Synthesis and synchrotron radiation X-ray structural analysis of Tm-metallofullerene single crystals

ツリウム金属内包フラーレンの
単結晶作製と放射光X線構造解析

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Synthesis and synchrotron radiation X-ray structural analysis of Tm-metallofullerene single crystals

by

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Contents

Glossary

XRD	X-ray diffraction
UV-Vis	Ultra Violet Visual
ESR	Electron Spin Resonance
XPS	X-ray photoelectron spectroscopy
NMR	Nuclear Magnetic Resonance
STM	Scanning Tunneling Microscope
LD-TOF	laser desorption time-of-flight
HPLC	High Perfomance Liquid Chromatography
DFT	Density Functional Theory
MEM	Maximum Entropy Method
CCDC	Cambridge Crystallographic Data Centre
Crystal A	co-crystal of one Ni(OEP) and one $Tm@C_{82}(I)$
Crystal B	co-crystal of one Ni(OEP) and two $Tm@C_{82}(I)$
Crystal C	co-crystal of one Ni(OEP) and one $Tm_2@C_{82}(I)$
Crystal D	co-crystal of one Ni(OEP) and one $Tm_2C_2@C_{82}(I)$
Tm(a1) – Tm(a8)	Metal atoms in crystal A
Tm(b1) – Tm(b5)	Metal atoms in crystal B
Tm(c1) – Tm(c9)	Metal atoms in crystal C
Tm(d1) – Tm(d10)	Metal atoms in crystal D
cage x1, x2 (x = a, b, c, d)	$C_{82}(C_s(6))$ cages in crystal A, B, C, D
F(xn) (x = a, b, c, d; n = 1, 2)	molecule consisting of cage x and Tm(xn) as below

F(xn)	F(a1)	F(a2)	F(b1)	F(b2)	F(c1)	F(c2)	F(d1)	F(d2)
cage x	cage a1	cage a2	cage b1	cage b2	cage c1	cage c2	cage d1	cage d2
Tm(xn)	Tm(a1)	Tm(a2)	Tm(b1)	Tm(b2)	Tm(c1), Tm(c2)	Tm(c3), Tm(c4)	Tm(d1), Tm(d2)	Tm(d3), Tm(d4)

1. Introduction

1.1 Fullerenes and metallofullerenes

1.1.1 Fullerene species

Empty fullerenes

Nano-size carbon clusters, "fullerenes" have spherical cage structures which consist of hexagons and pentagons. The first fullerene C_{60} has been synthesized by Kroto, Smalley and Carl in 1985[1]. Following the discovery, C_{70}, C_{76}, C_{78}, C_{80}, C_{84}, C_{86} and higher fullerenes were isolated and characterized[2-9]. While C_{60}, C_{70}, and C_{76} have identical structures, which other fullerenes higher than C_{76} have several structural isomers. These isomers are found to have different symmetries and properties. All characterized empty fullerenes satisfy an empirical rule known as isolated pentagon rule (IPR), which holds that pentagons cannot be adjacent in a carbon cage[10]. Adjacent pentagons make a fullerene cage unstable because the fused pentagons possess large curvature and distortion. Nowadays, empty fullerenes are utilized in several scientific fields, such as biology, physics and photochemistry.

Metallofullerenes

Fullerenes can encapsulate a metal atom in their hollow space. The first synthesis of metallofullerene was reported by Heath et al. in 1985[11]. They observed a peak of La@C_{60} in the mass spectrum. Here the symbol @ is used to denote the encapsulation of atom(s) or clusters. In contrast, a small amount of metallofullerenes prevented further research of the metal-carbon cluster. The next-stage investigation of metallofullerenes was started from the high-yield production of metallofullerenes

achieved by Chai et al[12]. They extracted the metallofullerene with toluene from the mixture of fullerene, metallofullerene and most of the impurities. Interestingly, although the most abundant metallofullerene is M@C_{60}, the extracted metallofullerenes are La@C_{82}. This fact suggests that La@C_{82} is more stable than La@C_{60}. Followed by the investigation of La@C_{82}, metallofullerenes that contains various metal atoms have been investigated such as Mg, Ca, Ti, Hf, Zr and most lanthanide atoms[13-17]. Metallofullerenes also have several isomers because its fullerene has several isomers.

Fullerenes can also encapsulate several materials such as M_2, M_2C_2 and M_3N clusters inside their hollow space. The first discovery of di-metallofullerenes, Sc_2@C_{80} and Sc@C_{84}, was reported by Shinohara et al. in 1992[18]. Metal-carbide cluster, Sc_2C_2@C_{84}, has firstly been reported by Wang et al. Several M_2 and M_2C_2 cluster encapsulated fullerenes are investigated such as Sc_2C_2@C_{82}, Y_2@C_{82}, Y_2C_2@C_{82}, Er_2@C_{82}, Er_2C_2@C_{82} and so on[19-28]. The first M_3N endohedral metallofullerene, Sc_3N@C_{82}(I_h(7)), was reported by Stevenson et al. in 1999[29]. Since the discovery of Sc_3N@C_{82}(I_h(7)), several M_3N cluster endohedral metallofullerenes are reported such as $ErSc_2N$@C_{80}(I_h(7)), Sc_3N@C_{78}(D_{3h}(5)), Sc_3N@C_{80}(D_{5h}(6)) and $CeSc_2N$@C_{80}(I_h(7))[29-34]. Here the Schönflies notation and number following the carbon cage (e. g. : I_h(7), D_{5h}(5)) shows cage symmetry and isomer number which is described in the textbook "An Atlas of Fullerenes"[10].

Further research of metallofullerenes revealed that metal atoms or carbides are encapsulated only in specific cage structures. For example, the structures of C_{82} cage which can encapsulate a La atom are C_{82}(C_{2v}(9)), C_{82}(C_s(6)) and C_{82}(C_{3v}(8)) whereas Y_2 and Y_2C_2 can only be encapsulated into C_{82}(C_2(5)), C_{82}(C_s(6)) and

$C_{82}(C_{3v}(8))$[16,21-24,35-38].

The investigation of metallofullerenes also revealed the existence of fullerene cages that violate IPR. Although most fullerene cages of metallofullerenes obey IPR, the fullerene cages of $Sc_2@C_{66}$, $La_2@C_{72}$ and $La@C_{72}$ contain fused-pentagon moiety, which are entirely absent in empty fullerenes [39-42].

1.1.2 Synthesis

Laser-vaporization method

The first synthesis of C_{60} was carried out with laser-vaporization method by Kroto et al[1]. In this method, fullerenes are synthesized when graphite is vapored by Nd : YAG laser irradiation in an atmosphere of helium flow at 1200°C followed by cooling down. First synthesis of La endohedral fullerenes is also achieved with this method utilizing graphite coating $LaCl_3$. Relatively high-yield of fullerenes and metallofullerenes compared with any other method can be obtained with Laser vaporization method. However this method has a severe problem in that only a small amount of fullerenes and metallofullerenes can be produced for several measurements.

Carbon evaporation method

Macroscopic quantities of C_{60} can firstly be obtained by carbon evaporation method performed by Krätschmer et al[43]. In this method, pure graphite is evaporated with electrodes in an atmosphere of ~100Torr of helium. This method enables production of 100 mg of C_{60} per day per person. Since the discovery of carbon evaporation method, several measurements that required over 1 mg of C_{60} have been achieved such as ^{13}C-nuclear magnetic resonance (NMR) and X-ray diffraction (XRD).

Arc discharge method

Fullerenes and metallofullerenes are usually synthesized by means of arc discharge method at the moment. In this method, a carbon electrode is utilized as the carbon source for fullerene synthesis. In order to produce metallofullerenes, metal atoms, usually in the form of metal oxide, are incorporated in the carbon electrode.

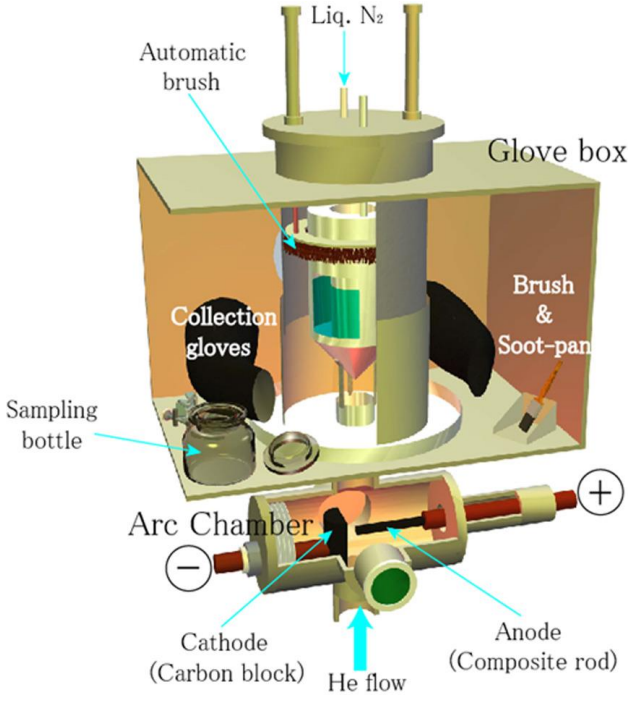


Figure 1. Arc reactor allowing anaerobic collection of soot. The raw soot containing fullerenes and metallofullerenes are synthesized in the arc chamber. The raw soot cooled down with liquid nitrogen is collected in the glove box.

Figure 1 shows the arc discharge apparatus in our laboratory. This apparatus has two chambers: arc discharge is performed in the lower chamber and the raw soot is collected in the upper chamber. The main feature of this machine is that the raw soot is collected and sampled in an inert atmosphere. Vaporization of graphite is

accomplished by driving a strong current between the two electrodes at 30 V and 500 A in a helium flow. The combined yield of empty fullerenes and endohedral metallofullerene is about 10 – 20 %.

1.1.3 Separation and isolation

HPLC separation

The amount of fullerenes and metallofullerenes in the raw soot synthesized by means of arc discharge method is about 10 – 20 %. Fullerenes are usually extracted with organic solvent such as *o*-dichlorobenzene, toluene and xylene. C_{60}, C_{70}, $M@C_{2n}$, $M_2@C_{2n}$, $M_2C_2@C_{2n}$ and other metallofullerenes are contained in the extracted solution. These fullerenes and metallofullerenes are separated by means of high-performance liquid chromatography (HPLC).

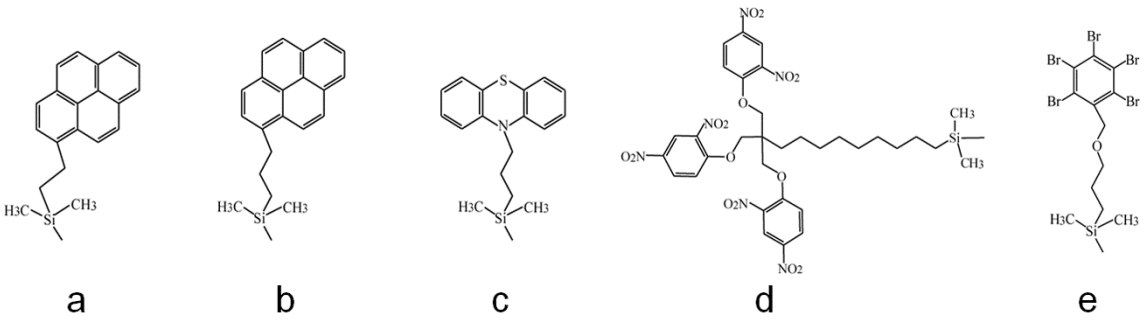


Figure 2. Functional structures on silica gel of 5PYE, Buckyprep, Buckyprep-M, Buckyclutcher-I and 5PBB columns are shown in Figs. a, b, c, d and e, respectively.

Figure 2 shows the functional structures on silica gel of 5PYE, Buckyprep, Buckyprep-M (Nakalai Tesque), and Buckyclutcher-I (Regis Chemical). These columns are usually utilized in the separation of metallofullerenes. Each column has specific features for separating the fullerenes. HPLC with Buckyprep-M and Buckyclutcher-I is efficient for separating empty fullerenes and metallofullerenes.

HPLC with Buckyprep is efficient for separating the fullerenes depending on the size and symmetries.

Separation of insoluble metallofullerenes

C_{74}, M@C_{60}, M@C_{70}, M@C_{72}, M@C_{74} and some other metallofullerenes are insoluble in organic solvents like toluene or xylene because their small-bandgap causes oligomerisation. These metallofullerenes can be dissolved in few solvents such as aniline and pyridine, which tends to cause serious damage to the HPLC column. Hence these metallofullerenes cannot be separated by usual HPLC method. Among these fullerenes and metallofullerenes, C_{74} was firstly separated by means of sublimation followed by reduction[44]. Sublimation from the mixture of fullerenes enable empty fullerenes with small size carbon cage to be separated from large fullerenes and impurities due to the difference of sublimation temperatures[45]. Then sublimed small fullerenes are reduced by means of cyclic voltammetry (CV) in order to be soluble and then C_{74} is separated by means of HPLC.

Metallofullerene with small carbon cage can also be separated by sublimation of the mixture of fullerenes and metallofullerenes[45]. Starting from the sublimed metallofullerenes, several M@C_{60} have been separated. Eu@C_{60} and Dy@C_{60} were forced to be separated by means of HPLC eluted by aniline[46,47]. Gd@C_{60} was separated by means of forming derivative as Gd@C_{60}[$C(COOH)_2$]$_{10}$ after elimination of C_{74} and other fullerenes by means of the reduction with $AlCl_3$[48].

1.1.4 Properties

Electronic structure of C_{60}

Figure 3 shows a schematic diagram of the frontier orbitals of C_{60} derived from the Hückel approximation[49]. The high symmetry of C_{60} possesses a high degree of degenerate orbitals. It can be seen that the LUMO and LUMO+1 levels are both triply degenerate while HOMO level is quintuply degenerate. The energy gap between HOMO-LUMO is 1.8 eV. This calculation also indicates that C_{60} behaves as electron acceptor rather than electron donor due to its low lying LUMO, which is proved with several experiments[50,51]. Not only C_{60} but also other empty fullerenes also behave as electron acceptors.

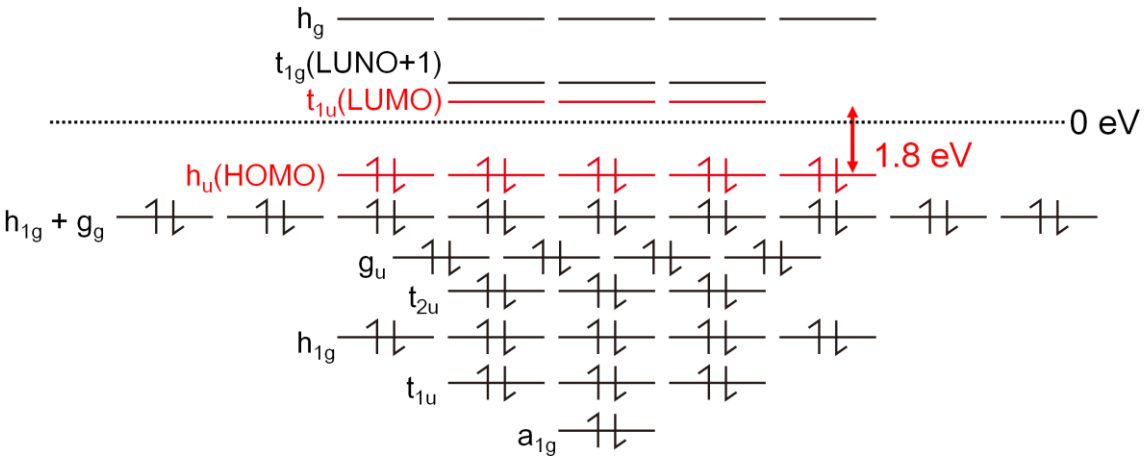


Figure 3. Frontier electronic energy levels of C_{60} within the Hückel approximation[49].

Superconductivity of alkali-metal doped C_{60}

Superconductivity was initially reported in K_3C_{60} and subsequently in other A_3C_{60} (A = alkali metal), compounds with the same structure[51-53]. Among them, the highest transition temperatures are found in the A_3C_{60} group, Cs_3C_{60} at 38 K with the application of pressure (~7 kbar)[54].

The superconductivity of C_{60} strongly depends on the degrees of orientational

disorder of C_{60}. For instance, pristine C_{60} molecule is almost freely rotating in the cubic close packed crystal at room temperature[55,56]. In contrast, K_3C_{60} and Rb_3C_{60} crystals, which are superconducting fullerides, show a merohedral disorder at room temperature[57,58]. Meanwhile the C_{60} molecule in Li_2CsC_{60} crystal, which is a non-superconducting fulleride, shows a hindered rotation even at 13 K[58,59]. These facts indicate that determination of fullerene orientation is also essential to understand the properties of the fulleride crystals.

Electron transfer of metallofullerenes

Endohedral metal(s) of metallofullerene tend to offer its fullerene cage to their electrons due to the electron acceptability of empty fullerene. Johnson et al. reported La atom of La@C_{82} transfer three electrons to carbon cage. Further experiments such as ESR and XPS measurements reveal that most lanthanide metal atoms of M@C_{82} (M = La, Ce, Pr, Nd, Pm, Gd, Tb, Dy, Ho, Er, Lu) are trivalent while others (M = Sm, Eu, Tm, Yb) are divalent[14,60-65]. M@C_{82} metallofullerenes whose valency of metals are the same show quite similar UV-Vis-NIR spectra, which strongly suggests their electric and molecular structures are almost the same even though metal atom is different[14,60-66].

Valency of metal atoms in M_2@C_{82} has been also investigated. Endohedral atoms of Er_2@C_{82} are found to be trivalent by means of fluorescence measurements[19]. Due to the similarity of UV-Vis-NIR spectra with that of Er_2@C_{82}, it is suggested that endohedral metal atoms of Tm_2@C_{82} and TmHo@C_{82} are also trivalent. In contrast, Er atoms of Er_2@C_{82} are trivalent according to theoretical calculation[67].

Other physical properties

Encapsulation of metal atoms and clusters such as metal carbide and nitride within the carbon cage induces interesting properties. For instance, the photoluminescence of $Er_2C_2@C_{82}$(III) is 100 times stronger than that of $Er_2@C_{82}$(III) even though the isomeric structures of the carbon cages are exactly the same[25]. STM tunneling current can control the orientation of metallofullerenes, which strongly implies the possibility of molecular switching with metallofullerenes[68,69]. The reduction potential of $Li@C_{60}$ is much higher than that of empty C_{60} due to the existence of endohedral metal, whose property is important of designing host-guest interaction following to synthesis of epochal solar cell[70,71]. These are entirely absent in empty fullerenes.

1.1.5 Supramolecular chemistry with metallofullerenes

Fullerene molecules form stable complexes with cyclodextrins (CDs), porphyrins and so on[72-79]. This supramolecular chemistry is important for application of fullerenes due to improvement of the solubility of fullerenes into various solvent like water, its strong host-guest interaction and so on. Since the first supramolecular complex of fullerenes has been achieved with γ-CD and C_{60}, anomalous ligands of fullerenes and metallofullerenes are synthesized[72-79]. The ligands which have metal porphyrins are also the strong association with (metallo)fullerenes. Sun et al. reported porphyrin-ligands are associated with C_{60}[73]. Pagona et al. shows these types of ligands are also associated with metallofullerenes[79]. Recently these ligands were utilized for separation of (metallo)fullerenes with cycloparaphenylene (CPP). Iwamoto et al. reported that the association of [10]CPP with C_{60} is the highest among the other [n]CPP[80]. Nakanishi et al. reported [12]CPP selectively formed a complex with $M@C_{82}$

among the mixture of (metallo)fullerenes.

1.2 Structure analysis of fullerenes and metallofullerenes

1.2.1 Structural determination by NMR and XRD

^{13}C-NMR spectroscopy is a useful tool for the characterization of the symmetry of the fullerene cage. The spectra consist of a number of peaks, each of which is derived from an equivalent set of carbon atoms and each of which has an intensity that is proportional to the number of atoms in each set. Thus symmetry analysis can be used to predict the numbers and relative intensities of peaks in the ^{13}C-NMR spectra of an isolated fullerene isomer. Taylor et al. have reported the structural characterization of C_{60} and C_{70} by using ^{13}C-NMR spectroscopy[3]. Up to date, diamagnetic metallofullerenes such as Ca@C_{2n}, Sc_2@C_{2n}, and Sc_2C_2@C_{2n} have been characterized by using the same method. NMR measurement is capable of reveal of the motion of endohedral materials. Multinuclear NMR spectroscopy has been performed to revealing of the metal rotation inside the fullerene cage. For instance Akasaka et al. have reported La atom rotation in La_2@C_{80} by using ^{139}La-NMR[81].

On the other hand, it is difficult to characterize symmetry of metallofullerenes whose metal atom ion is paramagnetic, which makes the chemical shift of the carbons on the fullerene cage broad. For instance although Dunsch et al. firstly assigned the symmetry of three Tm@C_{82} isomers, whose metal atom is paramagnetic, Kodama et al. re-assigned these symmetries[82]. Furthermore ^{13}C-NMR structural analysis of metallofullerenes with low-symmetry is challenging due to spectra with relatively large number of peaks and small intensities compared with high symmetry metallofullerenes.

XRD is a powerful method for characterizing the symmetry of the carbon cage, metal position and electronic state because atom positions can be directly determined[83]. The soccer-ball framework of C_{60} was firstly confirmed by X-ray structure analysis of osmylated C_{60}, $C_{60}O_2(OsO_2)$(4-tert-butylpyridine)$_2$[84]. Since the first structural analysis of C_{60}, dozens of structures of fullerenes and metallofullerenes have been revealed with XRD analysis[84-102]. In particular, several investigations of endohedral structures of metallofullerenes have contributed to the understanding of their properties. On the other hand, XRD structural analysis has the following problems: (i) the single crystal is scarcely obtained and (ii) the rotation of the spherical fullerene molecule tends to be disordered in the crystal[91]. These problems prevent the detailed analysis of metallofullerenes.

1.2.2 Principle of X-ray diffraction

Thomson scattering

Figure 4 shows the scattering of X-rays by a single electron. Since X-rays are electromagnetic waves, they cause vigorous vibration of the shell electrons of the atoms of substances through which they pass. When electrically charged particles such as electrons are accelerated, secondary radiation is always emitted. Because the secondary emission is stimulated by oscillating electric field of the incident X-rays, it is synchronous with it, consisting therefore of X-rays having the same frequency and wavelength as the incident X-rays. This scattering without change in wavelength is known as Thomson scattering and is the main type of scattering involved in X-ray diffraction.

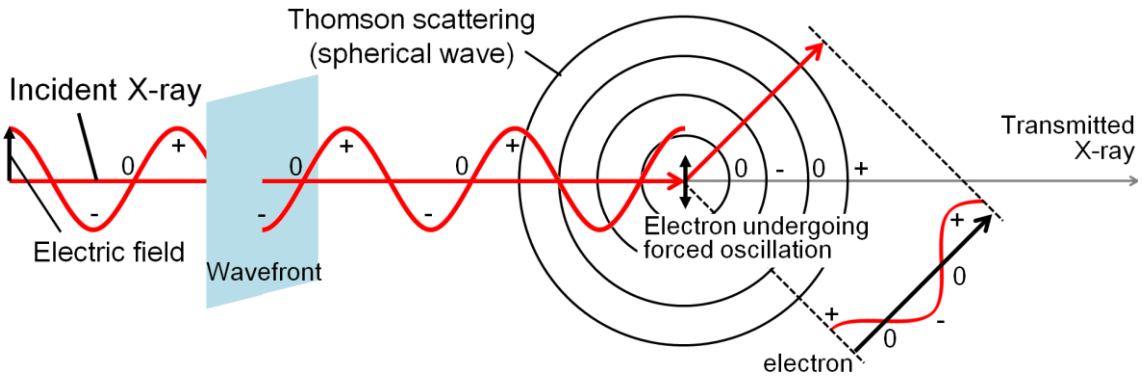


Figure 4. Thomson scattering of a spherical wave with amplitude.

The wave function of the scattered X-ray φ(***r***) can be described as Eq. 1.

$$\varphi(\boldsymbol{r}) = \exp\{2\pi i(\nu t + \delta(\boldsymbol{r}))\} \qquad \text{Equation 1}$$

where ***r*** is the scattered point of the incident X-ray, $\rho(\boldsymbol{r})$ is electron density at ***r***, ν is frequency, t is time and $\delta(\boldsymbol{r})$ is phase difference.

X-ray Diffraction

In the measurement of XRD, all the scattered X-rays arriving at given observation point are parallel, just as the incident X-ray beam is taken to be parallel because the observation distance should be thought of as effectively infinite. The overlapped X-ray scattered in parallel at an electron density distribution, E, as shown Fig. **5**a can be described as Eq. 2.

$$E = \int \rho(\boldsymbol{r})\exp\{(2\pi i(\nu t + \delta(\boldsymbol{r}))\}dv = F \cdot \exp(2\pi i\nu t)$$
$$F = \int \rho(\boldsymbol{r})\exp\{2\pi i\delta(\boldsymbol{r})\}dv \qquad \text{Equation 2}$$

where ν is a parameter of real space. F is called "structure factor", which only consists of charge density distribution scattering X-rays.

Every scattered X-ray wave has different $\delta(\boldsymbol{r})$ because the scattered position is different. As shown in Fig. 5b, the optical path difference between the two scattered X-rays at different position, *d*, can be described as

$$d = \boldsymbol{s}_1 \cdot \boldsymbol{r} - \boldsymbol{s}_0 \cdot \boldsymbol{r} \qquad \text{Equation 3}$$

where $\boldsymbol{s}_1$ and $\boldsymbol{s}_0$ are unit vectors of the incident and scattered X-rays, respectively. Equation 3 can be described as

$$2\pi\frac{d}{\lambda} = 2\pi\left(\frac{\boldsymbol{k}_1}{\lambda} - \frac{\boldsymbol{k}_0}{\lambda}\right)\cdot\boldsymbol{r} = 2\pi\boldsymbol{k}\cdot\boldsymbol{r}$$
$$\boldsymbol{k}_1 \equiv \frac{\boldsymbol{s}_1}{\lambda}, \qquad \boldsymbol{k}_0 \equiv \frac{\boldsymbol{s}_0}{\lambda}, \qquad \boldsymbol{k} \equiv \boldsymbol{k}_1 - \boldsymbol{k}_0 \qquad \text{Equation 4}$$

In the case, $\delta(\boldsymbol{r})$ can be described as $\frac{d}{\lambda}$, resulted in, therefore,

$$\delta(\boldsymbol{r}) = \boldsymbol{k} \cdot \boldsymbol{r} \qquad \text{Equation 5}$$

Hence structure factor *F* shown in Eq. **2** is

$$F(\boldsymbol{k}) = \int \rho(\boldsymbol{r}) \exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r})\, dv \qquad \text{Equation 6}$$

By the way, $\boldsymbol{k}$ is called scattering vector. As shown in Fig. 5c, absolute value of $\boldsymbol{k}$ is described as

$$|\boldsymbol{k}| = \frac{2sin\theta}{\lambda} \qquad \text{Equation 7}$$

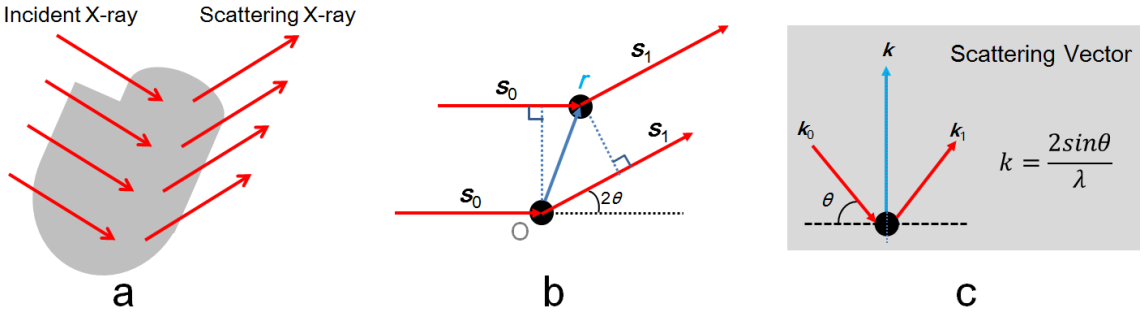


Figure 5. Panels show: a) The image of incident X-rays to electron density and scattering X-rays in parallel; b) two scattering X-rays in parallel c) scattering vector.

Structure factor of an atom

Figure 6a shows the image of electron density distribution of an atom, where $\boldsymbol{r}_j$ is the center of atom and $\boldsymbol{r}'$ is the vector from $\boldsymbol{r}_j$ to $\boldsymbol{r}$. From Eq. 6, structure factor of an atom, $f(\boldsymbol{k})$, can be described as

$$f(\boldsymbol{k}) = \int_{\text{atom}} \rho(\boldsymbol{r}) \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r})\, dv$$
$$= \int_{\text{atom}} \rho(\boldsymbol{r}_j + \boldsymbol{r}') \exp\{2\pi i k \cdot (\boldsymbol{r}_j + \boldsymbol{r}')\} dv \qquad \text{Equation 8}$$

Here $\rho(\boldsymbol{r}_j + \boldsymbol{r}')$can be described as $\rho(\boldsymbol{r}')$. Therefore

$$f(\boldsymbol{k}) = \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_j) \int_{\text{atom}} \rho(\boldsymbol{r}') \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}')\, dv$$
$$= f'(\boldsymbol{k}) \cdot \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_j) \qquad \text{Equation 9}$$

Structure factor of unit cell

Figure 6b illustrates atoms in a unit cell. Here it is assumed that there is no overlap of electron density distribution in each atom. Hence the structure factor of the unit cell, $F(\boldsymbol{k})$ can be described as

$$F(\boldsymbol{k}) = \sum_j f'_j(\boldsymbol{k}) \cdot \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_j) \qquad \text{Equation 10}$$

Crystal structure factor

Figure 6c shows the image of lattice points of a crystal. Every structure factor of the unit cell is the same except for the phase difference. When the structure factor of unit cell at original point represents $F(\boldsymbol{k})$, the structure factor of unit cell at r_j can be described as $F(\boldsymbol{k}) \cdot \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_j)$. Therefore the crystal structure factor, $F_L(\boldsymbol{k})$ can be described as

$$F_L(\boldsymbol{k}) = \sum_j F(\boldsymbol{k}) \cdot \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_j) \qquad \text{Equation 11}$$

In Eq. 11, $\boldsymbol{r}_j = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}$, where $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ is unit vector along with the unit cell. Therefore Eq. 11 can be described as

$$F_L(\boldsymbol{k}) = F(\boldsymbol{k}) \cdot \sum_m \exp(2\pi i m \boldsymbol{k} \cdot \boldsymbol{a}) \sum_n \exp(2\pi i n \boldsymbol{k} \cdot \boldsymbol{b}) \sum_p \exp(2\pi i m \boldsymbol{k} \cdot \boldsymbol{c}) \qquad \text{Equation 12}$$

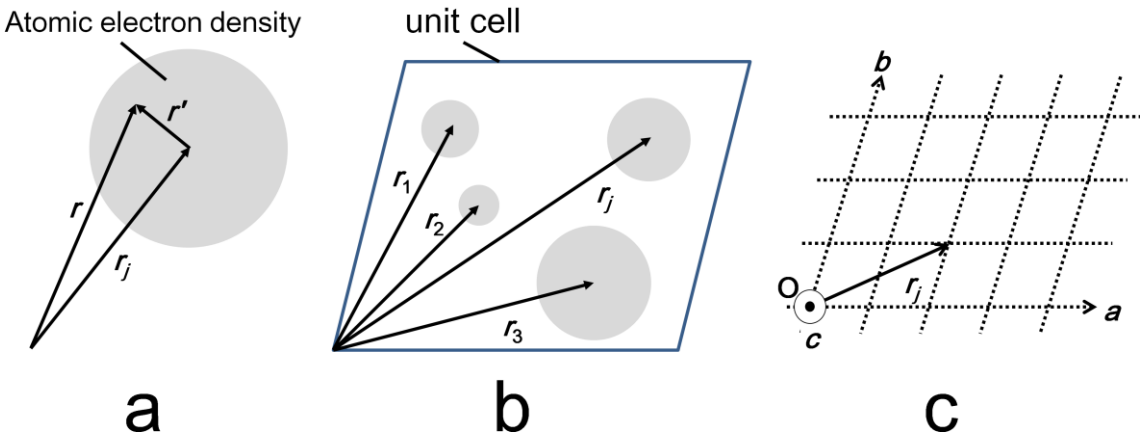


Figure 6. Panels show a) the image of electron density distribution of an atom b) atoms in a unit cell c) the image of lattice points of a crystal

Laue function

The function $\sum_q \exp(2\pi iqx)$is called Laue function. When q is large, the number of Laue function is 0 except when x is an integer number. Therefore $F_L(\boldsymbol{k})$ in Eq. 12 is 0 except when $\boldsymbol{k}\cdot\boldsymbol{x}$ ($\boldsymbol{x} = \boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$) is an integer number due to m, n and p being an Avogadro number. When $\boldsymbol{k}\cdot\boldsymbol{a} = h$, $\boldsymbol{k}\cdot\boldsymbol{b} = k$, $\boldsymbol{k}\cdot\boldsymbol{c} = l$ (h, k and l is an integer number), Eq. 13 is induced.

$$\boldsymbol{k} = h\cdot\boldsymbol{a}^* + k\cdot\boldsymbol{b}^* + l\cdot\boldsymbol{c}^* \qquad \text{Equation 13}$$

$$\left(\boldsymbol{a}^* = \frac{\boldsymbol{b}\times\boldsymbol{c}}{V}, \quad \boldsymbol{b}^* = \frac{\boldsymbol{c}\times\boldsymbol{a}}{V}, \quad \boldsymbol{c}^* = \frac{\boldsymbol{a}\times\boldsymbol{b}}{V}\right)$$

$$(V = \boldsymbol{a}\times\boldsymbol{b}\times\boldsymbol{c})$$

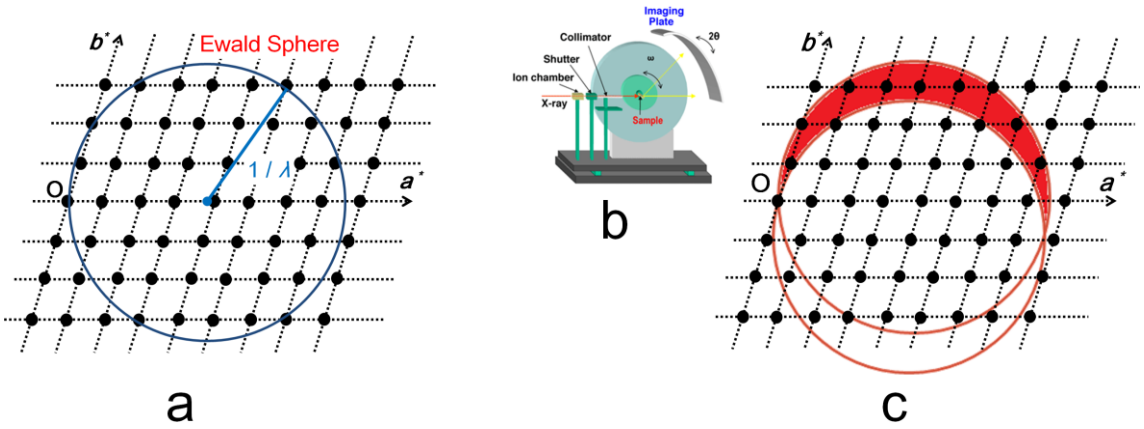


Figure 7. a) Reciprocal lattice with lattice points and the Ewald sphere b) the image of XRD measurement with crystal oscillation c) the locus of Ewald's sphere caused by the XRD measurement with crystal oscillation as shown in panel b.

Ewald sphere

Figure 7a shows the Cartesian coordinate consisting of $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$ with its lattice points. This Cartesian coordinate is called the reciprocal lattice. From Eq. 13, $F_L(\boldsymbol{k})$ has value only at the lattice point in Fig. 7a. From Eq. 7, furthermore, $\boldsymbol{k}$ must lie on the

sphere whose radius is 1 / λ and whose surface is at 0. This sphere is called Ewald sphere. Hence $\boldsymbol{k}$ must be (i) on Ewald sphere and (ii) on the lattice points when $F_L(\boldsymbol{k})$ has value. However the point that satisfies condition (i) and (ii) is rare. In XRD measurement, therefore, the crystal is oscillating during exposure in the X-ray as shown in Fig. 7b. In the measurement, the diffractions that satisfy the lattice points in the red area in Fig 7c can be seen.

Structure determination

$\rho(\boldsymbol{r})$ is obtained from inverse Fourier transformation of Eq. 6;

$$\rho(\boldsymbol{r}) = \int F(\boldsymbol{k}) \exp(-2\pi i \boldsymbol{k} \cdot \boldsymbol{r})\, dv^* \qquad \text{Equation 14}$$

In case of crystals, $F(k)$ has value other than 0 at reciprocal lattice point because the charge density distribution has almost infinite periodicity. Hence $\rho(\boldsymbol{r})$ can be described as:

$$\rho(x,y,z) = \sum_h \sum_k \sum_l F(hkl) \exp(hx + ky + lz) \qquad \text{Equation 15}$$

where V is volume of unit cell, x, y, z are parameters of Cartesian coordinates in the unit cell and h, k, l are described as reciprocal lattice point (h, k, l are integer number and $-\infty < h, k, l < \infty$).

In XRD measurement, the value $|F(\boldsymbol{k})|$ can be obtained. In order to obtain $F(\boldsymbol{k})$, the phase parameter of $F(\boldsymbol{k})$ is required. Direct method, firstly proposed by Harker et al., is a powerful tool for determination of the phase[103-105]. Combination of direct method

and Eq. 15, fundamental atomic positions in crystal are modeled. Based on the resultant atomic positions, the final atomic positions are refined by means of least square method. In the least square method, absolute structure factor calculated from the model, $|F_c(\boldsymbol{k})|$, is fitted on the observed structure factor, $|F_o(\boldsymbol{k})|$ and then the final atomic positions are determined.

1.2.3 Powder X-ray diffraction

Due to the low crystallinity of metallofullerenes, the combination of powder X-ray diffraction and charge density analysis using the maximum entropy method (MEM) has been utilized in the early age of structural analysis of metallofullerenes[16,38,85,86]. The MEM can visualize the charge density distribution of the molecule without actual structure model from the low-resolution diffraction data obtained by the powder diffraction.

Figure 8 shows the MEM charge density distributions of endohedral natures of $Y@C_{82}(C_{2v}(9))$, $La_2@C_{80}(I_h(7))$, $Y_2@C_{82}(C_{3v}(8))$ and $Y_2C_2@C_{82}(C_{3v}(8))$[21,85,88]. As shown in Fig. 8a, the first conclusive experimental evidence of the endohedral nature of metallofullerene was observed by means of synchrotron radiation XRD (SR-XRD) with powder crystal of $Y@C_{82}(C_{2v}(9))$[85]. Up to date, several molecular structure determinations of metallofullerenes have been carried out by means of powder crystal XRD measurement such as $Sc@C_{82}(C_{2v}(9))$, $La@C_{82}(C_{2v}(9))$, $La_2@C_{80}(I_h(7))$, $Sc_2C_2@C_{82}(C_{3v}(8))$, $Y_2C_2@C_{82}(C_{3v}(8))$ and so on[20-22,38,86,88,94]. As shown in Fig. 8b, the molecular structural analysis of $La_2@C_{80}(I_h(7))$ revealed that two endohedral La atoms occupy several positions instead of staying in one position. MEM charge density distribution analysis also revealed that the charge density of La atoms forms regular

dodecagon in the fullerene cage where entire metallofullerene possesses I_h symmetry of the cage[88]. Also the shape of the charge density distribution of endohedral metal atoms in $Y_2@C_{82}(C_{3v}(8))$, $Y_2C_2@C_{82}(C_{3v}(8))$ is determined as regular dodecagon and molecular structures of these metallofullerenes maintain the symmetries of their carbon cage as shown in Figs. 8c and d[21,22]. Comparison of molecular structures of $Y_2@C_{82}(C_{3v}(8))$ and $Y_2C_2@C_{82}(C_{3v}(8))$ reveals that the structures of both are quite similar except the existence of C_2 unit of $Y_2C_2@C_{82}(C_{3v}(8))$[21].

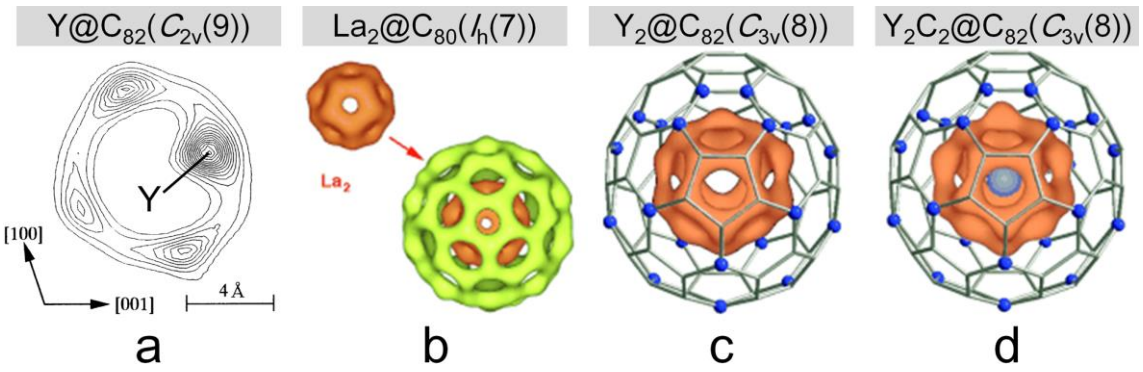


Figure 8. MEM electron charge density distribution of the endohedral natures of; a) $Y@C_{82}(C_{2v}(9))$; b) $La_2@C_{80}(I_h(7))$; c) $Y_2@C_{82}(C_{3v}(8))$; d) $Y_2C_2@C_{82}(C_{3v}(8))$[21,85,88]. The contour lines are drawn from 0.0 eÅ^{-3} with 0.5 eÅ^{-3} intervals in panel a. MEM charge density distributions of metal atoms are colored in orange in panels b-d whereas that of endohedral C_2 unit are colored in blue in panel d.

1.2.4 Single crystal structure analysis of functional (metallo)fullerenes

The powder X-ray diffraction has, however, difficulty to obtain a high-resolution diffraction data for more accurate structure determination because of generally weak diffraction intensity and peak overlapping. The high-resolution diffraction data can be achieved by single crystal X-ray diffraction. Single crystal XRD has been utilized for structure determination of functionalized metallofullerenes. Large single crystals can be

obtained for the functionalized molecules. The functionalization also has an advantage that the disorder of molecular orientation in the crystal is oftentimes prevented by steric barrier. Akasaka and co-workers have successfully determined the molecular structures of carbine derivative of La@C_{82}(C_{2v}(9)) and Gd@C_{82}(C_{2v}(9))[37,95]. They overcome the weakness of powder diffraction of low resolution with this method. Although the structure of Sc_3C_{82} was once determined as Sc_3@C_{82}(C_{3v}(8)) by powder crystal XRD, the single crystal structure analysis of Sc_3C_{82} adamantylidene carbene derivative revealed that the molecule is Sc_3C_2@C_{80}(I_h(7))[92,106]. The functionalization of metallofullerene also has an advantage that enables insoluble metallofullerene to be soluble in several solvents. The structure of La@C_{74}, which is one of the insoluble metallofullerenes, is successfully determined with isolated and crystallized by means of functionalizing dichlrorobenzene[93]. Unfortunately the functionalization seriously modifies the original molecular structure of the metallofullerenes, especially the positions of endohedral metals[107,108]. Furthermore the reaction of functionalization oftentimes needs abundant metallofullerene compared to its yield.

1.2.5 Single crystal structure analysis of co-crystal with *M*(OEP)

Co-crystallization with octaethylporphyrin metal, *M*(OEP), is an epochal method to obtain single crystals of endohedral metallofullerenes. This method is firstly reported by Olmstead et al. with crystallization of C_{60}, C_{70} and $(C_{60})_2O$ followed by metallofullerene, Sc_3N@C_{80}(I_h(7))[29,87]. This method has advantages in that (i) high-quality and large single crystals can be obtained with tiny amount (> 1 μg) of metallofullerene; and (ii) crystallization can be achieved with only one step. In this method, the crystallization is carried out by means of layering a saturated metallofullerene solution over a Ni(OEP)

solution and then co-crystal of Ni(OEP) and metallofullerene is obtained with size of ~0.1×0.1×0.1 mm^3.

Most typical co-crystal structures of M(OEP) – metallofullerenes are shown in Fig. 9. In the crystal, one Ni(OEP) is attached on metallofullerene. The unit cell consists of four Ni(OEP) and four metallofullerenes. The space group of the crystal is $C_{2/m}$, and the parameters of the unit cells are; a = 25 Å, b = 15 Å, c = 20 Å, β = 95° (monoclinic).

