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Fullerene C_{60} exhibiting a strong intermolecular interaction in a cocrystallite with C_4 symmetrical cobalt tetrakis(di-*tert*-butylphenyl)porphyrin

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Received 22nd May 2001, Accepted 16th August 2001
First published as an Advance Article on the web 2nd October 2001

A new cocrystallite is reported which contains C_{60} with the cobalt(II) complex 5,10,15,20-tetrakis[3,5-(di-*tert*-butyl)-phenyl]porphyrin (tbp). The inter-molecular distance between C_{60} and the Co^{II}(tbp) molecules in the cocrystallite Co^{II}(tbp)·C_{60} is quite short, having a value of 2.61 Å at room temperature for any covalent bonding arrangement. This is the first report of X-ray structural analysis at room temperature of metal porphyrin cocrystallites with fullerenes. The temperature dependence of the inter-molecular interaction between C_{60} and the Co^{II}(tbp) molecules has been investigated by ESR spectroscopy. C_4 symmetry of the C_{60} molecule has been observed in this cocrystallite which can be explained by the disorder of the fullerene molecules in the crystal packing, caused by the strong inter-molecular interaction with the C_4 symmetrical molecule of Co^{II}(tbp). This cocrystallite forms one of the most attractive packing arrangements for molecular 3-D design based on the fullerene C_{60}.

Introduction

Amongst the various types of fullerenes, C_{60} is quite exceptional[1] because of its high symmetry,[2,3] wide abundance and variety of solid-state properties in intercalation compounds (*e.g.* superconductivity[4] and ferromagnetism[5]). A variety of C_{60} cocrystallites have now been synthesized and amongst these, the 'host–guest' compounds of fullerene and other molecules have been discovered.[2,3]

The C_{60} molecule consists of 12 pentagons and 20 hexagons arrayed in a 'soccer ball'-like structure, which belongs to the icosahedral point group I_h and cascaded symmetry point groups (*i.e.* D_{5d}, D_{3d}, D_{2h}, S_6, C_{2h}, C_i *etc.*) but it has no element of 4-fold symmetry. It has been suggested that the round-shaped C_{60} is not appropriate for cocrystallization with planar molecules, since a curving of the planar molecule to match the concave structure would be required in order to fit to the C_{60} molecule.[6,7] In some circumstances, it has been reported that changing a planar molecule into a curved one is very appropriate for cocrystallization with the curved shape of fullerene.

Concerning the macrocyclic metal compounds, the complementary curvature based on non-planar molecules such as Ni(OMTAA),[8] Ni(TMTAA)[9] and Cu(TMTAA)[10] could be argued as assisting the host–guest interactions in order to form cocrystallites with C_{60}. Olmstead *et al.*[11,12] reported that the Co, Zn and Fe complexes of octaethylporphyrin (oep) cocrystallites with C_{60} were observed to form solids with a remarkably close contact between the curved π surface of the fullerene and the planar π surface of the porphyrin, without the need for matching convex with concave surfaces.[13] Such a strategy is effective for not only the pure fullerene molecules C_{60} and C_{70} but also the endohedral fullerenes $Sc_3N@C_{80}$,[14] and $ErSc_2N@C_{80}$.[15] Recently, we have also reported the first syntheses of Pd,[16] Cu,[16] Ag,[17] and Ni,[17] complexes of oep cocrystallites with C_{60} as examples of *anti*-formed metal complexes of oeps. In addition, unique cocrystallites of C_{60} and C_{70} fullerenes with tetraphenylporphyrins (tpps) have been also reported.[18] However, few cocrystallites of any metal tpp complexes with C_{60}, except the η^2-C_{60} cocrystallite with tetrakis(pentafluorophenyl)borate,[19] have been synthesized up to now. In the case of the metal tpp, only the cocrystallite with C_{70} has been reported.[18] It is well known that the lattice of a pristine metal porphyrin[20] is very flexible and that many kinds of constitutional isomers of cocrystallites with C_{60} are expected to be obtained. Lowering the temperature has also been required for the X-ray structural analysis of the porphyrin cocrystallites with C_{60} in order to weaken the effect of the disorder caused by the rotation of the fullerene molecule.

In metal tpps, a modification of the structure of the terminal phenyl groups is supposed to be very important in order to make the cocrystallite of the curved C_{60} surface match with the planar surface of the porphyrin. In this paper the synthesis and X-ray structural analysis of the cobalt complex of 5,10,15,20-tetrakis[3,5-(di-*tert*-butyl)phenyl]porphyrin (tbp) (Fig. 1) cocrystallized with C_{60} has been carried out, according to the strategy of structural modification by the addition of di-*tert*-butyl groups into the tpp. Although the X-ray structure analysis was performed at room temperature, the absolute positions of the carbon atoms on the fullerene C_{60} were determined completely. We also describe the inter-molecular interaction between the non-C_4 symmetrical ball-shaped C_{60} molecule and the typical C_4 symmetrical planar-shaped Co^{II}(tbp) by means of analysis of the ESR spectra.

