

Interaction of Curved and Flat Molecular Surfaces. The Structures of Crystalline Compounds Composed of Fullerene (C₆₀, C₆₀O, C₇₀, and C₁₂₀O) and Metal Octaethylporphyrin Units

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Abstract: Solutions of C₆₀, C₆₀O, or C₇₀ and metal complexes of octaethylporphyrin (OEPH₂) yield crystals that contain both the fullerene and the porphyrin. The structures of C₆₀·2Co^{II}(OEP)·CHCl₃, C₆₀·2Zn^{II}(OEP)·CHCl₃, and C₆₀O·2Co^{II}(OEP)·CHCl₃ are isomorphous and contain an ordered C₆₀ cage surrounded by two M^{II}(OEP) units. Although there is no covalent bond between the fullerene and porphyrin components, the separation between these units is shorter than normal van der Waals contact. Crystals of C₇₀·Co^{II}(OEP)·C₆H₆·CHCl₃, C₇₀·Ni^{II}(OEP)·C₆H₆·CHCl₃, and C₇₀·Cu^{II}(OEP)·C₆H₆·CHCl₃ are also isomorphous with an ordered fullerene, but have only one porphyrin/fullerene contact. Crystalline C₆₀·ClFe^{III}(OEP)·CHCl₃ lacks the close face-to-face porphyrin/porphyrin contact that is common to all of the other structures reported here but retains the intimate contact between the porphyrin and the fullerene. In (C₁₂₀O)·Co^{II}(OEP)·0.6C₆H₆·0.4CHCl₃ the fullerene dimer is enclosed by two Co^{II}(OEP) moieties. Unfortunately disorder in the fullerene portion obscures details of the geometry of the bridging region between the fullerenes.

Introduction

The unique three-dimensional shapes of the fullerenes coupled with their distinct physical properties make them attractive candidates for the construction of larger, supramolecular aggregates. While the synthetic chemist has had decades of experience using the flat surfaces of aromatic hydrocarbons in the construction of molecules and molecular arrays, the curved external surfaces of the fullerenes are unusual and present interesting challenges in the design of larger assemblies. There have been several approaches to obtaining curved surfaces that are able to encircle a fullerene by building complex structures from planar aromatic hydrocarbon units and other flat moieties. A number of bowl-shaped molecules including calixarenes,¹ cyclodextrins,² and cyclotrimeratrylene³ have been found to form weak complexes with C₆₀ and other fullerenes. Several of these assemblies have been structurally characterized. Metal binding ligands have been designed with portions that can allow flat benzene rings to encircle C₆₀.⁴ Solutions of silver nitrate and C₆₀ yield a black crystalline solid, C₆₀{Ag(NO₃)₃}₅, that contains an infinite, curved silver nitrate network that encapsulates the fullerene.⁵ Fullerenes are also well-known to cocrystallize with a variety of molecules that include organic (e.g. benzene⁶),

organometallic (e.g. ferrocene⁷), and inorganic species (e.g. Pd₆-Cl₁₂,⁸ P₄,⁹ S₈¹⁰).

Here we report that metal complexes of octaethylporphyrin cocrystallize with C₆₀ and C₇₀ to form solids in which the two components make remarkably close contact despite the differences in external shapes, planar versus highly curved. There have been a number of molecules created in which a fullerene and a porphyrin are covalently attached to one another,^{11–13} but

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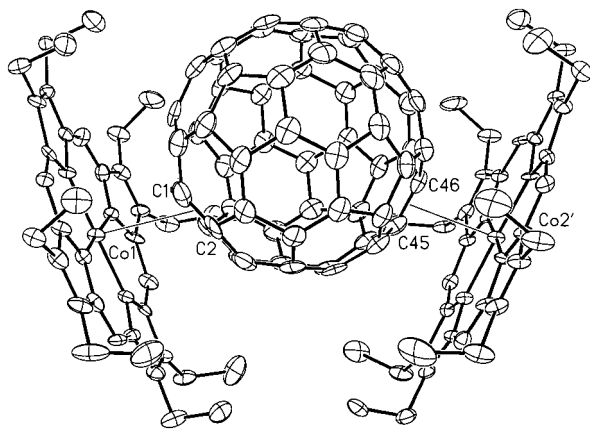


Figure 1. A view of the $C_{60} \cdot 2Co^{II}(OEP)$ unit in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ with 50% thermal ellipsoids showing how the two porphyrins surround the fullerene.

in the work presented here, no covalent links occur between the constituents.