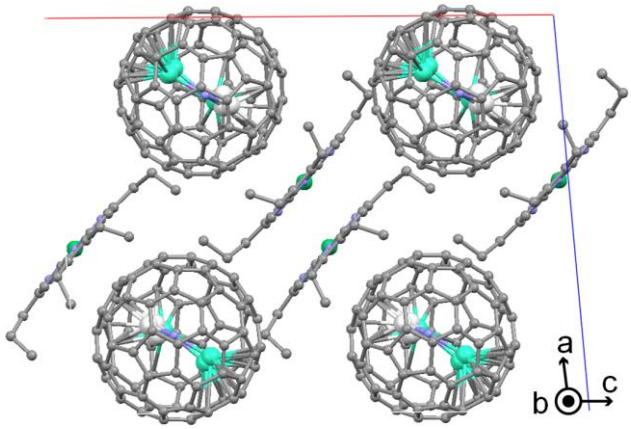


Figure 9. Typical unit cell structure of the co-crystal of Ni(OEP) – metallofullerene.

Table 1 summarizes a part of metallofullerenes whose structures have been determined with the co-crystal. A number of the molecular structures of endohedral metallofullerenes have been determined for the co-crystals with *M*(OEP). Several molecular structures of metallofullerenes whose fullerene cages violate IPR have been revealed with this method[109-113]. Comparisons of endohedral Yb, Sm and Sm_2 structures in different fullerene cages are performed. Also the investigations of endohedral structures of tri-metallic nitride in $C_{80}(I_h(7))$ have been carried out.

In contrast, few investigations of endohedral C_2 units of $M_2C_2@C_{2n}$ have been carried out. Furthermore the comparison of different endohedral structures in the same fullerene

cage is only carried out with $C_{80}(I_h(7))$ and M_3N cluster. One of the main reasons that these investigations have not been achieved is the existence of high degree of disordered structures of endohedral atoms and carbon cage in the co-crystals[91,97-99]. The molecular orientation of spherical endohedral metallofullerenes is readily disordered in the crystals, which sometimes misleads the space group of the crystal, detailed carbon cage structure (e.g. a couple of C-C bonds on fullerene cages are over 1.7 Å) and so on[91,114].

Table 1. The list of metallofullerenes whose molecular structures have been determined with co-crystal of Ni(OEP).

Size	mono-metallofullerene	Ref.	di-metallofullerene	Ref.	$M_3N@C_{2n}$	Ref.
$C_{68\text{-}78}$			$Sc_2S@C_{72}(C_s(10528))$	112	$Sc_3N@C_{68}(D_3(6140))$ $Sc_3N@C_{78}(D_{3h}(5))$ $Gd_3N@C_{78}(C_2(22010))$	113 31 111
C_{80}	$Yb@C_{80}(C_{2v}(3))$	107			$M_3N@C_{80}(D_{5h}(6))$ (M =Sc, Lu) $M_3N@C_{80}(I_h(7))$ (M = Sc, Gd, Lu) $MSc_2N@C_{80}(I_h(7))$ (M = Ce, Gd, Tb, Er) $Gd_2ScN@C_{80}(I_h(7))$	33 32,87 115 30,34 96 96
C_{82}	$M@C_{82}(C_s(6))$ (M = Sm, Yb) $M@C_{82}(C_2(5))$ (M = Sm, Yb) $M@C_{82}(C_{2v}(9))$ (M = Sm, Yb)	101,116 101,116 101,116	$Er_2@C_{82}(C_s(6))$ $Er_2@C_{82}(C_{3v}(8))$ $Sc_2(\mu_2\text{-}O)@C_{82}(C_{3v}(8))$	89 90 117	$Gd_3N@C_{82}(C_s(39663))$	110
$C_{84\text{-}88}$			$Sm_2@C_{88}(C_2(35))$	98	$Tb_3N@C_{84}(C_s(51365))$	109
C_{90}	$Sm@C_{90}(N)$ (N = C_2(40, 42, 45), C_{2v}(46))	99	$Sm_2@C_{90}(C_1(21))$	98		
C_{92}	$Sm@C_{92}(C_1(42))$ $Sm@C_{92}(C_s(24))$	118 118	$Sm_2@C_{92}(D_3(85))$ $Gd_2C_2@C_{92}(D_3(85))$	98 119		
C_{94}	$Sm@C_{94}(C_{3v}(134))$	118				

The disorder of metallofullerene tends to be reduced with coordination of two Ni(OEP)s. Most metallofullerene-M(OEP) co-crystals have a ratio of metallofullerene : M(OEP) = 1 : 1. The carbon cage often shows a disordered structure in the co-crystals[91]. In contrast, empty C_{60} and water-molecule encaged endohedral fullerene, $H_2O@C_{60}$, form 1 : 2 co-crystals with Ni(OEP) ligands[87,120]. The carbon cage orientation can be fixed in both crystals at 100 K, suggesting that the disorder of metallofullerene

orientation is also suppressed in the 1 : 2 co-crystals.

1.3 Aim of this work

Endohedral metallofullerenes are among the most attractive molecules because of their interesting properties such as anomalously enhanced photoluminescence, high reduction potential and molecular switching, which are entirely absent in empty fullerenes[68-70,121]. These properties are caused by their unique structures, where metal atom(s) are encapsulated into the hollow space of the fullerene. In particular the endohedral structure should affect the properties of metallofullerenes because the endohedral structure alters the symmetry of the metallofullerene and then the electronic structure such as the degeneracy of orbitals modifies. Hence the determination of endohedral structure of metallofullerenes is highly required for understanding the properties of metallofullerenes.

The endohedral atoms of metallofullerenes show valuable structures inside the fullerene cage. It has been known that an endohedral metal atom in mono-metallofullerene generally occupies one stable distinct position[122-124]. An endohedral metal atom in the vicinity of a six-membered ring has been found in La@C_{82}(C_{2v}(9)) and Sc@C_{82}(C_{2v}(9)) by X-ray diffraction studies[122,123]. In contrast, an endohedral metal atom of M_2@C_{2n} and M_2C_2@C_{2n} simultaneously occupies several positions such as La_2@C_{80}(I_h(7)), Y_2@C_{82}(C_{3v}(8)), Sc_2C_2@C_{82}(C_{3v}(8)) and so on[21,22,125,126]. These facts imply that metal atoms of di-metallofullerenes occupy multi-positions in the fullerene cage. In order to understand the relationship between the number of endohedral metal atoms and their occupation sites, comparison of endohedral structures is required where their fullerene cage and the species of endohedral metal atoms are the same but endohedral materials as a whole are different such as M, M_2 and M_2C_2 (each M is the same atom).

However this comparison usually has great difficulty because the fullerene cage structures of metallofullerenes are usually different depending on its endohedral materials. For example, the most abundant metallofullerene in $Y@C_{82}$ isomers is $Y@C_{82}(C_{2v}(9))$ and the others are quite little whereas the amount of three isomers of $Y_2@C_{82}$, $Y_2@C_{82}(C_s(6))$ $Y_2@C_{82}(C_2(5))$ and $Y_2@C_{82}(C_{3v}(8))$ are similar[23,24,38].

Endohedral structure analysis of metallofullerenes itself is also challenging because the high degree of orientational disorder of both endohedral atoms and fullerene cage oftentimes prevent the molecular structural analysis of metallofullerenes. It is difficult to identify whether these disordered endohedral atoms are generated by (i) disordered metal atom or (ii) molecular disorder as a whole though only one or a few stable positions existing in the metallofullerene. However there are only a few structural determinations that disordered endohedral structure are discussed in proper way. Structural determination of disordered fullerene cage is also difficult because of several overlapped atoms. For example, in case of $M@C_{82}$ with four orientational disorders, 324 carbon atoms (82×4) are onto the spherical surface whose radius is about 4.2 Å. These overlapped atoms can hardly be separated in the analysis.

In this work, single crystal X-ray structural analysis of $Tm@C_{82}$(I), $Tm_2@C_{82}$(I) and $Tm_2C_2@C_{82}$(I) are carried out with co-crystal with Ni(OEP), where the three metallofullerenes are suggested to have $C_{82}(C_s(6))$ fullerene cages from the combination of X-ray structural analysis and UV-Vis-NIR spectra. In order to determine the detailed endohedral structures, co-crystal of metallofullerene with two Ni(OEP) are utilized for the XRD structural analysis in order to reduce the rotation of metallofullerenes. Furthermore the ligand of metallofullerenes, which have two nickel porphyrins, are synthesized and then the crystallization of this complex and the metallofullerenes are

carried out.

In the structural analysis, the single-crystal X-ray diffraction (XRD) experiments utilizing third-generation synchrotron radiation with high counting statistics were performed at BL02B1 in SPring-8 (Hyogo, Japan). MEM charge density distribution analyses are carried out. Structural analysis involving disorder of carbon cage orientation is carried out considering not only *R* value but also valuable parameters such as occupancies of the disordered structures and thermal displacement of atoms. The resultant structures are compared to the theoretical ones.

2. Experimental and structural determination

2.1 Synthesis and isolation of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$, $Tm_2C_2@C_{82}(I)$

$Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ were synthesized by DC arc-discharge of Tm/graphite composite rods (15 × 15 × 300 mm^3, 0.8 at.% Tm/C, Toyo Tanso Co. Ltd.). The soot containing $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ was collected anaerobically under nitrogen atmosphere. These metallofullerenes and other fullerenes were extracted from the soot with *o*-xylene. $Tm@C_{82}(I)$ was isolated by means of four-stages of high-performance liquid chromatography (HPLC) method with 5PYE (φ21.1 × 250 mm; flow rate: 21 mL min^{-1}; Nacalai Tesque), Buckyprep-M (φ21.1 × 250 mm^2; flow rate: 21 mL min^{-1}; Nacalai Tesque) and Buckyprep (φ21.1 × 250 mm^2; flow rate: 21 mL min^{-1}; Nacalai Tesque). $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ were isolated by means of four-stages high-performance liquid chromatography (HPLC) method with 5PYE, Buckyclucher-I (φ21.1 × 500 mm; flow rate: 10 mL min^{-1}; Regis Chemical), Buckyprep-M and Buckyprep. Identification of the isolated metallofullerenes was performed by using laser desorption time-of-flight (LD-TOF) mass spectroscopy (AXIMA-CFR, Shimadzu) and UV-Vis-NIR absorption (Jasco V-570 spectrophotometer).

2.2 Co-crystallization with Ni(OEP)

Co-crystal of $Tm@C_{82}(I)$ and Ni(OEP) was obtained by means of layering a dusky red solution of saturated $Tm@C_{82}(I)$ in 1 ml toluene over a red solution of 0.6 mg Ni(OEP) solution in 1 ml chloroform. The two layers were diffused in a 5 mm diameter

glass tube with vapor of solvent slowly at room temperature. Two types of co-crystals, crystal A and B are obtained.

The isolated $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ were also co-crystallized with Ni(OEP) from the solution by diffusion in a sealed glass tube (φ0.5 mm). A dusky red solution of saturated $Tm_2@C_{82}(I)$ or $Tm_2C_2@C_{82}(I)$ in 5 μl chlorobenzene was layered over a red solution of 1.0 μg Ni(OEP) solution in 5 μl chloroform. The two layers were diffused in the glass tube at room temperature. Co-crystal of each $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$, crystal C and D, are obtained.

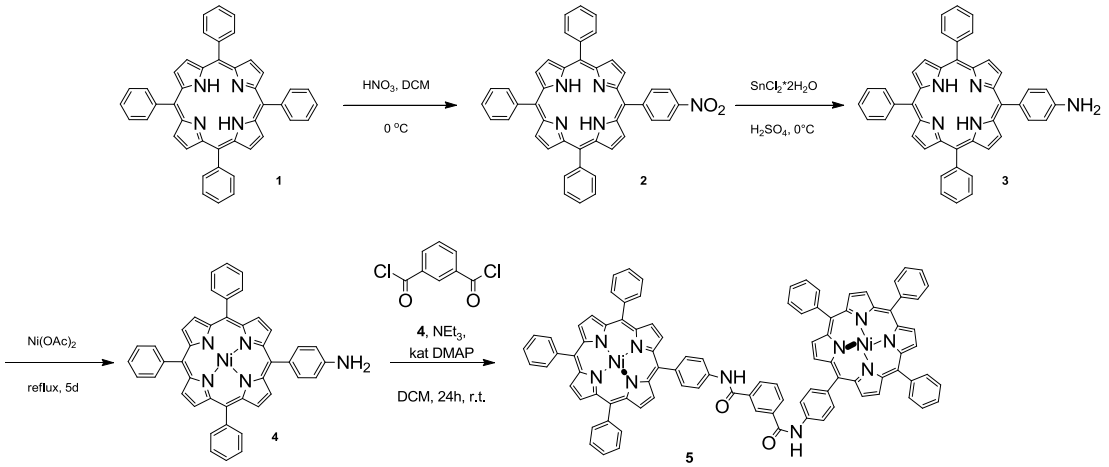
Crystals A-D are then put into paraffin liquid. The paraffin liquid coats crystals surface and then prevent the solvent in crystal from vapour. Next crystals are picked up with micro-loop (MiTeGen; M1-L19-100 and HAMPTON; HR4-955).

2.3 Complex of metallofullerenes and its ligand

2.3.1 Synthesis of the ligand of metallofullerene

Scheme 1 shows the scheme of the tweezers we synthesized. Firstly mono-nitration of phenyl-functionalized group on tetraphenylporphyrin (TPP WAKO; 325-83381) was carried out and produced nitrophenyltriphenylporphyrin (TPP-NO_2). Secondly, reduction of the nitro group was performed to obtain aminophenyltriphenylporphyrin (TPP-NH_2). Thirdly, nickel metal insertion into the porphyrin ring was carried out to be synthesized aminophenyltriphenylporphyrin nickel (NiTPP-NH_2). Lastly two NiTPP-NH_2 molecules were reacted with isophtaloyl chloride resulted in obtaining porphyrin nickel tweezers (NiTPP dimer). The electron spray ionization (ESI) mass spectra of produced TPP-NO_2, TPP-NH_2, Ni(TPP), and Ni(TPP) dimer were recorded with a MicroToF spectrometer (Bruker). ^{1}H-NMR spectra of produced TPP-NH_2 and

Ni(TPP) are measured with Bruker spectrometers (AV300, AV400).



Scheme 1. Scheme of NiTPP dimer synthesis. Nitration, reduction, nickel insertion, bridged by isophtaloyl chrolide.

2.3.2 Association of the ligand and metallofullerene

In order to investigate the association of Ni(TPP) dimer and metallofullerenes, titration of metallofullerene solution to Ni(TPP) dimer was carried out. When porphyrin ring molecule interacts with fullerenes, red-shift of Soret band occurs[79]. In order to investigate the association, titration of Ni(TPP) dimer and (metallo)fullerenes are performed. Here UV-Vis spectra measurement of Ni(TPP) dimer upon successive addition of C_{60}, C_{70}, Ce@C_{82}(I) and Tm@C_{82}(I) were carried out and investigate the shift of Soret band.

2.3.3 Crystallization of the complex of Ni(TPP) dimer and Tm@C_{82}(I)

Crystallization of the complex of Ni(TPP) dimer and Tm@C_{82}(I) are carried out by means of liquid/liquid diffusion method. Poor solvent was over the mixture solution of

1.0×10^{-4} mol · l^{-1} of Ni(TPP) dimer and $Tm@C_{82}$(I). In this method, methanol, ethanol, acetonitrile, hexane and acetone were utilized for poor solvent while toluene, chloroform, dichloromethane and tetrahydrofuran were used for good solvent.

2.4 XRD measurement in SPring-8

2.4.1 SR-XRD in SPring-8

The single crystal X-ray diffraction measurements of crystal, A, B, C and D were performed at BL02B1 in SPring-8 (Hyogo, Japan). SPring-8 is a large synchrotron radiation facility which delivers one of the most powerful synchrotron radiation currently available. High directional and narrow wavelength range of electromagnetic radiation beam is available within the wavelength of 2000 ~ 0.1 Å.

Synchrotron radiation is an electromagnetic wave generated by an electron traveling at almost light speed, toward its running direction when its path is bent by a magnetic field. In SPring-8, thermionic gun made of barium-impregnated tungsten generates an electron beam. The gun is located on a high voltage deck and extraction voltage is about 180 kV. The extracted beam is accelerated up to 1 GeV with 25 accelerator cavities. Next, the beam is accelerated again up to 8 GeV with the booster synchrotron. The booster has a racetrack shape and its circumference is 396 m long. Then the electron is stored in a circular accelerator whose circumference is 1436 m long. Synchrotron radiation from a bending magnet is extracted at the upper course of the electron orbit in the magnet.

BL02B1 is designed for XRD measurement of single crystal. This beamline has large cylindrical image-plate camera. In BL02B1, monochromatic X-ray (E = 8 – 115 keV) can be utilized for measurements.

2.4.2 XRD measurements of crystal A-D

The conditions of SR-XRD measurements of crystal A-D are summarized in Table 2, which shows temperature (T), wavelength (λ), oscillation angle of the crystals in one measurement ($\Delta\omega$), exposure time of X-ray for the crystals (t) and frame numbers of the measurements (N). During X-ray measurement, the angle of X-ray to the crystal oscillates within $\Delta\omega$. Frame number means the number of X-ray measurements in different angles.

Table 2. The conditions of X-ray measurement for crystals A-D at BL02B1.

	T / K	λ / Å	$\Delta\omega$	t / min.	N
Crystal A	50, 210	0.61900	6.5°	5	62
Crystal B	190	0.62029	6.5°	5	62
Crystal C	200	0.49521	5.5°	2	73
Crystal D	200	0.49521	5.5°	2	73

2.5 Theoretical calculation of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$

Geometry optimizations of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ were performed by using density functional theory (DFT) at the B3LYP/SV(P) level[127]. The TURBOMOLE program package was used for all DFT calculations[128]. The Stuttgart relativistic effective core potential (ECP) was used in order to model the core electrons in Tm[129]. The structure models of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ derived from the XRD analyses were used as the initial structures of the calculation. All molecular structures were optimized on the quintet electronic ground state potential energy surface.

2.6 Structural determination

2.6.1 Theory of MEM charge density analysis

The structures of Ni(OEP), solvents and metal atoms in the crystal A-D were obtained by the direct method using program *SIR2004*[130]. In contrast, the structure determination of fullerene cage is usually difficult by means of direct method due to the complicated disorder. In this work, alternatively, the cage structures are determined by means of fitting theoretical fullerene cage onto each charge density distributions of crystal A-D obtained by MEM[131]. The MEM charge density distributions were obtained by using program *ENIGMA*[132]. It is well known that the MEM map is consistent with the observed structure factors and least biased with respect to unobserved structure factors.

Although conventional Fourier transition method is useful to obtain charge density distribution, Equation 15 indicates that an infinite number of Fourier coefficients (h, k, l) are needed to perform a Fourier inversion without any ambiguity. It is, however, simply not possible to satisfy this condition experimentally. Conventionally, Fourier inversion is performed by using a limited number of Fourier coefficients obtained by experiment and ignoring experimental errors. This procedure implicitly means that all the missing Fourier coefficients are set to zero, simply because the experiment to measure them cannot be or was not carried out. In contrast, MEM can extract detailed information on the electron density distribution such as deformation of electron density distribution from free atoms while the conventional direct Fourier method fails to extract such information from the same data[131,133].

In information theory, "amount of information" expressed as $-\ln p(x)$ is used, where $p(x)$ is occurrence probability. Then the expected value (H) can be expressed as:

$$H = -\sum_{x \in X} p(x) \ln p(x) \qquad \text{Equation 16}$$

The Eq. 16 is called "information entropy" because it is the same as Boltzman entropy. MEM induces the result, which has the highest information entropy. In Eq. 16 the value is 0.5 which gives the highest entropy. When a priori occurrence probability is given, information entropy is described as;

$$S = -\sum_{x \in X} p(x) \ln \frac{p(x)}{q(x)} \qquad \text{Equation 17}$$

where $q(x)$ is a priori occurrence probability and S is information entropy. The maximum S is given when $p(x) = q(x)$.

Application of MEM theory for charge density analysis is investigated by D. M. Collins and M. Sakata[131,134]. In the analysis, the resultant charge density distribution has the highest information entropy in what satisfies observed structure factor. The charge density distribution is investigated by means of sequential calculation stating from $\rho(\boldsymbol{r})$ = constant until the charge density distribution satisfies observed structure factor within the margin of error.

In MEM charge density analysis, $p(x)$ and $q(x)$ are described as;

$$\rho'(\boldsymbol{r}) = \rho(\boldsymbol{r})/Q_{total}$$
$$\rho_0'(\boldsymbol{r}) = \rho_0(\boldsymbol{r})/Q_{total} \qquad \text{Equation 18}$$

where Q_{total} is the total electron number in unit cell, $\rho(\boldsymbol{r})$ is charge density distribution of unit cell and $\rho_0(\boldsymbol{r})$ is priori charge density which is already given. Therefore the

information entropy S is described as;

$$S = -\sum_{r} \rho(\boldsymbol{r}) \ln \frac{\rho'(\boldsymbol{r})}{\rho'_0(\boldsymbol{r})} \qquad \text{Equation 19}$$

ρ should satisfy Eq. 20 when resultant charge density distribution satisfies observed structure factor within margin error.

$$C = \frac{1}{N} \sum_{j=1}^{N} \left\{ \frac{|F_c(\boldsymbol{k}_j) - F_o(\boldsymbol{k}_j)|^2}{{\sigma_F}^2(\boldsymbol{k}_j)} \right\} \leq 1 \qquad \text{Equation 20}$$

where F_o is observed structure factor, F_c is obtained from equation (1) with using ρ, σ_F is root-mean-square deviation of F_o and N is the number of reflections for observed structure factor. Probable condition is that F_c derived from ρ coincides with F_o within error.

ρ satisfying Eq. 20 is given by means of Lagrange's method of undetermined multipliers as:

$$\rho(\boldsymbol{r}) = \rho_0(\boldsymbol{r}) \exp\left[\Lambda \frac{Q_{\text{total}}}{N} \sum_{j=1}^{N} \frac{\{F_o(\boldsymbol{k}_j) - F_c(\boldsymbol{k}_j)\} \cdot \exp(-2\pi i \boldsymbol{r} \cdot \boldsymbol{k}_j)}{{\sigma_F}^2(\boldsymbol{k}_j)} \right] \qquad \text{Equation 21}$$

where Λ is an undetermined coefficient.

2.6.2 Structural and orientational determinations of carbon cages

The modelings of orientations of fullerene cages in crystal A-D were carried out by fitting of theoretical rigid C_{82} cage onto the MEM charge density distributions[135]. The theoretical $C_{82}(C_s(6))$ was used in the analyses of crystal A-D. Additionally, the

theoretical $C_{82}(C_s(4))$ was used in the analysis of crystal B due to the assignment of the cage structure of Tm@C_{82}(I). The structural difference between the two isomers is shown in Fig. 10. $C_{82}(C_s(4))$ and $C_{82}(C_s(6))$ have eight independent pentagons and 18 independent hexagons. The eight independent pentagons were fitted to some pentagons seen in the MEM charge density distribution as shown in Fig. 11. When a pentagon of a rigid $C_{82}(C_s(4))$ and $C_{82}(C_s(6))$ molecule is fitted to a pentagon of charge density distribution, there are five possible molecular orientations. When a pentagon is fixed, forty candidates for the molecular orientation are obtained because the cages has eight independent pentagons. The orientation and position of the fitted rigid molecules were refined by the least-square method using the program *SHELX97*[136].

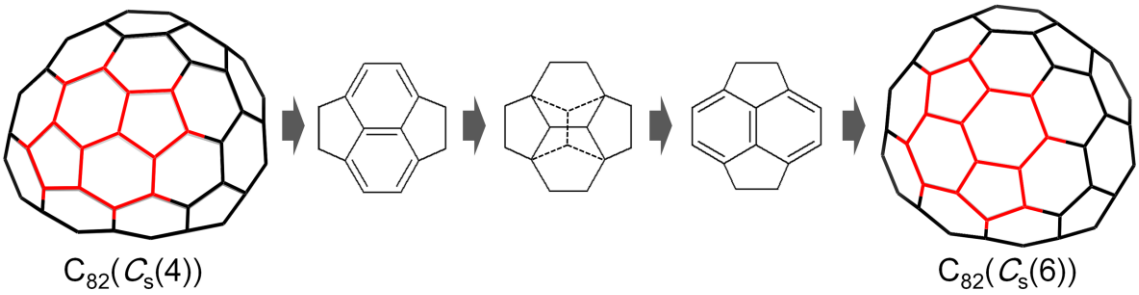


Figure 10. $C_{82}(C_s(4))$ and $C_{82}(C_s(6))$ isomer viewed from perpendicular to the molecular mirror plane. The transformation of the moiety colored in red on $C_{82}(C_s(4))$ cage as following the arrow in the figure gives $C_{82}(C_s(6))$. Note that all of black atoms in both isomers have similar locations and connectivities.

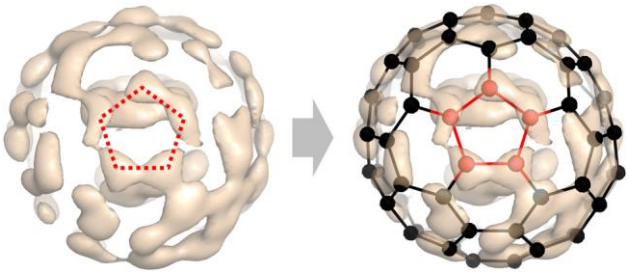


Figure 11. An example of the cage fittings. A pentagon of the rigid fullerene cage is fitted to a pentagon ring seen in the MEM charge density distribution.

3. Results

3.1 Isolation of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$

The separation scheme of $Tm@C_{82}(I)$ is shown in Fig. 12a-c. Figure 12a shows the first-stage HPLC chromatogram on the Buckyprep column. Figure 12b shows the second-stage HPLC chromatogram of fraction a on the Buckyprep M column. Three subfractions, b1 – b3, were obtained at this stage. Fraction b1 contains C_{78} and C_{80}. Fraction b2 contains C_{84}, $Tm@C_{78}$ and C_{82}. And fraction b3 contains $Tm@C_{82}$. Figure 12c shows the third-stage HPLC chromatogram of fraction b3 by recycling on the Buckyprep column. Two fractions, c1 and c2, were obtained at this stage. Fraction c1 contains $Tm@C_{82}(I)$ whereas fraction c2 contains other isomers. Finally at the fourth-stage by 18 recycling of fraction c1 on the Buckyprep column, a small amount of other isomers were completely eliminated and then the isolation of $Tm@C_{82}(I)$ was achieved as shown in Fig. 12d.

The separation scheme of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ is also shown in Fig. 12a and d-f. At first stage, fraction a2 in Fig. 12a is obtained. Figure 12d shows the second-stage HPLC chromatogram of the fraction a2 obtained at the first stage, on the 5PYE column. Five subfractions, d1 – d5, were obtained at this stage. Fraction d1 contains C_{88}, TmC_{84}, TmC_{86}, $Tm_2@C_{82}(I)$, $Tm_2C_2@C_{82}(I)$ and Tm_2C_{86}. Fraction d2 contains C_{90}, TmC_{84}, $Tm_2@C_{82}(II)$, $Tm_2C_2@C_{82}(II)$ and Tm_2C_{84}. Fraction d3 contains C_{90}, TmC_{88}, $Tm_2@C_{82}(III)$ and $Tm_2C_2@C_{82}(III)$. Fraction d4 contains C_{92}, TmC_{88}, and Tm_2C_{84}. Fraction d5 contains C_{90}, TmC_{90}, and Tm_2C_{86}. Figure 12e shows the third-stage HPLC chromatogram of the fraction b1 by recycling on the Buckyclutcher-I column. Two fractions, e1 and e2, were obtained at this stage. Fraction e1 contains C_{88}, TmC_{86}

and Tm_2C_{86} whereas fraction e2 contains TmC_{80}, TmC_{84}, $Tm_2@C_{82}(I)$, and $Tm_2C_2@C_{82}(I)$. Figure 12f shows the fourth-stage HPLC chromatogram of fraction e2 by recycling on the Buckyprep column. Four fractions, f1 – f4, were obtained at this stage. Fraction f1, f2, f3 and f4 contain TmC_{80}, TmC_{84}, $Tm_2C_2@C_{82}(I)$ and $Tm_2@C_{82}(I)$, respectively. Finally by recycling of fraction f3 and f4 on the Buckyprep column for eliminating a small amount of other fullerenes, the isolation of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ were achieved, respectively.

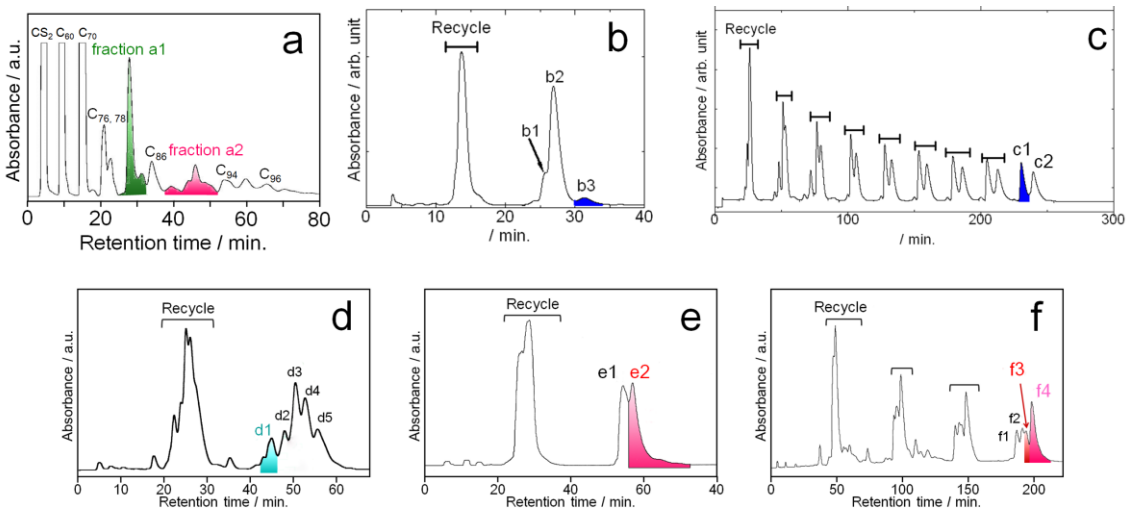


Figure 12. HPLC separation and isolation scheme of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$; (a) HPLC of extract containing thulium metallofullerenes on a Buckyprep column; (b) recycling HPLC of fraction a1 on Buckyprep M column; (c) recycling HPLC of fraction b3 on Buckyprep; (d) recycling HPLC of fraction a2 on 5PYE column; (e) recycling HPLC of fraction d1 on Buckyclutcher-I; (f) recycling HPLC of fraction e2 on Buckyprep column.

Figure 13 shows UV-Vis-NIR and LD-TOF-Mass spectra of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$. The mass spectra of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ on positive / negative mode only have one peak at 1159, 1322 and 1346, respectively. These values are consistent with molecular weights of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and

$Tm_2C_2@C_{82}$(I). The UV-Vis-NIR absorption spectra of the obtained $Tm@C_{82}$(I) is identical with that reported by Kodama and co-workers[82]. The UV-Vis-NIR spectra of $Tm_2@C_{82}$(I) and $Tm_2C_2@C_{82}$(I) are similar to those of $Y_2@C_{82}$(I), $Y_2C_2@C_{82}$(I) and $Er_2@C_{82}(C_s(6))$[23,89]. Thus the isomeric structures of the carbon cages are expected to be $C_{82}(C_s(6))$. The UV-Vis-NIR and mass spectra also ensure the encapsulation of the C_2 unit of $Tm_2C_2@C_{82}$(I).

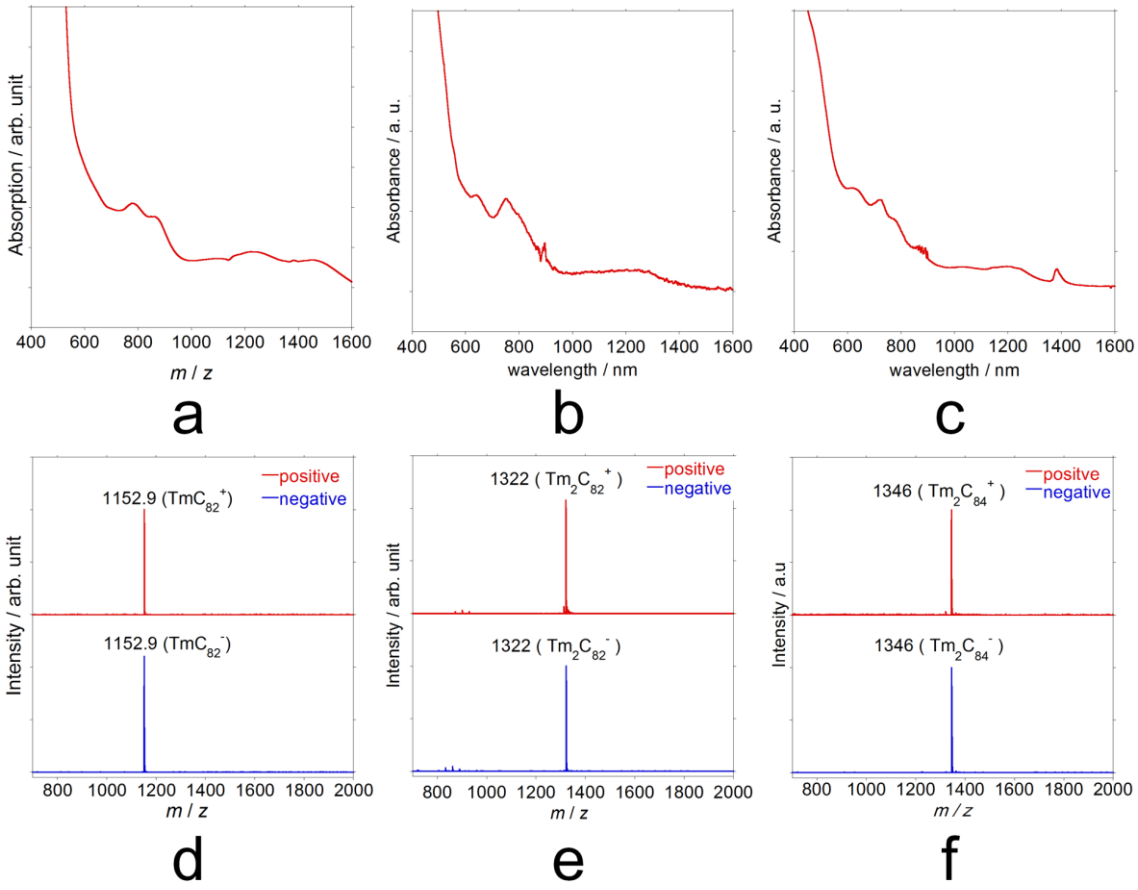


Figure 13. Panels a, b and c are UV-Vis-NIR spectra of $Tm@C_{82}$(I), $Tm_2@C_{82}$(I) and $Tm_2C_2@C_{82}$(I), respectively. Panels d, e and f are LD-TOF mass spectra of positive / negative mode of $Tm@C_{82}$(I), $Tm_2@C_{82}$(I) and $Tm_2C_2@C_{82}$(I), respectively.

3.2 Productions of crystal A-D

3.2.1 Synthesis of crystal A-D

The obtained crystals are shown in Fig. 14. Two types of crystals, crystal A and B, are obtained from synthesis of co-crystal with $Tm@C_{82}(I)$ and Ni(OEP) while one kind of co-crystals with Ni(OEP) of each $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$, which is referred to as crystal C and D, respectively, are obtained. All the resultant co-crystals have black parallelepiped shapes.

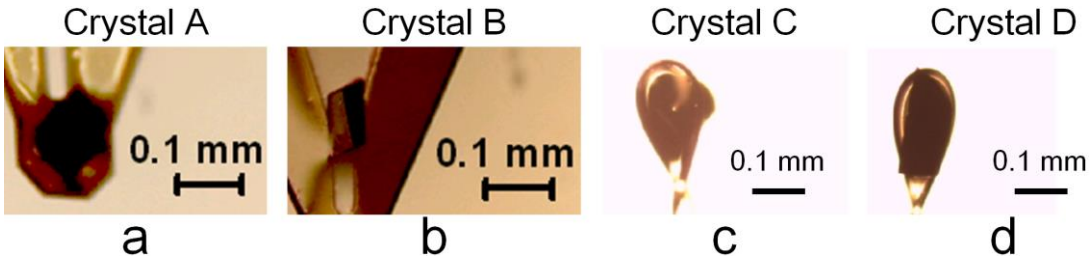


Figure 14. Images of crystal A-D observed by optical microscope.

3.2.2 XRD measurement

$Tm@C_{82}(I)$·Ni(OEP)·1.7$CHCl_3$ (crystal A)

The crystal structure at 50 K was determined as follows: formula weight; 1944, space group; *C*2/*m*, color of crystal; black, unit cell parameters; λ = 0.61900 Å; a = 25.1149(6) Å, b = 15.3088(5) Å, c = 19.6770(2) Å, β = 94.867(4)°; resolution is d > 0.65 Å; $R1$ is 0.1152 ($|F| > 3\sigma$) and wR is 0.3009 ($|F| > 3\sigma$); GOF (on F^2) = 1.903; R_{merge} is 0.0364; Completeness is 0.933; Redundancy is 4.29; Independent reflections are 13857. The crystal information file (CIF) is available from The Cambridge Crystallographic Data Centre (CCDC) with the deposition number, CCDC 904328 (the definitions of d, R1, wR, GOF, Rmerge, Completeness, Redundancy is shown in Apendix).

Tm@C$_{82}$(I)·2Ni(OEP)·2C$_6$H$_5$CH$_3$ (crystal B)

The crystal structure at 190 K was determined as follows: formula weight; 2521, space group; *C*2/*m*, color of crystal; black, unit cell parameters; λ = 0.62029 Å; *a* = 25.4136(5) Å, *b* = 14.9451(3) Å, *c* = 29.001 (1) Å, β = 97.199(3)°; resolution is *d* > 0.60 Å; *R*1 is 0.0728 ($|F| > 3\sigma$) and w*R* is 0.1786 ($|F| > 3\sigma$); GOF (on F^2) = 1.067; R_{merge} is 0.0438; Completeness is 0.901; Redundancy is 3.62; Independent reflections are 24597. The CIF is available from CCDC with the deposition number, CCDC 904327.

Tm$_2$@C$_{82}$(I)·Ni(OEP)·2C$_6$H$_5$Cl (crystal C)

The crystal structure at 200 K was determined as follows: formula weight; 2129, space group; *C*2/*m*, color of crystal; black, unit cell parameters; λ = 0.49521 Å; *a* = 25.405(2) Å, *b* = 14.9223(6) Å, *c* = 20.5026(4) Å, β = 97.312(4)°; resolution is *d* > 0.60 Å; *R*1 is 0.1134 ($|F| > 3\sigma$) and w*R* is 0.2704 ($|F| > 3\sigma$); GOF (on F^2) = 1.371; R_{merge} is 0.0562; Completeness is 0.997; Redundancy is 4.57; Independent reflections are 19195. The crystal information file (CIF) is available from The Cambridge Crystallographic Data Centre (CCDC) with the deposition number, CCDC 918323.

Tm$_2$C$_2$@C$_{82}$(I)·Ni(OEP)·1.9C$_6$H$_5$Cl (crystal D)

The crystal structure at 200 K was determined as follows: formula weight; 2146, space group; *C*2/*m*, color of crystal; black, unit cell parameters; λ = 0.49521 Å; *a* = 25.483(2) Å, *b* = 14.8653(6) Å, *c* = 20.5770(4) Å, β = 97.837(4)°; resolution is *d* > 0.70 Å; *R*1 is 0.1058 ($|F| > 3\sigma$) and w*R* is 0.2502 ($|F| > 3\sigma$); GOF (on F^2) = 1.124; R_{merge} is 0.0952; Completeness is 0.998; Redundancy is 6.46; Independent reflections are 12187. The CIF is available from CCDC with the deposition number, CCDC 918324.

3.2.3 Phase transition

Figure 15 shows a temperature dependence of a SR-XRD pattern of crystal B and C. A phase transition was observed for crystal B and C around 150 K. Diffraction spots that were observed as single peak at 200 K (Fig. 15b and e) were split below 150 K (Fig. 15c and f) due to the phase transition. Crystal A-D have *C*-centered monoclinic lattices with similar lattice constants at 200 K. No phase transition was observed for crystal A from 300 to 50 K. The data collection of crystal D for the crystal structure analyses was performed at 200 K in order to compare the crystal structure with that of crystal C at the same temperature.

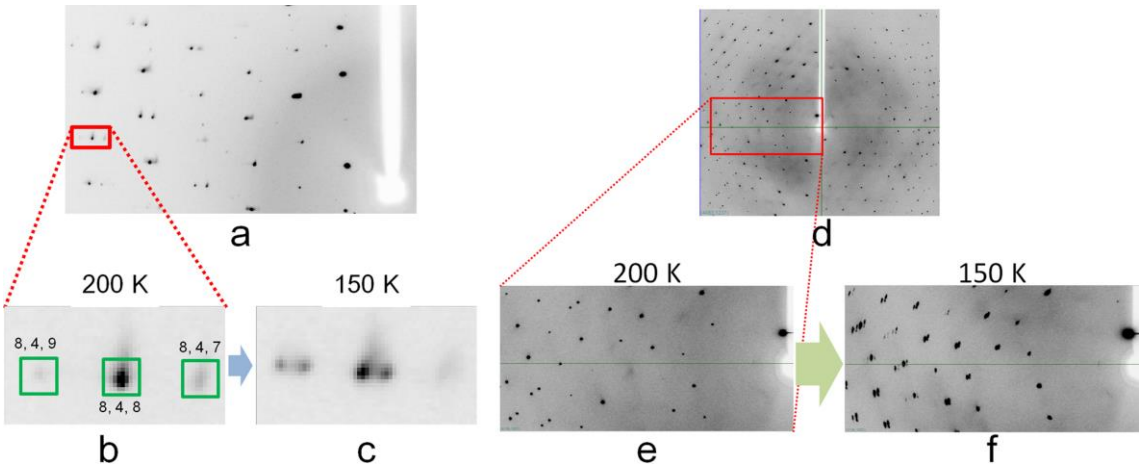


Figure 15. Temperature dependence of a SR-XRD pattern of crystal B and C. Parts of the pattern at 200 K of crystal B and C are shown in Fig. 15a and d, respectively. Panels b (e) and c (f) show the temperature dependence of enlarged Bragg peaks measured at 200 and 150 K of crystal B (C), respectively.

3.2.4 Molecular arrangement

The molecular arrangements in crystal A and B are compared in Fig. 16. In crystal A, double layers of Tm@C_{82}(I) and Ni(OEP) colored in blue are stacked along the *c*-axis. In crystal B, an additional bent Ni(OEP) layers colored in red are inserted between the

double layers. As a result, the length of the *c*-axis of crystal B is about 1.5 times longer than that of crystal A. Both crystals contain solvent molecules at the intermolecular voids of Tm@C_{82}(I) and Ni(OEP). Crystal A contains chloroform molecules, whereas crystal B contains toluene molecules. There are two kinds of voids where the solvent molecules can occupy. One is at an intermolecular position between Tm@C_{82}(I) molecules along the *b*-axis. The other is at an interlayer position between the double layers of Tm@C_{82}(I) and flat Ni(OEP). The molecular arrangement of crystal C and D are almost the same as that of crystal A. Crystal C and D contain two chlorobenzene molecules at intermolecular position between metallofullerene molecules and the intermolecular voids of metallofullerene molecule and Ni(OEP).

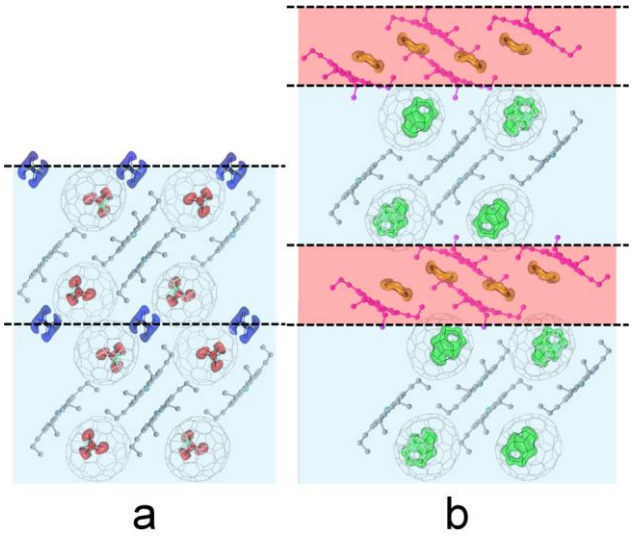


Figure 16. Molecular arrangement of crystal A and B. Panels a and b are the view from the *b* axis of crystal A and B, respectively. Blue layers consist of Tm@C_{82}(I) and flat Ni(OEP). Red layers consist of bent Ni(OEP). Solvent molecules are shown as colored charge density surfaces.