Results and discussion

The synthesis of Co^{II}(tbp) has been performed by modifying the terminal phenyl ligand of tpp into di-*tert*-butylphenyl groups. The compound Co^{II}(tbp)·C_{60} was obtained in a form suitable for single-crystal X-ray diffraction by the evaporation

DOI: 10.1039/b104514h

Table 1 Crystallographic data for $Co^{II}(tbp)\cdot C_{60}$

	At room temperature	At 83 K
Empirical formula	$C_{136}H_{92}N_4Co$	
M	1841.18	
Crystal system	Tetragonal	Tetragonal
Space group	I_4 (no. 79)	I_4 (no. 79)
Z	2	2
a/Å	20.399(2)	19.9711(4)
c/Å	12.0635(8)	11.9970(2)
V/Å^3	5020.1(6)	4784.9(1)
μ/mm^{-1}	0.228	0.239
T/K	296(1)	83(1)
ρ/g cm^{-3}	1.218	1.278
No. of reflections used for unit cell determination (2θ range/°)	21184 (3.9–55.0)	33349 (4.0–54.9)
No. of reflections measured total, unique	20345, 2875	22984, 2875
No. of observations ($I > 3\sigma(I)$)	4207 ($2\theta < 54.91°$)	1963 ($2\theta < 54.96°$)
parameters	347	342
R_1[a] ($I > 3\sigma(I)$)	0.056	0.032
R_w[b] (all data)	0.136	0.074

[a] $R_1 = (\Sigma \left| |F_o| - |F_c| \right|)(\Sigma |F_o|)^{-1}$. [b] $R_w = \{[\Sigma w(F_o^2 - F_c^2)][\Sigma w(F_o^2)^2]\}^{1/2}$, $w = [\sigma_c^2(F_o^2) + (p(\max(F_o^2,0) + 2F_c^2)/3)^2]^{-1}$.

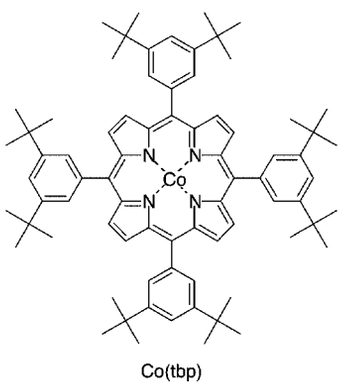

Fig. 1 5,10,15,20-Tetrakis[3,5-(di-*tert*-butyl)phenyl]porphyrin cobalt-(II) $Co^{II}(tbp)$.

of a mixture of a solution of the fullerene in toluene and a solution of the $Co^{II}(tbp)$ in toluene.

The crystal data are summarized in Table 1. Complex $Co^{II}(tbp)\cdot C_{60}$ crystallizes in the tetragonal space group I (no. 79), with cell dimensions at room temperature of a = 20.399(2) Å, c = 12.0635(8) Å, Z = 2, R = 0.056, R_w = 0.136, and GOF = 1.94. Although the X-ray structure analysis was performed at room temperature, the absolute positions of the carbon atoms on the fullerene C_{60} were determined completely. In addition, the orientation matrix for data collection corresponded to an I-centered tetragonal cell (Laue class: 4/m) in this compound. The C_4 symmetry corresponding to the tetragonal I space group, which is appropriate to the C_4 symmetrical molecule of tbp, is not suitable for the icosahedral I_h point group of C_{60} molecule.

The numbering system of the atoms of the compound is given in Fig. 2. Independent cobalt, nitrogen and 37 carbon atoms are observed which belong to the I point group. The occupancy of the central cobalt atom is 0.25, whereas that of the six carbon atoms from C(32) to C(37) is 0.5. Therefore the composition is $C_{34}NCo_{0.25}$, which denotes a quarter of the non-hydrogen chemical formula of $Co^{II}(tbp)\cdot C_{60}$ (*i.e.* $C_{136}N_4Co$). The unit cell in this compound consists of a C_{60} molecule and $Co^{II}(tbp)$, as shown in Figs. 3 and 4. Within this unit cell, the $Co^{II}(tbp)$ is positioned symmetrically between two fullerene units and the fullerene is very close to the atoms of the Co^{II}-(tbp), allowing for the possibility for covalent bonding between them. The fullerene is caught by two porphyrin planes from top and bottom. In addition, the fullerene is also surrounded by the four porphyrins placed side by side. The fullerene is located in the position of closest approach to the centred metal atom,