Results

The compounds reported here were obtained in a form suitable for single-crystal X-ray diffraction by allowing a solution of the fullerene in benzene to diffuse into a solution of the metalloporphyrin in chloroform.

The Isomorphous Series, $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$, and $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$. The asymmetric unit in these three compounds consists of a C_{60} molecule, two metalloporphyrins, and one molecule of chloroform. In each compound the C_{60} cage is fully ordered. These compounds crystallize so that two porphyrin molecules surround each fullerene as shown in Figure 1 for the cobalt complex $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$. Within this unit the fullerene is positioned asymmetrically between the two $Co^{II}(OEP)$ units, but the fullerene is too far from the cobalt atoms for any covalent bonding between them. The fullerene is positioned so that the closest approach to the cobalt atom involves 6:6 ring junctions. The distances from the cobalt atoms to the midpoints of these C—C bonds are 2.680 and 2.893 Å, respectively. The Co—C distances are $Co(1) \cdots C(1)$, 2.738; $Co(1) \cdots C(2)$, 3.198; $Co(2') \cdots C(45)$, 2.858; and $Co(2') \cdots C(46)$, 2.673 Å. While these distances are too long to represent coordination, they are shorter than normal van der Waals contact seen between graphite layers (3.4 Å),¹⁴ between adjacent porphyrins (3.2 Å and larger),¹⁵ and between neighboring fullerenes (greater than 3.2 Å).¹⁶

The ethyl groups of both $Co^{II}(OEP)$ portions lie on the same side of the porphyrin as the fullerene and form an octapoid embrace about the fullerene. The distances from the center of the fullerene to the methyl carbons span the range 6.94–7.87 Å. The van der Waals radius of C_{60} is 5.0 Å, and that of a methyl group is 2.0 Å.^{14,16} Thus, the eight methyl groups are within van der Waals contact of the fullerene. Additionally, the fullerene is surrounded by the ethyl groups from two other pairs of $Co^{II}(OEP)$ molecules. Figure 2 shows a drawing of the molecular packing that emphasizes how the fullerene is nestled within the ethyl groups of these other cobalt porphyrin molecules.

In addition to these fullerene/porphyrin interactions, there are significant porphyrin/porphyrin contacts with pairwise, face-to-face contact. The combination of fullerene/porphyrin and porphyrin/porphyrin contacts produces helical ribbons that wind

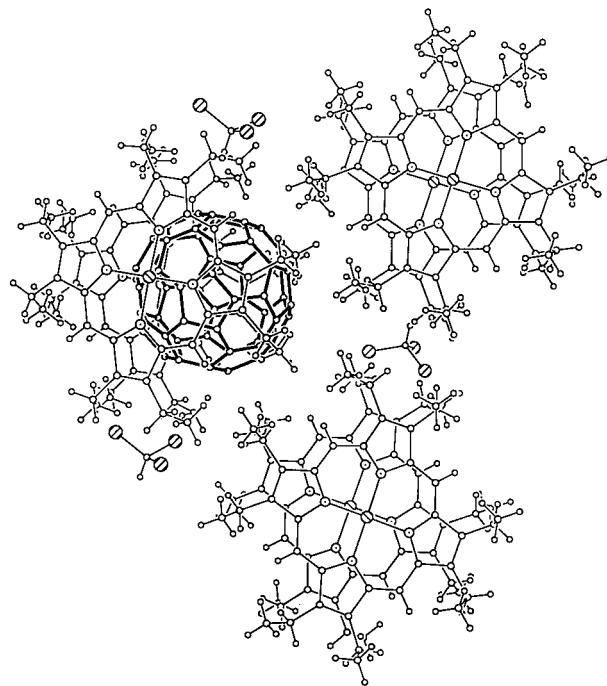


Figure 2. A view emphasizing the ethyl groups that surround the fullerene in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$.

their way through the crystal. A portion of a ribbon is shown in Figure 3. The contact between the two porphyrins places each cobalt atom nearly directly over a nitrogen atom of the adjacent porphyrin, but the $Co \cdots N$ separation is too long to represent a covalent interaction.