3.3 Crystal structures

3.3.1 MEM charge density distribution

As shown in Fig. 17, the coordination structure of crystal A, C and D, where corresponding metallofullerene molecules are coordinated by a flat Ni(OEP) ligand as shown in Fig. 17a, g and j, are similar to that of other typical *M*(OEP) co-crystals[29,91,97,102]. Tm@C_{82}(I) in crystal B is, in contrast, additionally coordinated by a bent Ni(OEP) molecule as shown in Fig. 17d.

The charge density distributions on the fullerene cages in crystal C and D are almost the same as shown in the figures, suggesting that the fullerene cages have the same isomeric structure and orientation. Very interestingly, the charge density peaks of Tm atoms in crystal D are very similar to those in crystal C (colored in green in Figs. 17e and f). Charge density peaks for the two endohedral carbon atoms (colored in red) are clearly found in crystal D near the barycenter of the fullerene cage.

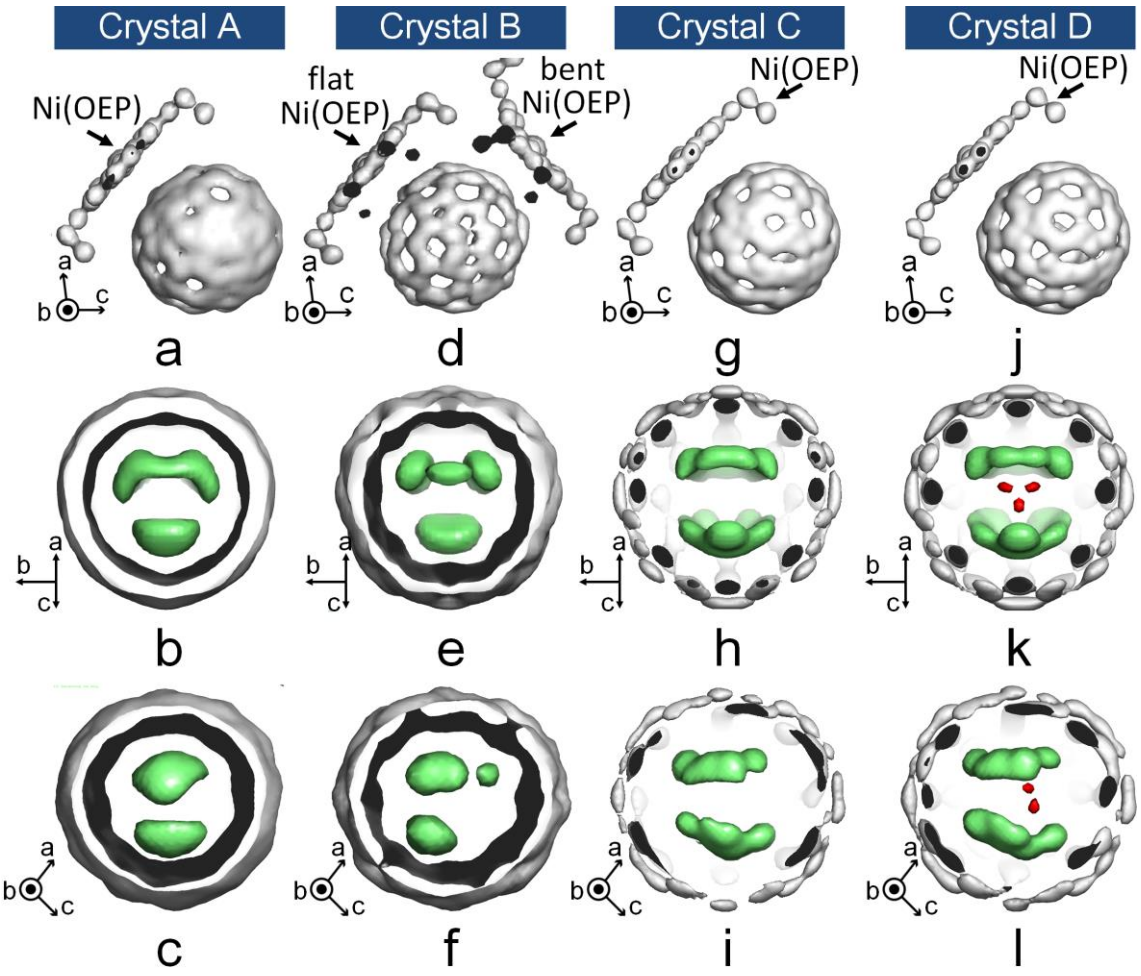


Figure 17. Charge density distributions of crystal A at 210 K (a-c), crystal B at 190 K (d-f), crystal C at 200 K (g-i) and crystal D (j-l) obtained by MEM. Equi-density surfaces for a metallofullerene molecule with a Ni(OEP) at 1.5 eÅ^{-3} are shown in a, d, g, j. Equi-density surfaces for a endohedral cluster at 0.8 eÅ^{-3} are shown in b, c, e and f. Equi-density surfaces for a endohedral cluster at 2.7 eÅ^{-3} are shown in h, i, k and l. The charge density peaks colored in red and green shown in the panels are for the endohedral carbon and Tm atoms, respectively.

3.3.2 Tm positions of crystal A, B, C and D

Refined structure models and charge density surfaces of the encapsulated Tm atom of crystal A, B, C and D are shown in Fig. 18. The disordered charge density distributions were modeled by a Tm atom for crystal A and B and two Tm atoms for

crystal C and D. These Tm atoms partially occupy independent eight (Tm(a1)-(a8)), five(Tm(b1)-(b5)), nine (Tm(c1)-(c9)) and ten (Tm(d1)-(d10)) positions in crystal A, B, C and D, respectively. The barycenter of the carbon cage is on the crystal mirror plane of the *C*2/*m* space group in all the crystals. Thus the number of Tm positions in a carbon cage is totally sixteen, ten, eighteen and twenty in crystal A, B, C and D, respectively. The equivalent Tm positions derived by the mirror symmetry operation are denoted by Tm(a1)'-(a8)' for crystal A, Tm(b1)'-(b5)' for crystal B, Tm(c1)'-(c9)' for crystal C and Tm(d1)'-(d10)' for crystal D. The positions, occupancies and anisotropic atomic displacement parameters of the partially occupied Tm atoms were refined by the least square method. The refined occupancies for crystal A are 0.11, 0.16, 0.04, 0.04, 0.05, 0.03, 0.03 and 0.03 (see Apendix). The refined occupancies for crystal B are 0.17, 0.17, 0.08, 0.03 and 0.05 (see Apendix). The refined occupancies for crystal C are 0.07, 0.08 0.13, 0.12, 0.09, 0.09, 0.20, 0.05 and 0.17 (see Apendix). The refined occupancies for crystal D are 0.13, 0.14, 0.09, 0.08, 0.08, 0.09, 0.19, 0.02, 0.16 and 0.02 (see Apendix).

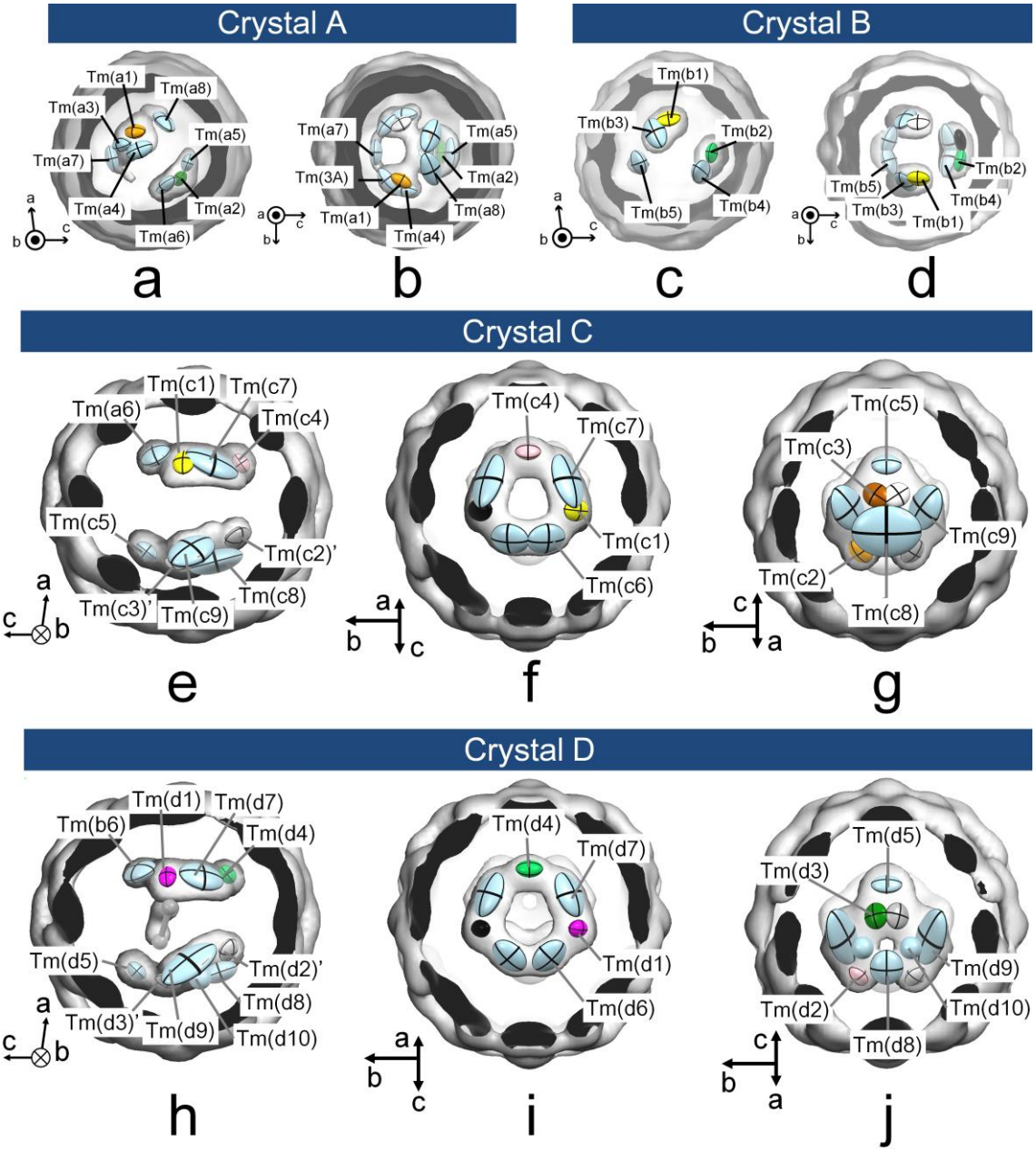


Figure 18. Charge density distributions and Tm atoms shown as ellipsoids at 50 % probability level of crystal A at 50 K (a and b), B at 190 K (c and d) C at 200 K (e-f) and D at 200 K (h-i).

3.3.3 Structure of endohedral C_2 unit in crystal D

As shown in Fig. 17, there are three charge density peaks for two carbon atoms in the middle of the carbon cage (colored in red) in crystal D. The triangular carbon peaks were modeled by disordered endohedral C_2 unit where the carbon atoms are on the corners and the interatomic distances are the same. In order to obtain the plausible C-C distance, geometry giving the smallest isotropic thermal displacement parameter of the carbon atoms was searched. The isotropic thermal displacement parameters of the three (two independent) carbon atoms are the same and refined by a least-square method for the rigid regular triangle carbon cluster.

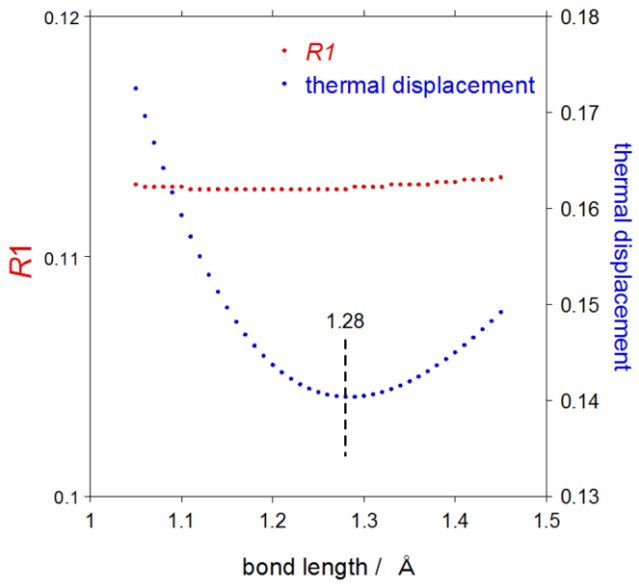


Figure 19. Reliable factors and the refined thermal displacement parameters of the endohedral C_2 unit against the C-C bond length for crystal B.

The reliable factors and the refined isotropic thermal displacement parameters of the carbon atom were plotted against the C-C bond length in Fig. 19. While changes of the reliable factor are negligible, the thermal displacement parameters have the minimum at

where the C-C bond length is 1.28 Å. This C-C bond length is consistent with that of other C_2 endohedral metallofullerenes. The C-C bond length optimized by means of the theoretical calculation is 1.26 Å, which also support that the value determined by XRD is reliable.

3.3.4 Modelling of the molecular orientations in crystals A-D

Modeling of disordered Tm@C_{82}(I) for crystal B

The reliable factors ($|F| > 3\sigma$, $d > 1.0$ Å) of forty C_{82}(C_s(6)) models for crystal B (model 1-40), forty C_{82}(C_s(4)) models for crystal B (model 41-80) and forty C_{82}(C_s(6)) models for crystal A (model 81-120) are summarized in Fig. 20. The model 1 has a remarkably low reliable factor. Thus C_{82}(C_s(6)) is found to be feasible for the cage structure of Tm@C_{82}(I). Further determination of cage orientation of Tm@C_{82}(I) in crystal B was performed by using model 1. The difference MEM charge density distribution, which is obtained by subtracting model MEM charge density distribution from the experimental one suggests existence of an additional C_{82}(C_s(6)) cage with different orientation. The refined two independent carbon cages are referred to as cage b1 and b2. The refined occupancies for cage b1 and b2 are 0.30 and 0.20, respectively. The remaining occupancy of 0.5 is provided by the crystal mirror plane perpendicular to the *b*-axis on the cage center. The carbon cage was treated as a rigid molecule in the refinement to preserve the theoretical interatomic lengths and angles and reduce the number of parameters in the refinement.

The anisotropic displacement parameters of carbon atoms on the fullerene cages were refined by the *TLS* approach in order to obtain physically acceptable parameters and reduce the number of parameters in the refinement[137]. Only two parameters ($T_{11} = T_{22} =$

T_{33} and $L_{11} = L_{22} = L_{33}$) were used in the refinement instead of 984 parameters (6×82×2; 6 U_{ij} parameters of 82 carbon atoms for 2 fullerene cages). An encapsulated Tm atom and solvent molecules were also modeled and refined based on the MEM charge density distribution. The reliable factor of the final model for crystal B at 190 K is $R1$ = 0.0742 (d > 0.60 Å, $|F| > 3\sigma$).

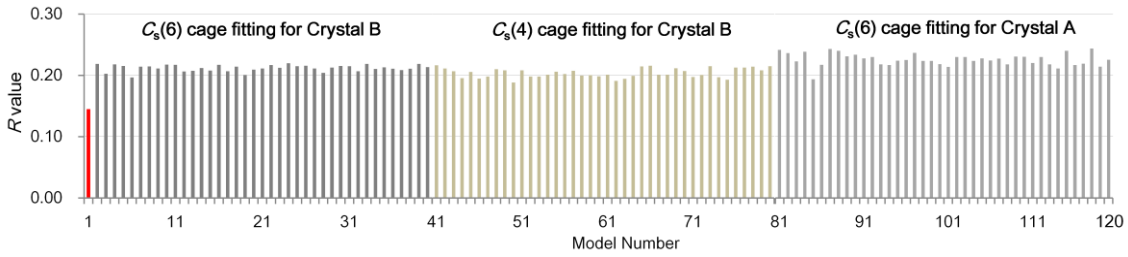


Figure 20. Panel a shows the values of reliable factors (d > 1.0 Å, $|F| > 3\sigma$) of 120 models; C_s(6) cage fittings for crystal B at 190 K (model number: 1-40), C_s(4) cage fittings for crystal B at 190 K (model number: 41-80) and C_s(6) cage fittings for crystal A at 210 K (model number: 81-120).

As shown in Fig. 21, eight possible positions are suggested for the Tm atom in the $C_{82}(C_s(6))$ cage from the present result because the endohedral Tm atom mainly occupies four positions (Tm(b1), Tm(b2) and the equivalent positions, Tm(b1)' and Tm(b2)') inside the $C_{82}(C_s(6))$ carbon cage. The four Tm positions relative to cage b1 are different from that relative to cage b2. On the other hand, the stable Tm position should be on the molecular mirror plane of $C_{82}(C_s(6))$ because Tm@C_{82}(I) molecule also has C_s symmetry[82]. The disorder of Tm atom is explained by an overlap of Tm@$C_{82}(C_s(6))$ where the Tm atom occupies only one stable position on the molecular mirror plane.

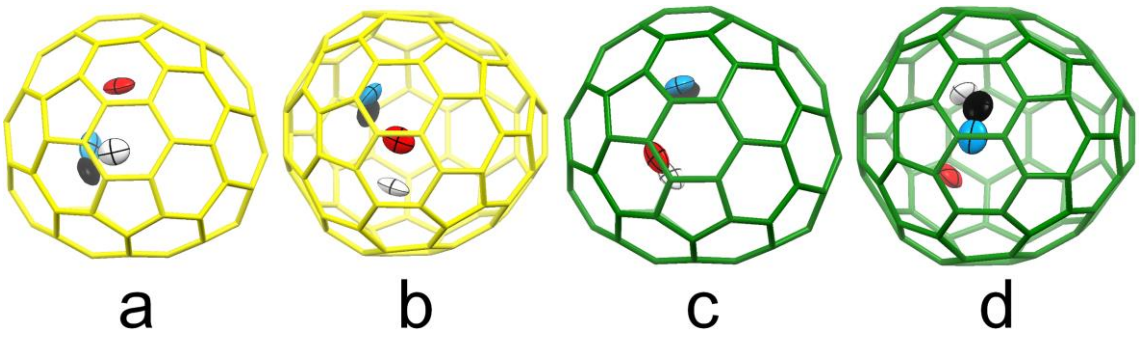


Figure 21. Possible Tm positions in $C_{82}(C_s(6))$ cage in crystal B. Only the major four Tm positions, Tm(b1) (red), Tm(b2) (waterblue) and the equivalent mirror sites, Tm(b1)' (white) and Tm(b2)' (black) are shown. The Tm positions in cage b1 shown in a and b are different from that in cage b2 shown in c and d. Panels a and b (c and d) are views perpendicular and parallel to the molecular mirror plane of cage b1 (b2), respectively.

Modeling of disordered Tm@C_{82}(I) for crystal A

Molecular structure of crystal A at 50 K was determined based on the structure of crystal B at 190 K. Position of Tm@C_{82}(I) relative to Ni(OEP) in crystal A is similar to that relative to flat Ni(OEP) in crystal B as shown in Figs. 17a and d. Although the charge density distribution on the fullerene cage of crystal A is more uniform than that of crystal B, the relative positions of carbon rings and Tm peaks seen in the charge density surface are also similar between crystal A and B. Hence the fullerene cage of crystal A has a disordered structure of Tm@C_{82}(I) similar to that found in crystal B. Two independent carbon cages used in the analysis of crystal A are referred to as cage a1 and a2. The occupancy, position, orientation, *T* and *L* parameters of the two rigid carbon cages were refined by the least-square method. The refined occupancies of cage a1 and a2 are 0.27 and 0.23, respectively, which are similar to those of cage b1 and b2 in crystal B. An encapsulated Tm atom and solvent molecules were also modeled and refined based on the MEM charge density distribution.

Modeling of disordered Tm@C_{82}(I) for crystal C and D

The modeling of orientations of the fullerene cage for crystal C and D were the same as that of crystal B. In the modeling, C_{82}(C_s(6)) were used. The reliable factors ($|F| > 3\sigma$, d > 1.0 Å) of forty C_{82}(C_s(6)) orientations for crystal C (model c1 – c40) and crystal D (model d1 – d40) are summarized in Fig. 22. The cage orientations of model c1 and d1 for crystal C and D, respectively, have the lowest reliable factors. Model c1 and d1 are hereafter referred as cage c1 and d1, respectively.

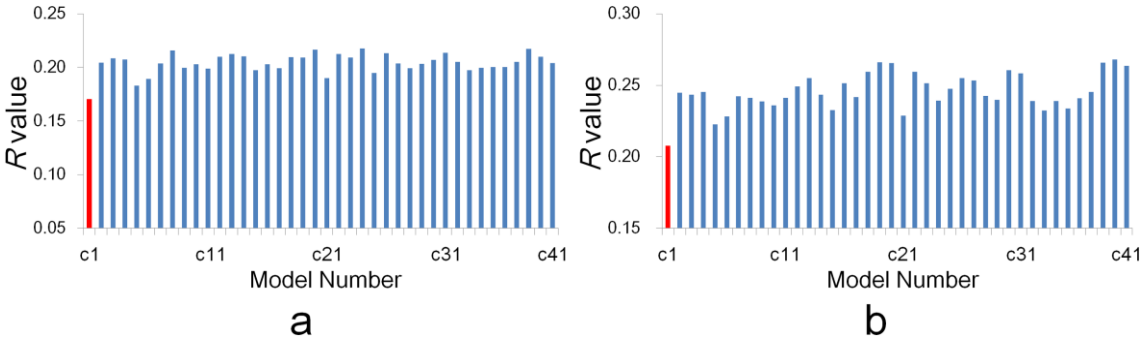


Figure 22. Reliable factors ($|F| > 3\sigma$, d > 1.0 Å) of forty C_{82}(C_s(6)) orientations for a: crystal C and b: crystal D.

Three candidates of the molecular structures were suggested from cage c1 and d1 for Tm_2@C_{82}(I) and Tm_2C_2@C_{82}(I), respectively, as shown in Fig. 23. Tm_2@C_{82}(I) and Tm_2C_2@C_{82}(I) should possess C_s symmetry because UV-Vis-NIR spectra of both molecules are similar to that of Y_2C_2@C_{82}(I), whose molecular symmetry has been assigned as C_s symmetry by means of ^{13}C-NMR[23]. Therefore two Tm atoms of both Tm_2@C_{82}(I) and Tm_2C_2@C_{82}(I) should be (i) both on the molecular mirror plane of C_{82}(C_s(6)) or (ii) on the two positions whose perpendicular bisector plane coincides with the molecular mirror plane. The combinations of Tm positions shown in Fig. 23 that nearly satisfy C_s symmetry in cage c1 for Tm_2@C_{82}(I) are (i) Tm(c1) and Tm(c2)

(candidate c1), (ii) Tm(c1)' and Tm(c5) (candidate c2), and (iii) Tm(c7)' and Tm(c9) (candidate c3) as shown in Figs. 23a-f. As well, the combinations of Tm positions shown in Fig. 18e-j that nearly satisfy C_s symmetry in cage d1 for $Tm_2C_2@C_{82}(I)$ are (i) Tm(d1) and Tm(d2) (candidate d1), (ii) Tm(d1)' and Tm(d5) (candidate d2), and (iii) Tm(d7)' and Tm(d9) (candidate d3) as shown in Figs. 23g-l.

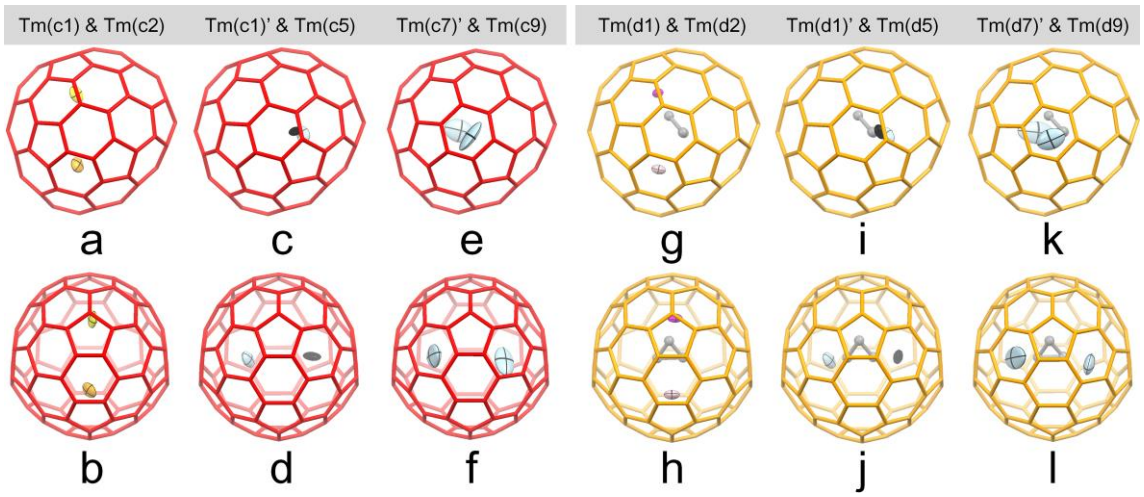


Figure 23. Three candidates of the molecular structures for $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$. a,b: candidate c1, c,d: candidate c2, and e,f: candidate c3 for $Tm_2@C_{82}(I)$. g,h: candidate d1, i,j: candidate d2, and k,l: candidate d3 for $Tm_2C_2@C_{82}(I)$. Upper and lower panels are views perpendicular and parallelel to the molecular mirror plane of the $C_{82}(C_s(6))$, respectively.

The remaining Tm positions that do not satisfy C_s symmetry in cage c1 and d1 should be explained by orientational disorder of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ with C_s symmetry. The MEM charge density distributions on the carbon cage of both crystal C and D also suggest orientational disorder of the carbon cage. In order to explain the disorder of Tm atoms and the charge density distribution of carbon cage, an additional carbon cage with different orientation should be introduced in the structure model. The

most reliable orientation of the additional carbon cage was investigated under a condition where the Tm positions in the additional carbon cage satisfy the C_s symmetry.

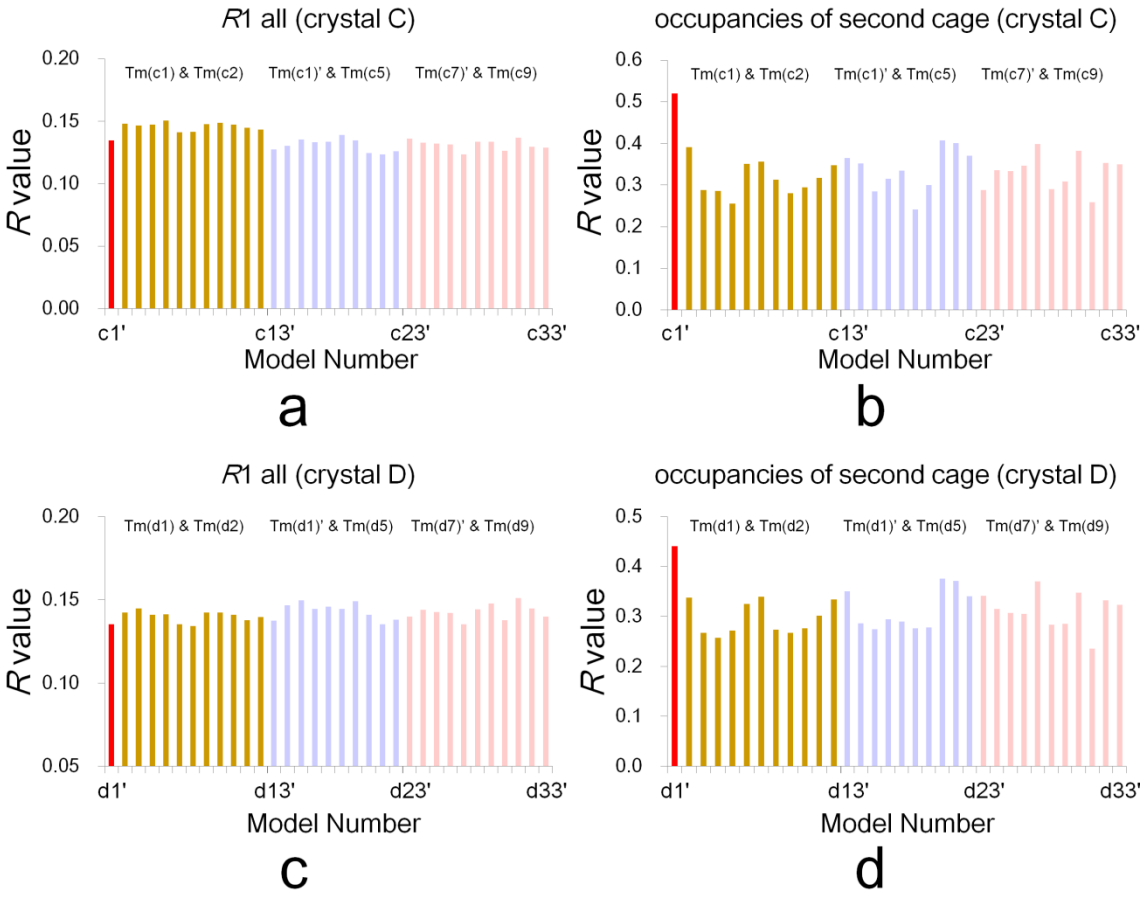


Figure 24. (a) Reliable factors ($|F| > 3\sigma$, $d > 0.6$ Å) and (b) refined occupancies of the additional cage of model c1' – c33' for $Tm_2@C_{82}(I)$. (c) Reliable factors ($|F| > 3\sigma$, $d >$ 0.7 Å) and (d) refined occupancies of the additional cage of model d1' – d33' for $Tm_2C_2@C_{82}(I)$.

Figure 24 shows the reliable factors and refined occupancies of the additional cage for thirty-three models for both crystal A and B. The structure models are denoted as c1'-c33' for crystal A and d1'-d33' for crystal B. While only a little differences of reliable factors exist among the models, we concluded that the model c1' and d1' are the

most reliable for crystal C and D, respectively, because they obviously have the highest ccupancies. Model c1' and d1' are hereafter referred as cage c2 and d2, respectively.

Tm positions shown in Figs. 18e-g relative to the two cages for $Tm_2@C_{82}(I)$ are shown in Figs. 25a and b, respectively. The cage orientations are consistent in the figure. Tm positions shown in Figs. 18h-j relative to the two cages in model b1' for $Tm_2C_2@C_{82}(I)$ are also shown in Figs. 25d and e, respectively. In Fig. 25, Tm(c8), Tm(d8) and Tm(d10) are ommited due to the relatively lower occupancies compared to the others. Figure 25c and f show the overlapped image of Fig. 25a and b, and 25d and e, respectively, where the barycenters and orientations of each fullerene cage coincide with each other. In Fig. 25c, four magenta Tm positions of Fig. 25a coincide with four yellow Tm positions of Fig. 25b. Also in Fig. 25f, four green Tm positions of Fig. 25d coincide with four orange Tm positions of Fig. 25e. If the molecular structure is not affected by the molecular orientation in the crystals, these Tm positions are more probable than the others. Futhermore, if the molecules have C_s symmetry, only the Tm positions that nearly satisfies C_s symmetry are acceptable. The acceptable Tm positions for $Tm_2@C_{82}(I)$ are only two blue ones on the molecular mirror plane in Fig. 25c. The $Tm_2@C_{82}(I)$ structure with the two Tm positions is exactly the same with candidate c1 shown in Fig. 23a and b. Also the acceptable Tm positions for $Tm_2C_2@C_{82}(I)$ are only two red ones on the molecular mirror plane in Fig. 23f. The $Tm_2C_2@C_{82}(I)$ structure with the two Tm positions is exactly the same with candidate d1 shown in Fig. 23g and h. Therefore the candidates c1 and d1 are the most feasible for the molecular structures of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$, respectively, in the analyses. The other Tm positions in Fig. 18c and f would be explained by the other molecules that coexist with different orientations.

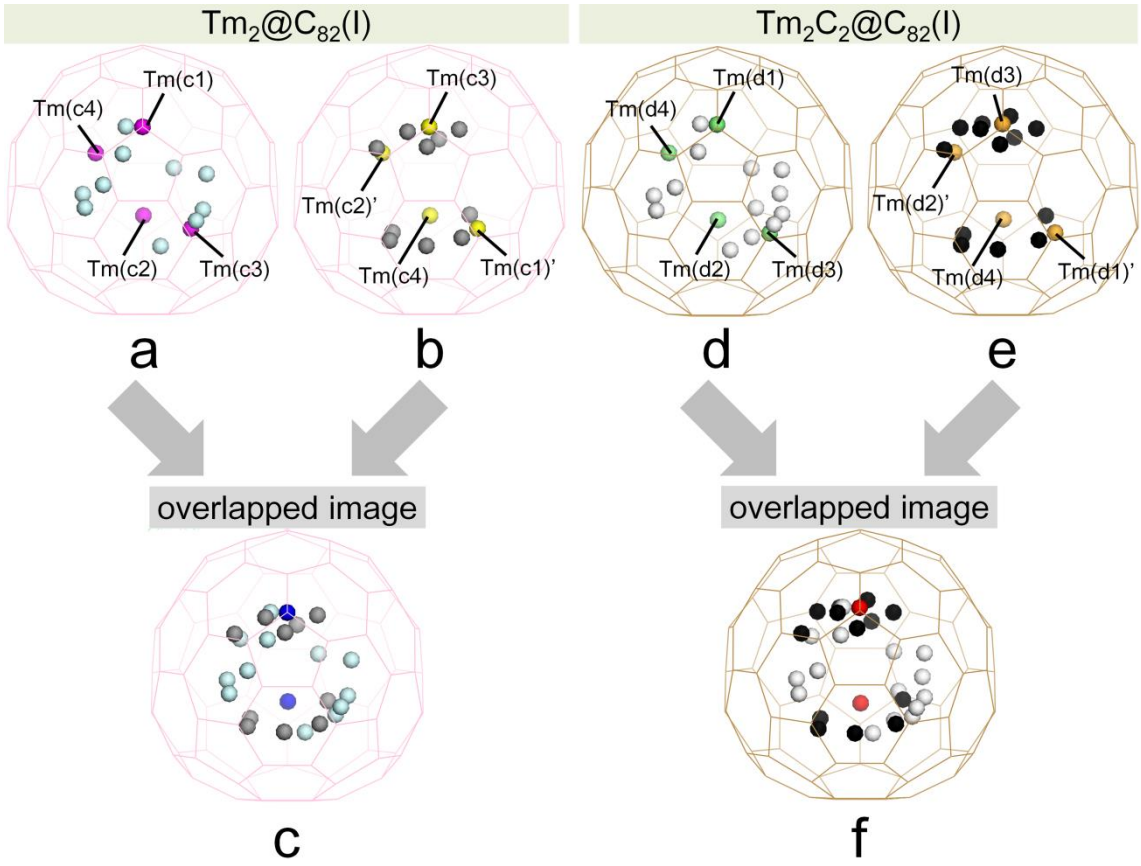


Figure 25. a and b: the Tm positions in cage c1 and c2 for $Tm_2@C_{82}(I)$ relative to the two cages, respectively. d and e: the Tm positions in cage d1 and d2 for $Tm_2C_2@C_{82}(I)$ relative to the two cages, respectively. Panels a and b (d and e) are overlapped in panel c (f). The barycenters and orientations of each fullerene cage coincide with each other in the figures. Four magenta Tm positions of panel a coincide with four yellow ones of panel b. Of the four coincided Tm positions, two positions nearly on the molecular mirror plane are colored in blue in panel c. Four green Tm positions of panel d coincide with four orange ones of panel e. Of the four coincided Tm positions, two positions nearly on the molecular mirror plane are colored in red in panel f.

Structure candidates c1-c3 for $Tm_2@C_{82}(I)$ and d1-d3 for $Tm_2C_2@C_{82}(I)$ are geometrically optimized by means of density functional B3LYP/SV(P) calculations. The calculations for candidates c2 and d2 were diverged, while those for candidates c1, c3, d1 and d3 could obtain converged geometries. The theoretical structure calculated

for candidate c1 (d1) is more stable than that for c3 (d3). The energy difference between c1 and c3 is 6.2 kcal/mol. This results strongly support that two Tm atoms selectively occupy positions on the molecular mirror plane of $C_{82}(C_s(6))$ in candidate c1 and d1. From the energy difference, the two Tm atoms can not occupy positions displaced from the molecular mirror plane in candidate c3 and d3 by the thermal excitation at 200 K and, possibly even at room temperature.

Figure 26 shows the endohedral C atoms, shown in Fig. 17, relative to cage d1 and d2. Although the candidates of the carbon positions are three in cage d1 and d2, one of the three carbon positions are unusually close (~1.3 Å) to one Tm atom in each cage. Also the other two carbon positions of each carbon cage maintain C_s symmetry. Therefore the structure of the endohedral C2 unit was determined in each cage. The three carbon atoms in Fig. 17 can be explained overlapping of the two determined $Tm_2C_2@C_{82}(I)$ molecules.

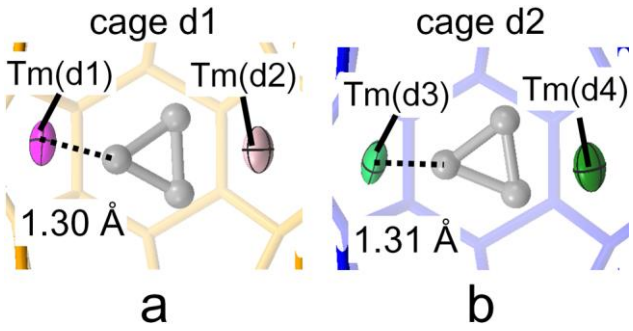


Figure 26. Three-disordered endohedral C atoms and a) Tm(d1) and Tm(d2) in cage d1; b) Tm(d3) and Tm(d4) in cage d2.

3.4 Molecular structures of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$

The occupancies of metal atoms and cages in each crystal are summarized in Apendix.

$Tm@C_{82}(I)$

The molecular structure of $Tm@C_{82}(I)$ derived from crystal A and B are shown in Figs. 27a-b and c-d, respectively. Only the molecular sturctures consisting of cage a1 and Tm(a1), and cage b1-Tm(b1) are shown in the figures. The cage structure of $Tm_2@C_{82}(I)$ was found to be $C_{82}(C_s(6))$. The encapsulated Tm atom occupy only the specific position on the molecular mirror plane of the $C_{82}(C_s(6))$ cage.

$Tm_2@C_{82}(I)$

The molecular structure of $Tm_2@C_{82}(I)$ is shown in Figs. 27e and f. Only the molecular sturctures consisting of cage c1, Tm(c1) and Tm(c2) are shown in the figures. The cage structure of $Tm_2@C_{82}(I)$ was found to be $C_{82}(C_s(6))$. The two encapsulated Tm atoms occupy only the specific positions on the molecular mirror plane of the $C_{82}(C_s(6))$ cage.

$Tm_2C_2@C_{82}(I)$

The carbon cage structure is also $C_{82}(C_s(6))$ and the Tm positions are similar to those of $Tm_2@C_{82}(I)$. Figures 27g and h depict the molecular structure of $Tm_2C_2@C_{82}(I)$ consisting of cage d1, Tm(d1) and Tm(d2). The Tm positions of $Tm_2C_2@C_{82}(I)$ are similar to but slightly different from those of $Tm_2@C_{82}(I)$ as discussed later. The two endohedral carbon atoms of $Tm_2C_2@C_{82}(I)$ located around the barycenter of the cage are displaced from the molecular mirror plane as shown in Figs. 27g and h.

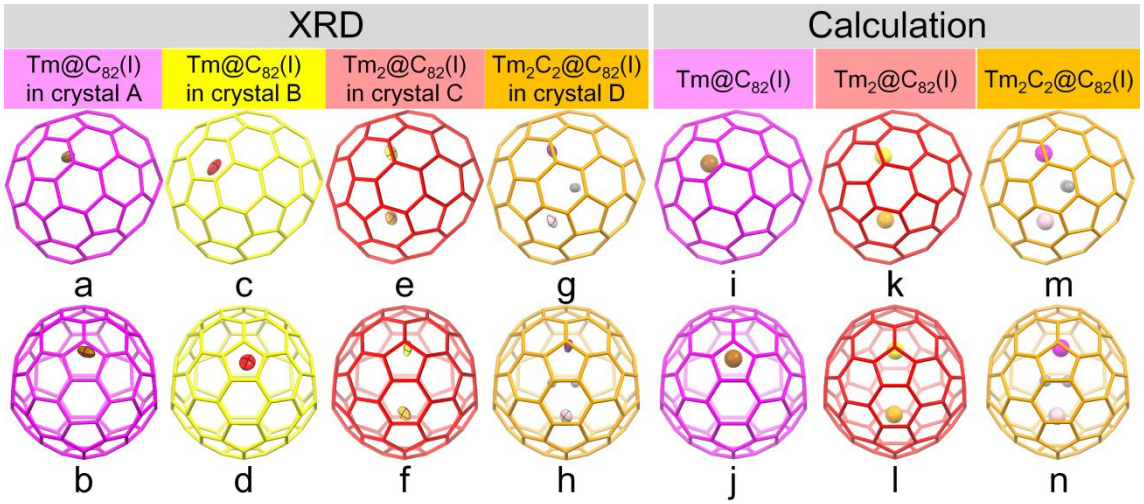


Figure 27. Experimentally determined molecular structures of $Tm@C_{82}(I)$ in crystal A (a and b), $Tm@C_{82}(I)$ in crystal B (c and d), $Tm_2@C_{82}(I)$ in crystal C (e and f) and $Tm_2C_2@C_{82}(I)$ in crystal D (g and h). The theoretical structures of $Tm@C_{82}(I)$ (i and j), $Tm_2@C_{82}(I)$ (e and f) and $Tm_2C_2@C_{82}(I)$ (g and h) are also shown[138]. Tm positions of $Tm@C_{82}(I)$ in crystal A and B, Tm(a1) and Tm(b1), are colored in brown and magenta, respectively, in panels a and b, and c and d. Two Tm positions of $Tm_2@C_{82}(I)$, Tm(c1) and Tm(c2), are colored in yellow and orange, respectively, in panel e and f. Two Tm positions of $Tm_2C_2@C_{82}(I)$, Tm(d1) and Tm(d2), are colored in magenta and pink, respectively, in panel g and h. Endohedral carbon atoms of $Tm_2C_2@C_{82}(I)$ are colored in gray in panel g and h. Panels a, c, e, g, i , k and m (b, d, f, h, j, l and n) are views perpendicular (parallel) to the molecular mirror plane of the $C_{82}(C_s(6))$ fullerene cage.

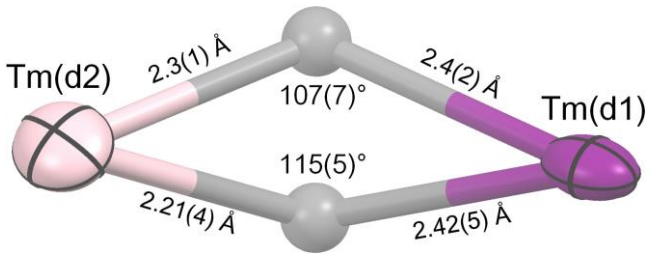


Figure 28. Geometry of the Tm_2C_2 cluster of $Tm_2C_2@C_{82}(I)$. Tm atoms are shown as thermal ellipsoids at 50 % probability level.

The positions of the two carbon atoms perpendicularly projected on the molecular mirror plane are almost identical within a differenece of 0.28 Å. The C-C bond length is

determined as 1.28 Å. The C-C bond length is similar to those of $Y_2C_2@C_{82}(C_{3v}(8))$ (1.3(1) Å), $Sc_2C_2@C_{82}(C_{3v}(8))$ (1.3 Å), where both values are determined by powder X-ray diffraction together with a theoretical value of 1.27 Å for $Y_2C_2@C_{92}(D_3(85)$[22,139].

The endohedral Tm_2C_2 cluster has a butterfly shape as shown in Fig. 28, which shows the geomeric details of the Tm_2C_2 cluster in $Tm_2C_2@C_{82}$(I). The butterfly-shape M_2C_2 clusters have been found in $Sc_2C_2@C_{82}(C_{3v}(8))$ and $Y_2C_2@C_{82}(C_{3v}(8))$[22,140,141]. The four Tm-C bond lengths are within a range from 2.2 to 2.4 Å. The bond lengths are comparable to the typical Tm-C bond length in thulium carbide compounds (2.4 – 2.6 Å)[142,143].