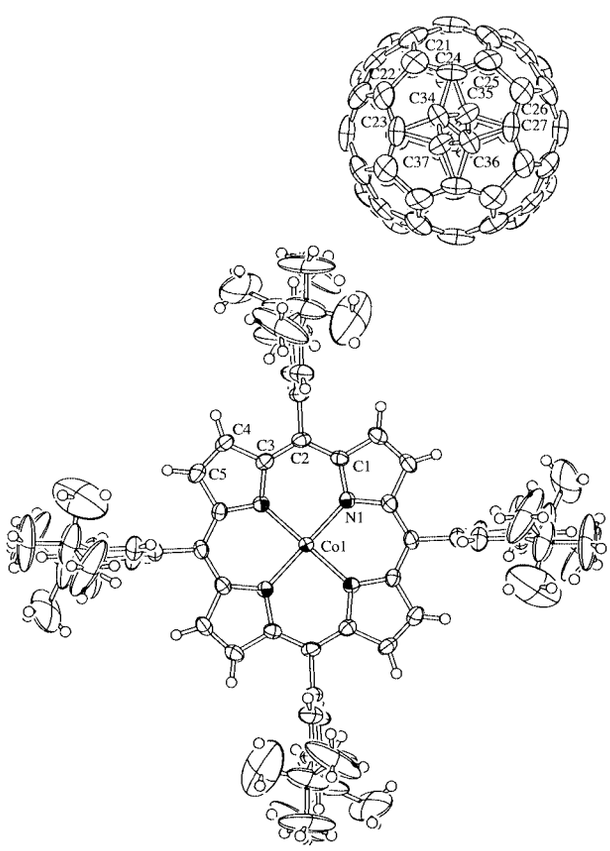

Fig. 2 Atom numbering in $Co^{II}(tbp)\cdot C_{60}$ with 50% thermal ellipsoids.

which involves an electron-rich π-bonding 6 : 6 carbon ring junction (hexagon–hexagon junction). The C_4 symmetrical disorder of the carbon atoms on C_{60} is observed, as shown in Fig. 5. The six carbon atoms from C(32) to C(37), whose occupancy is 0.5, are disordered in the six octahedral points on the C_{60} framework. Typical C_4 symmetry of the C_{60} molecule have been reported in the complexes $2(PPh_4^+)\cdot C_{60}^-\cdot Cl^-$,[21] $2(PPh_4^+)\cdot C_{60}^-\cdot Br^-$ [22] and $2(AsPh_4^+)\cdot C_{60}^-\cdot Cl^-$,[22] and in the calix-(4)arene adduct.[23] In the case of a porphyrazine complex,[24] the space group of the cocrystallite is tetragonal which is reflected by the typical C_4 symmetrical molecule of porphyrazine. Unfortunately, no 4-fold disorder of the carbon atoms on C_{60} was observed because of the weak inter-molecular interaction between C_{60} and the porphyrazine molecules. Such a phenomenon is explained by the two orientations, at 90° relative

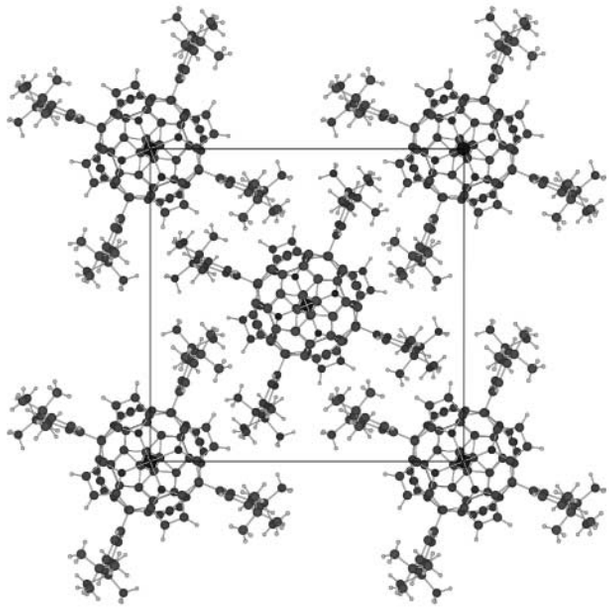

Fig. 3 Crystal structure of $Co^{II}(tbp)\cdot C_{60}$, view along the *c*-axis.

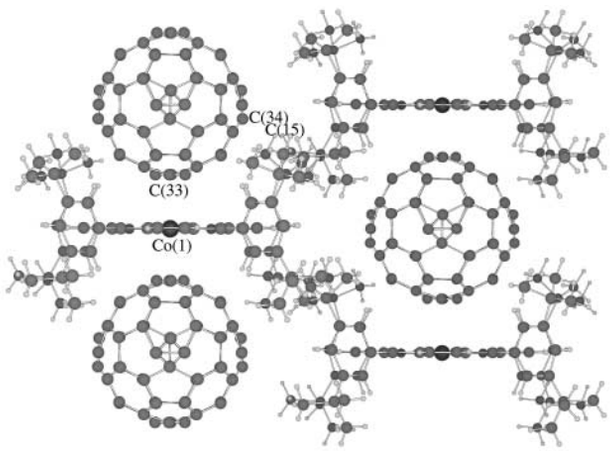

Fig. 4 Crystal structure of $Co^{II}(tbp)\cdot C_{60}$, view along the *a*-axis.