Selected interatomic distances within the porphyrin portion of these cocrystals are given in Table 1. The core molecular geometry of the cobalt porphyrin in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ is similar to that found in $Co^{II}(OEP)$ itself,¹⁷ as seen in Table 1 where parameters for some simple metalloporphyrins are also shown. Notice from this table that the face-to-face porphyrin/porphyrin contact is greater in the fullerene cocrystals than it is in $Co^{II}(OEP)$ itself. Thus, the lateral shift (LS) and the $Co \cdots Co$ separation ($M \cdots M$) in the fullerene compound are shorter than they are in $Co^{II}(OEP)$. Additionally the mean plane separation (MPS) and the LS are shorter in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ than in $Co^{II}(OEP)$ itself. This close face-to-face arrangement is facilitated by the positioning of all of the ethyl groups on the opposite side of the porphyrin from the adjacent porphyrin. In contrast $Co^{II}(OEP)$ has four ethyl groups on one side of the porphyrin plane and four on the opposite side.

While $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ and $C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$ are isomorphous, there are some slight differences in the structures. Again, there is no coordination of the fullerene to zinc, but the fullerene is more symmetrically positioned between the two porphyrins in the zinc cocrystal. The distances from the midpoints of the closest 6:6 fullerene ring junctions to the zinc ions are 2.971 and 3.082 Å, and the $Zn \cdots C$ distances are 2.943, 3.147, 2.985, and 3.321 Å.

$C_{60}O$,¹⁸ like C_{60} , forms a cocrystalline compound with $Co^{II}(OEP)$. The fullerene is again asymmetrically positioned between

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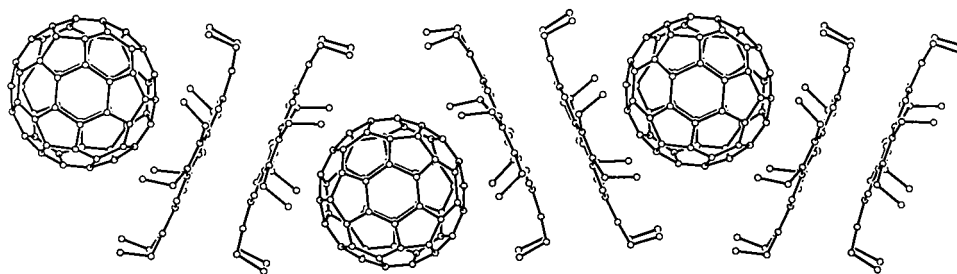


Figure 3. A view of the helical chains of $C_{60} \cdot 2Co^{II}(OEP)$ in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$.