Theoretical results

The theoretical structure of $Tm@C_{82}$(I) optimized in DFT calculation has been reported by Zheng et al. as shown in Fig. 27i and j[138]. The experimentally determined $Tm_2@C_{82}$(I) and $Tm_2C_2@C_{82}$(I) molecular structures were reoptimized in DFT calculations as shown in Figs. 27k, l, m and n.

3.5 The complex of Ni(TPP) dimer and metallofullerenes

3.5.1 Synthesis of Ni(TPP) dimer

Synthesis of 5- (4- nitrophenyl) - 10, 15, 20- triphenylporphyrin (TPP-NO_2)

TPP-NO_2 was prepared by the method of Rochford et al[144]. 1 g of 5, 10, 15, 20-tetraphenylporphyrin was dissolved in 150 ml of dry dichloromethane in round-bottomed flask fitted with additional funnel and argon inlet. The solution was purged with argon for 10 min. and 8.6 ml of dichloromethane was put into additional funnel followed by 1.4 ml fuming nitric acid and purged with argon for 10 min. The reaction flask and the additional funnel were maintained under an argon atmosphere. The nitric acid solution in additional funnel was added dropwise to the porphyrin

solution for a period of 2 hours at 0°C with vigorous stirring. During this addition, the porphyrin solution color changed from purple to green. The solution was then neutralized by addition of 20 g of $NaHCO_3$, thus the solution color changed from green to purple. The solid was removed by filtration followed by evaporation of the solvent. Over 1 g of crude product was obtained. The entire product was used for further synthesis without any purification.

The ESI mass spectrum is shown in Figure 29. There are three peaks at 615, 660 and 705. The peak at 660 suggests TPP-NO_2 was synthesized.

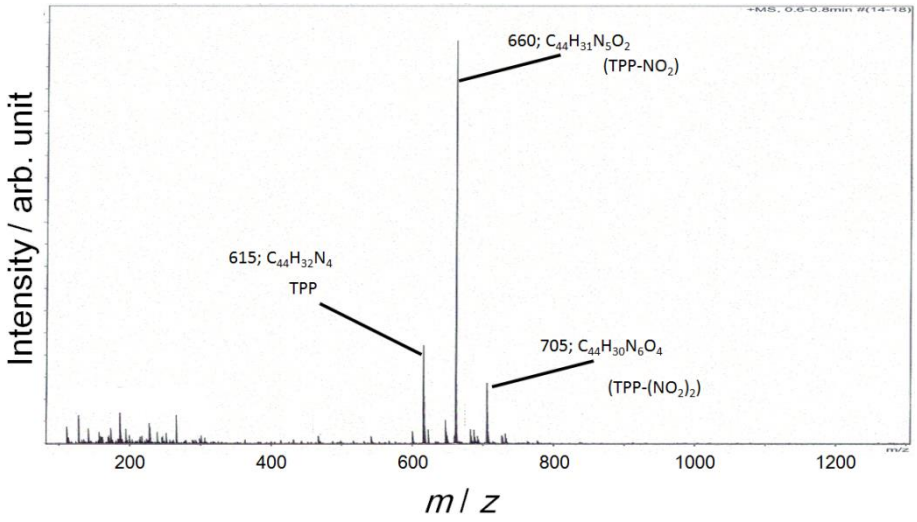


Figure 29. The ESI mass spectrum of the synthesized TPP-NO_2.

Synthesis of 5- (4- aminophenyl), 10, 15, 20- triphenylporphyrin (TPP-NH_2)

TPP-NH_2 was prepared by the method of Tay et al[145]. All the produced TPP-NO_2 was dissolved in 200 ml of 20% hydrochloride aqua solution followed by added 2.2 g of $SnCl_2$ and stirred for 1 hour at 65°C. The solution was poured into 100 ml of water and neutralized by NH_4OH until pH 8. The product was extracted by dichloromethane until colorless and washed saturated NaCl aq followed by dried $MgSO_4$ and separated by

silica chromatography eluted by CH_2Cl_2. After isolating and evaporating TPP-NH_2**,** its yield was 720 mg.

The ^{1}H-NMR and ESI mass spectrum are shown in Fig. 30. The peak at 630 derived from TPP-NH_2 was observed in the ESI spectrum. The broad peak at 3.9 ppm in the ^{1}H-NMR is derived from H atom on N because this broadness is caused by hydrogen bonding.

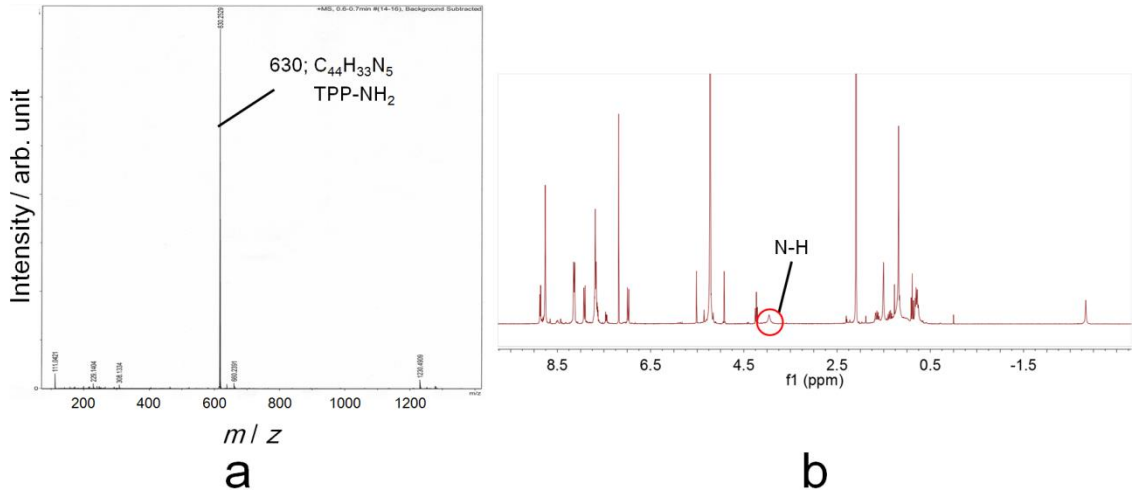


Figure 30. Panels a and b shows ESI mass spectrum and ^{1}H – NMR spectrum of the produced TPP-NH_2, respectively.

Synthesis of 5- (4- aminophenyl), 10, 15, 20- triphenylporphyrin nickel(II) (Ni(TPP)-NH_2)

100 mg of TPP-NH_2 dissolved in 10 ml of dry dichloromethane was added to Ni(OAc)2 dissolved in 10 ml of dry methanol under argon atmosphere followed by refluxed for five days at room temperature. The product was purified by silica chromatography eluted by dichloromethane. The product was then evaporated and 44 mg of Ni(TPP)-NH_2 was obtained.

ESI mass and ^{1}H-NMR spectrum are shown in Fig. 31. The peak at 686 derived from Ni(TPP)-NH_2 was observed in the ESI spectrum. All the peaks in ^{1}H-NMR spectrum are

broadened due to the magnetism of nickel.

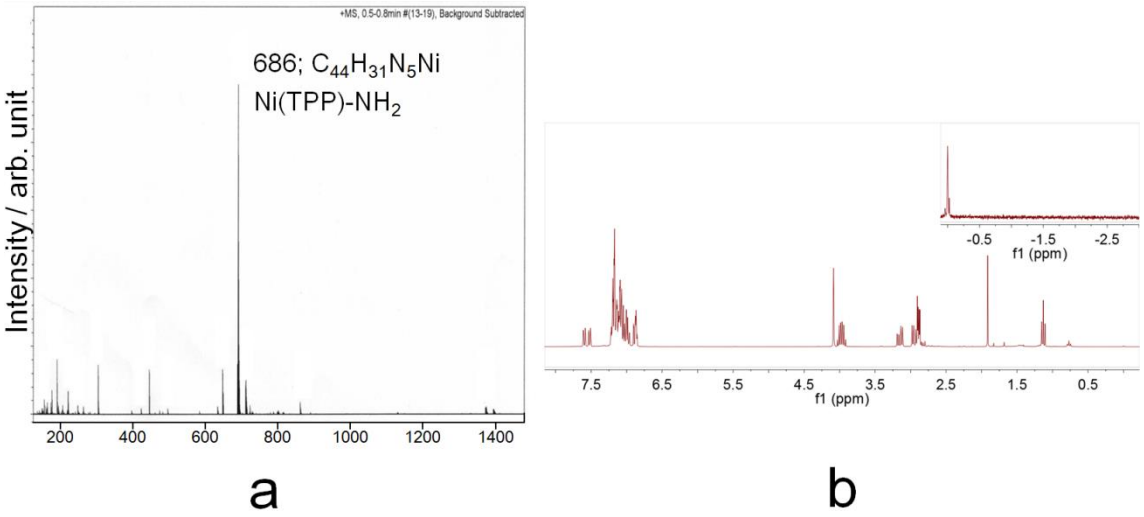


Figure 31. Panels a and b show ESI mass spectrum and ^1H – NMR spectrum of the produced Ni(TPP)-NH_2, respectively.

Synthesis of compound "Ni TPP dimer"

To a solution of 50 mg of Ni(TPP)-NH_2 and 4-dimethylaminopyridine dissolved in 20 ml of dichloromethane, a solution of isopthaloyl chloride in dichloromethane was added dropwise over a period of two hours using additional funnel. The resulting solution was stirred for 24 hours and then was concentrated under reduced pressure. The residue was dissolved in dichloromethane and then washed with saturated NaCl aq. followed by dried over $MgSO_4$. The product was evaporated and 28 mg of Ni(TPP)-NH_2 dimer was obtained.

ESI mass and UV-Vis-NIR spectrum is shown in Fig. 32. The peak at 1502.5 in Fig. 29a suggests Ni(TPP) dimer was synthesized. Figure 29b has two strong peaks at 418 nm and 528 nm called Soret band and Q band, respectively. This fact strongly suggests the molecule has a porphyrin ring.

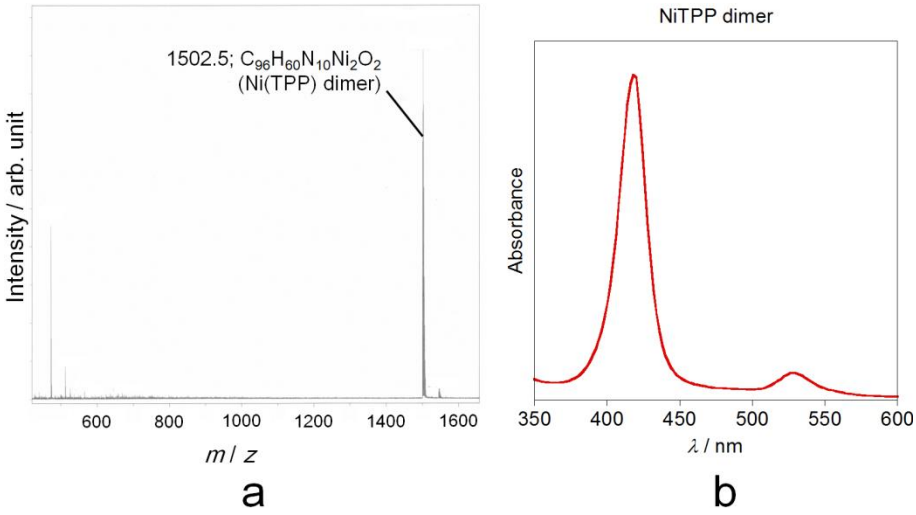


Figure 32. ESI mass spectrum of the produced Ni(TPP) dimer.

3.5.2 Association of Ni(TPP) dimer and metallofullerenes

Figs. 33a, b, c, d, and e show the UV-Vis spectra of Ni(TPP) dimer upon successive addition of C_{60}, C_{70}, C_{76}, Ce@C_{82}(I) and Tm@C_{82}(I), respectively. In the titration, every 100 µl of these (metallo)fullerenes in toluene (conc.; 2.0×10^{-6} mol · l^{-1}) are injected into 1 ml of Ni(TPP) dimer in dichloromethane (conc.; 2.0×10^{-5} mol · l^{-1}). The Soret band is slightly shifted in each titration. The peak shift amount of Soret band in case of 1:1 titration of NiTPP dimer with C_{60}, C_{70}, C_{76}, Ce@C_{82}(I) and Tm@C_{82}(I) are 0.2 nm, 0.3 nm, 0.5 nm, 0.5 nm and 0.5 nm, respectively. This fact strongly supported that these five fullerenes are associated with Ni(TPP) dimer. Furthermore Tm@C_{82}(I), Ce@C_{82}(I), and C_{76} can interact with Ni(TPP) dimer more strongly than C_{60} and C_{70}.

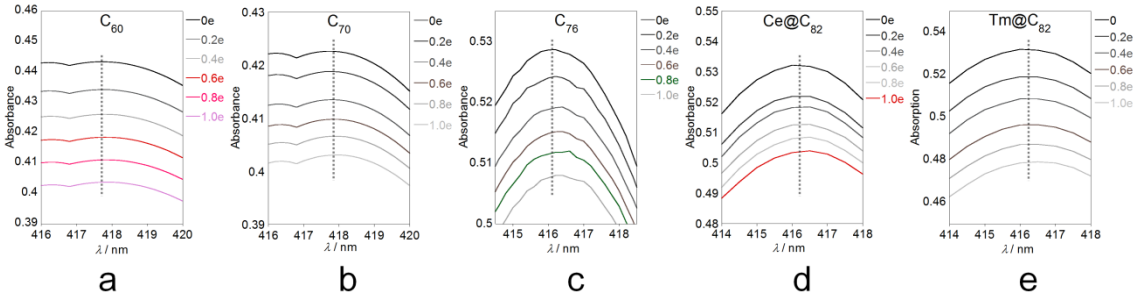


Figure 33. UV-Vis spectra of Ni(TPP) dimer upon successive addition of a) C_{60} b) C_{70} c) C_{76} d) Ce@C_{82}(I) e) Tm@C_{82}(I)

3.5.3 Crystallization of complex Ni(TPP) dimer and Tm@C_{82}(I)

Table 3 shows the result of the crystallization of the complex Ni(TPP) dimer and Tm@C_{82}(I). The precipitates were observed with an optical microscope (LEICA DM 2500 M). Only the case in the crystallization that good solvent is THF and poor solvent is methanol generated some solids whereas the others generate mud-like precipitates.

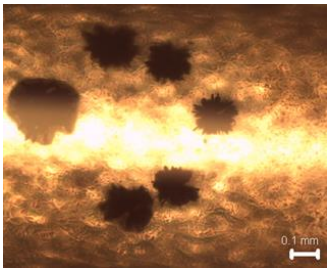


Figure 34. The optical microscope image of the crystal obtained by the case that good solvent is THF and poor solvent is methanol.

Table 3. The crystal qualities at all the combinations of good/poor solvents. "×" means mud-like precipitate.

		poor solvent				
		MeOH	EtOH	CH_3CN	hexane	acetone
good solvent	toluene	×	×	×	×	×
	$CHCl_3$	×	×	×	×	×
	CH_2Cl_2	×	×	×	×	×
	THF	Multi-crystal	×	×	×	×

Figure 34 shows the image of the crystal obtained by the case that good solvent is THF and poor solvent is methanol. Clusters consisting of needle crystals were observed, which are not obviously single crystal.

4. Discussion

4.1 Tm atom positions of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$, and $Tm_2C_2@C_{82}(I)$

Figure 35 shows that the Tm positions of $Tm@C_{82}(I)$ in crystal A (Tm(a1)), $Tm_2@C_{82}(I)$ in crystal C (Tm(c1) and Tm(c2)) and $Tm_2C_2@C_{82}(I)$ in crystal D (Tm(d1) and Tm(d2)) are contrastively, where these metallofullerenes are under the same condition that one Ni(OEP) is attached on each metallofullerene. The barycenters are shown as green crosses, and orientations of each fullerene cage coincide with each other.

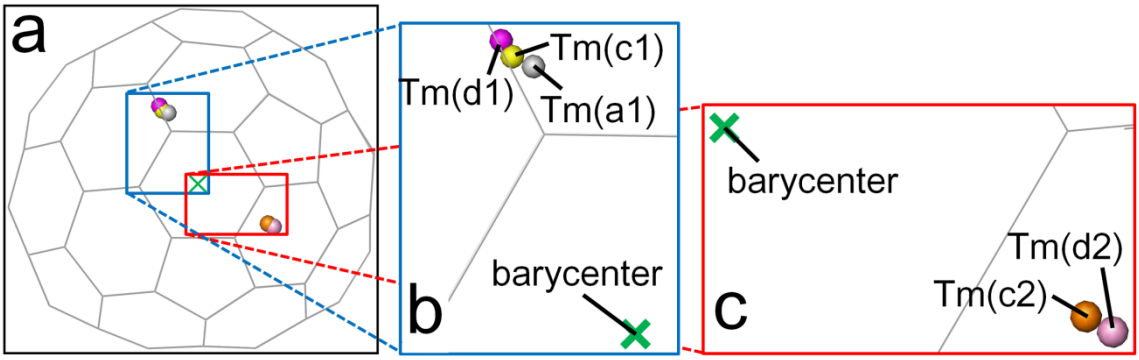


Figure 35. a) Overlapped Tm positions of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$. The barycenters (green cross) and orientations of $C_{82}(C_s(6))$ are coincided in the figure. Tm(a1) of $Tm@C_{82}(I)$, Tm(c1) of $Tm_2@C_{82}(I)$, Tm(d1) of $Tm_2C_2@C_{82}(I)$ and are enlarged in panel b. Tm(c2) of $Tm_2@C_{82}(I)$, Tm(d2) of $Tm_2C_2@C_{82}(I)$ are enlarged in panel c.

The positions of Tm(a1), Tm(c1) and Tm(d1) are adjacent but slightly different. The distances from the barycenter to the Tm positions are 1.86, 1.95 and 2.07 Å for Tm(a1), Tm(c1) and Tm(d1), respectively. The Tm positions are, thus, shifted off-center from

the $C_{82}(C_s(6))$ cage by the encapsulation of additional Tm and C atoms. The position of the additional Tm atom is also shifted by the encapsulation of the C_2 unit. The distances from the barycenter to the Tm positions are 1.86 and 2.01 Å for Tm(c2) and Tm(d2), respectively. The shift of Tm positions stems likely from repulsive interaction exerted between the additional Tm atoms while maintaining Tm – C bond length constant.

4.2 Orientations of metallofullerenes in the crystals

4.2.1 Rotation of metallofullerenes

The difference in coordination structure between crystal A and B affects also the rotational movement of metallofullerene molecule. The charge density distribution on the carbon cage in crystal A is more uniform than that in crystal B as shown in Figs. 17a and b, indicating the suppression of rotational movement of carbon cage in crystal B. The structures of endohedral Tm atom are also different between crystal A and B as shown in Figs. 17b, c, e and f. The charge density peaks locate at positions about 1.9 Å away from the center of the carbon cage. The charge density at the peaks for the Tm atom in crystal A (Fig. 17b and c) are 5.9 $eÅ^{-3}$ and 19.6 $eÅ^{-3}$, which are much lower than those in crystal B, 20.0 $eÅ^{-3}$ and 21.5 $eÅ^{-3}$, (Fig. 17e and f) indicating suppression of the rotational movements of Tm atom.

4.2.2 Relative orientations for Ni(OEP)s

Figures 36a-h show most probable molecular orientations of $Tm@C_{82}(I)$, $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ relative to the Ni(OEP) in crystals A, B, C and D. Two kinds of molecular orientation are obtained for each crystal (F(a1) and F(a2) for crystal A, F(b1) and F(b2) for crystal B, F(b1) and F(b2) for crystal B, F(c1) and F(c2) for

crystal C and F(d1) and F(d2) for crystal D) by the present structure analysis.

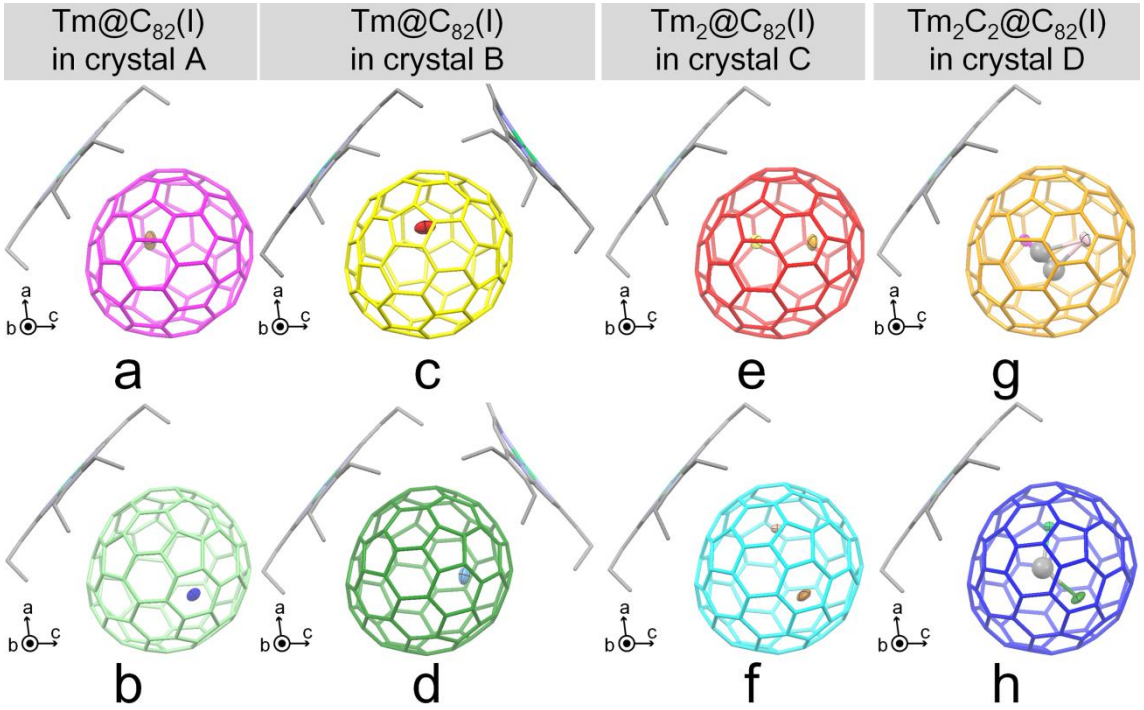


Figure 36. Molecular orientations relative to the Ni(OEP) viewed from the *b*-axis. a and b) F(a1) and F(a2) for $Tm@C_{82}(I)$ in crystal A, respectively. c and d) F(b1)and F(b2) for $Tm@C_{82}(I)$ in crystal B, respectively. e and f) F(c1) and F(c2) for $Tm_2@C_{82}(I)$ in crystal C, respectively. g and h) F(d1) and F(d2) for $Tm_2C_2@C_{82}(I)$ in crystal D, respectively. All endohedral Tm atoms are shown as thermal ellipsoids at 50% probability level.

Interestingly, orientations of F(a1) – F(d1) or F(a2) – F(d2) relative to the Ni(OEP) are almost identical as shown in the figure. The positions of Tm atom for $Tm@C_{82}(I)$ in crystal A is close to that in crystal B but slightly different as later discussed. The Tm atom for $Tm@C_{82}(I)$ is close to one of the two Tm atoms for $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$. This indicates that the stable endohedral Tm position and intermolecular interaction with *M*(OEP) are not fundamentally changed by an addition of endohedral atoms but rather depend on the cage structure.

4.2.3 Intermolecular interaction between metallofullerenes and Ni(OEP)

In order to understand the detailed interaction between the carbon cage and Ni(OEP), coodination structure of crystal B is suitable because (i) all the orientations of $Tm@C_{82}$(I), $Tm_2@C_{82}$(I) and $Tm_2C_2@C_{82}$(I) relative to flat Ni(OEP) are the same in crystal A-D (ii) additional Ni(OEP) exists.

The Ni atoms of the two Ni(OEP) molecules in crystal B are located near carbon atoms on a pentagon whose exocyclic bond is connected with a hexagon as shown in Fig. 37. The selective coordination of Ni(OEP) suggests an electrostatic attractive interaction between cationic Ni atoms and a locarized electron on the carbon atoms forming pentagon. The attraction between a metal atom of *M*(OEP) and carbon atoms forming pentagon is also found in other fullerene-*M*(OEP) co-crystals such as $Sm@C_{84}(C_2(13))$ · Ni(OEP), $Gd_2ScN@C_{80}(I_h(7))$ · Ni(OEP), $Sc_2O@C_{82}(C_s(6))$ · Ni(OEP), and $Ba@C_{74}$ · Co(OEP)[91,96,97,102]. The $C_{82}(C_s(6))$ cage has thirty-two independent carbon atoms forming pentagon. The Ni atoms of Ni(OEP) ligands are selectively attracted to the four of thirty-two carbon atoms colored in green in Fig. 37. Actually the green carbon atoms in Figs. 37b and d are equivalent in the $C_{82}(C_s(6))$ molecule. Cage b1 can coincide with cage b2' by a rotation around the axis from Ni(2) to the barycenter of the cage. The angle that cage b1 coincides with cage b2' is about 130°. This suggests that the bent Ni(OEP) is selectively attached on the pivot carbon atom, and then the $Tm@C_{82}$(I) orientation is restricted to the two independent orientations in crystal B. The same orientation relationship are observed between cage b1' and cage b2 because both Ni(2) and the barycenter of the cage are on the mirror plane of the *C*2/*m* space group.

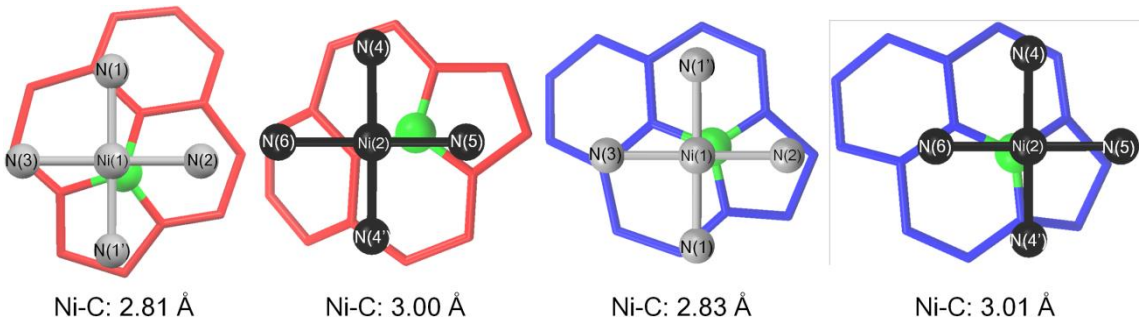


Figure 37. Partial structures of cage b1 (a and b) and b2' (c and d) around carbon atoms nearest to Ni atoms of Ni(OEP) ligands. Fifteen carbon atoms near flat (a and c) and bent Ni(OEP) (b and d) are shown with Ni and four N atoms of the Ni(OEP) in each panel. The carbon atoms nearest to the Ni atoms are colored in green. The shortest Ni-C interatomic distances for each partial structure are also shown.

The interatomic distances between the Ni atoms and the nearest fullerene carbon atoms are also shown in Fig. 37. The distances are within the range of that reported for other fullerene- *M*(OEP) co-crystals where the distances between Ni atom and the nearest carbon atom are 2.5 – 3.0 Å[91,96,97,99,102]. The distances for the bent Ni(OEP) (3.00 and 3.01 Å) are longer than that for the flat Ni(OEP) (2.81 and 2.83 Å). This difference is due to a stelic barrier, which leads to the molecular deformation and flipping of terminal ethyl groups of the bent Ni(OEP) as shown in Fig. 17b.

The positional relationship between the Tm positions of Crystal A-D and these Ni(OEP) is shown in Fig. 38. The relative positions of Tm(c1), Tm(c1)', Tm(c3) and Tm(c3)' in crystal C and Tm(d1), Tm(d1)', Tm(d3) and Tm(d3)' in crystal D from the Ni(OEP)s are quite similar to Tm(a1), Tm(a1)' and Tm(a2) in crystal A and Tm(b1), Tm(b1)', Tm(b2) and Tm(b2)' in crystal B from the flat Ni(OEP). Meanwhile the relative positions of Tm(c2), Tm(c2)' and Tm(c4) in crystal C and Tm(d2), Tm(d2)' and Tm(d4) in crystal D from the Ni(OEP)s are quite similar to Tm(b2) and Tm(b2)' in

crystal B from the bent Ni(OEP). The Tm atom tends to localize near the nitrogen atoms and at the far side from the nickel atom of Ni(OEP) in both crystals. A similar positional relationship between nitrogen atoms of *M*(OEP) and endohedral metal atoms can be seen in other co-crystals[91,98,101,102].

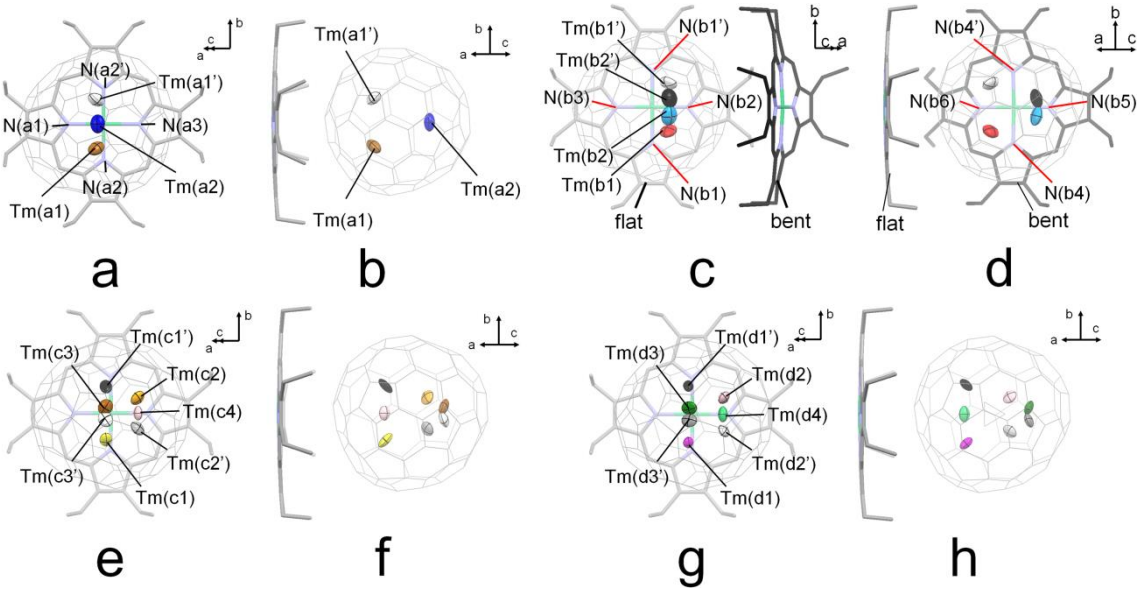


Figure 38. Positional relationship between the major Tm positions and the Ni(OEP) molecules of; a, b) crystal A; c, d) crystal B; e, f) crystal C; g, h) crystal D. Views perpendicular (parallel) to the molecular plane of flat Ni(OEP) are shown in a, c, e and g (b, d, f and h).

The Tm and Ni atom are positively charged by an intramolecular charge-transfer to the fullerene cage and four N atoms of the OEP, respectively. The Tm@C_{82}(I) molecule has a molecular dipole moment when the positively charged Tm atom is displaced from the barycenter of the excess electrons distributed on the fullerene cage. The molecular dipole moment should be oriented toward the negatively charged N atoms or the other side of the positively charged Ni atoms. The dipole interaction also restricts the orientation of Tm@C_{82}(I) in crystal B. A similar electrostatic intereaction between a

lithium cation encapsulated in C_{60} and its coordinated anion outside the carbon cage has been found in $Li^{+}@C_{60}$ crystals[71,100]. A single-molecule orientational switching of endohedral metallofullerene by applying an external electric field also has been found by the low-temperature ultrahigh vacuum scanning tunneling microscopy (STM)[69].

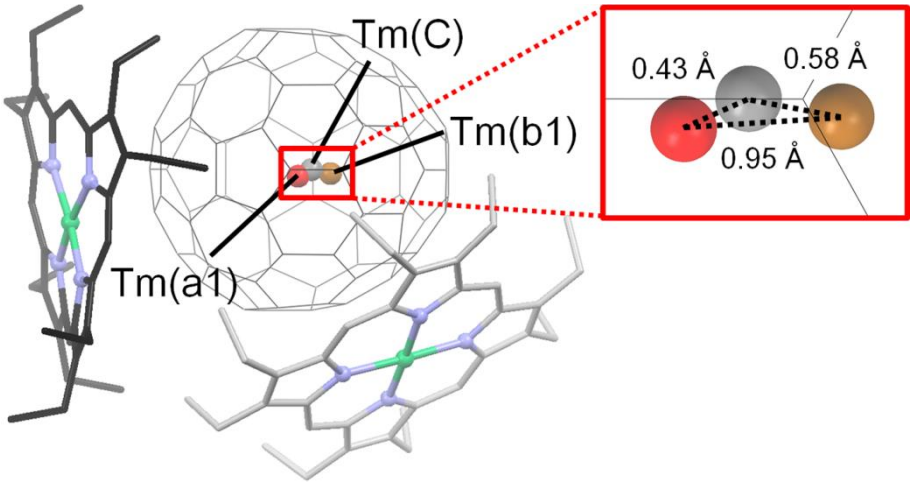


Figure 39. a) Overlapped Tm positions of $Tm@C_{82}(I)$s in crystal A, B and the calculation. The barycenters and orientations of $C_{82}(C_s(6))$ coincide in the figure. Tm(a1) of $Tm@C_{82}(I)$, Tm(b1) of $Tm@C_{82}(I)$, Tm(C) of theoretical $Tm@C_{82}(I)$ are enlarged.

4.3 Comparison of Tm atom positions in crystal A and B

The Ni(OEP)s and Tm positions of $Tm@C_{82}(I)$ in crystal A (Tm(a1)) and crystal B (Tm(b1)) are contrastively shown in Fig. 39. The Tm position of calculated $Tm@C_{82}(I)$ (Tm(C)) are also shown in the figure. The barycenters and orientations of each fullerene cage coincide with each other. The Ni(OEP) of crystal A are omitted due to the similar position of flat Ni(OEP) in crystal B as shown in Fig. 36. The positions of Tm(a1), Tm(b1) and Tm(C) are adjacent but slightly different. The distances of Tm(a1) – Tm(C), Tm(b1) – Tm(C) and Tm(a1) – Tm(b1) are 0.43, 0.58 and 0.95 Å, respectively. The Tm positions in crystal A and B are shifted to flat and bent Ni(OEP)s' direction of these

crystals, respectively. This fact strongly suggests that the attractive interaction between the endohedral Tm atom and four nitrogen atoms of Ni(OEP) alters the Tm positions.

4.4 The static endohedral atoms of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$

As well as the Tm atom of $Tm@C_{82}(I)$, the two endohedral Tm atoms of $Tm_2@C_{82}(I)$ and $Tm_2C_2@C_{82}(I)$ are found to statically occupy only the specific positions at 200 K in contrast to metal atoms of $La_2@C_{80}(I_h(7))$, $Y_2@C_{82}(C_{3v}(8))$ and $Sc_2C_2@C_{82}(C_{3v}(8))$ which are dynamically moving inside their fullerene cages at room temperture[21,22,88,146,147]. In the case of $La_2@C_{80}(I_h(7))$, $Y_2@C_{82}(C_{3v}(8))$ and $Sc_2C_2@C_{82}(C_{3v}(8))$, metal atoms can be thermally hopping among the symmetrically equivalent stable positions inside the fullerene cage. However, no other equivalent positions exist for two Tm atoms inside the $C_{82}(C_s(6))$ cage.

On the basis of theoretical structural searches, other stable positions for the endohedral Tm atoms displaced from the mirror plane can be suggested. In fact, their calculated total electronic energies suggest that the alternative positions are metastable. The occupation of Tm atoms at the metastable positions will not be achieved by the thermal excitation even at room temperature considering the corresponding energy difference.

Endohedral carbon atoms of $Tm_2C_2@C_{82}(I)$ are also static whereas those of $Sc_2C_2@C_{84}(D_{2d}(23))$ and $Y_2C_2@C_{92}(D_3(85))$ are dynamically moving as the C_2 unit rotates[139,148]. The C_2 unit of $Y_2C_2@C_{92}(D_3(85))$ has three stable orientations at every 120° rotation around D_3 axis of the $C_{92}(D_3(85))$ cage, which are symmetrically

equivalent positions for the carbon cage[139]. This fact strongly suggests the rotation of the C_2 unit also depends on the symmetry of its fullerene cage. In contrast, the rotational motion of the C_2 unit is excited more easily than the hopping of metal atoms.

The presence of the static endohedral Tm atoms and C_2 unit of $Tm_2C_2@C_{82}(I)$ suggests that the rotational motion of the C_2 unit is governed by the dynamics of endohedral metal atoms. The rotational motion of the C_2 unit is hindered by the covalent bond with the metal atoms. The Tm-C bond of the Tm_2C_2 cluster can be classified to a covalent bond because the bond length is comparable to those of thulium carbide compounds[142,143]. The C-C bond of the Tm_2C_2 cluster should also be covalent because the bond length is comparable to that of typical allene C-C bond (1.30 Å), which consists of a sp^2 – sp hybrid orbital. The order of the C-C bond is considered to be about 2.5. Because of this covalent character, the Tm_2C_2 cluster tends to behave as a rigid body in the carbon cage.

4.5 $Tm@C_{82}(I)$ and Ni(TPP) dimer

Due to red shift of Soret band, the association of Ni(TPP) dimer and $Tm@C_{82}(I)$ occurred[79]. However crystallization of the complex of $Tm@C_{82}(I)$ and Ni(TPP) dimer cannot be achieved. One hypothesis is that the Ni(TPP) dimer is ununiformly associated with $Tm@C_{82}(I)$, such as not 1 : 1 association. In order to validate this hypothesis, titration for Bensi-Hildebrand plot or Job plot are required as further experiment.

5. Conclusion

Single crystal structure analyses of 1 : 1 and 1 : 2 co-crystals of Tm@C_{82}(I) and Ni(OEP) reveal that the orientational disorder of Tm@C_{82}(I) is suppressed by increasing the coordination number of Ni(OEP) ligand. The carbon cage structure was determined as C_s(6)-C_{82} by the MEM charge density analysis of the 1 : 2 co-crystal.

Single crystal structure analysis of the co-crystals of Tm_2@C_{82}(I) and Tm_2C_2@C_{82}(I) with Ni(OEP) reveal that the endohedral Tm and C atoms are statically confined in the low-symmetry C_{82}(C_s(6)) cage in contrast to the endohedral atoms of La_2@C_{80}(I_h(7)), Y_2@C_{82}(C_{3v}(8)) and Sc_2C_2@C_{82}(C_{3v}(8)) which are dynamically moving inside the high-symmetry carbon cage. The relative metal positions of Tm@C_{82}(C_s(6)), Tm_2@C_{82}(I) and Tm_2C_2@C_{82}(I) are similar, and the Tm positions are slightly shifted off-center by the encapsulation of additional Tm and C atoms. The molecular orientations of Tm@C_{82}(C_s(6)), Tm_2@C_{82}(I) and Tm_2C_2@C_{82}(I) relative to Ni(OEP) are also similar with each other. The current study provides a fair understanding on the fundamental dynamics of the encapsulated atoms and intermolecular interactions of endohedral metallofullerenes.

The Ni atoms of Ni(OEP) molecules are always located near carbon atoms forming pentagon. The orientations of metallofullerenes in the co-crystal are restricted by the molecular dipole moment of Tm@C_{82}(I) that interacts with Ni(OEP) ligands. The interaction of Ni(OEP) slightly alters the endohedral metal positions. The intermolecular interaction between Ni(OEP) and metallofullerenes found in this study indicates that the molecular orientation of metallofullerenes can be controlled and ordered by a novel porphyrin based ligand such as fullerene tweezers[79]. Although Ni(TPP) dimer cannot be crystalized, further designing and synthesis of a novel

porphyrin based ligand will, in future, enable us to determine more detailed structure of metallofullerenes.

6. Apendix

6.1 Occupancy Information

6.1.1 Crystal A

	Tm(an)								cage an	
n	1	2	3	4	5	6	7	8	1	2
occupancy	0.11	0.16	0.04	0.04	0.05	0.03	0.03	0.03	0.53	0.47

6.1.2 Crystal B

	Tm(bn)					cage bn	
n	1	2	3	4	5	1	2
occupancy	0.17	0.17	0.08	0.03	0.05	0.60	0.40

6.1.3 Crystal C

	Tm (cn)									cage cn	
n	1	2	3	4	5	6	7	8	9	1	2
occupancy	0.07	0.08	0.13	0.12	0.09	0.09	0.20	0.05	0.05	0.45	0.55

6.1.4 Crystal D

	Tm (dn)										cage dn	
n	1	2	3	4	5	6	7	8	9	9	1	2
occupancy	0.13	0.14	0.09	0.08	0.08	0.09	0.19	0.02	0.16	0.02	0.59	0.41

6.2 Crystallographic information

Here crystallographic information files (CIFs) of crystal A – D are described. In addition, the indication number of each atom is not corresponding to that in the main body.