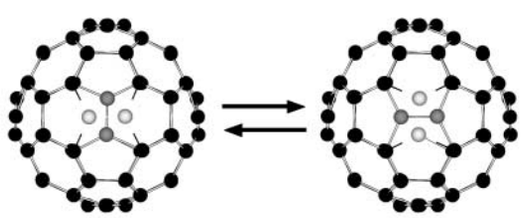

Fig. 5 A view of the C_4 symmetrical disorder of the carbon atoms of the C_{60} molecule in $Co^{II}(tbp)\cdot C_{60}$.

to each other, of the two porphyrazine molecules which are refined with 50% occupancy factor.[25,26] The C_{60} molecule belongs to the icosahedral point group and its cascade symmetry point group (*i.e.* D_{5d}, D_{3d}, D_{2h} *etc.*) but it does not belong to the C_4 symmetry group. Each individual fullerene molecule itself does not possess C_4 symmetry. On the other hand, the $Co^{II}(tbp)$ molecule belongs to the typical C_4 point group. This unusual C_4 symmetry of C_{60} observed in the $Co^{II}(tbp)\cdot C_{60}$ cocrystallite is expected to be related to the strong inter-molecular interaction between C_{60} and the C_4 symmetrical molecule of $Co^{II}(tbp)$.

The closest distance between the cobalt atom and a carbon atom on C_{60} is 2.61 Å (*i.e.* Co(1)···C(33)). On the other hand, the closest distance from the *tert*-butyl group of $Co^{II}(tbp)$ to the carbon atom on C_{60} is 3.50(1) Å (*i.e.* C(15)···C(34)). The X-ray structural analysis of this compound can be carried out at room temperature. Over a dozen porphyrin/fullerene or metalloporphyrin/fullerene structures have been reported using lower temperature in order not only to optimize accuracy but also to conceal the imperfect C_{60} structures with large anisotropic thermal parameters. So far, the crystal structure using X-ray analysis at room temperature, of none of the cocrystallites with fullerene have been determined with absolute atomic position because it is very difficult to reduce the effect of the free rotation of the fullerene molecule at higher temperatures. Therefore, this is the first example of an X-ray structural analysis performed at room temperature for a metal porphyrin cocrystallite with fullerene.

In order to investigate the lattice structure and the inter-molecular interaction of the $Co^{II}(tbp)\cdot C_{60}$ more precisely, X-ray structural analysis at low temperature has also been performed. The crystal data observed at 83 K are also summarized in Table 1. The structures at room temperature and at 83 K are isomorphous and belong to the same space group *I* (no. 79). The volume of the unit cell at 83 K is 4.7% smaller than that observed at room temperature. The effect of the thermal contraction on the intra-molecular bonds in $Co^{II}(tbp)$ is quite small, *i.e.* the average $Co–N^{porphyrin}$ bond distance at room temperature (1.99 Å) is very similar to that observed at 83 K (1.98 Å). This suggests that the inter-molecular interaction between C_{60} and the $Co^{II}(tbp)$ molecules is enhanced as the temperature is decreased. On the other hand, the closest distance from the cobalt atom to the carbon atom on C_{60} is shifted to 2.58 Å (*i.e.* Co(1)···C(34)). This distance is almost the covalent bond length and is shorter than in any other tpp complexes, such as $H_2(tpp)\cdot C_{60}\cdot 3C_6H_5CH_3$ (2.72 Å),[18] $H_2T_{3,5\text{-dibutyl}}PP\cdot C_{60}$ (2.69 Å),[18] $H_2T_{3,5\text{-dimethyl}}PP\cdot 1.5C_{60}\cdot 2C_6H_5CH_3$ (2.71 Å),[18] $H_2T_{piv}PP\cdot C_{60}$ (2.74 Å),[18] $H_2T_{3,5\text{-dimethyl}}PP\cdot C_{70}$ (2.86 Å),[18] $Zn(tpp)\cdot C_{70}$ (2.80 Å)[18] and $NiT_{4\text{-methyl}}PP\cdot 2C_{70}\cdot 2C_6H_5CH_3$ (2.85 Å) (where H_2T_RPP represents tetraphenylporphyrin having its phenyl groups substituted with R; piv = pivolyl).[18] The distance is also shorter than that in octaethylporphyrin (oep) complexes such as $C_{60}\cdot 2Co^{II}(oep)\cdot CHCl_3$ (2.67 Å),[11] $C_{60}\cdot 2Zn^{II}(oep)\cdot CHCl_3$ (2.943 Å),[11] $C_{60}O\cdot 2Co^{II}(oep)\cdot CHCl_3$ (2.67 Å),[11] $C_{70}\cdot Co^{II}(oep)\cdot C_6H_6\cdot CHCl_3$ (2.80 Å),[11] $C_{60}\cdot ClFe^{III}(oep)\cdot CHCl_3$ (2.75 Å),[11] $C_{60}\cdot Pd^{II}(anti\text{-}oep)\cdot 1.5C_6H_6$ (3.10 Å),[16] $C_{60}\cdot Cu^{II}(anti\text{-}oep)\cdot 2C_6H_6$ (3.02 Å),[16] $C_{60}\cdot Ru^{II}(CO)(oep)\cdot 2C_6H_5CH_3$ (2.83 Å),[16] $C_{60}\cdot 2Zn^{II}(oep)\cdot 2C_6H_6$ (2.97 Å),[16] $C_{60}\cdot Ag^{II}(anti\text{-}oep)\cdot 2C_6H_6$ (3.07 Å),[17] and $C_{60}\cdot 2Ni^{II}(anti\text{-}oep)\cdot 2C_6H_5Cl$ (2.99 Å).[17] Therefore, it is suggested that this is the strongest inter-molecular interaction between the planar molecule $Co^{II}(tbp)$ and the curved structure of C_{60}.