Table 1. Selected Interatomic Distances

	$C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$	$C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$	$C_{60}O \cdot 2Co^{II}(OEP) \cdot CHCl_3$	$C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$	$C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$	$C_{70} \cdot Cu^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$	$C_{60} \cdot ClFe^{III}(OEP) \cdot CHCl_3$	$C_{120}O \cdot Co^{II}(OEP) \cdot 0.4C_6H_6 \cdot 0.6CHCl_3$			
M—N	1.971(5)	1.983(5)	2.089(4)	2.042(5)	1.980(7)	1.986(7)	1.964(5)	1.950(6)	1.961(9)	2.073(8)	1.964(15)
	1.983(6)	1.985(6)	2.054(5)	2.081(5)	1.978(8)	1.967(8)	1.966(5)	1.956(6)	2.009(8)		1.966(11)
	1.979(6)	1.982(5)	2.030(4)	2.047(5)	1.978(8)	1.976(7)	1.964(5)	1.956(6)	1.964(9)		1.961(15)
	1.967(6)	1.954(6)	2.036(5)	2.033(4)	1.957(8)	1.962(8)	1.967(5)	1.960(6)	1.993(8)		
M—Cl										2.235(9)	
M···N	2.980	2.592	2.955	2.965	3.152	2.962					2.936
	2.970	2.674	2.981								
M···M	3.438	3.166	3.425	3.392	3.485	3.407	8.079	3.448			
Ct···Ct	3.63	3.68	3.61	3.60	3.65	3.66	8.45	3.68			
MPS	3.21	3.21	3.21	3.19	3.28	3.26	2.98	3.21			
LS	1.69	1.80	1.65	1.67	1.60	1.66	7.91	1.80			
M—N ₄ plane	0.0219	0.1605	0.0236	0.0320	0.0276	0.0255					
	0.0114	0.1402	0.0134								
	$Co^{II}(OEP)^a$			$Ni^{II}(OEP)^b$	$Cu^{II}(OEP)^d$	$ClFe^{III}(OEP)^c$					
M—N	1.967(3)			1.946(4)	1.996(3)	2.074					
	1.975(2)			1.958(4)	1.999(3)	2.076					
						2.064					
						2.067					
M—Cl						2.231					
M···M	4.742			4.802	4.805	7.877, 8.193					
Ct···Ct	4.74			4.802	4.805	8.24, 7.69					
MPS	3.33			3.44	3.43	3.41, 3.42					
LS	3.38			3.35	3.36	7.50, 6.89					

^a Data from Scheidt, W. R.; Turowska-Tyrk, I. *Inorg. Chem.* **1994**, *33*, 1314. ^b Data from Brennan, T. D.; Scheidt, W. R.; Shelnut, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3919. ^c Data from Senge, M. Private communication, Cambridge Crystallographic Data Base, TOYRUU. ^d Data from Pak, R.; Scheidt, W. R. *Acta Crystallogr., Sect. C*, **1991**, *C47*, 431.

the two porphyrin molecules with Co—C distances of 2.728, 3.219, 2.670, and 2.840 Å and separations of 2.669 and 2.902 Å between the cobalt atoms and the centers of the adjacent 6:6 ring junctions of the fullerene oxide. Although the C_{60} cage is fully ordered, the epoxide oxygen atoms are disordered over five sites as seen in Figure 4. (In crystalline $C_{60}O$ itself, the oxygen atoms are disordered over the entire surface of the fullerene.¹⁹) The sum of the occupancies is only 0.71, whereas the expected occupancy is 1. The reduction in oxygen atom occupancy may result from additional disorder of the oxygen atom over sites that are simply too sparsely occupied to be detected in the available X-ray diffraction data or from the loss of oxygen from $C_{60}O$ during the time required for crystal growth. (It is well-known that $C_{60}O$ readily reverts to C_{60} under a variety of conditions including chromatography on alumina.¹⁸) Nevertheless, the data indicate that the oxygen atoms are all situated above 6:6 ring junctions in epoxide functionalities as seen also in the crystallographically determined structures of $(\eta^2-C_{60}O)Ir(CO)Cl(PPh_3)_2$ and $(\eta^2-C_{60}O)Ir(CO)Cl(AsPh_3)_2$.^{20,21}

The Isomorphous Series, $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, $C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, and $C_{70} \cdot Cu^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$.