6.2.1 Crystal A

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F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
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Tm8 Tm 0.1492(8) 0.449(2) 0.1484(12) 0.160(11) Uani 0.0250(12) 1 d PU
C301 C 0.3406(2) 0.6025(5) 0.2969(4) 0.115 Uani 0.273(4) 1 d PG
C302 C 0.3481(2) 0.5118(5) 0.3100(4) 0.115 Uani 0.273(4) 1 d PG
C303 C 0.36658(17) 0.4584(5) 0.2561(5) 0.114 Uani 0.273(4) 1 d PG
C304 C 0.3162(3) 0.4720(5) 0.3564(3) 0.117 Uani 0.273(4) 1 d PG
C305 C 0.2747(3) 0.5196(5) 0.3855(3) 0.116 Uani 0.273(4) 1 d PG
C306 C 0.2634(3) 0.6069(5) 0.3668(3) 0.112 Uani 0.273(4) 1 d PG
C307 C 0.3000(3) 0.6493(4) 0.3261(4) 0.115 Uani 0.273(4) 1 d PG
C308 C 0.2990(3) 0.3816(5) 0.3473(4) 0.116 Uani 0.273(4) 1 d PG
C309 C 0.3139(3) 0.3325(4) 0.2916(4) 0.114 Uani 0.273(4) 1 d PG
C310 C 0.3501(2) 0.3721(5) 0.2473(5) 0.114 Uani 0.273(4) 1 d PG
C311 C 0.2771(3) 0.2693(3) 0.2629(4) 0.113 Uani 0.273(4) 1 d PG
C312 C 0.1802(3) 0.4844(5) 0.3910(2) 0.113 Uani 0.273(4) 1 d PG
C313 C 0.2325(3) 0.4578(5) 0.3972(2) 0.117 Uani 0.273(4) 1 d PG
C314 C 0.2469(3) 0.3732(4) 0.3705(3) 0.115 Uani 0.273(4) 1 d PG
C315 C 0.2083(3) 0.3176(4) 0.3373(3) 0.111 Uani 0.273(4) 1 d PG
C316 C 0.2261(3) 0.2606(2) 0.2864(4) 0.113 Uani 0.273(4) 1 d PG
C317 C 0.1924(3) 0.7050(3) 0.3157(4) 0.111 Uani 0.273(4) 1 d PG
C318 C 0.2075(3) 0.6356(4) 0.3607(3) 0.109 Uani 0.273(4) 1 d PG
C319 C 0.1671(3) 0.5742(5) 0.3729(3) 0.109 Uani 0.273(4) 1 d PG
C320 C 0.2729(3) 0.2510(2) 0.1891(5) 0.110 Uani 0.273(4) 1 d PG
C321 C 0.3064(3) 0.2959(3) 0.1447(5) 0.108 Uani 0.273(4) 1 d PG
C322 C 0.3460(2) 0.3527(4) 0.1740(5) 0.111 Uani 0.273(4) 1 d PG
C323 C 0.2843(3) 0.3140(4) 0.0771(4) 0.106 Uani 0.273(4) 1 d PG
C324 C 0.1380(3) 0.2581(3) 0.2235(4) 0.112 Uani 0.273(4) 1 d PG
C325 C 0.1902(4) 0.23310(13) 0.2286(4) 0.113 Uani 0.273(4) 1 d PG
C326 C 0.2196(3) 0.23260(6) 0.1681(4) 0.109 Uani 0.273(4) 1 d PG
C327 C 0.1949(3) 0.26277(18) 0.1032(4) 0.103 Uani 0.273(4) 1 d PG
C328 C 0.2285(3) 0.2969(3) 0.0575(4) 0.105 Uani 0.273(4) 1 d PG
C329 C 0.1393(3) 0.4282(5) 0.3579(3) 0.109 Uani 0.273(4) 1 d PG
C330 C 0.1523(3) 0.3458(4) 0.3310(3) 0.108 Uani 0.273(4) 1 d PG
C331 C 0.1180(3) 0.3143(4) 0.2757(4) 0.109 Uani 0.273(4) 1 d PG
C332 C 0.2993(3) 0.3888(5) 0.0414(4) 0.106 Uani 0.273(4) 1 d PG
C333 C 0.3360(2) 0.4505(5) 0.0731(4) 0.105 Uani 0.273(4) 1 d PG
C334 C 0.36057(19) 0.4294(5) 0.1389(5) 0.109 Uani 0.273(4) 1 d PG
C335 C 0.3282(3) 0.5405(5) 0.0570(4) 0.106 Uani 0.273(4) 1 d PG
C336 C 0.2529(3) 0.4175(5) -0.0030(3) 0.106 Uani 0.273(4) 1 d PG
C337 C 0.1909(3) 0.5361(5) -0.0304(2) 0.111 Uani 0.273(4) 1 d PG
C338 C 0.2438(3) 0.5082(5) -0.0173(3) 0.106 Uani 0.273(4) 1 d PG
C339 C 0.2818(3) 0.5697(5) 0.0125(3) 0.105 Uani 0.273(4) 1 d PG
C340 C 0.1561(3) 0.3919(4) 0.0016(3) 0.106 Uani 0.273(4) 1 d PG
C341 C 0.2101(3) 0.3618(4) 0.0070(3) 0.105 Uani 0.273(4) 1 d PG
C342 C 0.1469(3) 0.4765(5) -0.0248(2) 0.114 Uani 0.273(4) 1 d PG
C343 C 0.1191(3) 0.3550(4) 0.0474(3) 0.106 Uani 0.273(4) 1 d PG
C344 C 0.1111(3) 0.2824(3) 0.1576(4) 0.109 Uani 0.273(4) 1 d PG
C345 C 0.1386(3) 0.2909(3) 0.0986(4) 0.103 Uani 0.273(4) 1 d PG
C346 C 0.0734(2) 0.4043(5) 0.0591(4) 0.115 Uani 0.273(4) 1 d PG
C347 C 0.3398(2) 0.6055(5) 0.1069(4) 0.106 Uani 0.273(4) 1 d PG
C348 C 0.36121(19) 0.5837(5) 0.1741(5) 0.108 Uani 0.273(4) 1 d PG
C349 C 0.37323(15) 0.4998(5) 0.1886(5) 0.111 Uani 0.545(9) 2 d SPG
C350 C 0.3467(2) 0.6390(4) 0.2288(5) 0.112 Uani 0.273(4) 1 d PG
C351 C 0.3002(3) 0.6737(4) 0.0960(4) 0.104 Uani 0.273(4) 1 d PG
C352 C 0.2819(3) 0.7201(3) 0.1500(4) 0.103 Uani 0.273(4) 1 d PG
C353 C 0.3098(3) 0.7065(3) 0.2165(5) 0.110 Uani 0.273(4) 1 d PG
C354 C 0.2307(4) 0.7452(2) 0.2733(4) 0.113 Uani 0.273(4) 1 d PG
C355 C 0.2824(3) 0.7176(3) 0.2780(4) 0.114 Uani 0.273(4) 1 d PG
C356 C 0.1746(3) 0.6220(5) -0.0100(3) 0.113 Uani 0.273(4) 1 d PG
C357 C 0.2100(3) 0.6755(4) 0.0306(3) 0.105 Uani 0.273(4) 1 d PG
C358 C 0.2649(3) 0.6503(4) 0.0366(4) 0.104 Uani 0.273(4) 1 d PG
C359 C 0.1899(3) 0.7271(2) 0.0854(4) 0.105 Uani 0.273(4) 1 d PG
C360 C 0.2257(3) 0.74876(11) 0.1455(4) 0.103 Uani 0.273(4) 1 d PG
C361 C 0.2031(4) 0.76570(6) 0.2070(4) 0.110 Uani 0.273(4) 1 d PG
C362 C 0.1185(3) 0.6176(5) 0.0008(3) 0.122 Uani 0.273(4) 1 d PG
C363 C 0.0988(3) 0.6683(4) 0.0508(4) 0.122 Uani 0.273(4) 1 d PG
C364 C 0.1344(3) 0.7253(3) 0.0919(4) 0.114 Uani 0.273(4) 1 d PG
C365 C 0.0442(2) 0.5452(5) 0.0858(4) 0.122 Uani 0.273(4) 1 d PG
C366 C 0.0652(2) 0.4920(5) 0.0328(4) 0.123 Uani 0.273(4) 1 d PG
C367 C 0.1014(3) 0.5275(5) -0.0084(3) 0.122 Uani 0.273(4) 1 d PG
C368 C 0.0606(2) 0.6312(5) 0.0945(4) 0.122 Uani 0.273(4) 1 d PG
C369 C 0.0699(2) 0.3423(4) 0.1720(4) 0.112 Uani 0.273(4) 1 d PG
C370 C 0.03936(15) 0.4912(5) 0.1443(4) 0.114 Uani 0.273(4) 1 d PG
C371 C 0.0514(2) 0.4023(5) 0.1240(4) 0.115 Uani 0.273(4) 1 d PG
C372 C 0.1004(3) 0.4828(5) 0.3232(3) 0.105 Uani 0.273(4) 1 d PG
C373 C 0.0724(2) 0.6647(4) 0.1620(4) 0.113 Uani 0.273(4) 1 d PG
C374 C 0.0708(2) 0.6117(5) 0.2202(4) 0.104 Uani 0.273(4) 1 d PG
C375 C 0.05364(16) 0.5211(5) 0.2109(4) 0.104 Uani 0.273(4) 1 d PG
C376 C 0.0707(2) 0.4557(5) 0.2631(4) 0.103 Uani 0.273(4) 1 d PG
C377 C 0.0770(2) 0.3673(5) 0.2435(4) 0.108 Uani 0.273(4) 1 d PG
C378 C 0.1138(3) 0.7308(3) 0.1576(4) 0.115 Uani 0.273(4) 1 d PG
C379 C 0.1476(3) 0.7507(2) 0.2138(4) 0.112 Uani 0.273(4) 1 d PG
C380 C 0.1415(3) 0.7067(3) 0.2783(4) 0.109 Uani 0.273(4) 1 d PG
C381 C 0.1052(3) 0.6364(4) 0.2816(4) 0.103 Uani 0.273(4) 1 d PG
C382 C 0.1177(3) 0.5734(5) 0.3325(3) 0.105 Uani 0.273(4) 1 d PG
C201 C 0.34328(13) 0.34373(12) 0.2165(3) 0.113 Uani 0.227(4) 1 d PG
C202 C 0.33984(10) 0.37125(15) 0.2849(3) 0.114 Uani 0.227(4) 1 d PG
C203 C 0.29867(9) 0.33278(14) 0.3224(2) 0.114 Uani 0.227(4) 1 d PG
C204 C 0.35683(8) 0.45640(18) 0.3025(3) 0.117 Uani 0.227(4) 1 d PG
C205 C 0.37306(10) 0.51548(16) 0.2519(3) 0.116 Uani 0.227(4) 1 d PG
C206 C 0.37087(14) 0.49137(13) 0.1827(3) 0.111 Uani 0.227(4) 1 d PG
C207 C 0.35970(15) 0.40184(12) 0.1670(3) 0.112 Uani 0.227(4) 1 d PG
C208 C 0.33076(6) 0.50000(18) 0.3531(2) 0.117 Uani 0.455(9) 2 d SPG
C209 C 0.28801(4) 0.47050(17) 0.3854(2) 0.114 Uani 0.227(4) 1 d PG
C210 C 0.27377(6) 0.38051(15) 0.3708(2) 0.114 Uani 0.227(4) 1 d PG
C211 C 0.24704(4) 0.52806(15) 0.40326(18) 0.113 Uani 0.227(4) 1 d PG
C212 C 0.34410(13) 0.66473(13) 0.2244(3) 0.115 Uani 0.227(4) 1 d PG
C213 C 0.35909(10) 0.60308(16) 0.2727(3) 0.118 Uani 0.227(4) 1 d PG
C214 C 0.33075(7) 0.59638(17) 0.3340(3) 0.117 Uani 0.227(4) 1 d PG
C215 C 0.28731(8) 0.65134(15) 0.3448(2) 0.113 Uani 0.227(4) 1 d PG
C216 C 0.24744(6) 0.61679(14) 0.38488(19) 0.114 Uani 0.227(4) 1 d PG
C217 C 0.33054(19) 0.52977(8) 0.0672(3) 0.108 Uani 0.227(4) 1 d PG
C218 C 0.35516(16) 0.55740(10) 0.1309(3) 0.108 Uani 0.227(4) 1 d PG
C219 C 0.34217(16) 0.64250(10) 0.1525(3) 0.110 Uani 0.227(4) 1 d PG
C220 C 0.19102(3) 0.50000(12) 0.40061(14) 0.109 Uani 0.455(9) 2 d SPG
C221 C 0.17674(5) 0.41055(10) 0.38086(13) 0.107 Uani 0.227(4) 1 d PG
C222 C 0.21793(6) 0.35161(12) 0.36912(17) 0.111 Uani 0.227(4) 1 d PG
C223 C 0.12588(6) 0.39762(7) 0.34454(10) 0.105 Uani 0.227(4) 1 d PG
C224 C 0.17751(9) 0.70716(7) 0.32673(16) 0.111 Uani 0.227(4) 1 d PG
C225 C 0.19202(6) 0.64434(10) 0.37380(15) 0.112 Uani 0.227(4) 1 d PG
C226 C 0.15797(4) 0.56858(9) 0.37998(12) 0.107 Uani 0.227(4) 1 d PG
C227 C 0.11018(6) 0.55670(7) 0.33437(9) 0.100 Uani 0.227(4) 1 d PG
C228 C 0.09329(6) 0.47154(7) 0.32177(7) 0.102 Uani 0.227(4) 1 d PG
C229 C 0.29993(13) 0.72327(10) 0.2344(2) 0.112 Uani 0.227(4) 1 d PG
C230 C 0.27138(11) 0.71769(11) 0.2933(2) 0.110 Uani 0.227(4) 1 d PG
C231 C 0.21759(11) 0.74583(6) 0.28623(19) 0.111 Uani 0.227(4) 1 d PG
C232 C 0.11726(9) 0.33064(6) 0.29551(11) 0.107 Uani 0.227(4) 1 d PG
C233 C 0.16008(11) 0.27537(4) 0.27923(15) 0.107 Uani 0.227(4) 1 d PG
C234 C 0.20997(9) 0.28496(8) 0.31866(18) 0.110 Uani 0.227(4) 1 d PG
C235 C 0.16116(14) 0.24681(3) 0.21044(16) 0.109 Uani 0.227(4) 1 d PG
C236 C 0.07740(10) 0.36167(9) 0.24239(8) 0.107 Uani 0.227(4) 1 d PG
C237 C 0.05966(15) 0.39392(15) 0.12201(7) 0.113 Uani 0.227(4) 1 d PG

C238 C 0.07949(14) 0.33560(11) 0.17283(9) 0.108 Uani 0.227(4) 1 d PG
C239 C 0.12135(15) 0.27758(9) 0.15701(13) 0.109 Uani 0.227(4) 1 d PG
C240 C 0.04865(11) 0.51046(12) 0.20684(5) 0.105 Uani 0.227(4) 1 d PG
C241 C 0.06312(9) 0.44711(10) 0.25844(6) 0.104 Uani 0.227(4) 1 d PG
C242 C 0.04121(14) 0.47975(16) 0.13931(5) 0.114 Uani 0.227(4) 1 d PG
C243 C 0.06420(11) 0.60137(11) 0.21949(7) 0.103 Uani 0.227(4) 1 d PG
C244 C 0.12747(10) 0.69972(5) 0.28377(13) 0.108 Uani 0.227(4) 1 d PG
C245 C 0.09534(9) 0.62449(7) 0.28307(9) 0.101 Uani 0.227(4) 1 d PG
C246 C 0.06728(14) 0.65616(13) 0.16237(9) 0.113 Uani 0.227(4) 1 d PG
C247 C 0.21011(16) 0.236407(5) 0.18110(19) 0.108 Uani 0.227(4) 1 d PG
C248 C 0.25992(14) 0.25136(6) 0.2195(2) 0.109 Uani 0.227(4) 1 d PG
C249 C 0.25922(11) 0.27254(9) 0.2890(2) 0.112 Uani 0.227(4) 1 d PG
C250 C 0.30312(15) 0.28402(8) 0.1831(2) 0.110 Uani 0.227(4) 1 d PG
C251 C 0.20220(18) 0.26319(5) 0.11059(19) 0.106 Uani 0.227(4) 1 d PG
C252 C 0.24234(19) 0.30395(6) 0.0779(2) 0.103 Uani 0.227(4) 1 d PG
C253 C 0.29488(18) 0.30656(5) 0.1144(2) 0.108 Uani 0.227(4) 1 d PG
C254 C 0.3183(2) 0.43782(7) 0.0536(3) 0.110 Uani 0.227(4) 1 d PG
C255 C 0.33201(18) 0.37643(8) 0.1021(3) 0.111 Uani 0.227(4) 1 d PG
C256 C 0.08323(18) 0.39932(17) 0.05776(8) 0.115 Uani 0.227(4) 1 d PG
C257 C 0.1306(2) 0.35376(14) 0.04785(12) 0.107 Uani 0.227(4) 1 d PG
C258 C 0.14646(18) 0.28773(10) 0.09663(14) 0.107 Uani 0.227(4) 1 d PG
C259 C 0.1717(2) 0.39569(13) 0.01092(15) 0.105 Uani 0.227(4) 1 d PG
C260 C 0.2277(2) 0.37148(9) 0.02633(19) 0.102 Uani 0.227(4) 1 d PG
C261 C 0.2671(2) 0.43260(9) 0.0128(2) 0.107 Uani 0.227(4) 1 d PG
C262 C 0.07397(19) 0.48649(19) 0.03141(7) 0.123 Uani 0.227(4) 1 d PG
C263 C 0.1117(2) 0.52548(18) -0.00557(10) 0.122 Uani 0.227(4) 1 d PG
C264 C 0.1600(2) 0.47875(16) -0.01763(13) 0.114 Uani 0.227(4) 1 d PG
C265 C 0.10051(19) 0.66464(16) 0.05437(11) 0.122 Uani 0.227(4) 1 d PG
C266 C 0.06071(17) 0.62303(17) 0.09325(8) 0.122 Uani 0.227(4) 1 d PG
C267 C 0.04789(17) 0.53623(18) 0.08202(6) 0.122 Uani 0.227(4) 1 d PG
C268 C 0.1254(2) 0.61704(17) 0.00617(12) 0.122 Uani 0.227(4) 1 d PG
C269 C 0.13547(13) 0.74607(5) 0.22241(15) 0.112 Uani 0.227(4) 1 d PG
C270 C 0.13143(18) 0.72298(11) 0.09875(14) 0.114 Uani 0.227(4) 1 d PG
C271 C 0.10618(15) 0.72478(10) 0.16275(13) 0.114 Uani 0.227(4) 1 d PG
C272 C 0.27324(16) 0.74026(5) 0.1694(2) 0.107 Uani 0.227(4) 1 d PG
C273 C 0.1815(2) 0.62700(13) 0.00146(16) 0.113 Uani 0.227(4) 1 d PG
C274 C 0.2134(2) 0.68011(9) 0.04700(19) 0.104 Uani 0.227(4) 1 d PG
C275 C 0.18723(18) 0.73019(7) 0.09776(18) 0.105 Uani 0.227(4) 1 d PG
C276 C 0.21808(16) 0.757687(15) 0.1610(2) 0.105 Uani 0.227(4) 1 d PG
C277 C 0.19184(14) 0.767848(14) 0.22153(18) 0.110 Uani 0.227(4) 1 d PG
C278 C 0.2011(2) 0.54319(14) -0.02140(17) 0.114 Uani 0.227(4) 1 d PG
C279 C 0.2535(2) 0.52015(10) -0.0066(2) 0.110 Uani 0.227(4) 1 d PG
C280 C 0.2899(2) 0.58019(7) 0.0313(2) 0.107 Uani 0.227(4) 1 d PG
C281 C 0.2703(2) 0.65766(6) 0.0597(2) 0.103 Uani 0.227(4) 1 d PG
C282 C 0.29941(17) 0.69018(6) 0.1186(2) 0.106 Uani 0.227(4) 1 d PG
Ni1 Ni 0.02153(3) 0.50000(12) 0.41936(4) 0.0329(2) Uani 1 2 d SG
N1 N 0.07886(4) 0.50000(14) 0.49309(6) 0.0356(12) Uani 1 2 d SG
N2 N -0.03388(4) 0.50001(15) 0.34314(6) 0.0361(13) Uani 1 2 d SG
N3 N 0.02250(5) 0.62697(12) 0.41817(7) 0.0362(8) Uani 1 1 d G
C101 C 0.10436(6) 0.42832(16) 0.52295(7) 0.0368(10) Uani 1 1 d G
C102 C -0.05611(6) 0.42967(18) 0.30878(8) 0.0410(11) Uani 1 1 d G
C103 C 0.05469(7) 0.31753(12) 0.45808(8) 0.0369(10) Uani 1 1 d G
C104 C -0.00734(7) 0.31878(13) 0.37472(8) 0.0396(11) Uani 1 1 d G
C105 C 0.09271(7) 0.34415(15) 0.50724(9) 0.0393(11) Uani 1 1 d G
H105 H 0.1121 0.3011 0.5318 0.047 Uiso 1 1 calc R
C106 C -0.04444(18) 0.3427(3) 0.3228(3) 0.0390(11) Uani 1 1 d
H106 H -0.0622 0.2995 0.2965 0.047 Uiso 1 1 calc R
C107 C 0.14591(17) 0.4551(3) 0.5756(3) 0.0395(11) Uani 1 1 d
C108 C -0.09157(19) 0.4554(4) 0.2499(3) 0.0424(11) Uani 1 1 d
C109 C 0.04462(18) 0.2259(3) 0.4404(3) 0.0431(12) Uani 1 1 d
C110 C 0.00648(19) 0.2260(3) 0.3885(3) 0.0408(11) Uani 1 1 d
C111 C 0.18456(18) 0.3948(4) 0.6134(3) 0.0465(13) Uani 1 1 d
H11A H 0.1657 0.3435 0.6275 0.056 Uiso 1 1 calc R
H11B H 0.2004 0.4237 0.6540 0.056 Uiso 1 1 calc R
C112 C -0.1198(2) 0.3932(4) 0.2003(3) 0.0521(14) Uani 1 1 d
H11C H -0.1483 0.4243 0.1740 0.063 Uiso 1 1 calc R
H11D H -0.1361 0.3474 0.2255 0.063 Uiso 1 1 calc R
C113 C 0.0739(2) 0.1492(3) 0.4761(3) 0.0488(14) Uani 1 1 d
H11E H 0.0528 0.0966 0.4683 0.059 Uiso 1 1 calc R
H11F H 0.0780 0.1601 0.5248 0.059 Uiso 1 1 calc R
C114 C -0.0172(2) 0.1495(4) 0.3474(4) 0.0532(15) Uani 1 1 d
H11G H -0.0552 0.1592 0.3373 0.064 Uiso 1 1 calc R
H11H H -0.0128 0.0968 0.3747 0.064 Uiso 1 1 calc R
C115 C 0.2288(2) 0.3666(5) 0.5693(3) 0.0602(17) Uani 1 1 d
H11I H 0.2134 0.3354 0.5301 0.090 Uiso 1 1 calc R
H11J H 0.2536 0.3294 0.5954 0.090 Uiso 1 1 calc R
H11K H 0.2472 0.4173 0.5547 0.090 Uiso 1 1 calc R
C116 C -0.0831(2) 0.3518(4) 0.1516(3) 0.0568(15) Uani 1 1 d
H11L H -0.0659 0.3969 0.1275 0.085 Uiso 1 1 calc R
H11M H -0.1038 0.3154 0.1195 0.085 Uiso 1 1 calc R
H11N H -0.0565 0.3171 0.1770 0.085 Uiso 1 1 calc R
C117 C 0.1290(2) 0.1353(4) 0.4503(4) 0.0567(16) Uani 1 1 d
H11O H 0.1253 0.1274 0.4017 0.085 Uiso 1 1 calc R
H11P H 0.1453 0.0843 0.4715 0.085 Uiso 1 1 calc R
H11Q H 0.1511 0.1854 0.4614 0.085 Uiso 1 1 calc R
C118 C 0.0085(3) 0.1357(4) 0.2803(4) 0.0663(19) Uani 1 1 d
H11R H 0.0055 0.1884 0.2538 0.099 Uiso 1 1 calc R
H11S H -0.0093 0.0890 0.2552 0.099 Uiso 1 1 calc R
H11T H 0.0456 0.1213 0.2900 0.099 Uiso 1 1 calc R
C11 C 0.1809(2) 1.0138(6) 0.2123(3) 0.079(5) Uani 0.351(5) 1 d PGU
Cl11 Cl 0.24602(15) 0.9884(15) 0.1990(2) 0.061(4) Uani 0.351(5) 1 d PGU
Cl12 Cl 0.1377(2) 0.9701(4) 0.1487(3) 0.108(3) Uani 0.351(5) 1 d PGU
Cl13 Cl 0.1656(2) 0.9764(11) 0.2909(3) 0.100(4) Uani 0.351(5) 1 d PGU
H11 H 0.1765 1.0854 0.2113 0.120 Uiso 0.351(5) 1 d PG
C21 C 0.1616(15) 1.035(4) 0.212(2) 0.072(9) Uiso 0.051(5) 1 d PGU
Cl21 Cl 0.2182(13) 1.004(9) 0.1698(16) 0.072(9) Uiso 0.051(5) 1 d PGU
Cl22 Cl 0.1093(12) 0.971(2) 0.1781(18) 0.072(9) Uiso 0.051(5) 1 d PGU
Cl23 Cl 0.1744(16) 1.013(9) 0.2981(15) 0.072(9) Uiso 0.051(5) 1 d PGU
H21 H 0.1504 1.1038 0.2058 0.087 Uiso 0.051(5) 1 d PG
C31 C 0.0027(5) 0.1019(8) -0.0104(10) 0.123(10) Uani 0.260(10) 1 d PGU
Cl31 Cl -0.0453(8) 0.148(2) 0.0359(11) 0.237(18) Uani 0.260(10) 1 d PGU
Cl32 Cl -0.0078(11) 0.1306(18) -0.0950(8) 0.192(11) Uani 0.260(10) 1 d PGU
Cl33 Cl 0.0656(5) 0.1337(19) 0.0222(14) 0.182(12) Uani 0.260(10) 1 d PGU
H31 H -0.0002 0.0303 -0.0063 0.219 Uiso 0.260(10) 1 d PG
C41 C 0.0264(6) 0.1809(10) -0.0091(13) 0.16(6) Uani 0.171(9) 1 d PG
Cl41 Cl -0.0258(9) 0.220(2) 0.0337(14) 0.180(17) Uani 0.171(9) 1 d PG
Cl42 Cl 0.0579(7) 0.0959(13) 0.0355(11) 0.152(14) Uani 0.171(9) 1 d PG
Cl43 Cl 0.0038(8) 0.1476(19) -0.0900(9) 0.19(2) Uani 0.171(9) 1 d PG
H41 H 0.0554 0.2341 -0.0133 0.227 Uiso 0.171(9) 1 d PG

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Tm1 0.0532(12) 0.1072(19) 0.0478(13) 0.000 0.0180(10) 0.000
Tm2 0.073(4) 0.209(8) 0.041(3) 0.000 0.020(2) 0.000

Tm3 0.080(5) 0.129(10) 0.111(8) 0.049(6) 0.056(4) 0.054(5)
Tm4 0.0495(17) 0.0628(18) 0.102(3) 0.0305(18) 0.0107(16) -0.0057(13)
Tm5 0.084(6) 0.054(5) 0.170(10) 0.016(5) 0.047(7) 0.001(4)
Tm6 0.048(6) 0.118(9) 0.091(6) 0.054(6) 0.012(3) 0.006(5)
Tm7 0.156(17) 0.156(12) 0.039(7) 0.000 -0.014(7) 0.000
Tm8 0.103(7) 0.26(3) 0.110(10) 0.055(13) -0.053(8) -0.110(13)
C301 0.087 0.133 0.116 -0.022 -0.044 -0.031
C302 0.080 0.147 0.108 -0.003 -0.052 -0.004
C303 0.056 0.145 0.134 0.006 -0.035 0.015
C304 0.114 0.149 0.077 0.009 -0.052 0.006
C305 0.140 0.150 0.052 -0.008 -0.033 -0.003
C306 0.139 0.129 0.064 -0.037 -0.025 -0.011
C307 0.122 0.117 0.099 -0.040 -0.036 -0.029
C308 0.125 0.131 0.085 0.036 -0.041 0.022
C309 0.109 0.107 0.118 0.034 -0.033 0.039
C310 0.074 0.125 0.137 0.016 -0.028 0.041
C311 0.132 0.072 0.132 0.035 -0.016 0.035
C312 0.145 0.151 0.047 0.006 0.026 -0.001
C313 0.153 0.151 0.043 0.016 -0.007 0.001
C314 0.148 0.128 0.066 0.044 -0.016 0.008
C315 0.145 0.098 0.087 0.052 0.004 -0.004
C316 0.148 0.067 0.122 0.046 -0.004 0.007
C317 0.144 0.085 0.103 -0.051 0.010 0.012
C318 0.143 0.117 0.067 -0.045 0.006 0.004
C319 0.135 0.138 0.059 -0.027 0.031 0.009
C320 0.128 0.057 0.144 0.004 -0.002 0.038
C321 0.102 0.083 0.139 -0.013 0.011 0.048
C322 0.071 0.115 0.145 -0.002 0.002 0.048
C323 0.114 0.092 0.116 -0.035 0.026 0.036
C324 0.128 0.064 0.143 0.019 0.009 -0.041
C325 0.147 0.047 0.143 0.024 0.003 -0.013
C326 0.142 0.041 0.142 -0.006 0.000 0.008
C327 0.134 0.054 0.120 -0.033 -0.002 -0.004
C328 0.134 0.079 0.102 -0.045 0.011 0.014
C329 0.121 0.139 0.072 0.023 0.043 -0.013
C330 0.127 0.110 0.090 0.042 0.029 -0.023
C331 0.110 0.096 0.124 0.032 0.027 -0.041
C332 0.102 0.125 0.097 -0.028 0.042 0.026
C333 0.070 0.138 0.115 -0.010 0.044 0.015
C334 0.051 0.138 0.141 -0.005 0.019 0.025
C335 0.078 0.140 0.107 0.009 0.048 -0.013
C336 0.128 0.132 0.062 -0.027 0.032 0.011
C337 0.146 0.144 0.042 0.014 -0.001 0.000
C338 0.131 0.141 0.050 0.003 0.030 -0.001
C339 0.113 0.134 0.075 0.022 0.043 -0.014
C340 0.131 0.121 0.062 -0.035 -0.021 -0.010
C341 0.137 0.111 0.068 -0.044 0.007 0.005
C342 0.139 0.147 0.049 -0.008 -0.029 -0.003
C343 0.111 0.105 0.094 -0.035 -0.031 -0.027
C344 0.108 0.075 0.142 -0.009 -0.006 -0.048
C345 0.118 0.071 0.117 -0.031 -0.015 -0.031
C346 0.087 0.135 0.114 -0.021 -0.046 -0.028
C347 0.069 0.125 0.129 0.014 0.030 -0.034
C348 0.050 0.132 0.142 0.001 0.003 -0.031
C349 0.040 0.146 0.145 0.000 -0.004 0.000
C350 0.074 0.117 0.139 -0.013 -0.020 -0.045
C351 0.100 0.094 0.121 0.027 0.025 -0.040
C352 0.112 0.065 0.132 0.012 0.007 -0.040
C353 0.105 0.082 0.140 -0.014 -0.011 -0.049
C354 0.147 0.062 0.128 -0.042 -0.005 -0.010
C355 0.131 0.081 0.126 -0.039 -0.020 -0.035
C356 0.146 0.126 0.063 0.043 -0.011 0.006
C357 0.137 0.093 0.085 0.048 0.006 -0.005
C358 0.121 0.106 0.090 0.040 0.029 -0.024
C359 0.135 0.061 0.115 0.039 -0.003 0.006
C360 0.132 0.044 0.131 0.016 0.002 -0.012
C361 0.143 0.042 0.142 -0.013 0.000 0.004
C362 0.135 0.138 0.083 0.039 -0.041 0.021
C363 0.120 0.117 0.119 0.040 -0.039 0.040
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C365 0.064 0.155 0.137 0.008 -0.044 0.017
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C367 0.124 0.157 0.075 0.010 -0.053 0.006
C368 0.082 0.134 0.141 0.021 -0.036 0.044
C369 0.075 0.112 0.147 -0.002 -0.003 -0.050
C370 0.043 0.148 0.145 -0.001 -0.018 -0.003
C371 0.061 0.136 0.142 -0.010 -0.026 -0.035
C372 0.088 0.140 0.092 0.004 0.050 -0.005
C373 0.080 0.109 0.148 0.005 -0.007 0.052
C374 0.062 0.118 0.132 -0.008 0.017 0.037
C375 0.043 0.135 0.134 -0.001 0.014 0.008
C376 0.059 0.134 0.120 0.007 0.035 -0.015
C377 0.074 0.119 0.134 0.015 0.026 -0.042
C378 0.118 0.074 0.149 0.009 -0.006 0.050
C379 0.133 0.057 0.145 -0.016 0.006 0.036
C380 0.124 0.083 0.122 -0.037 0.021 0.035
C381 0.091 0.110 0.113 -0.026 0.033 0.035
C382 0.102 0.133 0.086 -0.021 0.046 0.017
C201 0.077 0.112 0.147 0.007 -0.010 0.050
C202 0.084 0.123 0.127 0.022 -0.035 0.039
C203 0.120 0.106 0.108 0.040 -0.033 0.033
C204 0.071 0.148 0.122 0.009 -0.047 0.015
C205 0.049 0.151 0.143 -0.001 -0.029 -0.005
C206 0.040 0.146 0.146 0.000 0.005 0.004
C207 0.056 0.134 0.147 -0.005 0.012 0.037
C208 0.100 0.150 0.090 0.001 -0.055 0.001
C209 0.128 0.145 0.060 0.011 -0.040 0.005
C210 0.135 0.126 0.073 0.040 -0.030 0.016
C211 0.145 0.147 0.044 -0.010 -0.017 -0.002
C212 0.080 0.114 0.149 -0.009 -0.013 -0.052
C213 0.069 0.139 0.139 -0.015 -0.036 -0.035
C214 0.099 0.138 0.104 -0.024 -0.049 -0.026
C215 0.126 0.114 0.091 -0.042 -0.033 -0.025
C216 0.145 0.130 0.062 -0.040 -0.017 -0.008
C217 0.078 0.145 0.109 0.006 0.050 -0.009
C218 0.053 0.139 0.135 0.006 0.029 -0.020
C219 0.072 0.118 0.142 0.010 0.017 -0.046
C220 0.141 0.144 0.043 0.001 0.018 0.000
C221 0.135 0.130 0.059 0.031 0.024 -0.009
C222 0.145 0.113 0.072 0.049 0.000 0.000
C223 0.109 0.125 0.087 0.029 0.041 -0.022
C224 0.142 0.087 0.106 -0.050 0.015 0.018
C225 0.146 0.119 0.071 -0.047 0.014 0.009
C226 0.128 0.136 0.060 -0.023 0.034 0.009
C227 0.091 0.130 0.087 -0.014 0.045 0.014
C228 0.080 0.136 0.098 0.007 0.047 -0.009
C229 0.114 0.076 0.142 -0.017 -0.011 -0.047
C230 0.130 0.077 0.120 -0.040 -0.018 -0.030
C231 0.145 0.061 0.125 -0.042 -0.002 -0.003
C232 0.107 0.100 0.117 0.032 0.030 -0.038
C233 0.131 0.068 0.124 0.036 0.013 -0.028
C234 0.145 0.077 0.108 0.050 0.002 -0.002
C235 0.134 0.049 0.141 0.008 0.002 -0.028
C236 0.074 0.113 0.135 0.013 0.020 -0.044
C237 0.069 0.129 0.134 -0.014 -0.030 -0.036
C238 0.081 0.101 0.140 -0.006 -0.008 -0.049
C239 0.115 0.069 0.138 -0.015 -0.009 -0.043
C240 0.041 0.137 0.136 0.000 0.007 0.003
C241 0.054 0.134 0.128 0.007 0.029 -0.019

C242 0.047 0.147 0.141 -0.002 -0.026 -0.009
C243 0.056 0.121 0.133 -0.005 0.012 0.033
C244 0.115 0.087 0.123 -0.033 0.023 0.039
C245 0.080 0.111 0.114 -0.020 0.032 0.033
C246 0.076 0.114 0.146 0.009 -0.013 0.049
C247 0.141 0.040 0.141 -0.006 0.000 0.003
C248 0.132 0.052 0.140 0.012 -0.004 0.031
C249 0.137 0.070 0.124 0.040 -0.014 0.025
C250 0.108 0.077 0.145 -0.004 0.003 0.050
C251 0.137 0.056 0.122 -0.036 0.000 0.001
C252 0.127 0.078 0.104 -0.042 0.015 0.021
C253 0.109 0.089 0.129 -0.028 0.022 0.043
C254 0.091 0.142 0.103 -0.016 0.051 0.018
C255 0.082 0.126 0.130 -0.021 0.036 0.039
C256 0.098 0.133 0.105 -0.026 -0.046 -0.027
C257 0.121 0.106 0.088 -0.039 -0.029 -0.023
C258 0.128 0.073 0.117 -0.038 -0.015 -0.027
C259 0.134 0.120 0.058 -0.036 -0.012 -0.006
C260 0.129 0.109 0.069 -0.040 0.016 0.010
C261 0.123 0.137 0.068 -0.023 0.040 0.012
C262 0.102 0.158 0.097 -0.005 -0.059 -0.005
C263 0.133 0.158 0.066 0.009 -0.048 0.004
C264 0.145 0.148 0.045 -0.009 -0.020 -0.002
C265 0.123 0.121 0.113 0.041 -0.040 0.037
C266 0.084 0.137 0.135 0.022 -0.042 0.039
C267 0.070 0.156 0.129 0.007 -0.050 0.012
C268 0.141 0.140 0.077 0.039 -0.038 0.018
C269 0.127 0.062 0.145 -0.013 0.006 0.042
C270 0.130 0.079 0.128 0.038 -0.019 0.035
C271 0.113 0.079 0.148 0.012 -0.009 0.051
C272 0.122 0.059 0.139 0.010 0.005 -0.038
C273 0.148 0.126 0.063 0.044 -0.007 0.003
C274 0.135 0.091 0.086 0.047 0.007 -0.007
C275 0.135 0.062 0.115 0.040 -0.004 0.007
C276 0.136 0.043 0.134 0.015 0.001 -0.009
C277 0.143 0.043 0.142 -0.014 0.001 0.010
C278 0.150 0.148 0.043 0.016 0.006 -0.001
C279 0.134 0.148 0.055 0.007 0.036 -0.003
C280 0.110 0.136 0.083 0.023 0.046 -0.017
C281 0.116 0.102 0.095 0.038 0.029 -0.027
C282 0.103 0.090 0.128 0.026 0.022 -0.043
Ni1 0.0264(4) 0.0331(4) 0.0382(5) 0.000 -0.0026(3) 0.000
N1 0.027(2) 0.037(3) 0.042(3) 0.000 0.000(2) 0.000
N2 0.028(2) 0.036(3) 0.043(3) 0.000 -0.003(2) 0.000
N3 0.0255(15) 0.039(2) 0.044(2) 0.000(2) -0.0006(15) 0.0015(16)
C101 0.0277(19) 0.041(3) 0.042(3) 0.003(2) 0.0021(18) 0.0017(18)
C102 0.031(2) 0.046(3) 0.046(3) 0.001(2) -0.0016(19) -0.001(2)
C103 0.029(2) 0.035(2) 0.047(3) -0.002(2) 0.0004(18) 0.0011(18)
C104 0.029(2) 0.042(3) 0.048(3) -0.004(2) 0.0022(19) -0.0010(19)
C105 0.031(2) 0.039(3) 0.047(3) 0.006(2) 0.0006(19) 0.0047(19)
C106 0.033(2) 0.040(3) 0.043(3) -0.004(2) -0.0007(19) -0.0052(19)
C107 0.0292(19) 0.046(3) 0.043(3) 0.003(2) 0.0007(18) 0.0018(19)
C108 0.035(2) 0.049(3) 0.041(3) 0.000(2) -0.0069(19) -0.002(2)
C109 0.033(2) 0.032(2) 0.065(4) 0.000(2) 0.008(2) 0.0014(19)
C110 0.036(2) 0.038(2) 0.048(3) -0.005(2) -0.002(2) -0.0007(19)
C111 0.031(2) 0.055(3) 0.052(3) 0.008(3) -0.005(2) 0.002(2)
C112 0.043(3) 0.056(3) 0.054(3) 0.000(3) -0.013(2) -0.010(2)
C113 0.037(2) 0.034(2) 0.075(4) 0.005(3) 0.000(2) 0.004(2)
C114 0.042(3) 0.036(3) 0.079(4) -0.007(3) -0.006(3) -0.005(2)
C115 0.038(3) 0.078(4) 0.064(4) 0.022(3) 0.000(2) 0.021(3)
C116 0.059(3) 0.060(4) 0.049(3) -0.008(3) -0.006(3) -0.015(3)
C117 0.047(3) 0.043(3) 0.080(5) 0.002(3) 0.005(3) 0.010(2)
C118 0.060(4) 0.052(3) 0.086(5) -0.026(4) 0.001(3) -0.005(3)
C11 0.070(7) 0.082(19) 0.087(9) 0.009(10) 0.015(7) 0.017(10)
Cl11 0.058(2) 0.066(12) 0.061(3) 0.000(3) 0.0145(18) -0.002(3)
Cl12 0.079(4) 0.104(6) 0.133(6) 0.036(4) -0.034(4) -0.003(3)
Cl13 0.118(6) 0.094(9) 0.099(4) -0.024(4) 0.067(4) -0.036(5)
C31 0.049(12) 0.13(3) 0.19(2) 0.06(3) 0.022(14) 0.020(18)
Cl31 0.153(15) 0.33(3) 0.25(2) 0.21(3) 0.154(18) 0.15(2)
Cl32 0.27(3) 0.152(16) 0.151(13) -0.016(13) 0.009(12) 0.014(17)
Cl33 0.108(9) 0.21(3) 0.23(2) -0.11(2) 0.032(10) -0.064(12)
C41 0.3(2) 0.07(3) 0.09(5) 0.01(4) 0.02(8) 0.09(6)
Cl41 0.106(15) 0.20(3) 0.23(3) -0.14(3) -0.021(16) 0.043(16)
Cl42 0.061(9) 0.087(12) 0.30(4) 0.001(16) -0.007(14) 0.028(10)
Cl43 0.080(10) 0.31(5) 0.19(3) 0.19(3) 0.068(13) 0.088(18)

_geom_special_details;

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. ;

loop_
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_geom_bond_site_symmetry_2
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Tm1 Tm3 0.888(15) .
Tm1 Tm3 0.888(15)
Tm1 C217 2.255(2)
Tm1 C217 2.255(2) .
Tm1 C254 2.3249(17) .
Tm1 C254 2.3249(18)
Tm1 C335 2.361(4) .
Tm1 C335 2.361(5)
Tm1 C280 2.364(2)
Tm2 Tm3 1.562(19) .
Tm2 Tm3 1.562(19)
Tm2 C279 2.274(5) .
Tm2 C279 2.274(5)
Tm2 C261 2.305(5) .
Tm2 C261 2.305(5)
Tm2 Tm8 2.38(2)
Tm2 Tm8 2.38(2) .
Tm2 C338 2.383(7) .
Tm3 Tm3 1.01(2)
Tm3 C218 2.285(9)
Tm3 C347 2.368(11)
Tm3 C255 2.414(9) .
Tm3 C334 2.415(9) .
Tm3 Tm5 2.435(17) .
Tm3 C217 2.432(11)
Tm3 C348 2.430(12)
Tm4 Tm6 0.890(15) .
Tm4 Tm5 0.989(13) .
Tm4 Tm8 1.55(2) .
Tm4 Tm7 2.162(17) .
Tm4 C381 2.195(7)
Tm4 C380 2.281(8)
Tm4 C331 2.291(4) .
Tm4 C245 2.355(3)
Tm4 C232 2.388(3) .
Tm4 C244 2.400(3)
Tm5 Tm6 0.99(2) .
Tm5 Tm8 2.02(3) .
Tm5 Tm7 2.224(19) .
Tm5 C361 2.319(11)
Tm5 C235 2.364(11) .
Tm5 C277 2.370(10)
Tm5 C325 2.376(10) .
Tm5 C247 2.382(13) .
Tm5 C354 2.396(14)
Tm6 Tm7 1.52(2) .
Tm6 C330 2.166(12) .
Tm6 C317 2.211(15)
Tm6 C315 2.229(13) .
Tm6 C318 2.233(16)
Tm6 C380 2.344(17)

Tm6 Tm8 2.33(2) .
Tm6 C233 2.370(15) .
Tm7 Tm6 1.52(2)
Tm7 Tm4 2.162(16)
Tm7 Tm5 2.224(19)
Tm7 C313 2.357(17)
Tm7 C313 2.357(16) .
Tm7 C305 2.394(19) .
Tm7 C305 2.394(19)
Tm8 Tm8 1.57(6)
Tm8 C237 2.416(16) .
Tm8 C257 2.47(3) .
Tm8 C256 2.449(17) .
Tm8 C343 2.52(3) .
Tm8 C238 2.54(2) .
Ni1 N3 1.944(4)
Ni1 N3 1.9440 .
Ni1 N1 1.9554 .
Ni1 N2 1.9575 .
N1 C101 1.3767 .
N1 C101 1.377(4)
N2 C102 1.365(4)
N2 C102 1.3654 .
N3 C104 1.369(2)
N3 C103 1.373(2)
C101 C105 1.3514 .
C101 C107 1.466(5) .
C102 C106 1.386(6) .
C102 C108 1.454(5) .
C103 C105 1.3627 .
C103 N3 1.373(2)
C103 C109 1.463(5) .
C104 N3 1.369(2)
C104 C106 1.372(5) .
C104 C110 1.482(6) .
C107 C107 1.376(10)
C107 C111 1.491(7) .
C108 C108 1.366(11)
C108 C112 1.498(7) .
C109 C110 1.340(7) .
C109 C113 1.524(7) .
C110 C114 1.516(7) .
C111 C115 1.529(8) .
C112 C116 1.524(9) .
C113 C117 1.529(8) .
C114 C118 1.533(10) .
C301 C307 1.4065 .
C301 C302 1.4224 .
C301 C350 1.4722(15) .
C302 C304 1.4054 .
C302 C303 1.4450 .
C303 C310 1.391(2) .
C303 C349 1.4938(13) .
C304 C305 1.4298 .
C304 C308 1.457(3) .
C305 C306 1.4087(11) .
C305 C313 1.453(3) .
C306 C307 1.427(5) .
C306 C318 1.4659(12) .
C307 C355 1.4532 .
C308 C309 1.4044 .
C308 C314 1.4274 .
C309 C311 1.4211(15) .
C309 C310 1.446(3) .
C310 C322 1.4680 .
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6.2.2 Crystal B