Three types of metal porphyrin cocrystallites with fullerene C_{60} have been reported up to now. As shown in Fig. 6, these are; **(i)** ***syn*-M(oep)·C_{60}**, **(ii)** ***anti*-M(oep)·C_{60}** and **(iii) M(tbp)·C_{60}**. In **(i)** ***syn*-M(oep)·C_{60}**, cocrystallites such as $C_{60}\cdot 2Co^{II}(syn\text{-}oep)\cdot CHCl_3$,[11] $C_{60}\cdot 2Zn^{II}(syn\text{-}oep)\cdot CHCl_3$,[11] $C_{60}O\cdot 2Co^{II}(syn\text{-}oep)\cdot CHCl_3$,[11] $C_{60}\cdot ClFe^{III}(syn\text{-}oep)\cdot CHCl_3$,[11] $C_{60}\cdot Ru^{II}(CO)(syn\text{-}oep)\cdot 2C_6H_5CH_3$,[16] and $C_{60}\cdot 2Zn^{II}(syn\text{-}oep)\cdot 2C_6H_6$,[16] have been reported. In these compounds the eight ethyl groups of the metal oep portion lie on the same side of the porphyrin, toward the fullerene. In addition to these fullerene/porphyrin interactions, there are significant porphyrin/porphyrin contacts with either pair-wise or face-to-face contact. The face-to-face interaction is facilitated by the positioning of the ethyl groups on the same side of the porphyrin, which constructs the *syn*-formed metal oep. In the case of **(ii)** ***anti*-M(oep)·C_{60}**, our group has reported the syntheses and structures of cocrystallites such as $C_{60}\cdot Pd^{II}(anti\text{-}oep)\cdot 1.5C_6H_6$,[16] $C_{60}\cdot Cu^{II}(anti\text{-}oep)\cdot 2C_6H_6$,[16] $C_{60}\cdot Ag^{II}(anti\text{-}oep)\cdot 2C_6H_6$,[17] and $C_{60}\cdot 2Ni^{II}(anti\text{-}oep)\cdot 2C_6H_5Cl$.[17] In these compounds the fullerene is peculiarly positioned in the closest approach to the metal atom involving a 5 : 6 ring junction, which indicates π antibonding between the carbon atoms. These cocrystallites consist of the *anti*-formed oeps' and C_{60}, that is the four ethyl groups of both metal oep portions lie on the same side of the porphyrin toward the fullerene, and the

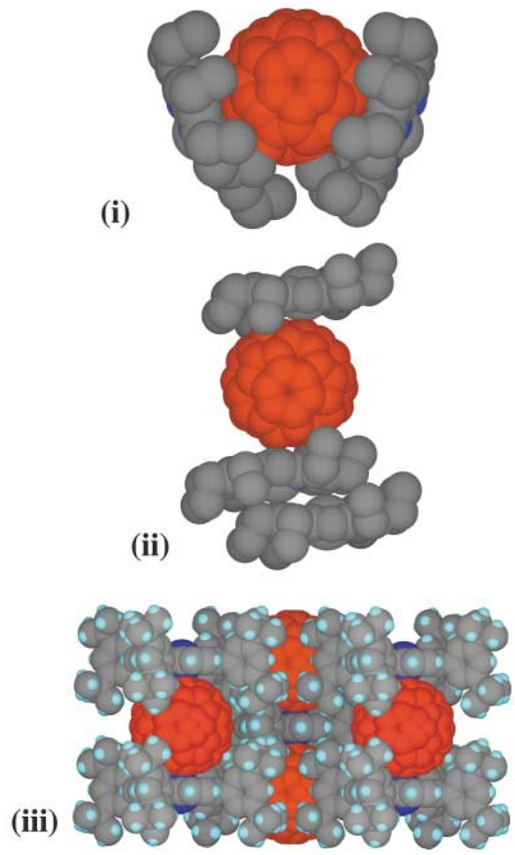

Fig. 6 View of the molecular packing of metal porphyrin cocrystallites with C_{60}. **(i)** ***syn*-M(oep)·C_{60}**, **(ii)** ***anti*-M(oep)·C_{60}** and **(iii) M(tbp)·C_{60}**.