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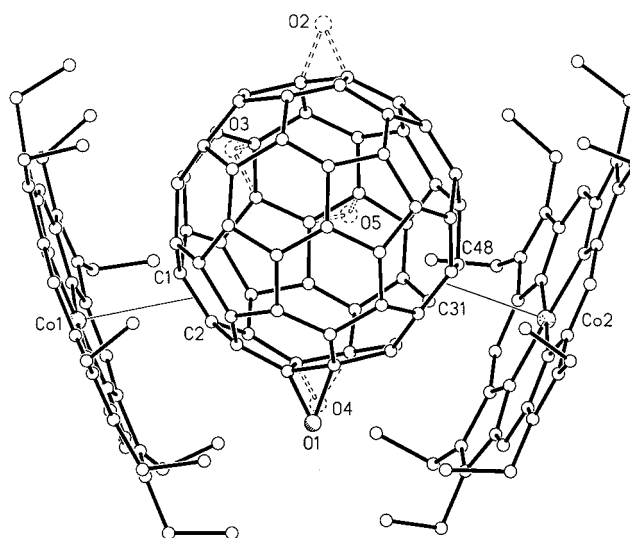


Figure 4. A drawing showing the locations of the five, partially occupied oxygen atom positions in $C_{60}O \cdot 2Co^{II}(OEP) \cdot CHCl_3$. The occupancies are O1, 0.21(1); O2, 0.17(1); O3, 0.13(1); O4, 0.16(1); and O5, 0.07(1).

The asymmetric unit in each consists of one fully ordered C_{70} molecule, one metalloporphyrin, and two solvent sites which may be occupied by chloroform or benzene. The porphyrin/fullerene interaction, which involves only a single $M^{II}(OEP)$

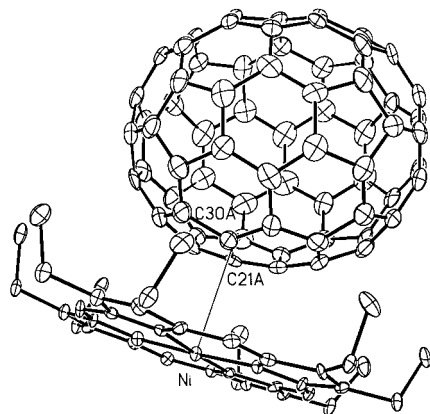


Figure 5. A view of the fullerene/porphyrin unit in $C_{70}\cdot Ni^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$ with 30% thermal ellipsoids. The arrows show the location of the 5-fold axis in C_{70} .

molecule, is shown in Figure 5. The fullerene is positioned so that the C_5 axis of the fullerene makes an angle of 16.4° with the porphyrin plane in $C_{70}\cdot Co^{II}(OEP)\cdot CHCl_3\cdot C_6H_6$, 16.2° in $C_{70}\cdot Ni^{II}(OEP)\cdot CHCl_3\cdot C_6H_6$, and 16.6° in $C_{70}\cdot Cu^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$. Again, there is no covalent bonding between the metal ions and the fullerene. The fullerene is positioned so that one of the carbon atoms (an atom in layer c of the fullerene) is positioned almost directly over the metal at the center of the porphyrin. These short, but nonbonded $Co\cdots C$, $Ni\cdots C$, and $Cu\cdots C$ distances are 2.800, 2.835, and 2.919 Å, respectively.

The ethyl groups on the porphyrin molecules are arranged so that they again encircle the C_{70} molecule and also avoid contact with the adjacent porphyrin molecules which make close face-to-face contact. An overall view of the molecular packing of these solids is shown in Figure 6.

The internal dimensions of the porphyrins are similar to those previously reported for $Co^{II}(OEP)$, for the triclinic B form of $Ni^{II}(OEP)$,²² and for $Cu^{II}(OEP)$ as can be seen from the data in Table 1. However, the face-to-face interactions between the metalloporphyrin components are more extensive in the fullerene cocrystals than in the simple porphyrin crystals.

$C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$. The asymmetric unit consists of one-quarter of the iron porphyrin at a site of mm symmetry, a fullerene (also at a site of mm symmetry), which is disordered over four positions, and a chloroform molecule. A view of the porphyrin/fullerene interaction in this solid is shown in Figure 7, while Figure 8 shows a view of the overall molecular packing. As seen in Figure 7 there is one porphyrin/fullerene interaction. Again, there is no coordination of the fullerene to the metal; indeed the iron ion is on the opposite side of the porphyrin from the fullerene. The distance from the closest fullerene carbon atom to the N_4 plane is 2.748 Å. The ethyl groups are arranged to embrace the fullerene.