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 'Ni'   'Ni'    0.2798    0.8728
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 'Tm'   'Tm'   -0.7442    4.1838
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; Refinement of F^2^ against reflections with F^2^ > 1.5sigma(F^2^).
The weighted R-factor wR and goodness of fit S are based on F^2^,
conventional R-factors R are based on F. The threshold expression of
F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement.  R-factors based
on F^2^ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
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P=(Fo^2^+2Fc^2^)/3'
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C564 C 0.65575(7) 0.04018(7) 0.16472(8) 0.069 Uani 0.2995(18) 1 d PG
C565 C 0.70799(9) -0.15908(4) 0.12061(8) 0.072 Uani 0.2995(18) 1 d PG
C566 C 0.74210(10) -0.12202(6) 0.08862(7) 0.076 Uani 0.2995(18) 1 d PG
C567 C 0.73740(10) -0.03316(6) 0.07589(6) 0.077 Uani 0.2995(18) 1 d PG
C568 C 0.67089(8) -0.10498(5) 0.13813(8) 0.077 Uani 0.2995(18) 1 d PG
C569 C 0.83371(9) -0.25453(4) 0.16284(6) 0.065 Uani 0.2995(18) 1 d PG
C570 C 0.73853(9) -0.22078(3) 0.15076(7) 0.068 Uani 0.2995(18) 1 d PG
C571 C 0.78974(10) -0.22937(4) 0.13343(6) 0.069 Uani 0.2995(18) 1 d PG
C572 C 0.78492(6) -0.23654(5) 0.27743(7) 0.064 Uani 0.2995(18) 1 d PG
C573 C 0.66364(7) -0.11173(7) 0.18612(9) 0.066 Uani 0.2995(18) 1 d PG
C574 C 0.69530(6) -0.16807(6) 0.21710(8) 0.063 Uani 0.2995(18) 1 d PG
C575 C 0.73434(8) -0.22498(4) 0.19863(8) 0.065 Uani 0.2995(18) 1 d PG
C576 C 0.78084(7) -0.25670(2) 0.22970(7) 0.064 Uani 0.2995(18) 1 d PG
C577 C 0.82902(8) -0.273654(12) 0.21136(6) 0.064 Uani 0.2995(18) 1 d PG
C578 C 0.64800(6) -0.02309(8) 0.20044(9) 0.071 Uani 0.2995(18) 1 d PG
C579 C 0.65745(4) 0.00000(10) 0.24615(9) 0.070 Uani 0.599(4) 2 d SPG
C580 C 0.68260(4) -0.06042(10) 0.28058(8) 0.065 Uani 0.2995(18) 1 d PG
C581 C 0.70286(5) -0.14309(9) 0.26655(8) 0.064 Uani 0.2995(18) 1 d PG
C582 C 0.74584(5) -0.17963(8) 0.29589(7) 0.064 Uani 0.2995(18) 1 d PG
Ni1 Ni 1.028322(19) 0.00000(9) 0.407885(18) 0.03763(14) Uani 1 2 d SG
N11 N 1.09257(2) 0.00000(11) 0.37707(3) 0.0394(8) Uani 1 2 d SG
N12 N 0.96866(2) 0.00000(10) 0.44423(2) 0.0404(8) Uani 1 2 d SG
N13 N 1.02605(3) 0.13059(8) 0.40447(3) 0.0417(6) Uani 1 1 d G
C11 C 0.99070(4) 0.18715(9) 0.42276(3) 0.0448(7) Uani 1 1 d G
C12 C 1.05746(4) 0.18574(9) 0.38152(3) 0.0460(7) Uani 1 1 d G
C13 C 0.94362(3) -0.07353(11) 0.46068(3) 0.0433(7) Uani 1 1 d G
C14 C 1.12210(3) 0.07273(12) 0.36693(3) 0.0421(7) Uani 1 1 d G
C15 C 0.95375(4) -0.16043(10) 0.45048(4) 0.0461(7) Uani 1 1 d G
H15 H 0.9342 -0.2046 0.4632 0.055 Uiso 1 1 calc R
C16 C 1.10430(13) 0.1598(2) 0.36597(12) 0.0470(7) Uani 1 1 d
H16 H 1.1250 0.2036 0.3542 0.056 Uiso 1 1 calc R
C17 C 0.99908(14) 0.2791(2) 0.40828(13) 0.0519(8) Uani 1 1 d
C18 C 1.03950(14) 0.2785(2) 0.38178(14) 0.0535(9) Uani 1 1 d
C19 C 0.90163(12) -0.0453(2) 0.48741(11) 0.0478(8) Uani 1 1 d
C20 C 1.17362(12) 0.0452(2) 0.35452(12) 0.0473(8) Uani 1 1 d
C21 C 0.96643(16) 0.3568(3) 0.42140(17) 0.0664(11) Uani 1 1 d
H21A H 0.9853 0.4119 0.4168 0.080 Uiso 1 1 calc R
H21B H 0.9626 0.3525 0.4542 0.080 Uiso 1 1 calc R
C22 C 1.06166(17) 0.3532(3) 0.35600(17) 0.0670(11) Uani 1 1 d
H22A H 1.1000 0.3483 0.3596 0.080 Uiso 1 1 calc R
H22B H 1.0527 0.4098 0.3695 0.080 Uiso 1 1 calc R
C23 C 0.86525(14) -0.1087(3) 0.50868(13) 0.0586(10) Uani 1 1 d
H23A H 0.8515 -0.0786 0.5343 0.070 Uiso 1 1 calc R
H23B H 0.8858 -0.1597 0.5214 0.070 Uiso 1 1 calc R
C24 C 1.21703(14) 0.1082(3) 0.34688(15) 0.0610(10) Uani 1 1 d
H24A H 1.2020 0.1591 0.3291 0.073 Uiso 1 1 calc R
H24B H 1.2413 0.0784 0.3286 0.073 Uiso 1 1 calc R
C25 C 0.91152(18) 0.3616(3) 0.39370(18) 0.0763(13) Uani 1 1 d
H25A H 0.9149 0.3653 0.3611 0.114 Uiso 1 1 calc R
H25B H 0.8933 0.4136 0.4029 0.114 Uiso 1 1 calc R
H25C H 0.8918 0.3090 0.3995 0.114 Uiso 1 1 calc R
C26 C 1.0407(2) 0.3532(3) 0.30422(18) 0.0842(14) Uani 1 1 d
H26A H 1.0504 0.2981 0.2904 0.126 Uiso 1 1 calc R
H26B H 1.0559 0.4026 0.2893 0.126 Uiso 1 1 calc R
H26C H 1.0028 0.3590 0.3004 0.126 Uiso 1 1 calc R
C27 C 0.81913(16) -0.1423(4) 0.47521(16) 0.0750(13) Uani 1 1 d
H27A H 0.7974 -0.0927 0.4636 0.113 Uiso 1 1 calc R
H27B H 0.7984 -0.1832 0.4910 0.113 Uiso 1 1 calc R
H27C H 0.8323 -0.1725 0.4497 0.113 Uiso 1 1 calc R
C28 C 1.24785(19) 0.1415(4) 0.39168(19) 0.0891(16) Uani 1 1 d
H28A H 1.2250 0.1769 0.4084 0.134 Uiso 1 1 calc R
H28B H 1.2771 0.1775 0.3847 0.134 Uiso 1 1 calc R
H28C H 1.2610 0.0914 0.4104 0.134 Uiso 1 1 calc R
Ni2 Ni 0.986075(18) 0.0000 0.057629(19) 0.03020(12) Uani 1 2 d S
N21 N 0.92512(12) 0.0000 0.00909(12) 0.0332(7) Uani 1 2 d S
N22 N 1.04516(12) 0.0000 0.10792(12) 0.0325(7) Uani 1 2 d S
N23 N 0.98489(8) 0.13133(15) 0.05864(8) 0.0321(5) Uani 1 1 d
C31 C 0.95048(11) 0.1878(2) 0.03226(11) 0.0375(6) Uani 1 1 d
C32 C 1.01745(11) 0.18811(19) 0.08722(10) 0.0351(6) Uani 1 1 d
C33 C 1.07025(10) -0.0728(2) 0.13045(10) 0.0350(6) Uani 1 1 d
C34 C 0.89771(10) -0.0731(2) -0.01123(10) 0.0344(6) Uani 1 1 d
C35 C 0.91011(11) 0.1607(2) -0.00073(11) 0.0373(6) Uani 1 1 d
H35 H 0.8898 0.2048 -0.0171 0.045 Uiso 1 1 calc R
C36 C 1.05771(11) 0.1608(2) 0.12025(11) 0.0382(6) Uani 1 1 d
H36 H 1.0779 0.2048 0.1369 0.046 Uiso 1 1 calc R
C37 C 0.96165(11) 0.2810(2) 0.04452(13) 0.0427(7) Uani 1 1 d
C38 C 1.00306(11) 0.2811(2) 0.07838(13) 0.0431(7) Uani 1 1 d
C39 C 1.10996(11) -0.0452(2) 0.16763(11) 0.0400(7) Uani 1 1 d
C40 C 0.85327(10) -0.0455(2) -0.04400(10) 0.0378(6) Uani 1 1 d
C41 C 1.02917(14) 0.3585(2) 0.10538(15) 0.0562(9) Uani 1 1 d
H41A H 1.0208 0.4132 0.0880 0.067 Uiso 1 1 calc R
H41B H 1.0673 0.3504 0.1086 0.067 Uiso 1 1 calc R
C42 C 0.92935(14) 0.3586(2) 0.02313(16) 0.0592(10) Uani 1 1 d
H42A H 0.9223 0.3495 -0.0102 0.071 Uiso 1 1 calc R
H42B H 0.9500 0.4131 0.0284 0.071 Uiso 1 1 calc R
C43 C 1.14130(12) -0.1085(3) 0.20098(13) 0.0499(8) Uani 1 1 d
H43A H 1.1730 -0.0784 0.2153 0.060 Uiso 1 1 calc R
H43B H 1.1523 -0.1595 0.1838 0.060 Uiso 1 1 calc R
C44 C 0.81403(12) -0.1082(2) -0.06998(12) 0.0455(7) Uani 1 1 d
H44A H 0.8326 -0.1601 -0.0798 0.055 Uiso 1 1 calc R
H44B H 0.7969 -0.0785 -0.0976 0.055 Uiso 1 1 calc R
C45 C 1.01194(18) 0.3687(3) 0.15356(18) 0.0795(14) Uani 1 1 d
H45A H 0.9746 0.3807 0.1507 0.119 Uiso 1 1 calc R
H45B H 1.0310 0.4174 0.1695 0.119 Uiso 1 1 calc R
H45C H 1.0194 0.3144 0.1708 0.119 Uiso 1 1 calc R
C46 C 0.87690(16) 0.3706(3) 0.0426(2) 0.0889(17) Uani 1 1 d
H46A H 0.8568 0.3161 0.0387 0.133 Uiso 1 1 calc R
H46B H 0.8571 0.4182 0.0264 0.133 Uiso 1 1 calc R
H46C H 0.8836 0.3849 0.0751 0.133 Uiso 1 1 calc R
C47 C 0.77132(14) -0.1393(3) -0.03977(15) 0.0688(12) Uani 1 1 d
H47A H 0.7882 -0.1685 -0.0123 0.103 Uiso 1 1 calc R
H47B H 0.7475 -0.1803 -0.0572 0.103 Uiso 1 1 calc R
H47C H 0.7518 -0.0883 -0.0310 0.103 Uiso 1 1 calc R
C48 C 1.10980(16) 0.1419(3) 0.23908(14) 0.0617(10) Uani 1 1 d
H48A H 1.1320 0.1793 0.2603 0.093 Uiso 1 1 calc R

H48B H 1.0979 0.0917 0.2556 0.093 Uiso 1 1 calc R
H48C H 1.0797 0.1757 0.2253 0.093 Uiso 1 1 calc R
C101 C 0.83211(17) 0.5000 0.20213(16) 0.0620(19) Uani 0.730(9) 2 d SPGU
C102 C 0.88688(18) 0.500(3) 0.19829(16) 0.064(2) Uani 0.730(9) 2 d SPGU
C103 C 0.92441(15) 0.499(3) 0.2380(2) 0.072(2) Uani 0.730(9) 2 d SPGU
C104 C 0.9076(2) 0.4877(18) 0.28218(17) 0.067(5) Uani 0.365(4) 1 d PGU
C105 C 0.8533(3) 0.488(3) 0.28634(18) 0.071(7) Uani 0.365(4) 1 d PGU
C106 C 0.81570(18) 0.500(3) 0.24665(19) 0.069(2) Uani 0.730(9) 2 d SPGU
C107 C 0.7909(3) 0.5099(10) 0.1592(2) 0.080(4) Uani 0.365(4) 1 d PGU
C201 C 0.8390(6) 0.5000 0.2506(5) 0.090(5) Uiso 0.270(9) 2 d SPGU
C202 C 0.7862(6) 0.498(3) 0.2290(6) 0.090(5) Uiso 0.270(9) 2 d SPGU
C203 C 0.7750(7) 0.497(4) 0.1805(7) 0.090(5) Uiso 0.270(9) 2 d SPGU
C204 C 0.8162(8) 0.506(3) 0.1528(5) 0.090(5) Uiso 0.135(4) 1 d PGU
C205 C 0.8688(7) 0.509(4) 0.1740(6) 0.090(5) Uiso 0.135(4) 1 d PGU
C206 C 0.8805(5) 0.501(3) 0.2226(6) 0.090(5) Uiso 0.270(9) 2 d SPGU
C207 C 0.8523(10) 0.4876(18) 0.3034(5) 0.090(5) Uiso 0.135(4) 1 d PGU
C301 C 0.8447(4) 0.4335(8) 0.5477(4) 0.086(5) Uani 0.287(5) 1 d PGU
C302 C 0.8932(4) 0.4367(10) 0.5288(5) 0.081(5) Uani 0.287(5) 1 d PGU
C303 C 0.9137(4) 0.5186(12) 0.5154(4) 0.095(6) Uani 0.287(5) 1 d PGU
C304 C 0.8861(6) 0.5986(10) 0.5207(6) 0.168(19) Uani 0.287(5) 1 d PGU
C305 C 0.8378(7) 0.5961(9) 0.5394(7) 0.107(7) Uani 0.287(5) 1 d PGU
C306 C 0.8172(5) 0.5142(10) 0.5529(5) 0.093(5) Uani 0.287(5) 1 d PGU
C307 C 0.8219(7) 0.3451(10) 0.5625(8) 0.112(7) Uani 0.287(5) 1 d PGU
C401 C 0.8544(6) 0.4584(10) 0.5305(6) 0.088(7) Uani 0.213(5) 1 d PGU
C402 C 0.8876(6) 0.5174(12) 0.5094(6) 0.097(7) Uani 0.213(5) 1 d PGU
C403 C 0.8869(9) 0.6097(11) 0.5185(8) 0.117(10) Uani 0.213(5) 1 d PGU
C404 C 0.8531(9) 0.6443(11) 0.5489(8) 0.17(2) Uani 0.213(5) 1 d PGU
C405 C 0.8200(6) 0.5862(14) 0.5700(6) 0.084(5) Uani 0.213(5) 1 d PGU
C406 C 0.8206(5) 0.4994(13) 0.5609(6) 0.079(4) Uani 0.426(10) 2 d SPGU
C407 C 0.8547(12) 0.3580(11) 0.5209(12) 0.129(11) Uani 0.213(5) 1 d PGU

loop_
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Tm1 0.0533(8) 0.0556(8) 0.1227(18) 0.0040(8) 0.0189(8) -0.0239(6)
Tm2 0.196(6) 0.092(3) 0.109(3) 0.039(3) -0.012(4) -0.088(4)
Tm3 0.0902(10) 0.1147(15) 0.0399(6) -0.0193(6) 0.0202(6) 0.0057(8)
Tm4 0.131(9) 0.31(5) 0.096(9) -0.070(16) 0.018(7) 0.079(17)
Tm5 0.128(5) 0.181(11) 0.070(3) 0.046(4) -0.014(3) 0.017(4)
C601 0.078 0.080 0.057 0.012 -0.013 0.009
C602 0.070 0.086 0.064 0.001 -0.020 0.002
C603 0.082 0.087 0.045 -0.006 -0.014 0.001
C604 0.066 0.085 0.058 -0.001 -0.025 0.002
C605 0.041 0.083 0.080 0.003 -0.019 0.007
C606 0.047 0.070 0.074 0.011 -0.017 0.021
C607 0.073 0.069 0.066 0.016 -0.011 0.017
C608 0.061 0.081 0.064 -0.013 -0.026 -0.010
C609 0.081 0.074 0.066 -0.016 -0.009 -0.008
C610 0.085 0.081 0.036 -0.022 -0.011 -0.003
C611 0.075 0.043 0.071 -0.027 -0.012 -0.021
C612 0.030 0.085 0.086 0.000 0.014 0.000
C613 0.030 0.086 0.086 -0.003 -0.010 -0.005
C614 0.044 0.076 0.088 -0.005 -0.007 -0.011
C615 0.065 0.058 0.086 0.002 0.009 -0.025
C616 0.075 0.045 0.087 -0.003 -0.002 -0.018
C617 0.067 0.047 0.082 -0.008 0.008 0.026
C618 0.037 0.067 0.084 0.001 0.006 0.024
C619 0.042 0.076 0.079 -0.007 0.019 0.019
C620 0.085 0.043 0.072 -0.026 -0.001 -0.005
C621 0.080 0.076 0.068 -0.016 0.004 0.003
C622 0.087 0.070 0.059 -0.021 -0.003 0.000
C623 0.062 0.068 0.070 -0.019 0.019 0.024
C624 0.085 0.051 0.083 0.014 0.006 -0.007
C625 0.081 0.051 0.086 0.003 0.002 -0.012
C626 0.084 0.033 0.084 -0.006 0.000 0.001
C627 0.077 0.050 0.074 0.001 -0.002 0.008
C628 0.065 0.050 0.081 -0.005 0.004 0.023
C629 0.043 0.079 0.077 0.006 0.019 -0.014
C630 0.070 0.065 0.080 0.008 0.012 -0.018
C631 0.075 0.057 0.086 0.007 0.010 -0.017
C632 0.073 0.076 0.063 -0.012 0.021 0.018
C633 0.073 0.080 0.057 -0.009 0.022 0.008
C634 0.077 0.083 0.046 -0.020 0.019 0.006
C635 0.068 0.081 0.071 0.003 0.024 -0.007
C636 0.029 0.078 0.083 -0.004 0.020 0.027
C637 0.033 0.087 0.092 0.000 -0.004 -0.001
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C640 0.031 0.080 0.076 0.008 -0.015 0.024
C641 0.049 0.066 0.083 0.000 0.000 0.024
C642 0.036 0.093 0.077 0.002 -0.026 0.008
C643 0.064 0.079 0.055 0.015 -0.019 0.013
C644 0.084 0.054 0.070 0.020 0.003 0.003
C645 0.078 0.045 0.063 0.026 -0.007 0.013
C646 0.086 0.076 0.054 0.018 -0.010 0.011
C647 0.075 0.072 0.050 0.023 0.026 -0.010
C648 0.087 0.077 0.062 0.008 0.004 0.001
C649 0.091 0.082 0.036 0.000 0.001 0.000
C650 0.086 0.067 0.046 0.026 -0.001 0.005
C651 0.068 0.061 0.071 0.021 0.018 -0.019
C652 0.082 0.044 0.073 0.017 0.011 -0.011
C653 0.086 0.049 0.061 0.029 0.003 0.005
C654 0.080 0.031 0.085 0.003 0.004 0.020
C655 0.083 0.048 0.075 0.019 -0.001 0.014
C656 0.029 0.086 0.089 -0.004 -0.005 -0.023
C657 0.053 0.053 0.082 -0.003 -0.001 -0.028
C658 0.047 0.064 0.083 0.010 0.019 -0.031
C659 0.063 0.043 0.084 -0.010 -0.003 -0.027
C660 0.078 0.033 0.081 0.008 0.006 -0.013
C661 0.086 0.029 0.085 -0.005 0.004 0.006
C662 0.066 0.089 0.082 -0.009 -0.012 -0.014
C663 0.072 0.078 0.072 -0.023 -0.015 -0.020
C664 0.070 0.053 0.077 -0.024 -0.010 -0.032
C665 0.083 0.089 0.059 -0.008 -0.012 -0.002
C666 0.072 0.092 0.072 0.001 -0.018 0.001
C667 0.065 0.091 0.077 -0.001 -0.018 -0.002

C668 0.082 0.084 0.055 -0.018 -0.014 -0.009
C669 0.089 0.065 0.052 0.025 0.002 0.004
C670 0.088 0.084 0.045 0.003 -0.002 0.001
C671 0.088 0.077 0.049 0.020 -0.005 0.005
C672 0.054 0.082 0.058 0.000 0.030 0.000
C673 0.085 0.067 0.049 -0.026 0.002 -0.006
C674 0.074 0.069 0.038 -0.024 0.014 0.003
C675 0.078 0.079 0.043 0.000 0.012 -0.003
C676 0.073 0.074 0.031 0.002 0.031 -0.002
C677 0.082 0.068 0.060 0.016 0.015 -0.006
C678 0.090 0.047 0.069 -0.028 0.001 -0.008
C679 0.087 0.035 0.079 -0.025 0.005 0.003
C680 0.077 0.041 0.072 -0.025 0.016 0.019
C681 0.062 0.068 0.059 -0.018 0.023 0.015
C682 0.048 0.076 0.068 -0.009 0.028 0.011
C501 0.086 0.074 0.055 -0.020 0.004 0.001
C502 0.080 0.078 0.054 -0.016 -0.015 -0.007
C503 0.079 0.067 0.068 -0.017 -0.010 -0.014
C504 0.082 0.084 0.047 -0.008 -0.016 -0.004
C505 0.085 0.085 0.036 -0.001 -0.008 -0.001
C506 0.087 0.082 0.038 -0.005 0.012 0.003
C507 0.085 0.074 0.051 -0.019 0.013 0.007
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C509 0.057 0.086 0.069 -0.002 -0.023 0.001
C510 0.057 0.078 0.074 -0.009 -0.022 -0.010
C511 0.033 0.084 0.083 0.000 -0.017 0.010
C512 0.086 0.064 0.047 0.031 0.001 0.003
C513 0.084 0.082 0.045 0.017 -0.010 0.006
C514 0.067 0.082 0.054 0.013 -0.023 0.011
C515 0.063 0.065 0.068 0.017 -0.016 0.022
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C517 0.060 0.081 0.063 0.001 0.031 -0.002
C518 0.074 0.083 0.046 0.007 0.019 -0.001
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C520 0.027 0.084 0.088 -0.001 0.002 0.002
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C532 0.064 0.068 0.078 0.012 0.017 -0.018
C533 0.070 0.055 0.085 0.008 0.008 -0.022
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C539 0.084 0.050 0.070 0.022 0.001 0.005
C540 0.079 0.081 0.036 -0.004 0.013 -0.002
C541 0.074 0.078 0.039 0.007 0.026 -0.004
C542 0.087 0.086 0.039 0.002 -0.004 0.001
C543 0.076 0.069 0.043 -0.022 0.011 0.003
C544 0.075 0.043 0.072 -0.025 0.015 0.021
C545 0.065 0.069 0.057 -0.017 0.019 0.012
C546 0.085 0.068 0.049 -0.025 -0.001 -0.005
C547 0.083 0.043 0.084 0.008 0.002 -0.004
C548 0.082 0.045 0.082 -0.011 -0.002 -0.009
C549 0.075 0.053 0.087 -0.011 -0.005 -0.013
C550 0.086 0.051 0.068 -0.023 -0.001 -0.003
C551 0.077 0.034 0.080 0.004 -0.003 0.015
C552 0.063 0.040 0.080 -0.008 0.009 0.027
C553 0.077 0.054 0.074 -0.018 0.015 0.016
C554 0.064 0.081 0.066 -0.009 0.024 0.014
C555 0.074 0.072 0.063 -0.017 0.022 0.012
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C568 0.058 0.087 0.078 -0.010 -0.019 -0.015
C569 0.086 0.030 0.077 -0.027 0.005 0.006
C570 0.069 0.054 0.076 -0.022 -0.011 -0.028
C571 0.087 0.050 0.068 -0.026 -0.001 -0.007
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C573 0.024 0.083 0.088 -0.004 -0.007 -0.024
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N22 0.0306(15) 0.0271(16) 0.0409(19) 0.000 0.0083(13) 0.000 -0.0055(14)
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C38 0.0379(14) 0.0259(14) 0.067(2) -0.0030(14) 0.0116(14) -0.0027(11)
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C40 0.0319(12) 0.0432(16) 0.0384(15) -0.0024(13) 0.0053(11) -0.0025(12)
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C42 0.0517(18) 0.0271(15) 0.098(3) 0.0081(18) 0.0064(19) 0.0027(14)
C43 0.0399(15) 0.052(2) 0.056(2) 0.0057(17) -0.0037(14) 0.0076(15)
C44 0.0389(14) 0.052(2) 0.0450(18) -0.0071(15) 0.0023(13)

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C47 0.0488(18) 0.086(3) 0.073(3) -0.023(2) 0.0126(18) -0.032(2)
C48 0.067(2) 0.064(3) 0.054(2) -0.0131(19) 0.0058(18) -0.015(2)
C101 0.069(4) 0.034(3) 0.078(4) 0.000 -0.009(3) 0.000
C102 0.076(4) 0.046(5) 0.071(5) 0.000 0.009(3) 0.000
C103 0.060(4) 0.074(6) 0.083(5) 0.000 0.010(3) 0.000
C104 0.086(4) 0.041(16) 0.071(4) -0.010(6) -0.008(4) 0.001(5)
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C106 0.069(4) 0.048(4) 0.091(5) 0.000 0.011(3) 0.000
C107 0.091(7) 0.055(10) 0.087(7) -0.014(8) -0.017(5) -0.019(8)
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C302 0.085(8) 0.108(13) 0.051(10) -0.001(10) 0.016(7) 0.026(7)
C303 0.073(8) 0.149(15) 0.067(9) -0.043(11) 0.028(7) -0.047(9)
C304 0.25(3) 0.093(11) 0.19(4) 0.002(11) 0.15(3) -0.047(12)
C305 0.131(14) 0.079(8) 0.111(16) 0.014(12) 0.022(12) 0.017(11)
C306 0.068(11) 0.082(7) 0.134(12) 0.005(8) 0.033(9) 0.009(6)
C307 0.080(12) 0.082(8) 0.16(2) 0.016(12) -0.022(11) -0.026(10)
C401 0.073(8) 0.078(8) 0.12(2) -0.018(9) 0.044(12) -0.018(7)
C402 0.080(9) 0.097(12) 0.12(2) -0.002(8) 0.033(10) -0.028(10)
C403 0.21(2) 0.101(11) 0.049(17) 0.001(11) 0.048(18) -0.056(12)
C404 0.17(3) 0.087(11) 0.27(6) -0.02(2) 0.10(4) -0.018(15)
C405 0.045(9) 0.105(11) 0.100(16) -0.018(12) -0.001(8) 0.017(10)
C406 0.046(10) 0.095(8) 0.100(12) 0.000 0.020(8) 0.000
C407 0.14(3) 0.060(10) 0.19(3) 0.009(13) 0.03(2) 0.022(11)

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.;

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Tm1 C525 2.403(2)	Tm4 C581 2.46(2)	C609 C611 1.4205	C624 C625 1.3623
Tm1 C533 2.411(2)	Tm5 Tm5 0.960(18)	C609 C610 1.4461	C624 C644 1.4586
Tm1 C522 2.440(2)	Tm5 C537 2.471(6)	C610 C622 1.4679	C624 C631 1.4612
Tm2 C680 2.313(5)	Tm5 Tm2 2.484(9)	C611 C616 1.4059	C625 C626 1.4638
Tm2 C681 2.383(6)	Tm5 C671 2.532(6)	C611 C620 1.4755	C626 C627 1.4438
Tm2 C631 2.392(5)	Tm5 C556 2.552(6)	C612 C613 1.3620	C627 C628 1.3939
Tm2 C624 2.404(4)	Tm5 C646 2.559(6)	C612 C629 1.4327	C627 C645 1.4741
Tm3 Tm3 0.960(3)	Tm5 C670 2.589(7)	C612 C619 1.4784	C628 C641 1.4522
Tm3 Tm4 1.002(17)	Tm5 C542 2.592(6)	C613 C614 1.4533	C629 C672 1.4164
Tm3 Tm4 1.34(2)	C601 C607 1.4062	C614 C615 1.4075	C629 C630 1.4170
Tm3 C648 2.266(4)	C601 C602 1.4224	C615 C616 1.4273	C630 C631 1.4138
Tm3 C634 2.317(3)	C601 C650 1.4730	C615 C630 1.4667	C631 C677 1.4191
Tm3 C506 2.327(2)	C602 C604 1.3736	C616 C625 1.4533	C632 C633 1.4263
Tm3 C518 2.327(2)	C602 C603 1.4452	C617 C618 1.4135	C632 C636 1.4637
Tm3 C507 2.3773(19)	C603 C610 1.3902	C617 C680 1.4204	C633 C634 1.4235
Tm3 C519 2.400(2)	C603 C649 1.4335	C617 C654 1.4613	C633 C635 1.4242
Tm3 C622 2.439(3)	C604 C605 1.3910	C618 C619 1.4187	C634 C649 1.3406
Tm4 Tm4 0.84(6)	C604 C608 1.5339	C619 C682 1.4167	C635 C647 1.4110
Tm4 Tm3 1.34(2)	C605 C606 1.4079	C620 C626 1.3880	C635 C639 1.4658
Tm4 C633 2.391(13)	C605 C613 1.4534	C620 C621 1.4383	C636 C641 1.4124
Tm4 C635 2.396(13)	C606 C607 1.4273	C621 C622 1.4055	C636 C638 1.5060
Tm4 C517 2.424(15)	C606 C618 1.4664	C621 C623 1.4238	C637 C638 1.3817
Tm4 C554 2.427(14)	C607 C655 1.4539	C622 C634 1.4260	C637 C642 1.4433

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Refinement of F^2^ against reflections with F^2^ > 1.5sigma(F^2^).
The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.
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C018 C -0.1066(3) 0.1460(5) 0.1650(3) 0.0567(17) Uani 1 1 d
H01C H -0.1281 0.1858 0.1361 0.085 Uiso 1 1 calc R
H01D H -0.0943 0.0977 0.1400 0.085 Uiso 1 1 calc R
H01E H -0.0767 0.1783 0.1869 0.085 Uiso 1 1 calc R
C019 C 0.1242(3) 0.3681(5) 0.4459(5) 0.078(2) Uani 1 1 d
H01F H 0.1426 0.4184 0.4673 0.117 Uiso 1 1 calc R
H01G H 0.1194 0.3775 0.3992 0.117 Uiso 1 1 calc R
H01H H 0.1447 0.3146 0.4560 0.117 Uiso 1 1 calc R
C020 C 0.0703(2) 0.3581(3) 0.4701(3) 0.0463(14) Uani 1 1 d
H02A H 0.0754 0.3500 0.5175 0.056 Uiso 1 1 calc R
H02B H 0.0500 0.4127 0.4606 0.056 Uiso 1 1 calc R
C021 C 0.0395(2) 0.2808(3) 0.4391(3) 0.0350(11) Uani 1 1 d
C022 C -0.00244(19) 0.2803(3) 0.3909(3) 0.0349(11) Uani 1 1 d
C023 C -0.0291(3) 0.3577(3) 0.3529(3) 0.0489(15) Uani 1 1 d
H02C H -0.0203 0.4127 0.3771 0.059 Uiso 1 1 calc R
H02D H -0.0673 0.3498 0.3494 0.059 Uiso 1 1 calc R
C024 C -0.0131(3) 0.3673(5) 0.2842(4) 0.079(2) Uani 1 1 d
H02E H -0.0312 0.4177 0.2625 0.119 Uiso 1 1 calc R
H02F H -0.0226 0.3138 0.2594 0.119 Uiso 1 1 calc R
H02G H 0.0245 0.3764 0.2873 0.119 Uiso 1 1 calc R
Ni01 Ni 0.01525(3) 0.0000 0.41931(4) 0.02204(19) Uani 1 2 d S
N001 N 0.0760(2) 0.0000 0.4881(3) 0.0245(10) Uani 1 2 d S
N002 N 0.01619(14) 0.1312(2) 0.41774(19) 0.0248(7) Uani 1 1 d
N003 N -0.0432(2) 0.0000 0.3482(3) 0.0258(11) Uani 1 2 d S
C101 C 0.1666(4) 0.1644(5) 0.0177(4) 0.097 Uani 0.225(4) 1 d PG
C102 C 0.1133(4) 0.1352(5) 0.0173(4) 0.099 Uani 0.225(4) 1 d PG
C103 C 0.0829(4) 0.1735(5) 0.0654(4) 0.100 Uani 0.225(4) 1 d PG
C104 C 0.1005(4) 0.0480(6) -0.0052(3) 0.101 Uani 0.225(4) 1 d PG
C105 C 0.1405(4) -0.0117(6) -0.0222(3) 0.099 Uani 0.225(4) 1 d PG
C106 C 0.1944(4) 0.0139(6) -0.0149(3) 0.093 Uani 0.225(4) 1 d PG
C107 C 0.2058(4) 0.1058(5) 0.0004(4) 0.095 Uani 0.225(4) 1 d PG
C108 C 0.0606(3) -0.0044(6) 0.0230(4) 0.102 Uani 0.225(4) 1 d PG
C109 C 0.0342(3) 0.0312(6) 0.0733(5) 0.100 Uani 0.225(4) 1 d PG
C110 C 0.0448(3) 0.1234(6) 0.0924(5) 0.100 Uani 0.225(4) 1 d PG
C111 C 0.0196(2) -0.0289(6) 0.1217(5) 0.099 Uani 0.225(4) 1 d PG
C112 C 0.1621(4) -0.1650(5) 0.0138(4) 0.098 Uani 0.225(4) 1 d PG
C113 C 0.1245(4) -0.1020(6) -0.0071(4) 0.101 Uani 0.225(4) 1 d PG
C114 C 0.0760(3) -0.0965(6) 0.0235(4) 0.101 Uani 0.225(4) 1 d PG
C115 C 0.0668(3) -0.1538(5) 0.0754(5) 0.098 Uani 0.225(4) 1 d PG
C116 C 0.0344(3) -0.1196(6) 0.1218(5) 0.099 Uani 0.225(4) 1 d PG

C117 C 0.2836(3) -0.0248(6) 0.0416(4) 0.090 Uani 0.225(4) 1 d PG
C118 C 0.2347(4) -0.0535(5) 0.0071(4) 0.090 Uani 0.225(4) 1 d PG
C119 C 0.2179(4) -0.1413(5) 0.0210(4) 0.092 Uani 0.225(4) 1 d PG
C120 C 0.0202(2) 0.0002(6) 0.1905(5) 0.095 Uani 0.449(8) 2 d SPG
C121 C 0.0348(3) 0.0906(6) 0.2099(5) 0.093 Uani 0.225(4) 1 d PG
C122 C 0.0446(3) 0.1520(5) 0.1608(5) 0.097 Uani 0.225(4) 1 d PG
C123 C 0.0618(3) 0.1034(5) 0.2745(5) 0.091 Uani 0.225(4) 1 d PG
C124 C 0.0786(4) -0.2130(4) 0.2102(5) 0.096 Uani 0.225(4) 1 d PG
C125 C 0.0419(3) -0.1489(5) 0.1899(5) 0.097 Uani 0.225(4) 1 d PG
C126 C 0.0359(3) -0.0718(6) 0.2317(5) 0.092 Uani 0.225(4) 1 d PG
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C128 C 0.0791(3) 0.0272(6) 0.3151(4) 0.087 Uani 0.225(4) 1 d PG
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C130 C 0.1069(4) -0.2216(4) 0.0977(5) 0.095 Uani 0.225(4) 1 d PG
C131 C 0.1113(4) -0.2514(3) 0.1636(5) 0.095 Uani 0.225(4) 1 d PG
C132 C 0.0995(4) 0.1725(5) 0.2886(4) 0.092 Uani 0.225(4) 1 d PG
C133 C 0.1129(4) 0.2302(3) 0.2379(5) 0.094 Uani 0.225(4) 1 d PG
C134 C 0.0834(4) 0.2208(4) 0.1743(5) 0.097 Uani 0.225(4) 1 d PG
C135 C 0.1664(4) 0.26041(19) 0.2412(5) 0.095 Uani 0.225(4) 1 d PG
C136 C 0.1401(4) 0.1406(5) 0.3405(4) 0.092 Uani 0.225(4) 1 d PG
C137 C 0.2336(4) 0.1087(5) 0.3697(4) 0.098 Uani 0.225(4) 1 d PG
C138 C 0.1942(4) 0.1682(5) 0.3426(4) 0.094 Uani 0.225(4) 1 d PG
C139 C 0.2072(4) 0.2287(3) 0.2930(4) 0.095 Uani 0.225(4) 1 d PG
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C143 C 0.1589(4) -0.1052(5) 0.3563(4) 0.088 Uani 0.225(4) 1 d PG
C144 C 0.1108(4) -0.2058(4) 0.2741(5) 0.092 Uani 0.225(4) 1 d PG
C145 C 0.1102(4) -0.1292(5) 0.3140(4) 0.085 Uani 0.225(4) 1 d PG
C146 C 0.2038(4) -0.1607(5) 0.3558(4) 0.097 Uani 0.225(4) 1 d PG
C147 C 0.1904(4) 0.27232(2) 0.1834(5) 0.094 Uani 0.225(4) 1 d PG
C148 C 0.1617(4) 0.25747(18) 0.1200(5) 0.095 Uani 0.225(4) 1 d PG
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C171 C 0.2047(4) -0.2304(4) 0.3078(5) 0.098 Uani 0.225(4) 1 d PG
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C203 0.081(12) 0.094(14) 0.082(13) 0.013(11) 0.025(10) -0.002(11)
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Cl07 0.122(5) 0.090(4) 0.156(6) 0.052(4) 0.044(4) 0.021(4)
C007 0.043(3) 0.075(5) 0.058(4) -0.016(3) 0.007(3) -0.027(3)
C008 0.030(2) 0.041(3) 0.038(3) -0.006(2) -0.0055(19) -0.005(2)
C009 0.027(2) 0.032(2) 0.029(2) -0.0039(18) 0.0032(17) -0.0028(18)
C010 0.0233(18) 0.027(2) 0.030(2) -0.0007(18) 0.0055(16) -0.0010(17)
C011 0.029(2) 0.023(2) 0.036(3) -0.0054(18) 0.0047(18) -0.0043(18)
C012 0.029(2) 0.0207(19) 0.037(2) -0.0021(18) 0.0060(18) -0.0007(17)
C013 0.030(2) 0.023(2) 0.036(2) 0.0011(19) 0.0057(18) 0.0020(18)
C014 0.030(2) 0.027(2) 0.033(2) 0.0066(19) 0.0020(18) 0.0070(19)
C015 0.0255(19) 0.029(2) 0.033(2) 0.0026(19) 0.0047(17) 0.0046(18)
C016 0.026(2) 0.039(3) 0.036(3) 0.001(2) -0.0023(18) 0.0021(19)
C017 0.043(3) 0.046(3) 0.042(3) 0.005(3) -0.011(2) 0.009(3)
C018 0.073(4) 0.059(4) 0.037(3) 0.009(3) 0.000(3) 0.022(3)
C019 0.057(4) 0.052(4) 0.125(7) 0.008(4) 0.010(4) -0.024(4)
C020 0.044(3) 0.022(2) 0.070(4) -0.006(2) -0.003(3) -0.005(2)
C021 0.038(2) 0.022(2) 0.045(3) -0.003(2) 0.006(2) 0.0001(19)
C022 0.034(2) 0.020(2) 0.051(3) 0.002(2) 0.003(2) 0.0044(18)
C023 0.054(3) 0.025(2) 0.066(4) 0.004(3) 0.002(3) 0.005(2)
C024 0.098(6) 0.052(4) 0.088(6) 0.040(4) 0.017(5) 0.008(4)
Ni01 0.0213(3) 0.0185(3) 0.0262(4) 0.000 0.0026(3) 0.000
N001 0.025(2) 0.018(2) 0.031(3) 0.000 0.005(2) 0.000
N002 0.0257(16) 0.0185(14) 0.0299(18) 0.0004(16) 0.0018(13) -0.0019(15)
N003 0.024(2) 0.025(2) 0.028(3) 0.000 0.003(2) 0.000
C101 0.128 0.095 0.064 0.046 0.000 0.000
C102 0.118 0.106 0.063 0.038 -0.025 0.015
C103 0.101 0.092 0.095 0.035 -0.030 0.032
C104 0.116 0.127 0.048 0.015 -0.034 0.006
C105 0.128 0.130 0.033 -0.005 -0.012 -0.001
C106 0.122 0.125 0.035 0.004 0.018 -0.001
C107 0.122 0.115 0.051 0.032 0.022 -0.009
C108 0.090 0.130 0.071 -0.001 -0.049 -0.001
C109 0.061 0.127 0.099 0.006 -0.044 0.009
C110 0.070 0.110 0.109 0.019 -0.034 0.033
C111 0.041 0.128 0.120 -0.003 -0.028 -0.009
C112 0.129 0.096 0.065 -0.047 -0.002 -0.001
C113 0.127 0.119 0.049 -0.033 -0.021 -0.008
C114 0.101 0.118 0.071 -0.026 -0.041 -0.018
C115 0.086 0.096 0.099 -0.028 -0.032 -0.034
C116 0.057 0.111 0.120 -0.012 -0.025 -0.035
C117 0.078 0.124 0.079 -0.006 0.047 0.006
C118 0.105 0.119 0.052 -0.016 0.035 0.008
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C123 0.063 0.110 0.106 -0.016 0.033 0.029
C124 0.087 0.074 0.126 0.010 0.009 -0.047
C125 0.057 0.102 0.129 0.002 0.003 -0.043
C126 0.042 0.119 0.119 0.005 0.021 -0.022
C127 0.062 0.113 0.090 0.010 0.038 -0.014
C128 0.071 0.119 0.082 -0.007 0.044 0.008
C129 0.124 0.062 0.094 -0.043 -0.006 -0.008
C130 0.107 0.063 0.107 -0.031 -0.016 -0.031
C131 0.108 0.049 0.124 -0.008 -0.004 -0.036
C132 0.093 0.087 0.101 -0.030 0.028 0.035
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C134 0.092 0.066 0.127 0.005 -0.004 0.046
C135 0.123 0.039 0.119 -0.024 0.003 0.013
C136 0.112 0.098 0.070 -0.038 0.026 0.018
C137 0.125 0.112 0.051 -0.036 -0.016 -0.007
C138 0.124 0.087 0.068 -0.046 0.003 0.002
C139 0.124 0.057 0.099 -0.041 -0.004 -0.006
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C141 0.102 0.117 0.054 -0.017 0.036 0.009
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C158 0.107 0.059 0.107 -0.030 -0.014 -0.029
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C179 0.035 0.127 0.123 -0.001 0.020 0.004
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_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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 _geom_bond_atom_site_label_2
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Tm01 Tm07 0.888(8)	Tm07 C418 2.310(8)	C019 C020 1.524(9)	C127 C145 1.4743
Tm01 Tm06 1.251(8)	Tm07 C430 2.350(7)	C020 C021 1.490(7)	C128 C141 1.4520
Tm01 Tm06 2.144(8)	Tm07 C431 2.379(4)	C021 C022 1.358(7)	C129 C172 1.4174
Tm01 Tm04 2.249(6)	Tm07 Tm06 2.413(7)	C022 C023 1.505(7)	C129 C130 1.4179
Tm01 C476 2.137(8)	Tm07 C124 2.484(10)	C023 C024 1.521(10)	C130 C131 1.4143
Tm01 C477 2.194(6)	Tm08 Tm03 1.18(4)	Ni01 N003 1.944(5)	C131 C177 1.4191
Tm01 C145 2.222(11)	Tm08 Tm09 1.479(17)	Ni01 N001 1.953(5)	C132 C133 1.4243
Tm01 C144 2.279(11)	Tm08 Tm09 1.479(17)	Ni01 N002 1.959(3)	C132 C136 1.4655
Tm01 C132 2.312(9)	Tm08 Tm02 1.27(3)	Ni01 N002 1.959(3)	C133 C134 1.4239
Tm01 C417 2.315(10)	Tm08 C432 2.57(3)	N001 C010 1.384(5)	C133 C135 1.4255
Tm02 Tm09 1.513(8)	Tm08 C432 2.57(3)	N003 C015 1.387(5)	C134 C149 1.4262
Tm02 Tm02 1.638(9)	Tm08 C117 2.55(3)	C101 C107 1.4056	C135 C147 1.4121
Tm02 Tm08 1.27(3)	Tm09 Tm03 1.059(8)	C101 C102 1.4210	C135 C139 1.4647
Tm02 Tm03 2.007(5)	Tm09 Tm02 1.513(8)	C101 C150 1.4730	C136 C141 1.4000
Tm02 Tm03 2.256(5)	Tm09 C428 2.098(5)	C102 C104 1.4047	C136 C138 1.4307
Tm02 C420 2.229(8)	Tm09 C182 2.153(10)	C102 C103 1.4462	C137 C138 1.3995
Tm02 Tm07 2.381(8)	Tm09 C181 2.192(11)	C103 C110 1.3910	C137 C142 1.4444
Tm02 C101 2.390(11)	Tm09 C427 2.173(7)	C103 C149 1.4659	C137 C156 1.4450
Tm02 C403 2.274(5)	Tm09 C153 2.208(6)	C104 C105 1.4288	C138 C139 1.4306
Tm02 C102 2.343(10)	C201 Cl07 1.7389	C104 C108 1.4572	C139 C158 1.3996
Tm03 Tm08 1.18(4)	C201 C206 1.3941	C105 C106 1.4084	C140 C142 1.4063
Tm03 Tm03 0.648(9)	C201 C202 1.384(9)	C105 C113 1.4542	C140 C141 1.4273
Tm03 Tm09 1.059(8)	C202 C203 1.427(10)	C106 C107 1.4290	C140 C143 1.4604
Tm03 Tm05 1.082(4)	C203 C204 1.3946	C106 C118 1.4654	C142 C167 1.4429
Tm03 Tm09 1.652(14)	C204 C205 1.3954	C107 C155 1.4528	C143 C146 1.4113
Tm03 C436 2.318(6)	C205 C206 1.3956	C108 C109 1.4050	C143 C145 1.4608
Tm03 C180 2.270(6)	C006 C001 1.3829	C108 C114 1.4285	C144 C145 1.4052
Tm03 C432 2.320(6)	C006 C005 1.39207(11)	C109 C111 1.4218	C144 C169 1.4284
Tm03 C154 2.328(9)	C001 C002 1.4028	C109 C110 1.4458	C146 C171 1.4333
Tm04 Tm07 1.466(9)	C002 C003 1.39192(12)	C110 C122 1.4670	C146 C166 1.4466
Tm04 Tm07 1.466(9)	C003 C004 1.3928	C111 C116 1.4048	C147 C148 1.4243
Tm04 Tm01 2.249(6)	C004 C005 1.3905	C111 C120 1.4730	C147 C151 1.4443
Tm04 C120 2.241(6)	C005 Cl01 1.7211	C112 C113 1.3691	C148 C149 1.4061
Tm04 C412 2.297(6)	C306 C301 1.3748	C112 C119 1.4511	C148 C150 1.4400
Tm04 C412 2.298(6)	C306 C305 1.40422(11)	C112 C129 1.4515	C150 C153 1.3958
Tm04 C111 2.397(6)	C301 C302 1.3954	C113 C114 1.4528	C151 C152 1.3871
Tm04 C111 2.397(6)	C302 C303 1.40359(10)	C114 C115 1.4096	C151 C158 1.4523
Tm04 C413 2.296(5)	C303 C304 1.3743	C115 C116 1.4283	C152 C153 1.4470
Tm05 Tm03 1.082(4)	C304 C305 1.3952	C115 C130 1.4652	C152 C160 1.4751
Tm05 Tm08 2.13(4)	C305 Cl02 1.72496(11)	C116 C125 1.4532	C153 C155 1.4532
Tm05 Tm09 1.840(10)	C007 C008 1.515(8)	C117 C118 1.4140	C154 C155 1.3620
Tm05 Tm09 1.840(10)	C008 C009 1.495(6)	C117 C180 1.4198	C154 C161 1.4593
Tm05 C438 2.214(6)	C009 C009 1.352(9)	C117 C154 1.4609	C156 C157 1.4057
Tm05 C438 2.214(6)	C009 C010 1.443(6)	C118 C119 1.4179	C156 C162 1.4427
Tm05 C179 2.245(7)	C010 C011 1.369(6)	C119 C182 1.4164	C157 C158 1.4277
Tm05 C179 2.245(7)	C010 N001 1.384(5)	C120 C126 1.3958	C157 C159 1.4611
Tm05 C437 2.362(5)	C011 C012 1.363(6)	C120 C121 1.4397	C159 C164 1.4108
Tm06 Tm06 1.065(11)	C012 N002 1.382(5)	C121 C122 1.4060	C159 C160 1.4607
Tm06 Tm07 1.829(10)	C012 C021 1.456(6)	C121 C123 1.4247	C160 C161 1.4041
Tm06 Tm01 2.144(8)	C013 C014 1.366(6)	C122 C134 1.4261	C161 C179 1.4293
Tm06 C475 2.121(6)	C013 N002 1.369(5)	C123 C132 1.4119	C162 C163 1.3784
Tm06 C143 2.142(9)	C013 C022 1.444(6)	C123 C128 1.4446	C162 C167 1.4521
Tm06 C474 2.179(7)	C014 C015 1.377(6)	C124 C125 1.3630	C163 C164 1.4462(10)
Tm06 C140 2.221(8)	C015 N003 1.387(5)	C124 C144 1.4592	C163 C168 1.4570
Tm06 C474 2.295(7)	C015 C016 1.448(6)	C124 C131 1.4602	C164 C178 1.4344
Tm06 C140 2.306(8)	C016 C016 1.363(10)	C125 C126 1.4528	C165 C168 1.3859
Tm07 Tm07 2.329(9)	C016 C017 1.501(7)	C126 C127 1.4475	C165 C170 1.4306
Tm07 Tm02 2.381(8)	C017 C018 1.508(9)	C127 C128 1.3877	C165 C166 1.4567(11)