other four ethyl groups lie on the opposite side of the porphyrin from the fullerene. In addition, there are significant *anti*-formed porphyrin/porphyrin contacts with pair-wise character. This combination of fullerene/porphyrin and porphyrin/porphyrin contacts produces a "soccer ball on stackable chairs-like" structure. The disorder of the C_{60} molecule is quite small in the *anti*-formed M(oep) cocrystallites. X-Ray structural analyses at room temperature of these **(i)** ***syn*-M(oep)·C_{60}** and **(ii)** ***anti*-M(oep)·C_{60}** cocrystallites have never been successful because of their incomplete 3-D lattice packing.

On the other hand, the structure of the Co^{II}(tbp)·C_{60} cocrystallite is in an ideal 3-D packing form with a highly symmetrical C_4 point group. The fullerene C_{60} molecule is caught tightly by six Co^{II}(tbp) portions in the octahedral position of the C_{60}. As a result, X-ray structural analysis of this compound at room temperature can be obtained because of a diminishing effect of the rotation of the C_{60} molecule. The inter-molecular distance between C_{60} and the Co^{II}(tbp) molecules is quite short, *i.e.* 2.61 Å at room temperature and it decreases to 2.58 Å at 83 K. This is the shortest length of all reported values, allowing for the possibility for covalent bonding between them. It is well known that the Co^{II} ion in the cobalt porphyrin complex easily forms metal–carbon bonds along the axial direction. Such a short contact distance for metal–carbon bonds in cobalt porphyrin complexes has been reported in compounds such as CH_3COCH_2–Co(tpp),[27] $CHOCH_2$–Co(tpp),[28] CH_3–Co(oep),[29] C_2H_5–Co(oep),[30] and maleic anhydride–Co(tmp) (tmp = tetramesitylporphyrin),[31] *etc*. Therefore employing the cobalt atom as the central metal of Co^{II}(tbp) is one of the most important reasons for having the inter-molecular interaction between C_{60} and the Co^{II}(tbp) molecules in the Co^{II}(tbp)·C_{60} cocrystallite.

In order to discuss the inter-molecular interaction between C_{60} and the Co^{II}(tbp) molecules, the angular dependence of the ESR spectra of the Co^{II}(tbp)·C_{60} were measured. Fig. 7 shows

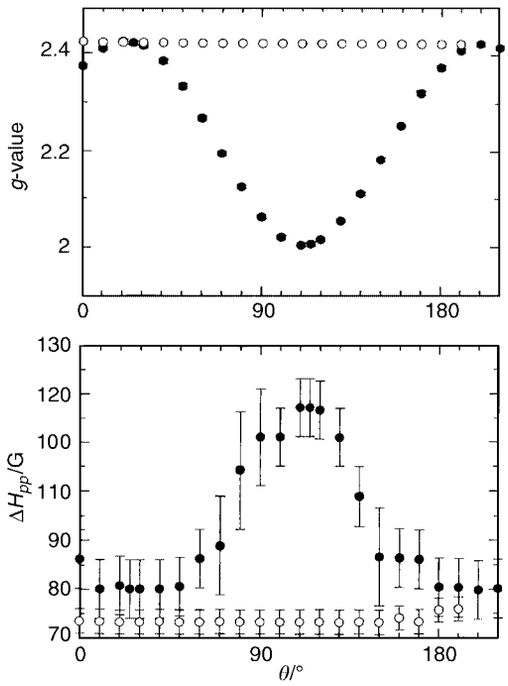

Fig. 7 The *g*-values (top) and the ESR line width (bottom) of Co^{II}(tbp)·C_{60} at room temperature. Full and open circles represent the magnetic field parallel and perpendicular to the tetragonal axis, respectively.

the *g*-values and line widths of the ESR spectra with the magnetic field applied either parallel or perpendicular to the tetragonal axis of Co^{II}(tbp)·C_{60}. The *g*-values in the parallel and perpendicular cases are estimated to be $g_{||} = 2.005$ and $g_{\perp} = 2.423$, respectively. These values suggests that a low spin state Co(II) ion is observed during ESR spectroscopy. Both of the *g*-values and the line widths of the ESR spectra reveal obvious significant anisotropy in the magnetic field. This result suggests that the spin moment from the d_{z^2} orbital of the Co(II) d^7 unpaired electron has been observed and not the one from the $d_{x^2-y^2}$ orbital. The difference between the bond lengths of Co(1)–N(1) at room temperature (1.991(2) Å) and at 83 K (1.981(2) Å) is much less than that of the inter-molecular distance Co(1)···C(34) mentioned above, suggesting that the change in the inter-molecular interaction is much larger than that in the intra-molecular interaction. This result is consistent with the fact that the d_{z^2} orbital of Co(II) is more sensitive to the change of the lattice parameters of Co^{II}(tbp)·C_{60} than the $d_{x^2-y^2}$ orbital. Consequently, in order to discuss the temperature dependence of the inter-molecular interaction between C_{60} and the Co^{II}(tbp) molecules, the temperature dependence of the ESR spectra of Co^{II}(tbp)·C_{60} were measured. The changes in the *g*-values and the ΔH, applying the magnetic field parallel to the tetragonal axis, are very small and negligible. On the other hand, significant changes in the *g*-values and the ΔH are observed when the magnetic field is applied perpendicular to the tetragonal axis. Therefore, only the changes in the case of applying the magnetic field perpendicular to the tetragonal axis are discussed. Fig. 8 shows the ESR spectra of Co^{II}(tbp)·C_{60} with the magnetic field applied perpendicular to the tetragonal axis at a variety of temperatures. The shape of the ESR signal is shown to be intermediate between Gaussian and Lorentzian-type functions. The temperature dependences of the *g*-value and the line width of the ESR spectra are summarized in Fig. 9. It is suggested that the *g*-value of the ESR spectra decreases as the temperature decreases. The change in the *g*-value of the ESR spectra, when the radical spin comes from the d_{z^2} orbital of the low spin state Co(II) ion, is explained in the following equation,

$$g_{\perp} = 2.0023 - 6\left(\frac{\lambda}{\Delta E}\right),$$

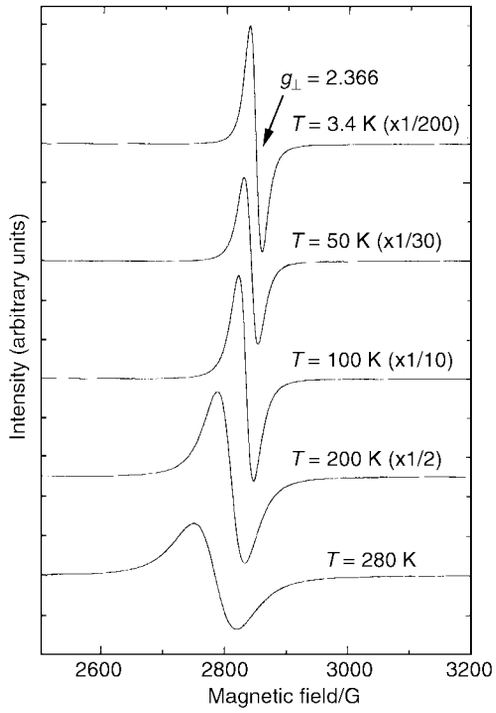

Fig. 8 ESR spectra of $Co^{II}(tbp)\cdot C_{60}$ applying the magnetic field perpendicular to the tetragonal axis at different temperatures.

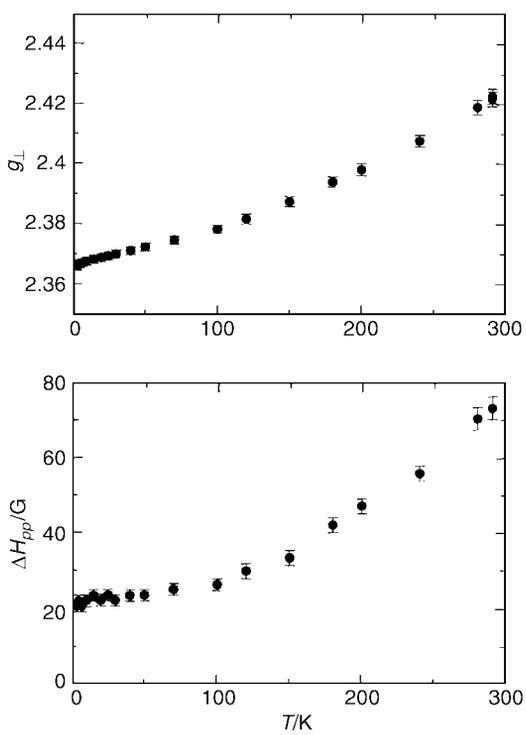

Fig. 9 Temperature dependence of the *g*-value (top) and the ESR line width (bottom) of $Co^{II}(tbp)\cdot C_{60}$ from 3.4 to 280 K applying the magnetic field perpendicular to the tetragonal axis.