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C168 C173 1.4305
C169 C171 1.3706
C169 C177 1.4558
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C172 C176 1.4075(13)
C172 C182 1.4581
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 Refinement of F^2^ against reflections with F^2^ > 1.5sigma(F^2^). The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.
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C302 C 0.1829(8) 0.0431 0.2097(9) 0.128(6) Uiso 0.686(15) 1 d PD
Tm01 Tm 0.16097(13) 0.1022(2) 0.24384(13) 0.0380(10) Uani 0.134(2) 1 d P
Tm02 Tm 0.15958(13) -0.0601(2) 0.09908(12) 0.0462(13) Uani 0.138(2) 1 d P
Tm03 Tm 0.24163(18) -0.0222(4) 0.1336(2) 0.050(3) Uani 0.085(2) 1 d P
Tm04 Tm 0.10159(11) 0.0000 0.17948(14) 0.0462(15) Uani 0.160(2) 2 d SP
Tm05 Tm 0.26378(12) 0.0000 0.17960(19) 0.0546(15) Uani 0.163(2) 2 d SP
Tm06 Tm 0.1833(3) 0.0415(5) 0.2793(3) 0.091(3) Uani 0.0873(16) 1 d P
Tm07 Tm 0.1288(2) 0.0836(3) 0.2058(3) 0.124(3) Uani 0.193(3) 1 d P
Tm08 Tm 0.1851(17) 0.0000 0.0858(14) 0.09(2) Uani 0.033(6) 2 d SP
Tm09 Tm 0.2083(5) 0.0932(7) 0.1284(4) 0.206(6) Uani 0.164(4) 1 d P
Tm10 Tm 0.2085(12) 0.051(3) 0.1010(16) 0.052(10) Uiso 0.019(3) 1 d P
C406 C 0.12901(16) 0.5000(16) 0.1766(2) 0.0504(16) Uiso 0.772(8) 2 d SPG
C401 C 0.1009(2) 0.4864(16) 0.2297(3) 0.0504(16) Uiso 0.386(4) 1 d PG
C402 C 0.1271(3) 0.4999(3) 0.2936(3) 0.0504(16) Uiso 0.772(8) 2 d SPG
C403 C 0.1822(3) 0.5000(16) 0.30431(18) 0.0504(16) Uiso 0.772(8) 2 d SPG
C404 C 0.2111(2) 0.5001(16) 0.25087(18) 0.0504(16) Uiso 0.772(8) 2 d SPG
C405 C 0.18414(16) 0.5001(3) 0.18741(17) 0.0504(16) Uiso 0.772(8) 2 d SPG
Cl01 Cl 0.21928(17) 0.5117(7) 0.12131(18) 0.0642(16) Uiso 0.386(4) 1 d PG
Cl03 Cl 0.0924(3) 0.4999(12) 0.2751(4) 0.0642(16) Uiso 0.164(6) 2 d SPG
C501 C 0.1963(2) 0.4891(14) 0.2619(2) 0.0504(16) Uiso 0.082(3) 1 d PG
C502 C 0.2383(2) 0.487(2) 0.2258(3) 0.0504(16) Uiso 0.082(3) 1 d PG
C503 C 0.22868(16) 0.5002(9) 0.1580(2) 0.0504(16) Uiso 0.164(6) 2 d SPG
C504 C 0.17709(18) 0.5001(12) 0.12622(17) 0.0504(16) Uiso 0.164(6) 2 d SPG
C505 C 0.13507(15) 0.5089(17) 0.1623(3) 0.0504(16) Uiso 0.082(3) 1 d PG
C506 C 0.1447(2) 0.5000(4) 0.2301(2) 0.0504(16) Uiso 0.164(6) 2 d SPG
C601 C 0.4503(2) -0.0576(5) 0.0650(3) 0.072(6) Uani 0.50 1 d PG
C602 C 0.4808(4) -0.0013(7) 0.1108(4) 0.089(5) Uani 1 2 d SG
C603 C 0.4792(5) 0.0901(7) 0.1039(6) 0.100(8) Uani 0.50 1 d PG
C604 C 0.4471(6) 0.1291(5) 0.0511(7) 0.114(12) Uani 0.50 1 d PG
C605 C 0.4166(5) 0.0747(6) 0.0052(6) 0.093(9) Uani 0.50 1 d PG
C606 C 0.4182(4) -0.0186(6) 0.0122(4) 0.086(10) Uani 0.50 1 d PG
Cl07 Cl 0.4524(4) -0.1739(5) 0.0738(5) 0.129(3) Uani 0.50 1 d PG
C007 C 0.2282(3) 0.1397(6) 0.5567(4) 0.057(2) Uani 1 1 d.
H00A H 0.2531 0.1797 0.5812 0.086 Uiso 1 1 calc R
H00B H 0.2104 0.1706 0.5190 0.086 Uiso 1 1 calc R
H00C H 0.2467 0.0886 0.5426 0.086 Uiso 1 1 calc R
C008 C 0.1877(2) 0.1084(5) 0.5999(3) 0.0356(15) Uani 1 1 d.
H00D H 0.2058 0.0782 0.6383 0.043 Uiso 1 1 calc R
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H00E H 0.1695 0.1604 0.6147 0.043 Uiso 1 1 calc R
C009 C 0.1475(2) 0.0454(4) 0.5638(2) 0.0288(13) Uani 1 1 d.
C010 C 0.1032(2) 0.0729(4) 0.5169(2) 0.0254(12) Uani 1 1 d.
C011 C 0.0901(2) 0.1613(4) 0.5026(3) 0.0288(13) Uani 1 1 d.
H011 H 0.1100 0.2058 0.5264 0.035 Uiso 1 1 calc R
C012 C 0.0496(2) 0.1881(4) 0.4556(3) 0.0268(13) Uani 1 1 d.
C013 C -0.0170(2) 0.1889(4) 0.3786(3) 0.0279(13) Uani 1 1 d.
C014 C -0.0573(2) 0.1618(5) 0.3314(3) 0.0294(13) Uani 1 1 d.
H014 H -0.0777 0.2061 0.3083 0.035 Uiso 1 1 calc R
C015 C -0.0695(2) 0.0732(4) 0.3162(3) 0.0274(13) Uani 1 1 d.
C016 C -0.1095(2) 0.0461(5) 0.2634(3) 0.0344(15) Uani 1 1 d.
C017 C -0.1403(3) 0.1099(5) 0.2166(3) 0.0434(17) Uani 1 1 d.
H01A H -0.1521 0.1601 0.2411 0.052 Uiso 1 1 calc R
H01B H -0.1716 0.0795 0.1950 0.052 Uiso 1 1 calc R
C018 C -0.1084(3) 0.1461(6) 0.1645(3) 0.057(2) Uani 1 1 d.
H01C H -0.1299 0.1866 0.1360 0.085 Uiso 1 1 calc R
H01D H -0.0974 0.0969 0.1393 0.085 Uiso 1 1 calc R
H01E H -0.0777 0.1774 0.1855 0.085 Uiso 1 1 calc R
C019 C 0.1254(3) 0.3675(7) 0.4476(5) 0.078(3) Uani 1 1 d.
H01F H 0.1437 0.4181 0.4690 0.117 Uiso 1 1 calc R
H01G H 0.1213 0.3762 0.4009 0.117 Uiso 1 1 calc R
H01H H 0.1455 0.3137 0.4587 0.117 Uiso 1 1 calc R
C020 C 0.0707(3) 0.3586(5) 0.4700(4) 0.051(2) Uani 1 1 d.
H02A H 0.0753 0.3512 0.5172 0.061 Uiso 1 1 calc R
H02B H 0.0512 0.4138 0.4596 0.061 Uiso 1 1 calc R
C021 C 0.0390(3) 0.2819(5) 0.4394(3) 0.0354(15) Uani 1 1 d.
C022 C -0.0031(3) 0.2813(5) 0.3910(3) 0.0354(15) Uani 1 1 d.
C023 C -0.0292(3) 0.3586(5) 0.3536(4) 0.0474(18) Uani 1 1 d.
H02C H -0.0198 0.4137 0.3777 0.057 Uiso 1 1 calc R
H02D H -0.0673 0.3515 0.3502 0.057 Uiso 1 1 calc R
C024 C -0.0137(4) 0.3675(6) 0.2843(4) 0.071(3) Uani 1 1 d.
H02E H -0.0315 0.4184 0.2627 0.106 Uiso 1 1 calc R
H02F H -0.0237 0.3139 0.2598 0.106 Uiso 1 1 calc R
H02G H 0.0240 0.3758 0.2873 0.106 Uiso 1 1 calc R
Ni01 Ni 0.01482(4) 0.0000 0.41965(5) 0.0218(3) Uani 1 2 d S
N001 N 0.0762(3) 0.0000 0.4884(3) 0.0247(15) Uani 1 2 d S
N002 N 0.01629(19) 0.1321(3) 0.4186(2) 0.0236(10) Uani 1 1 d.
N003 N -0.0441(3) 0.0000 0.3481(3) 0.0259(15) Uani 1 2 d S
C101 C 0.1628(4) 0.1656(4) 0.0212(3) 0.091 Uani 0.294(4) 1 d PG
C102 C 0.1098(3) 0.1359(5) 0.0213(3) 0.093 Uani 0.294(4) 1 d PG
C103 C 0.0801(3) 0.1740(4) 0.0696(4) 0.094 Uani 0.294(4) 1 d PG
C104 C 0.0969(3) 0.0485(5) -0.0013(3) 0.095 Uani 0.294(4) 1 d PG
C105 C 0.1368(3) -0.0112(5) -0.0187(3) 0.093 Uani 0.294(4) 1 d PG
C106 C 0.1904(3) 0.0148(5) -0.0119(3) 0.087 Uani 0.294(4) 1 d PG
C107 C 0.2018(4) 0.1071(4) 0.0035(3) 0.089 Uani 0.294(4) 1 d PG
C108 C 0.0577(3) -0.0046(6) 0.0272(3) 0.096 Uani 0.294(4) 1 d PG
C109 C 0.0321(2) 0.0308(6) 0.0777(4) 0.094 Uani 0.294(4) 1 d PG
C110 C 0.0427(3) 0.1234(5) 0.0968(4) 0.094 Uani 0.294(4) 1 d PG
C111 C 0.0183(2) -0.0298(6) 0.1261(4) 0.093 Uani 0.294(4) 1 d PG
C112 C 0.1590(3) -0.1651(4) 0.0168(3) 0.092 Uani 0.294(4) 1 d PG
C113 C 0.1212(3) -0.1020(5) -0.0036(3) 0.095 Uani 0.294(4) 1 d PG
C114 C 0.0733(3) -0.0969(5) 0.0274(3) 0.095 Uani 0.294(4) 1 d PG
C115 C 0.0650(3) -0.1547(5) 0.0792(4) 0.092 Uani 0.294(4) 1 d PG
C116 C 0.0333(2) -0.1208(5) 0.1259(4) 0.093 Uani 0.294(4) 1 d PG
C117 C 0.2801(3) -0.0236(5) 0.0436(4) 0.085 Uani 0.294(4) 1 d PG
C118 C 0.2310(3) -0.0526(5) 0.0096(3) 0.085 Uani 0.294(4) 1 d PG
C119 C 0.2147(3) -0.1409(4) 0.0235(3) 0.087 Uani 0.294(4) 1 d PG
C120 C 0.0197(2) -0.0008(5) 0.1948(4) 0.089 Uani 0.587(9) 2 d SPG
C121 C 0.0344(2) 0.0899(5) 0.2142(4) 0.088 Uani 0.294(4) 1 d PG
C122 C 0.0434(3) 0.1518(5) 0.1652(4) 0.091 Uani 0.294(4) 1 d PG
C123 C 0.0621(3) 0.1026(5) 0.2784(4) 0.086 Uani 0.294(4) 1 d PG
C124 C 0.0786(3) -0.2145(4) 0.2136(5) 0.090 Uani 0.294(4) 1 d PG
C125 C 0.0417(3) -0.1504(5) 0.1938(5) 0.091 Uani 0.294(4) 1 d PG
C126 C 0.0360(2) -0.0732(5) 0.2357(4) 0.087 Uani 0.294(4) 1 d PG
C127 C 0.0711(3) -0.0613(5) 0.2967(4) 0.081 Uani 0.294(4) 1 d PG
C128 C 0.0801(3) 0.0262(5) 0.3187(3) 0.082 Uani 0.294(4) 1 d PG
C129 C 0.1514(3) -0.2265(3) 0.0695(4) 0.089 Uani 0.294(4) 1 d PG
C130 C 0.1053(3) -0.2226(3) 0.1010(4) 0.089 Uani 0.294(4) 1 d PG
C131 C 0.1106(3) -0.2527(2) 0.1667(5) 0.090 Uani 0.294(4) 1 d PG
C132 C 0.0996(3) 0.1722(4) 0.2924(4) 0.087 Uani 0.294(4) 1 d PG
C133 C 0.1122(4) 0.2304(3) 0.2416(4) 0.088 Uani 0.294(4) 1 d PG
C134 C 0.0820(3) 0.2211(3) 0.1785(4) 0.091 Uani 0.294(4) 1 d PG
C135 C 0.1655(4) 0.26113(15) 0.2445(4) 0.089 Uani 0.294(4) 1 d PG
C136 C 0.1409(4) 0.1403(4) 0.3437(3) 0.086 Uani 0.294(4) 1 d PG
C137 C 0.2345(4) 0.1088(5) 0.3720(3) 0.092 Uani 0.294(4) 1 d PG
C138 C 0.1947(4) 0.1684(4) 0.3454(3) 0.088 Uani 0.294(4) 1 d PG
C139 C 0.2069(4) 0.2294(3) 0.2958(4) 0.089 Uani 0.294(4) 1 d PG
C140 C 0.1694(4) -0.0130(5) 0.3794(3) 0.084 Uani 0.294(4) 1 d PG
C141 C 0.1289(3) 0.0516(5) 0.3594(3) 0.083 Uani 0.294(4) 1 d PG
C142 C 0.2216(4) 0.0196(5) 0.3927(3) 0.092 Uani 0.294(4) 1 d PG
C143 C 0.1603(4) -0.1064(4) 0.3589(3) 0.083 Uani 0.294(4) 1 d PG
C144 C 0.1116(4) -0.2074(3) 0.2771(4) 0.086 Uani 0.294(4) 1 d PG
C145 C 0.1114(3) -0.1306(4) 0.3170(4) 0.080 Uani 0.294(4) 1 d PG
C146 C 0.2051(4) -0.1618(4) 0.3579(3) 0.091 Uani 0.294(4) 1 d PG
C147 C 0.1886(4) 0.27347(2) 0.1866(4) 0.089 Uani 0.294(4) 1 d PG
C148 C 0.1592(4) 0.25861(17) 0.1235(4) 0.089 Uani 0.294(4) 1 d PG
C149 C 0.1054(4) 0.2356(3) 0.1202(4) 0.092 Uani 0.294(4) 1 d PG
C150 C 0.1880(4) 0.2267(3) 0.0726(4) 0.089 Uani 0.294(4) 1 d PG
C151 C 0.2435(4) 0.2470(2) 0.2001(4) 0.086 Uani 0.294(4) 1 d PG
C152 C 0.2694(3) 0.2066(3) 0.1526(4) 0.083 Uani 0.294(4) 1 d PG
C153 C 0.2416(4) 0.2045(3) 0.0865(4) 0.087 Uani 0.294(4) 1 d PG
C154 C 0.2899(3) 0.0710(5) 0.0602(4) 0.087 Uani 0.294(4) 1 d PG
C155 C 0.2518(4) 0.1336(4) 0.0412(4) 0.088 Uani 0.294(4) 1 d PG
C156 C 0.2847(3) 0.1048(5) 0.3468(3) 0.095 Uani 0.294(4) 1 d PG
C157 C 0.2924(3) 0.1531(4) 0.2901(4) 0.088 Uani 0.294(4) 1 d PG
C158 C 0.2540(4) 0.2206(3) 0.2685(4) 0.088 Uani 0.294(4) 1 d PG
C159 C 0.3217(3) 0.1115(5) 0.2417(4) 0.086 Uani 0.294(4) 1 d PG
C160 C 0.3099(3) 0.1376(4) 0.1728(4) 0.083 Uani 0.294(4) 1 d PG
C161 C 0.3212(3) 0.0759(5) 0.1249(4) 0.086 Uani 0.294(4) 1 d PG
C162 C 0.3056(3) 0.0154(6) 0.3588(4) 0.101 Uani 0.294(4) 1 d PG
C163 C 0.3350(3) -0.0233(6) 0.3146(4) 0.101 Uani 0.294(4) 1 d PG
C164 C 0.3443(2) 0.0263(6) 0.2568(4) 0.094 Uani 0.294(4) 1 d PG
C165 C 0.2893(3) -0.1678(5) 0.3235(4) 0.099 Uani 0.294(4) 1 d PG
C166 C 0.2585(4) -0.1266(5) 0.3702(3) 0.099 Uani 0.294(4) 1 d PG
C167 C 0.2666(4) -0.0374(5) 0.3872(3) 0.100 Uani 0.294(4) 1 d PG
C168 C 0.3267(3) -0.1174(5) 0.2964(4) 0.100 Uani 0.294(4) 1 d PG
C169 C 0.1597(4) -0.2538(2) 0.2705(4) 0.090 Uani 0.294(4) 1 d PG
C170 C 0.2556(4) -0.2279(3) 0.2828(4) 0.092 Uani 0.294(4) 1 d PG
C171 C 0.2056(4) -0.2315(3) 0.3098(4) 0.092 Uani 0.294(4) 1 d PG
C172 C 0.2018(3) -0.2435(2) 0.1056(4) 0.085 Uani 0.294(4) 1 d PG
C173 C 0.3308(2) -0.1262(5) 0.2281(5) 0.092 Uani 0.294(4) 1 d PG
C174 C 0.2960(3) -0.1810(4) 0.1862(4) 0.084 Uani 0.294(4) 1 d PG
C175 C 0.2568(3) -0.2340(3) 0.2147(4) 0.084 Uani 0.294(4) 1 d PG
C176 C 0.2080(4) -0.26269(9) 0.1732(4) 0.084 Uani 0.294(4) 1 d PG
C177 C 0.1609(4) -0.27481(8) 0.2017(5) 0.088 Uani 0.294(4) 1 d PG
C178 C 0.3481(2) -0.0390(6) 0.2063(5) 0.092 Uani 0.294(4) 1 d PG
C179 C 0.3369(2) -0.0143(5) 0.1418(5) 0.088 Uani 0.294(4) 1 d PG
C180 C 0.3081(3) -0.0760(5) 0.0947(4) 0.085 Uani 0.294(4) 1 d PG
C181 C 0.2864(3) -0.1567(4) 0.1162(4) 0.082 Uani 0.294(4) 1 d PG
C182 C 0.2411(3) -0.1904(3) 0.0771(4) 0.084 Uani 0.294(4) 1 d PG
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C202 C 0.0903(4) -0.1575(6) 0.0487(5) 0.093 Uani 0.206(4) 1 d PG
C203 C 0.1264(5) -0.1206(7) 0.0072(4) 0.093 Uani 0.206(4) 1 d PG
C204 C 0.0501(4) -0.1013(7) 0.0660(5) 0.096 Uani 0.206(4) 1 d PG
C205 C 0.0321(3) -0.1092(7) 0.1285(6) 0.094 Uani 0.206(4) 1 d PG
C206 C 0.0551(4) -0.1716(6) 0.1756(6) 0.090 Uani 0.206(4) 1 d PG
C207 C 0.0912(4) -0.2353(4) 0.1544(6) 0.092 Uani 0.206(4) 1 d PG
C208 C 0.0478(4) -0.0068(7) 0.0470(5) 0.096 Uani 0.206(4) 1 d PG
C209 C 0.0856(4) 0.0298(7) 0.0109(5) 0.094 Uani 0.206(4) 1 d PG
C210 C 0.1241(5) -0.0305(7) -0.0110(4) 0.093 Uani 0.206(4) 1 d PG

C211 C 0.1006(5) 0.1210(6) 0.0230(5) 0.094 Uani 0.206(4) 1 d PG
C212 C 0.0228(3) 0.0003(7) 0.2120(6) 0.091 Uani 0.413(9) 2 d SPG
C213 C 0.0163(3) -0.0200(7) 0.1473(6) 0.095 Uani 0.206(4) 1 d PG
C214 C 0.0282(3) 0.0436(7) 0.0977(6) 0.095 Uani 0.206(4) 1 d PG
C215 C 0.0475(4) 0.1306(6) 0.1146(6) 0.092 Uani 0.206(4) 1 d PG
C216 C 0.0810(4) 0.1708(6) 0.0725(6) 0.094 Uani 0.206(4) 1 d PG
C217 C 0.1032(5) -0.1857(5) 0.2882(5) 0.087 Uani 0.206(4) 1 d PG
C218 C 0.0619(4) -0.1457(6) 0.2449(6) 0.086 Uani 0.206(4) 1 d PG
C219 C 0.0457(4) -0.0585(7) 0.2618(6) 0.086 Uani 0.206(4) 1 d PG
C220 C 0.1552(5) 0.1507(6) 0.0190(5) 0.090 Uani 0.206(4) 1 d PG
C221 C 0.1944(5) 0.0883(7) 0.0020(4) 0.087 Uani 0.206(4) 1 d PG
C222 C 0.1783(5) 0.0003(7) -0.0155(4) 0.090 Uani 0.413(9) 2 d SPG
C223 C 0.2477(5) 0.1019(6) 0.0314(5) 0.085 Uani 0.206(4) 1 d PG
C224 C 0.1276(5) 0.2603(3) 0.1618(7) 0.091 Uani 0.206(4) 1 d PG
C225 C 0.1220(5) 0.2346(4) 0.0977(6) 0.093 Uani 0.206(4) 1 d PG
C226 C 0.1687(5) 0.2170(4) 0.0663(6) 0.089 Uani 0.206(4) 1 d PG
C227 C 0.2212(5) 0.2221(4) 0.1033(6) 0.083 Uani 0.206(4) 1 d PG
C228 C 0.2602(5) 0.1690(5) 0.0819(6) 0.084 Uani 0.206(4) 1 d PG
C229 C 0.0419(4) 0.0940(7) 0.2311(6) 0.087 Uani 0.206(4) 1 d PG
C230 C 0.0543(4) 0.1572(6) 0.1838(7) 0.088 Uani 0.206(4) 1 d PG
C231 C 0.0930(5) 0.2225(4) 0.2058(7) 0.089 Uani 0.206(4) 1 d PG
C232 C 0.2829(4) 0.0291(7) 0.0458(5) 0.085 Uani 0.206(4) 1 d PG
C233 C 0.2655(4) -0.0611(7) 0.0334(5) 0.085 Uani 0.206(4) 1 d PG
C234 C 0.2132(5) -0.0741(7) 0.0002(4) 0.088 Uani 0.206(4) 1 d PG
C235 C 0.2869(4) -0.1294(6) 0.0779(6) 0.086 Uani 0.206(4) 1 d PG
C236 C 0.3192(4) 0.0520(7) 0.1050(6) 0.085 Uani 0.206(4) 1 d PG
C237 C 0.3513(3) 0.0090(7) 0.2169(6) 0.092 Uani 0.206(4) 1 d PG
C238 C 0.3393(3) -0.0160(7) 0.1510(6) 0.087 Uani 0.206(4) 1 d PG
C239 C 0.3232(4) -0.1070(6) 0.1371(6) 0.087 Uani 0.206(4) 1 d PG
C240 C 0.3117(4) 0.1597(5) 0.1948(6) 0.086 Uani 0.206(4) 1 d PG
C241 C 0.3052(4) 0.1367(6) 0.1268(6) 0.085 Uani 0.206(4) 1 d PG
C242 C 0.3404(4) 0.0988(7) 0.2383(6) 0.093 Uani 0.206(4) 1 d PG
C243 C 0.2723(5) 0.2181(4) 0.2184(6) 0.085 Uani 0.206(4) 1 d PG
C244 C 0.1803(5) 0.27251(4) 0.1986(6) 0.088 Uani 0.206(4) 1 d PG
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C246 C 0.2676(5) 0.2149(5) 0.2860(6) 0.093 Uani 0.206(4) 1 d PG
C247 C 0.2553(5) -0.2026(5) 0.0929(6) 0.087 Uani 0.206(4) 1 d PG
C248 C 0.2019(5) -0.2123(5) 0.0627(5) 0.088 Uani 0.206(4) 1 d PG
C249 C 0.1820(5) -0.1492(6) 0.0147(4) 0.090 Uani 0.206(4) 1 d PG
C250 C 0.1654(5) -0.2545(3) 0.1008(6) 0.090 Uani 0.206(4) 1 d PG
C251 C 0.2700(4) -0.2246(4) 0.1613(6) 0.086 Uani 0.206(4) 1 d PG
C252 C 0.2331(5) -0.2555(2) 0.1997(6) 0.084 Uani 0.206(4) 1 d PG
C253 C 0.1811(5) -0.27799(8) 0.1662(6) 0.089 Uani 0.206(4) 1 d PG
C254 C 0.1403(5) -0.2486(3) 0.2644(6) 0.090 Uani 0.206(4) 1 d PG
C255 C 0.1347(5) -0.2716(2) 0.1998(6) 0.091 Uani 0.206(4) 1 d PG
C256 C 0.3441(3) -0.0532(7) 0.2690(6) 0.094 Uani 0.206(4) 1 d PG
C257 C 0.3190(4) -0.1364(6) 0.2545(6) 0.088 Uani 0.206(4) 1 d PG
C258 C 0.3127(4) -0.1646(6) 0.1876(6) 0.087 Uani 0.206(4) 1 d PG
C259 C 0.2819(4) -0.1705(5) 0.2969(6) 0.087 Uani 0.206(4) 1 d PG
C260 C 0.2386(5) -0.2294(3) 0.2695(6) 0.084 Uani 0.206(4) 1 d PG
C261 C 0.1929(5) -0.2324(4) 0.3005(5) 0.088 Uani 0.206(4) 1 d PG
C262 C 0.3347(4) -0.0005(7) 0.3252(6) 0.101 Uani 0.413(9) 2 d SPG
C263 C 0.3012(5) -0.0338(7) 0.3668(5) 0.101 Uani 0.206(4) 1 d PG
C264 C 0.2760(5) -0.1203(7) 0.3537(5) 0.094 Uani 0.206(4) 1 d PG
C265 C 0.2611(5) 0.1159(7) 0.3736(5) 0.099 Uani 0.206(4) 1 d PG
C266 C 0.2966(5) 0.1504(6) 0.3297(6) 0.100 Uani 0.206(4) 1 d PG
C267 C 0.3323(4) 0.0933(7) 0.3062(6) 0.101 Uani 0.206(4) 1 d PG
C268 C 0.2633(5) 0.0261(7) 0.3918(4) 0.099 Uani 0.206(4) 1 d PG
C269 C 0.1747(6) 0.2558(3) 0.2657(6) 0.090 Uani 0.206(4) 1 d PG
C270 C 0.2107(6) 0.1587(6) 0.3574(5) 0.091 Uani 0.206(4) 1 d PG
C271 C 0.2174(6) 0.2273(4) 0.3086(6) 0.092 Uani 0.206(4) 1 d PG
C272 C 0.0735(5) 0.0865(6) 0.2931(6) 0.083 Uani 0.206(4) 1 d PG
C273 C 0.2152(6) -0.0226(7) 0.3940(4) 0.091 Uani 0.206(4) 1 d PG
C274 C 0.1651(5) 0.0164(7) 0.3747(4) 0.082 Uani 0.206(4) 1 d PG
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C276 C 0.1164(5) 0.1448(6) 0.3120(6) 0.081 Uani 0.206(4) 1 d PG
C277 C 0.1225(5) 0.2179(4) 0.2694(6) 0.087 Uani 0.206(4) 1 d PG
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C279 C 0.1853(5) -0.1710(6) 0.3519(5) 0.090 Uani 0.206(4) 1 d PG
C280 C 0.1314(5) -0.1366(6) 0.3410(5) 0.085 Uani 0.206(4) 1 d PG
C281 C 0.1211(5) -0.0441(7) 0.3501(4) 0.080 Uani 0.206(4) 1 d PG
C282 C 0.0759(5) -0.0080(7) 0.3121(5) 0.082 Uani 0.206(4) 1 d PG

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Tm03 0.042(3) 0.053(7) 0.061(3) -0.010(2) 0.029(3) 0.011(2)
Tm04 0.0248(16) 0.074(4) 0.0396(16) 0.000 0.0033(11) 0.000
Tm05 0.0218(16) 0.096(3) 0.046(2) 0.000 0.0059(14) 0.000
Tm06 0.112(5) 0.117(7) 0.050(3) -0.036(3) 0.036(3) -0.024(4)
Tm07 0.112(4) 0.094(3) 0.183(5) 0.024(3) 0.082(4) 0.063(3)
Tm08 0.12(3) 0.11(4) 0.061(15) 0.000 0.046(16) 0.000
Tm09 0.416(14) 0.113(7) 0.104(4) 0.027(4) 0.084(6) -0.118(8)
C601 0.059(12) 0.092(17) 0.070(11) 0.036(12) 0.025(10) 0.018(12)
C602 0.065(10) 0.097(15) 0.103(12) 0.000 0.004(9) 0.000
C603 0.12(2) 0.10(2) 0.095(17) 0.032(16) 0.041(15) -0.005(17)
C604 0.17(3) 0.07(2) 0.12(3) 0.03(2) 0.07(2) 0.00(2)
C605 0.11(2) 0.057(18) 0.110(19) 0.012(15) 0.019(16) 0.013(15)
C606 0.099(14) 0.11(3) 0.051(8) 0.029(13) 0.009(8) 0.025(16)
Cl07 0.136(7) 0.098(7) 0.157(7) 0.035(6) 0.036(5) 0.012(6)
C007 0.044(4) 0.068(6) 0.062(4) -0.015(5) 0.012(4) -0.024(4)
C008 0.032(3) 0.039(4) 0.035(3) -0.006(3) 0.001(2) -0.003(3)
C009 0.024(3) 0.033(4) 0.028(2) -0.003(2) -0.001(2) -0.004(3)
C010 0.023(3) 0.026(3) 0.028(2) 0.000(3) 0.004(2) -0.002(3)
C011 0.032(3) 0.022(3) 0.033(3) -0.005(3) 0.005(2) -0.005(3)
C012 0.027(3) 0.019(3) 0.035(3) -0.003(3) 0.003(2) -0.001(3)
C013 0.031(3) 0.021(3) 0.033(3) 0.002(3) 0.008(2) -0.001(3)
C014 0.028(3) 0.027(4) 0.034(3) 0.003(3) 0.005(2) 0.006(3)
C015 0.025(3) 0.029(4) 0.028(2) 0.005(3) 0.007(2) 0.007(3)
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C018 0.074(6) 0.055(6) 0.038(3) 0.011(4) -0.002(3) 0.024(5)
C019 0.055(6) 0.052(6) 0.128(8) 0.009(6) 0.013(5) -0.022(5)
C020 0.044(4) 0.020(4) 0.087(6) -0.008(4) 0.002(4) -0.005(3)
C021 0.034(4) 0.020(3) 0.052(4) -0.004(3) 0.003(3) -0.002(3)
C022 0.036(4) 0.018(3) 0.053(4) 0.003(3) 0.008(3) 0.005(3)
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N001 0.027(4) 0.017(4) 0.031(3) 0.000 0.007(3) 0.000
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C103 0.095 0.086 0.090 0.032 -0.028 0.029
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C107 0.114 0.107 0.049 0.029 0.020 -0.008
C108 0.085 0.121 0.067 -0.001 -0.044 -0.001
C109 0.058 0.118 0.093 0.005 -0.040 0.008
C110 0.066 0.103 0.102 0.018 -0.031 0.030

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C130 0.100 0.060 0.100 -0.028 -0.015 -0.028
C131 0.101 0.047 0.116 -0.007 -0.003 -0.033
C132 0.087 0.082 0.095 -0.027 0.025 0.032
C133 0.097 0.055 0.111 -0.018 0.010 0.034
C134 0.087 0.063 0.118 0.004 -0.003 0.042
C135 0.115 0.039 0.111 -0.022 0.003 0.012
C136 0.104 0.092 0.066 -0.034 0.024 0.017
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C139 0.115 0.055 0.092 -0.038 -0.003 -0.006
C140 0.108 0.112 0.035 0.002 0.018 0.000
C141 0.095 0.109 0.052 -0.015 0.032 0.008
C142 0.120 0.120 0.033 -0.009 -0.008 -0.001
C143 0.104 0.099 0.048 0.026 0.019 -0.008
C144 0.094 0.070 0.098 0.028 0.019 -0.031
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C281 0.086 0.107 0.055 0.010 0.034 -0.007
C282 0.062 0.112 0.081 0.001 0.039 -0.001

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are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.;

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Tm03 Tm10 1.48(3)
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Tm06 C274 2.111(10)
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Tm06 C274 2.249(10)
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C220 C226 C225 107.3
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C247 C235 C239 107.9
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C241 C236 C232 108.4
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8. List of Publications

I. Main Publications （副論文）

1) “Structure of $Tm@C_{82}$(I) Metallofullerene by Single-Crystal X-ray Diffraction Using the 1:2 Co-crystal with Octaethylporphyrin Nickel (Ni(OEP))”

Yuki Sado, Shinobu Aoyagi, Ryo Kitaura, Yasumitsu Miyata, Eiji Nishibori, Hiroshi Sawa, Kunihisa Sugimoto and Hisanori Shinohara

Journal of Physical Chemistry C (Accepted)

2) “Structure of Tm_2 and Tm_2C_2 Encapsulated in Low-Symmetry $C_{82}(C_s(6))$ Fullerene Cage by Single Crystal X-ray Diffraction”

Yuki Sado, Shinobu Aoyagi, Noriko Izumi, Ryo Kitaura, Tim Kowalczyk, Jian Wang, Stephan Irle, Eiji Nishibori, Kunihisa Sugimoto and Hisanori Shinohara

Inorganic Chemistry (submitted)

II. Reference Publication （参考論文）

1) “Rock-Salt-Type Crystal of Thermally Contracted C_{60} with Encapsulated Lithium Cation

Shinobu Aoyagi, Yuki Sado, Eiji Nishibori, Hiroshi Sawa, Hiroshi Okada, Hiromi Tobita, Yasuhiko Kashima, Ryo Kitaura and Hisanori Shinohara

Angewandte Chemie International Edition, **2012,** *51*, 3377 (Hot paper)

III. International Conference （国際学会）

1) **"Development of new method of isolating M@C_{60}"**

Yuki Sado, Hisanori Shinohara

ATI 2009 Nano-Carbon meeting and Zao09 meeting, Zao, Japan (2^{nd} – 3^{rd}, August, 2009)

2) **"Synthesis and Sturcture Determination of Tm@C82(I) – Ni(OEP) Co-Crystals"**

Yuki Sado, Shinobu Aoyagi, Eiji Nishibori, Hiroshi Sawa, Yasumitsu Miyata, Ryo Kitaura, Hisanori Shinohara

The 221^{st} ECS meeting, Seattle, Washington, USA, (5^{th} – 12^{nd}, May, 2012)

(Won "ECS Fullerenes, Nanotubes, and Carbon Nanostructures Division 3^{rd} Place-Student Poster Award" & "Journal of Materials Chemistry Poster Prize at 221^{st} Meeting

Main Publications （副論文）

1) “Structure of $Tm@C_{82}$(I) Metallofullerene by Single-Crystal X-ray Diffraction Using the 1:2 Co-crystal with Octaethylporphyrin Nickel (Ni(OEP))”
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Journal of Physical Chemistry C (Accepted)

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Structure of $Tm@C_{82}$(I) Metallofullerene by Single-Crystal X-ray Diffraction Using the 1:2 Co-Crystal with Octaethylporphyrin Nickel (Ni(OEP))

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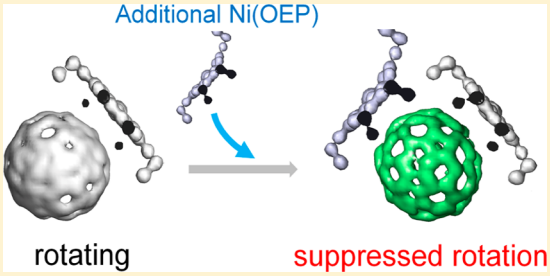
Supporting Information

ABSTRACT: The molecular structure of $Tm@C_{82}$ (isomer I) is revealed by single-crystal X-ray diffraction of the 1:2 cocrystal with nickel octaethylporphyrin (Ni(OEP)). A rotational movement of $Tm@C_{82}$(I) molecule in the 1:1 cocrystal is dramatically suppressed by the coordination of two Ni(OEP) ligands in the 1:2 cocrystal. The structure of $Tm@C_{82}$(I) in the crystal is explained by the orientation disorder with two different orientations. The so-obtained carbon cage structure is $C_s(6)$–C_{82}. The restricted molecular orientations of $Tm@C_{82}$(I) in the 1:2 cocrystal are achieved by the molecular dipole moment of $Tm@C_{82}$(I) that interacts with two Ni(OEP) ligands. The present study suggests that the intermolecular interactions can reduce the degree of freedom in the orientation of spherical metallofullerene molecules in the crystals and complexes.



INTRODUCTION

Endohedral metallofullerenes are among the most attractive fullerene molecules because of their unique structure and electronic properties.[1] Encapsulation of metal atoms and clusters within the carbon cage induces interesting properties such as anomalously enhanced photoluminescence and molecular switching.[2−4] These properties have been found to depend strongly on metal species and carbon cage structure, and thus detailed molecular structure determination is essential to understand the properties of endohedral metallofullerenes.

The structures of endohedral metallofullerenes have been determined by an X-ray diffraction technique.[5−18] The monometallofullerene, $M@C_{82}$, is one of the highest yield metallofullerenes and is well investigated by many studies, such as X-ray diffraction.[15,16,19,20] These studies concentrate on the trivalent monometallofullerene, $M^{3+}@C_{82}^{3-}$ (M = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu). The study of divalent monometallofullerene, $M^{2+}@C_{82}^{2-}$, (M = Sm, Eu, Tm, Yb, and the alkaline earth metals) would give an important clue for understanding the properties, stabilization, and growth-mechanism of $M@C_{82}$ molecules. Recently, single-crystal structures of $Sm@C_{82}$ and $Yb@C_{82}$ were determined.[12,18] For the molecular structure of a divalent thulium endohedral metallofullerene $Tm@C_{82}$(isomer I), two structural isomers with C_s symmetry, $C_s(4)$–C_{82} and $C_s(6)$–C_{82}, have been proposed by ^{13}C nuclear magnetic resonance (^{13}C NMR), ultraviolet photoelectron spectroscopy (UPS) and theoretical studies.[21−23] To determine the cage structure of $Tm@C_{82}$(I), an accurate X-ray structural analysis detectable to small structural differences between two isomers is required.

Co-crystallization with metal octaethylporphyrin, M(OEP), is an epochal method to obtain single crystals of endohedral metallofullerenes.[5,6,8−11,24−27] A number of the molecular structures of endohedral metallofullerenes have been determined for the cocrystals with M(OEP). Most metallofullerene–M(OEP) cocrystals have a ratio of metallofullerene/M(OEP) = 1:1. The carbon cage often shows a disordered structure in the cocrystals.[6] In contrast, empty C_{60} and water-molecule encaged endohedral fullerene, $H_2O@C_{60}$, form 1:2 cocrystals with Ni(OEP) ligands.[28,29] The carbon cage orientation can be fixed in the both crystals at 100 K, suggesting that the disorder of metallofullerene orientation is also suppressed in the 1:2 cocrystals.

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Here, we report synthesis and single-crystal structure analysis of a 1:2 cocrystal of Tm@C_{82}(I) and Ni(OEP). Two kinds of the cocrystals with ratios, 1:1 and 1:2, were simultaneously obtained in exactly the same crystal growth by solution diffusion with vapor of solvent at room temperature. The high-resolution diffraction data (d > 0.6 Å) were obtained by the single crystal X-ray diffraction using third-generation synchrotron radiation at BL02B1 in SPring-8 (Hyogo, Japan). A rotational movement of Tm@C_{82}(I) in the 1:1 cocrystal was dramatically reduced in the 1:2 cocrystal.

EXPERIMENTAL SECTION

Synthesis and Separation. Tm@C_{82}(I) was synthesized by DC arc-discharge of Tm/graphite composite rods (15 × 15 × 300 mm^3, 0.8 atom % Tm/C, Toyo Tanso Co., Ltd.). The soot containing Tm@C_{82}(I) was collected anaerobically under nitrogen atmosphere. Tm@C_{82}(I) and other fullerenes were extracted from the soot with *o*-xylene. Tm@C_{82}(I) was isolated by the multistage high performance liquid chromatography (HPLC) method using two kinds of columns with toluene as eluent, Bukeyprep (20 mm diameter × 250 mm, Nakalai Tesque) and Bukeyprep-M (20 mm diameter × 250 mm, Nakalai Tesque) (Figure S1 in the Supporting Information). Other isomers of Tm@C_{82} were completely eliminated by an extensive recycling HPLC process. The purity of Tm@C_{82}(I) (>99%) was checked by laser desorption time-of-flight (TOF) mass spectroscopy (Axima CFR, Shimazu) as well as HPLC analysis (Figure S2b in the Supporting Information). UV−vis−NIR absorption spectra of Tm@C_{82}(I) were measured by using a JASCO V-570 spectrophotometer for identification of its isomer (Figure S2a in the Supporting Information).