where λ and ΔE denote the spin–orbit interaction ($\lambda < 0$,($\because d > 5$)) and the difference in the energy levels between the d_{z^2} and $d_{yz,zx}$ orbitals of the Co(II) ion, respectively. From the results of X-ray structural analyses, it is revealed that the distance between the carbon atom on C_{60} and the cobalt atom on the $Co^{II}(tbp)$ molecule decreases as the temperature decreases. The distance between them (Co(1)···C(33), 2.61 Å) at room temperature decreases and reaches a value of 2.58 Å at 83 K. It is expected that the energy level of the d_{z^2} orbital of the Co(II) ion becomes more unstable when the inter-atomic distance is shorter at low temperature. Therefore it is also expected that the difference between the energy levels of the d_{z^2} and $d_{yz,xy}$ orbitals becomes larger as the temperature is decreased. As a result, the *g*-value of the ESR spectra decreases as the temperature is decreased. On the other hand, it is revealed that the line width of the ESR spectra of $Co^{II}(tbp)\cdot C_{60}$ also decreases as the temperature decreases. If the line width depends on the spin–phonon interaction, the line width could be explained as being proportional to the shift of the *g*-value, as in the following equation,

$$\Delta H_{pp} \propto \Delta g = |2.0023 - g|$$

where ΔH_{pp} denotes the line width of the ESR spectra. The *g*-value decreases and approaches the value of the free electron, 2.0023, as the temperature is decreased. Therefore, the line width of the ESR spectra decreases as the temperature is decreased. In addition, the spin–phonon interaction decreases as the temperature is decreased. Another reason for the decrease of ΔH_{pp}, is that the energy of the phonon of the shrunk $Co^{II}(tbp)\cdot C_{60}$ lattice packing is reduced as the temperature is decreased.

Conclusion

In our previous work,[16] the orientation of the terminal ethyl groups on the oep was suggested to be very important in order to make the cocrystallite of the curved surface C_{60} with the planar surfaced porphyrin. It is suggested that the introduction of the terminal *tert*-butyl groups onto the tpp is a requirement to obtain a strong inter-molecular interaction in the cocrystallite with C_{60}. Significantly short distances between the porphyrin plane and the fullerene C_{60} were observed in this cocrystallite. As a result of the strong inter-molecular attraction, X-ray structural analysis can be performed at room temperature. Therefore, this is the first report of an X-ray structural analysis at room temperature of metal porphyrin cocrystallites with fullerene.

Experimental

Chemicals and reagents

All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions were dried by conventional methods and freshly distilled under nitrogen. 3,5-Di-*tert*-butyltoluene was reagent grade (Aldrich). 3,5-Di-*tert*-butylbenzaldehyde was readily available.[32] As a result of our mechanistic studies on the synthesis of 5,10,15,20-tetrakis[3,5-(di-*tert*-butyl)phenyl]-21*H*,23*H*-porphyrin (H_2(tbp)), we have performed a synthesis which represents an improvement on methods previously reported in the literature.[33,34] The preparation of $Co^{II}(tbp)$ was performed according to methods in the literature.[35]

Synthesis of $Co^{II}(tbp)\cdot C_{60}$

A 0.020 g (0.028 mmol) sample of C_{60} was dissolved in 40 ml of toluene. The solution was filtered and then mixed with a filtered solution of 0.030 g (0.028 mmol) of $Co^{II}(tbp)$ dissolved in 10 ml of toluene. The resultant mixture was allowed to stand for a couple of weeks, during which dark crystals were formed. These were collected by decanting the solvent to yield 0.036 g (70%) of product.

X-Ray data collection

The black, needle-like, crystals having approximate dimensions of 0.10 × 0.10 × 0.10 mm were coated with a light hydrocarbon oil and mounted on a glass fiber. Data for $Co^{II}(tbp)\cdot C_{60}$ were

collected on a Rigaku RAXIS-RAPID 2 Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at room temperature and at 83 ± 1 K in a cold dinitrogen stream to a maximum 2θ value of 55.0°. Data were processed using the PROCESS-AUTO program package.[36] A symmetry-related absorption correction using the program ABSCOR[37] was applied. The data were corrected for Lorentz and polarization effects. Check reflections were stable throughout the data collection. The crystal data, including the previous data are summarized in Table 1.

The structure was solved by direct methods[38] and expanded using Fourier techniques.[39] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Hydrogen atoms were included through the use of a riding model. A numerical absorption correction was also employed. Neutral atom scattering factors were taken from Cromer and Waber.[40] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[41] All calculations were performed using the teXsan[42] crystallographic software package.

CCDC reference numbers 164971 and 164972.

See http://www.rsc.org/suppdata/dt/b1/b104514h/ for crystallographic data in CIF or other electronic format.

ESR spectroscopy

ESR measurements were performed on single crystal samples by using a Bruker E500 X-band spectrometer equipped with a gas-flow type cryostat (Oxford ESR-900). The absolute g value was calibrated using diphenylpicrylhydrazyl (DPPH) as a standard.

Acknowledgements

The authors thank Professors H. Imahori and Y. Sakata (Osaka University) for their kind advice on the syntheses of tbp. This research was supported partly by a Grant-in-Aid for Scientific Research on Priority Areas (Nos. 10149104 and 11165235), "Metal-Assembled Complexes" and "Fullerenes and Nanotubes Networks" from the Ministry of Education, Science and Culture, Japan.

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