Crystal Growth. The 1:1 and 1:2 cocrystals of Tm@C_{82}(I) and Ni(OEP), referred hereafter to as crystal A and B, respectively, were obtained by means of layering a dusky red solution of saturated Tm@C_{82}(I) in 1 mL of toluene over a red solution of 0.6 mg of Ni(OEP) solution in 1 mL of chloroform. The two layers were diffused in a 5 mm diameter glass tube with vapor of solvent slowly at room temperature, which resulted in growth of black parallelepiped crystals.

X−ray Structure Determination. The single crystal X-ray diffraction measurements of both crystals of Tm@C_{82}(I) were performed at BL02B1 in SPring-8 (Hyogo, Japan). The X-ray wavelength was 0.62 Å.

Tm@C_{82}(I)·Ni(OEP)·1.7$CHCl_3$ (Crystal A). The crystal structure at 50 K was determined as follows: formula weight, 1944; space group, $C2/m$; color of crystal, black; unit cell parameters, a = 25.1149(6) Å, b = 15.3088(5) Å, c = 19.6770(2) Å, β = 94.867(4)°; resolution is d > 0.65 Å; $R1$ is 0.1152 ($|F| > 3\sigma$) and wR is 0.3009 ($|F| > 3\sigma$); GOF (on F^2) = 1.903. The crystal information file (CIF) is available from The Cambridge Crystallographic Data Centre (CCDC) with the deposition number, CCDC 904328.

Tm@C_{82}(I)·2Ni(OEP)·2$C_6H_5CH_3$ (Crystal B). The crystal structure at 190 K was determined as follows: formula weight, 2521; space group, $C2/m$; color of crystal, black; unit cell parameters, a = 25.4136(5) Å, b = 14.9451(3) Å, c = 29.001 (1) Å, β = 97.199(3)°; resolution is d > 0.60 Å; $R1$ is 0.0728 ($|F| > 3\sigma$) and wR is 0.1786 ($|F| > 3\sigma$); GOF (on F^2) = 1.067. The CIF is available from CCDC with the deposition number, CCDC 904327.

RESULTS AND DISCUSSION

Suppression of Orientation Disorder of Tm@C_{82}(I). The coordination structures of crystal A and B are shown in Figure 1 panels a and b, respectively. The coordination

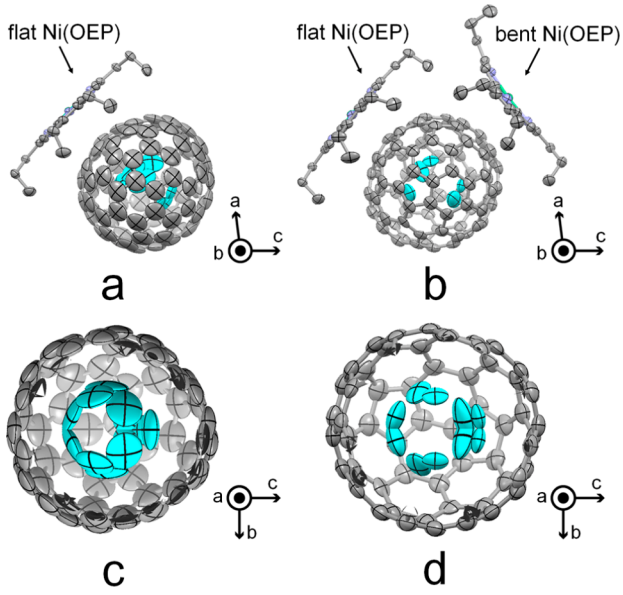

Figure 1. Molecular structures of crystal A at 210 K (a and c) and crystal B at 190 K (b and d). All atoms are shown as ellipsoids at 50% probability level. Only one of four overlapped cages is shown in the figures for each crystal A and B. The disordered Tm atom positions are colored in aqua-blue while carbon atoms are colored in gray.

structure of crystal A, where a Tm@C_{82}(I) molecule is coordinated by a flat Ni(OEP) ligand as shown in Figure 1a, is similar to that of other typical M(OEP) cocrystals.[5,6,13,25] Tm@C_{82}(I) in crystal B is, in contrast, additionally coordinated by a bent Ni(OEP) molecule as shown in Figure 1b. The additional coordination of bent Ni(OEP) elongates the intermolecular distance along the c axis as shown in Figure S4 of Supporting Information. The cell parameters of crystal A are comparable to other typical 1:1 cocrystals of endohedral metallofullerene and M(OEP). The a and b cell parameters of crystal B are also comparable to those of the 1:1 cocrystals, whereas the c and cell volume of crystal B is about 1.5 times larger than that of the 1:1 cocrystals. The solvent molecules in crystals A and B are also different, which contain chloroform and toluene molecules, respectively (see Figure S4 in the Supporting Information).

The difference in coordination structure between crystal A and B affects the rotational movement of Tm@C_{82}(I) molecule. The thermal displacement parameters of the carbon cage in crystal B is smaller than that in crystal A as shown in Figures 1a and b, indicating the suppression of rotational movement of carbon cage in crystal B. The thermal displacement parameters of the 82 fullerene carbon atoms were refined by using only two parameters, U_T and U_L that are parallel and perpendicular component to the radius vector from the barycenter of the carbon cage. The refined parameters are U_T = 0.037 Å^2 and U_L = 0.23 Å^2 for crystal A, and are U_T = 0.032 Å^2 and U_L = 0.09 Å^2 for crystal B, respectively. The thermal displacement parameters of the Tm atom of crystal B are also smaller than those of crystal A as shown in Figure 1c,d. Although only one Tm atom is confined inside the carbon cage,

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the Tm atom occupies several positions due to a disorder inside the carbon cage (see Supporting Information). The Tm atoms locate at positions about 1.9 Å away from the barycenter of the carbon cage. The site number and thermal displacement parameters of the Tm atoms in crystal B are smaller than those in crystal A, indicating that rotational movements of the Tm atom are suppressed in crystal B.

Molecular Structure of Tm@C_{82}(I). The structure of the C_{82} cage of crystal B (Figure 1b) was satisfactorily reconstructed by an overlap of two independent $C_s(6)$–C_{82} carbon cages with different orientation as shown in the Supporting Information. The two independent carbon cages in crystal B, which are referred to as cage 1 and 2 viewed along the *a* and *b*-axis, respectively, are shown in Figures 2a,b. The

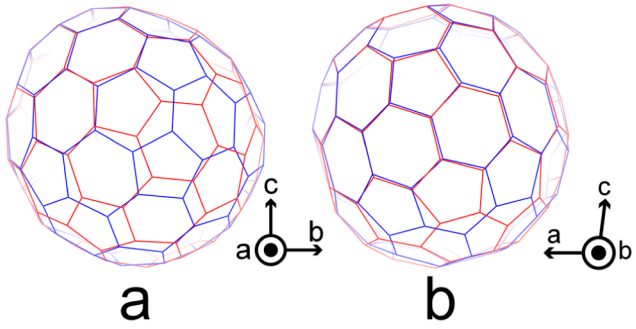

Figure 2. Determined carbon cage structure of crystal B. The independent carbon cages, 1 (red framework) and 2 (blue framework) viewed from the *a*-and *b*-axis are shown in structures a and b, respectively. The additional two cage frameworks (cage 1′ and 2′) provided by the crystal mirror plane are omitted.

barycenters of the carbon cages are on the mirror planes of the *C*2/*m* space group on $y = 0$ and 0.5. The $C_s(6)$–C_{82} carbon cage also has a mirror plane through the barycenter of the cage. But the "molecular" mirror plane of C_s symmetry for cage 1 and 2 does not coincide with the mirror plane of the *C*2/*m* space group. In total, four $C_s(6)$–C_{82} carbon cages (cages 1, 2, 1′ and 2′) with different orientation are thus overlapped with each other. The refined occupancies for cage 1 and 2 are 0.30 and 0.20, respectively.

Also the endohedral Tm atom mainly occupies four positions (Tm(1), Tm(2), and the equivalent positions, Tm(1)′ and Tm(2)′) inside the $C_s(6)$–C_{82} carbon cage as shown in Figure 3 and the Supporting Information. The refined occupancies for

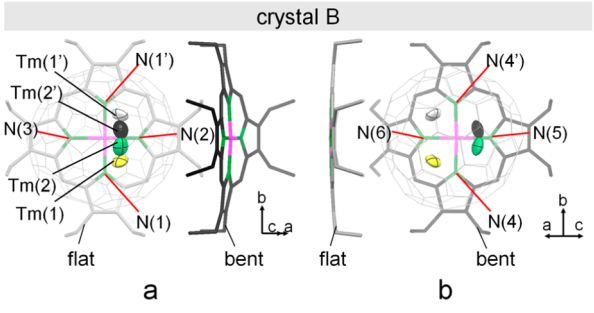

Figure 3. Positional relationship between the major four Tm positions (Tm(1), Tm(2), and the equivalent positions, Tm(1)′ and Tm(2)′) and the Ni(OEP) molecules of crystal B. Views perpendicular and parallel to the molecular plane of flat Ni(OEP) are shown in panels a and b, respectively.

Tm(1) and Tm(2) are both 0.17. The four Tm positions relative to cage 1 are different from that relative to cage 2. Thus eight possible positions are suggested for the Tm atom in the $C_s(6)$–C_{82} cage from the present result. On the other hand, the stable Tm position should be on the molecular mirror plane of $C_s(6)$–C_{82} because the Tm@C_{82}(I) molecule also has C_s symmetry.[21] If the Tm atom occupies only one stable position on the molecular mirror plane, the disorder of the Tm atom is explained by an overlap of the stable Tm@$C_s(6)$–C_{82} molecules with different orientations as discussed in the following sections.

Of the eight possible Tm positions, Tm(1) in cage 1 and Tm(2) in cage 2 are very close to the C_s mirror plane of each cage and have similar local structure as shown in Figures 4, 5a,

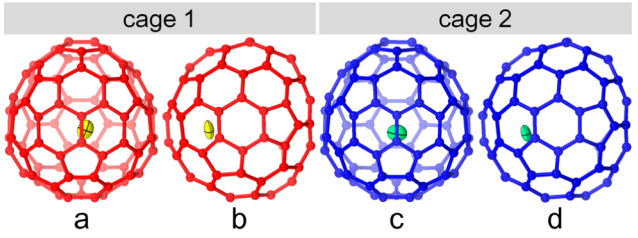

Figure 4. Molecular structure of (a) Tm(1) in cage 1 and (b) Tm(2) in cage 2. Panels a and b (c and d) are views parallel and perpendicular to the molecular mirror plane of cages 1 and 2, respectively.

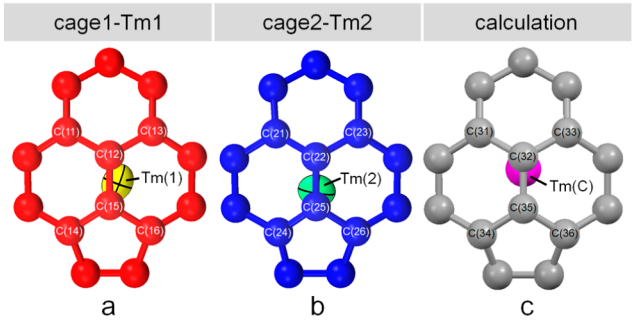

Figure 5. Local structure of (a) Tm(1) in cage 1 and (b) Tm(2) in cage 2. The figures are enlarged views of Figure 4 structures a and c. Theoretical structure (c) proposed by Zheng et al. is also shown for comparison.[23]

and 5b. Tm(1)′ and Tm(2)′ are assigned to cage 1′ and cage 2′, respectively. The molecular structures of Tm(1)′ in cage 1′ and Tm(2)′ in cage 2′ are the same as those of Tm(1) in cage 1 and Tm(2) in cage 2, respectively. The local structures are also consistent with the theoretically stable structure proposed by Zheng et al. as shown in Figure 4c.[23] The Tm(1) and Tm(2) positions relative to the carbon cage are slightly displaced from the theoretically stable Tm position by 0.44 and 0.61 Å, respectively. The interatomic distances between the two Tm positions and six adjacent carbon atoms are summarized in Table 1 together with the theoretical values. The nearest carbon atoms of Tm(1) and Tm(2) (C(15) and C(25)) are crystallographically independent but equivalent in the molecule of $C_s(6)$–C_{82}. The shortest Tm–C distances of 2.38 Å are slightly shorter than the theoretical 2.48 Å.

The present molecular structure of Tm@C_{82}(I) should be compared with that of Sm@C_{82}(I) and Yb@C_{82}(I) recently reported.[12,18] Three of the meallofullerenes may have the same carbon cage structure together with the oxidation state of the

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Table 1. The Interatomic Distances (Å) between Thulium and Carbon Atoms of Crystal B[a]

n	Tm(1)−C(1n)	Tm(2)−C(2n)	Tm(C)−C(3n)
1	2.85(1)	2.92(1)	2.65
2	2.50(1)	2.56(1)	2.48
3	2.76(1)	2.87(1)	2.65
4	2.60(1)	2.50(1)	2.82
5	2.38(1)	2.38(1)	2.57
6	2.50(1)	2.44(1)	2.82

[a]The values for experimental Tm(1)−C(1n) and Tm(2)−C(2n) bonds are listed with that for theoretical Tm(C)−C(3n) bonds.[21] The numbers of thulium and carbon atoms are corresponding to that shown in Figure 5.

metal atom since the UV−vis−NIR absorption spectra are very similar each other. In the reported 1:1 cocrystal of Sm@C_{82}(I) and Ni(OEP), Sm@C_s(6)−C_{82} coexists with another isomer of Sm@C_{3v}(7)−C_{82} which comes from residual isomer II. In contrast, the present Tm@C_{82}(I) isomer has been completely isolated from the other isomers by extensive recycling HPLC process as shown in the Supporting Information. The relative yield of Tm@C_{3v}(7)−C_{82} isomer, which has never been reported in literature, should be much lower than that of Tm@C_s(6)−C_{82}. The main metal position of the Sm@C_s(6)−C_{82} and Yb@C_s(6)−C_{82} is similar to that of Tm@C_s(6)−C_{82}. The nearest carbon atom to the Sm atom in Sm@C_s(6)−C_{82} and Yb atom in Yb@C_s(6)−C_{82} corresponds to C(12) in Figure 5a.

Intermolecular Interaction between Tm@C_{82}(I) and Ni(OEP). The Ni atoms of the two Ni(OEP) molecules in crystal B are located near carbon atoms on a pentagon whose exocyclic bond is connected with a hexagon as shown in Figure 6. The selective coordination of Ni(OEP) suggests an electrostatic attractive interaction between cationic Ni atoms and a localized electron on the carbon atoms forming the pentagon. The attraction between a metal atom of M(OEP) and carbon atoms forming the pentagon is also found in other fullerene−M(OEP) cocrystals such as Sm@C_2(13)−C_{84}·Ni(OEP), Gd_2ScN@I_h(7)−C_{80}·Ni(OEP), Sc_2O@C_s(6)−C_{82}·Ni(OEP), and Ba@C_{74}·Co(OEP).[6,9,13,25] The C_s(6)−C_{82} cage has 32 independent carbon atoms forming the pentagon. The Ni atoms of Ni(OEP) ligands are selectively attracted to the 4 of 32 carbon atoms colored in green in Figure 6. Actually the green carbon atoms in Figures 6b and d are equivalent in the C_s(6)−C_{82} molecule. Cage 1 can be coincide with cage 2′ by a rotation around the axis from Ni(2) to the barycenter of the cage. The angle that the cage 1 coincide with the cage 2′ is about 130°. This suggests that the bent Ni(OEP) is selectively attached on the pivot carbon atom, and then the Tm@C_{82}(I) orientation is restricted to the two independent orientations in crystal B. The same orientation relationships are observed between cage 1′ and cage 2 because both Ni(2) and the barycenter of the cage are on the mirror plane of the $C2/m$ space group.

The interatomic distances between the Ni atoms and the nearest fullerene carbon atoms are also shown in Figure 6. The distances are within the range of that reported for other fullerene-M(OEP) cocrystals where the distances between Ni atom and the nearest carbon atom are 2.5−3.0 Å.[6,9,13,25,27] The distances for the bent Ni(OEP) (3.00 and 3.01 Å) are longer than that for the flat Ni(OEP) (2.81 and 2.83 Å). This difference is due to a steric barrier, which leads to the molecular

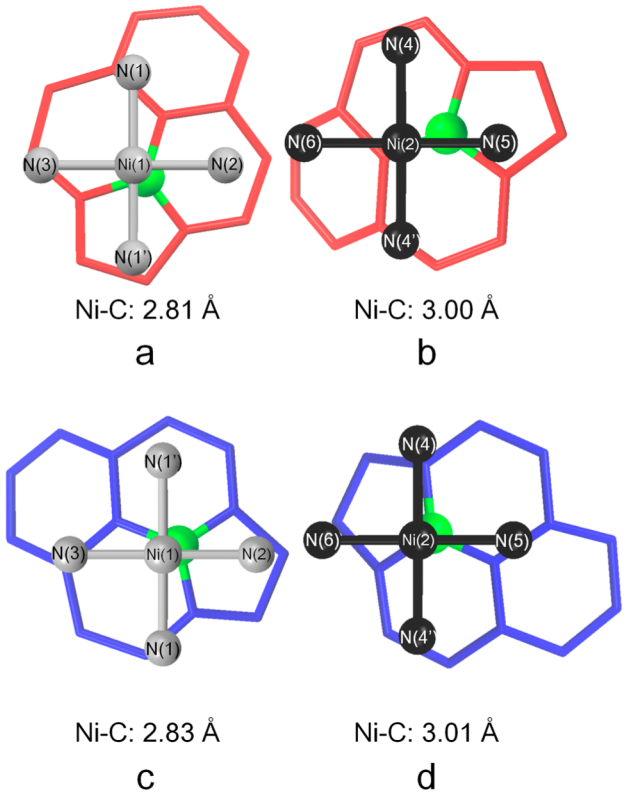

Figure 6. Partial structures of cage 1 (a and b) and 2′ (c and d) around carbon atoms nearest to Ni atoms of Ni(OEP) ligands. Fifteen carbon atoms near flat (a and c) and bent Ni(OEP) (b and d) are shown with Ni and four N atoms of the Ni(OEP) in each panel. The carbon atoms nearest to the Ni atoms are colored in green. The shortest Ni−C interatomic distances for each partial structure are also shown.

deformation and flipping of terminal ethyl groups of the bent Ni(OEP) as shown in Figure 1b.

The positional relationship between the four major Tm positions (Tm(1), Tm(2), and the equivalent positions, Tm(1)′ and Tm(2)′) and the Ni(OEP) molecules is shown in Figure 3. The atoms of flat and bent Ni(OEP) nearest to the position of Tm(1) are nitrogen atoms labeled as N(1) and N(4), respectively. The coresponding interatomic distances are 5.86 Å for Tm(1)−N(1) and 6.34 Å for Tm(1)−N(4). The interatomic distances between Tm(2), that is located at the far side from the Ni atom of flat Ni(OEP), and the nearest nitrogen atom of bent Ni(OEP), N(5), is 5.92 Å. A similar positional relationship between nitrogen atoms of M(OEP) and endohedral metal atoms can be seen in other cocrystals.[6,12,13,26]

The Tm and Ni atom are positively charged by an intramolecular charge-transfer to the fullerene cage and four N atoms of the OEP, respectively. The Tm@C_{82}(I) molecule has a molecular dipole moment when the positively charged Tm atom is displaced from the barycenter of the excess electrons distributed on the fullerene cage. The molecular dipole moment should be oriented toward the negatively charged N atoms or the other side of the positively charged Ni atoms. The dipole interaction also restricts the orientation of Tm@C_{82}(I) in crystal B. A similar electrostatic intereaction between a lithium cation encapsulated in C_{60} and its coordinated anion outside the carbon cage has been found in Li^+@C_{60} crystals.[30,31] A single-molecule orientation switching of endohedral metallofullerene by applying an external electric

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field also has been found by the low-temperature ultrahigh vacuum scanning tunneling microscopy (STM).[3]

CONCLUSION

Single crystal structure analyses of 1:1 and 1:2 cocrystals of Tm@C_{82}(I) and Ni(OEP) reveal that the carbon cage structure of Tm@C_{82}(I) was determined as $C_s(6)$–C_{82}. The endohedral divalent metal position of Tm@C_{82}(I) is similar to that of Sm@$C_s(6)$–C_{82}.[12] The distance between the endohedral metal and the nearest carbon atom of Tm@C_{82}(I) is about 0.2 Å shorter than that of Sm@$C_s(6)$–C_{82}. The Ni atoms of Ni(OEP) molecules are always located near carbon atoms forming the pentagon. The orientation disorder of Tm@C_{82}(I) is suppressed by increasing the coordination number of the Ni(OEP) ligand. The intermolecular interactions between Ni(OEP) and Tm@C_{82}(I) found in this study indicate that the molecular orientation of metallofullerenes can be controlled and ordered by a novel porphyrin-based ligand such as fullerene tweezers.[32] Design and synthesis of a novel porphyrin-based ligand will in future enable us to determine more detailed structure of endohedral metallofullerenes.

ASSOCIATED CONTENT

Supporting Information

Separation and isolation of Tm@C_{82}(I); phase transition of crystal B; molecular arrangement of crystal A and B; modeling of disordered Tm@C_{82}(I) for crystal A and B; Tm positions of crystal A and B; crystallographic data for crystals A and B. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Reference Publication （参考論文）

1) “Rock-Salt-Type Crystal of Thermally Contracted C_{60} with Encapsulated Lithium Cation
Shinobu Aoyagi, Yuki Sado, Eiji Nishibori, Hiroshi Sawa, Hiroshi Okada, Hiromi Tobita, Yasuhiko Kashima, Ryo Kitaura and Hisanori Shinohara

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Rock-Salt-Type Crystal of Thermally Contracted C_{60} with Encapsulated Lithium Cation**

Shinobu Aoyagi, Yuki Sado, Eiji Nishibori, Hiroshi Sawa, Hiroshi Okada, Hiromi Tobita, Yasuhiko Kasama, Ryo Kitaura, and Hisanori Shinohara*

Metallofullerenes encapsulating metal atoms within the hollow carbon cage are promising materials for molecular devices such as a single molecular memory.[1,2] However, the yield of metallofullerenes is usually extremely low.[3] Recently, the macroscopic synthesis and complete isolation of metallofullerenes encapsulating a lithium cation, $Li^+@C_{60}$, have been achieved by the present group.[4] The cationic $Li^+@C_{60}$ has a high tendency to form ion-pair states with an anion such as $SbCl_6^-$. The electrostatic attraction between Li^+ and anions through the cage suggests an external control of the position and thermal motion of Li^+ inside the cage by the species and arrangement of anions outside the cage. The molecular arrangement and endohedral structure of $Li^+@C_{60}$ in the ionic crystals could be changed by replacing the anion.

The rock-salt (Na^+Cl^-) structure is one of the most well-known and stable structures for ionic crystals, in which a cation (Na^+) is octahedrally coordinated by six anions (Cl^-). A rock-salt-type $Li^+@C_{60}$ crystal could also be produced by pairing with adequate anions. In fact, a rock-salt-type hollow C_{60} crystal has been found in alkali-metal-doped fullerenes, MC_{60} (M = K, Rb, or Cs), wherein cations (M) occupy octahedral voids of the face-centered-cubic (fcc) lattice of freely rotating C_{60} anions at high temperature.[5]

Herein we report the synthesis and crystal structure analysis of the cationic metallofullerene rock salt $[Li^+@C_{60}](PF_6)^-$. The detailed molecular structure of the cation, $Li^+@C_{60}$, octahedrally coordinated by six PF_6^- anions is revealed by means of the synchrotron radiation (SR) X-ray diffraction (XRD) at SPring-8 (Hyogo, Japan).

The crystal structure of $[Li^+@C_{60}](PF_6)^-$ at 400 K is shown in the inset of Figure 1. The anions, PF_6^-, having a disordered

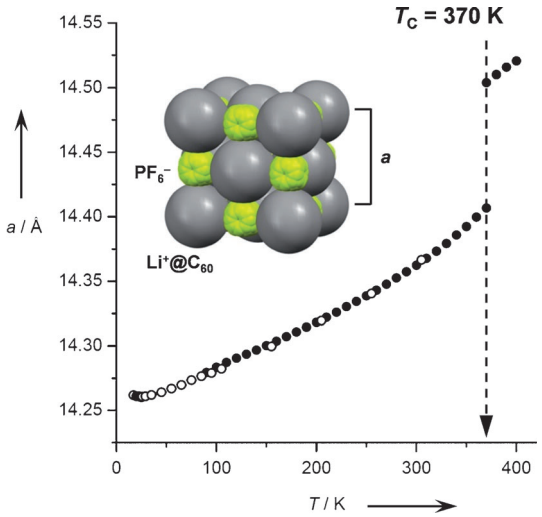

Figure 1. Temperature dependence of the lattice constant of $[Li^+@C_{60}](PF_6)^-$ measured for the single crystal (open circle) and powder sample (solid circle). The inset is the rock-salt-type fcc structure at a temperature above the T_C value.

orientation just fit into the octahedral voids of the fcc lattice of the almost freely rotating cations, $Li^+@C_{60}$, in the structure.[6] The fcc structure of rotating C_{60} cages is similar to that of pristine C_{60} at 300 K.[7] The crystal is the first example of a cationic metallofullerene crystal having symmetry (space group: $Fm\bar{3}m$) that is exactly the same as that of the rock salt.

The rotating $Li^+@C_{60}$ can be modeled by a uniform double spherical shell centered on the 4*a* sites at 0, 0, 0. The refined radii of the outer shell for C_{60} and inner shell for Li^+ are 3.548(1) and 1.3(1) Å, respectively. The rotational motion is regarded as a hindered rotation rather than a free rotation from the charge-density distribution obtained by the maximum entropy method (MEM; see Figure S5a in the Supporting Information). The charge density is not uniform for each shell. The charge density on the C_{60} shell is increased and decreased in the ⟨111⟩ and ⟨100⟩ directions, respectively (see Figure S5b). The non-uniform charge-density distribution which demonstrates the hindered rotation of C_{60} is different

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from the atomic-density distribution of pristine C_{60} as it decreases in the ⟨111⟩ direction,[8] but similar to that of C_{60} in Li_2CsC_{60}.[9] In contrast, the charge density on the Li^+ shell is increased in the ⟨100⟩ direction (see Figure S5c). This result demonstrates that an attractive interaction exists between Li^+ and PF_6^-, whereas a repulsive interaction exists between the carbon atoms and the Li^+ and/or PF_6^-.

PF_6^- anions having a disordered orientation can be modeled by a P atom on the 4*b* sites at 1/2, 1/2, 1/2, and partially occupied F atoms on the 48*i* sites at $1/2+\delta_1$, $1/2+\delta_1$, 1/2, and 96*k* sites at $1/2+\delta_2$, $1/2-\delta_2$, $1/2+\delta_3$ with the site occupancy of 1/6. The restricted rotational motion may be due to the concave shape of the voids surrounded by rotating $Li^+@C_{60}$ cations. The PF_6^- anions have a concave face to match the convex face of the adjacent rotating C_{60} cages (the inset of Figure 1 and Figure S5a). A similar "rotor-stator" molecular arrangement has been reported in the fullerene/cubane solid, $C_{60}{\cdot}C_8H_8$, in which static cubane molecules fill the octahedral voids of the fcc lattice of rotating C_{60}.[10]

The high-temperature fcc phase undergoes a phase transition to a low-temperature simple cubic (sc) phase at $T_C=370$ K with a jump in the lattice constant (Figure 1; see Figure S2 in the Supporting Information). The orientations of the C_{60} cages and PF_6^- are perfectly ordered in the sc phase (space group: $Pa\bar{3}$) at 300 K. A similar transition due to the ordering of the orientations is observed for pristine C_{60} and the hydrogen-encapsulating C_{60} $H_2@C_{60}$ at around 260 K.[7,11,12] The higher T_C value in $[Li^+@C_{60}](PF_6)^-$ suggests that an interaction preventing the C_{60} rotation exists. In contrast, decreases in the T_C value as a result of encapsulation of Ar and Kr have been reported for $Ar@C_{60}$ ($T_C=256$ K) and $Kr@C_{60}$ ($T_C=251$ K), respectively.[13]

The lattice constants of $[Li^+@C_{60}](PF_6)^-$ ($a=14.3666(4)$ Å at 300 K) are larger than those of pristine C_{60} ($a=14.17(1)$ Å at 300 K).[7] Such lattice expansion has also been reported for $Ar@C_{60}$.[13] The difference in the lattice constants between $Ar@C_{60}$ and pristine C_{60} is 0.002 Å at 300 K. The lattice expansion of $[Li^+@C_{60}](PF_6)^-$ is much greater than that of $Ar@C_{60}$, and mainly results from the filling of the octahedral voids with PF_6^-. A similar lattice expansion has been reported for $C_{60}{\cdot}C_8H_8$ ($a=14.74$ Å at 300 K),[10] whereas a lattice contraction has been reported for the rock-salt-type MC_{60} (M = K, $a=14.07$ Å at 473 K).[5] The lattice contraction in MC_{60} is due to an electrostatic attraction between M^+ and C_{60}^-. Such an electrostatic attraction between Li^+ and PF_6^- could also be present in $[Li^+@C_{60}](PF_6)^-$.

At a temperature below the T_C value, the orientation of C_{60} within $[Li^+@C_{60}](PF_6)^-$ is similar to the major of two orientations that coexist for pristine C_{60} even at 5 K;[11] the minor orientation is not observed in $[Li^+@C_{60}](PF_6)^-$. The C_{60} orientation can be represented by an angle, ϕ, which is an anticlockwise rotation about the [111] direction of an ideal molecular configuration with $Fm\bar{3}$ symmetry.[11] The angle $\phi=100.92(2)°$ for $[Li^+@C_{60}](PF_6)^-$ at 22 K is calculated from the refined atomic coordinates, and is slightly larger than that of for pristine C_{60} at 5 K ($\phi\approx98°$) as determined by the neutron powder diffraction.[11c]

The perfectly ordered C_{60} cages in $[Li^+@C_{60}](PF_6)^-$ enable us to determine the detailed cage structure. The radial distances of the ten independent carbon atoms from the cage center range from 3.5409(8) to 3.5556(9) Å at 22 K. The carbon atoms having the longer and shorter distances are oriented in the ⟨111⟩ and ⟨100⟩ directions, respectively.[6] The spherical C_{60} cage is, thus, slightly compressed along the unit-cell axes in $[Li^+@C_{60}](PF_6)^-$. The radial distances of carbon atoms are comparable with those for pristine C_{60} at 5 K which range from 3.541(5) to 3.556(6) Å within the experimental error.[11c]

The C_{60} cage radii, *r*, are estimated by averaging the radial distances of the carbon atoms and plotted against temperature (Figure 2). The cage radius for $[Li^+@C_{60}](PF_6)^-$ ($r=3.550(1)$ Å at 22 K) is also comparable with that for pristine C_{60} as determined by the neutron powder diffraction ($r=3.548(6)$ Å at 5 K) within the experimental error.[11c]

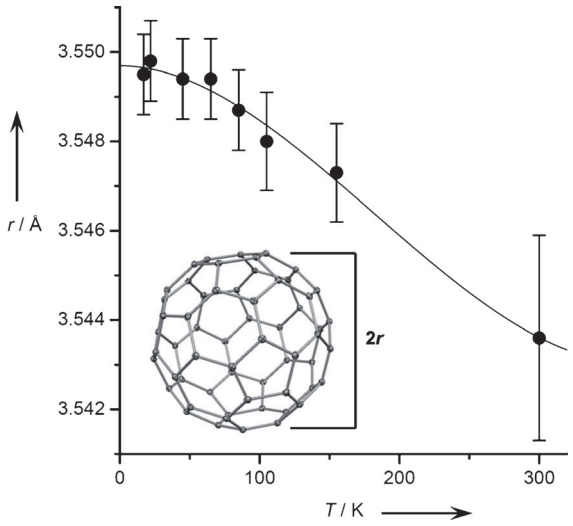

Figure 2. Temperature dependence of the C_{60} cage radius *r* of $[Li^+@C_{60}](PF_6)^-$ as estimated by averaging the radial distances of the carbon atoms from the cage center.

Although the experimental errors are not satisfactorily small to accurately detect the small changes of *r*, the negative thermal expansion (NTE) below 300 K can be seen in Figure 2. The NTE of C_{60} has been proposed on the basis of theoretical and experimental data.[14,15] The volumetric thermal expansion coefficient at around 100 K was estimated from the data in Figure 2 to be about -2×10^{-5} K^{-1}, a value larger than that predicted theoretically (-1×10^{-5} K^{-1}),[14] and smaller than that determined by EXAFS measurements of $Ar@C_{60}$ (-5×10^{-5} K^{-1}).[15] The NTE of C_{60} slightly elongates the C–C bond lengths. The temperature dependence of the C–C bond lengths are summarized in the Supporting Information.

Interestingly, the temperature dependence of the lattice constants given in Figure 1 and Figure S3 in the Supporting Information also show a small NTE at a temperature below 25 K. The usual positive thermal expansion of the lattice constant above 25 K is contrary to the NTE of the cage radius, and is mainly due to the increase of the intermolecular distance. The linear thermal expansion coefficients of the

lattice constant above 25 K is comparable with that for pristine C_{60} (see Figure S4).

In contrast to the static C_{60} cages, Li^+ cations are moving inside the cages. Our previous charge-density analysis of $[Li^+@C_{60}](SbCl_6)^-$ at 370 K using MEM clearly reconstructed charge-density peaks for one Li^+ inside the cage.[4] Nevertheless, no MEM charge-density peaks are found inside the cage of $[Li^+@C_{60}](PF_6)^-$ at 155 K (Figure 3a). To visualize the delocalized Li^+, model MEM charge densities calculated based on the refined structure model without any Li^+ are subtracted from the experimental values.

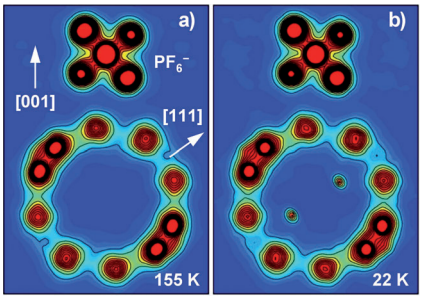

Figure 3. MEM charge-density maps of $[Li^+@C_{60}](PF_6)^-$ on the (1–10) plane at a) 155 and b) 22 K, respectively. The contour lines are drawn from 0 to 4.0 e Å^{-3} at intervals of 0.2 e Å^{-3}.

The equidensity surface of the difference-MEM charge densities at 0.015 e Å^{-3} inside the C_{60} cage at 155 K is shown as purple in Figure 4a. A shell-like positive difference-MEM charge density for the delocalized Li^+ is clearly found inside the C_{60} cage. The equidensity surface exhibits a dynamic or static positional disordering of Li^+ on the shell with a radius of about 1.5 Å. The shell-like charge densities are a little higher at near the centers of the six-membered rings, thus suggesting that Li^+ can occupy space under the twenty six-membered rings of the C_{60} cage. Remarkably, the Li^+ selectively occupies the positions with the highest charge densities (0.025 e Å^{-3}) under the eight six-membered rings around the threefold inversion axis. Four of these are shown as red sticks in Figure 4a. The other four are obtained by the inversion of these six-membered rings at the cage center.

The disordered Li^+ cations are gradually localized below 100 K without changes of the crystal symmetry. The MEM charge-density map and difference-MEM equidensity surface inside the cage at 22 K are shown in Figures 3b and 4b, respectively. The delocalized charge densities for Li^+ at 155 K are gradually condensed into two equivalent (crystallographic) positions within the C_{60} cage on the threefold inversion axis (8c sites at x, x, x) by decreasing the temperature (see also Figure S6 in the Supporting Information). The two positions having a charge density of 1.2 e Å^{-3} at 22 K are the most stable for Li^+ given the twenty possible positions beneath the six-membered rings. The Li^+ localization through decreasing the temperature implies that the disordered distribution of Li^+ over the twenty positions at 155 K (Figure 4a) is not static but rather a dynamic hopping, which is thermally excited. The thermal hopping of Li^+ is consistent with the ^{13}C NMR spectrum of $[Li^+@C_{60}](SbCl_6)^-$

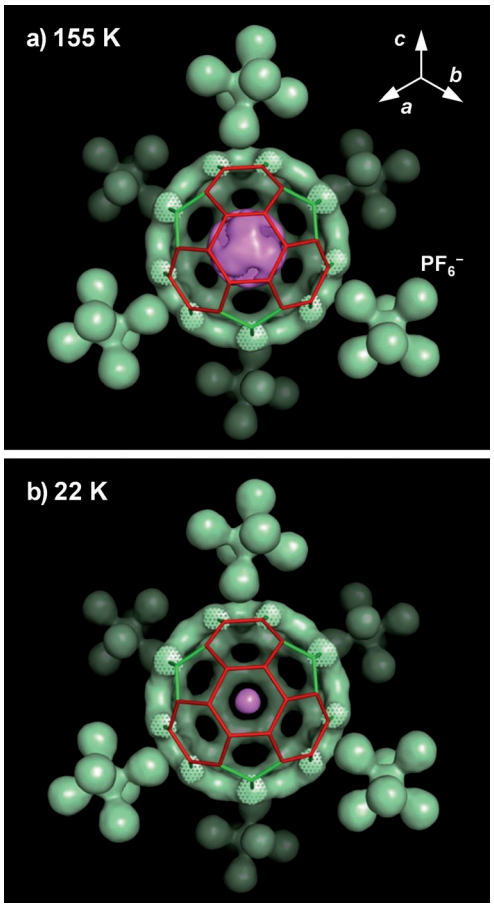

Figure 4. Equidensity surfaces of the difference-MEM charge densities for Li^+ (purple) at a) 155 K and b) 22 K as viewed from the [111] threefold inversion axis with the MEM charge densities (green). The purple surfaces represent difference-MEM charge densities inside the C_{60} cage at 0.015 and 0.100 e Å^{-3} in a) and b), respectively. The green surfaces represent MEM charge densities (not difference) at 1.0 e Å^{-3}, which are partially cut to show the inside of the C_{60} cage.

in solution which shows a single peak.[4] More detailed dynamics of Li^+ confined within a static C_{60} should be revealed by a solid NMR study of $[Li^+@C_{60}](PF_6)^-$.

The position and anisotropic atomic displacement parameters of Li^+ assumed at the 8c sites with the occupancy of 1/2 were refined.[6,16] The displacement of Li^+ from the cage center is 1.40(1) Å, which is close to the theoretical values.[17,18] The off-centered endohedral structure is common in mono-metallofullerenes,[3c,19] but is different from the centered structure of the nonmetal endohedral C_{60}.[12,13a,20] The nearest six-membered ring to Li^+ has three adjoined six-membered rings facing the coordinated PF_6^-. This arrangement tends to decrease the potential energy for Li^+ trapped under the six-membered rings (colored red in Figure 4) through the attractive Li–F electrostatic interaction. The symmetrical octahedral coordination of the PF_6^- anions around the C_{60} cage, on the other hand, should weaken the electrostatic potential on Li^+. As a result, the Li^+ cations in $[Li^+@C_{60}](PF_6)^-$ show a large thermal motion even at 155 K.

The attractive Li–F electrostatic interaction through the six-membered rings should prevent the rotational motion of

the C_{60} cage. The Li–F interaction increases the charge density of Li^+ within the vicinity of the PF_6^- anions at 155 K (Figure 4a), and also at 400 K above the T_C value (see Figure S5c in the Supporting Information). The electrostatic attraction between PF_6^- and Li^+ hopping among sites under twenty six-membered rings tends to fix the C_{60} orientation so that the six-membered rings face PF_6^-. The charge density on the C_{60} shell decreased in the $\langle 100 \rangle$ direction at 400 K (see Figure S5b) and can also be explained by the six-membered rings facing the PF_6^-. When the C_{60} cage is in the major and minor orientation of pristine C_{60}, the six- and five-membered rings are facing the PF_6^- anions. The fraction having the major orientation in pristine C_{60} can be expressed by using a Boltzmann distribution in which the energy difference between the major and minor orientations is 11.0 meV.[11b] The energy difference must be increased by the Li–F interaction, which prefers the major orientation in $[Li^+@C_{60}](PF_6)^-$. As a result, the major orientation is stabilized and C_{60} cages exhibits no disorder of orientation in $[Li^+@C_{60}](PF_6)^-$ at a temperature below the T_C value.

The substantially higher observed T_C value, relative to that of pristine C_{60}, could also be due to the Li–F interaction. The T_C value of pristine C_{60} increases with a lattice compression by pressure that increases the C_{60}–C_{60} interaction driving the ordering of the orientation.[21] Accordingly, the transition temperature should decrease with a lattice expansion. In fact, a decrease of the T_C value involving a lattice expansion has been reported for $C_{60}{\cdot}C_8H_8$ ($T_C = 140$ K) and $Ar@C_{60}$ ($T_C = 256$ K).[10,13] Importantly, the higher T_C value for $[Li^+@C_{60}](PF_6)^-$, involving the lattice expansion, is contrary to this effect. A similar increase of the T_C value involving a lattice expansion has been found in the Na-intercalated C_{60} $Na_{1.3}C_{60}$ ($T_C = 325$ K), wherein the electrostatic interaction between the C_{60} and Na^+ at the tetrahedral voids stabilizes the ordered phase.[22] The Li–F electrostatic attractive interaction which tends to fix the C_{60} orientation should stabilize the ordered phase for $[Li^+@C_{60}](PF_6)^-$. This interaction is one of the main reasons for the observed higher T_C value. The difference between the T_C values of $[Li^+@C_{60}](PF_6)^-$ ($T_C = 370$ K) and pristine C_{60} ($T_C = 260$ K) may correspond to the excitation energy needed for Li^+ to hop within the C_{60} cage.

The anisotropic thermal ellipsoids of the refined atomic displacement parameters for Li^+, at the two positions within the cage at 22 K, do not overlap with each other.[16] Thus, Li^+ occupying two positions within the cage at low temperature could not be explained by thermal hopping but rather by static disorder or tunneling. A static-disorder model for Li^+ is illustrated in Figure S10 in the Supporting Information. The Li^+ cations that were localized at either one of the two possible polar positions in the model can be explained by static disorder of the orientation of polar $Li^+@C_{60}$ cations. A theoretical tunneling model for the dynamics of Li within a C_{60} cage has been proposed.[18]

The crystal structure of the cationic metallofullerene rock salt $[Li^+@C_{60}](PF_6)^-$ reported here evidently demonstrates a strong interaction between Li^+, residing inside the C_{60} cage, and PF_6^- residing outside the cage; the interaction occurs through the six-membered rings. The interaction strongly restricts the rotational motion of the C_{60} cages. The detailed structure analysis of the perfectly ordered C_{60} cage at a temperature below the T_C value revealed a NTE and slight compression along the unit-cell axes. The Li^+ hops thermally inside the C_{60} cage even at 155 K, and is localized at the two polar positions at temperatures below 100 K because of the Li–F interaction. The orientation of the polar $Li^+@C_{60}$ cations at low temperature should be biased by applying an external electric field.[1] The external control of the molecular orientation and Li^+ position will be evaluated by dielectric measurements and X-ray structure analysis under an electric field.

Experimental Section

The high purity $[Li^+@C_{60}](PF_6)^-$ was obtained from $[Li^+@C_{60}](SbCl_6)^-$, which was synthesized by a previously reported method.[4,6] The anion replacement was performed by high-performance liquid chromatography (HPLC) using tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as an electrolyte. The crystals of the resultant $[Li^+@C_{60}](PF_6)^-$ were grown by slow vaporization of the chlorobenzene/acetonitrile solution in a refrigerator.

The SR-XRD experiments for the $[Li^+@C_{60}](PF_6)^-$ crystals were carried out at SPring-8 (Hyogo, Japan).[6] The X-ray oscillation photographs of the single crystal were corrected by the large cylindrical imaging plate camera at BL02B1 beamline. The crystal structures at 17, 22, 45, 65, 85, 105, 155, 300 and 400 K were successfully determined with good reliability factors, i.e., $R1 = 0.0366$ (for $|F| > 3\sigma_F$, $d > 0.33$ Å) for 22 K.[6,16] The powder diffraction experiments of $[Li^+@C_{60}](PF_6)^-$ were also performed by the large Debye–Scherrer camera at BL02B2 beamline.

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