The geometry of the porphyrin core and the iron coordination in $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$ are similar to those in $ClFe^{III}(OEP)$ ²³ itself, as seen from the data in Table 1. However, in $ClFe^{III}(OEP)$ the molecular packing gives rise to a different distribution of ethyl group orientations, with five lying on one side of the porphyrin and three on the opposite side, the side that includes the Fe—Cl portion.

$C_{120}O\cdot Co^{II}(OEP)\cdot 0.4C_6H_6\cdot 0.6CHCl_3$. The fullerene oxide, $C_{120}O$, which consists of two C_{60} cages joined by a tetrahydro-

furan-like bridge,^{24–27} was obtained by the solid-state thermolysis of a mixture $C_{60}O$ and C_{60} and purified by HPLC.^{23,24} Figure 9 shows a view of the packing of the fullerene and porphyrin units within this solid. The $Co^{II}(OEP)$ /fullerene and $Co^{II}(OEP)$ / $Co^{II}(OEP)\cdot CHCl_3$ and $C_{70}\cdot Co^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$. The fullerene dimer unfortunately suffers from a complex disorder as described in the Experimental Section. The two C_{60} units are clearly linked by a carbon—carbon single bond. However, the connections to the oxygen atom of the dimer are poorly defined.

Discussion

Eight new compounds that involve cocrystallization of fullerenes with porphyrins have been examined by single-crystal X-ray diffraction. Although fullerenes have a remarkable propensity for disorder,²⁸ the fullerenes are ordered in $C_{60}\cdot 2M^{II}(OEP)\cdot CHCl_3$ ($M = Co, Zn$) and in $C_{70}\cdot M^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$ ($M = Co, Ni, Cu$). In $C_{60}O\cdot 2Co^{II}(OEP)\cdot CHCl_3$, there is disorder in the location of the epoxide oxygen atom, but the carbon cage is ordered. Because the fullerene carbon cages are ordered in these structures, it is anticipated that cocrystallization with metalloporphyrins may offer a method of obtaining suitable crystals of related compounds, i.e. endohedral metallofullerenes, higher fullerenes, and chemically modified fullerenes, for study by single-crystal X-ray diffraction. However, in $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$ the fullerene is disordered over four positions, and in $C_{120}O\cdot Co^{II}(OEP)\cdot 0.6C_6H_6\cdot 0.4CHCl_3$ the bridged fullerene dimer is also disordered.

Within these new compounds the fullerene/porphyrin contacts are all unusually close (with $M\cdots C$ distances as short as 2.68 Å), but there is no direct coordination of the fullerene to the metalloporphyrin. This point is particularly clear in the structure of $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$, where the metal and the fullerene reside on opposite sides of the porphyrin plane. The close fullerene/porphyrin contacts seen here can be compared to previously reported cases where arene molecules interact with metalloporphyrins. For example, in $Mn^{II}(TPP)\cdot (CH_3C_6H_5)$ a toluene molecule sits over the center of the porphyrin with distances from the mean porphyrin plane to the carbon atoms of the toluene that range from 3.12 to 3.4 Å.²⁹ In $(ClO_4)Fe^{III}(TPP)\cdot 0.5(m-(CH_3)_2C_6H_4)$, a similar situation occurs with porphyrin mean plane to *m*-xylene carbon atom distances ranging from 3.32 to 3.66 Å.³⁰ Closer arene to metalloporphyrin contacts are seen in $[Fe(TTP)][Ag(Br_6CB_{11}H_6)_2]\cdot 4(p\text{-xylene})$ where two *p*-xylene molecules make face-to-face contact with the center of the porphyrin.³¹ The closest distance between a xylene carbon atom and the porphyrin mean plane is 2.89 Å, where the $[Fe(TPP)]^+$ unit is tightly solvated by its neighbors.

In all structures reported here, the eight ethyl groups of each metalloporphyrin are arranged so that they form an octopus-

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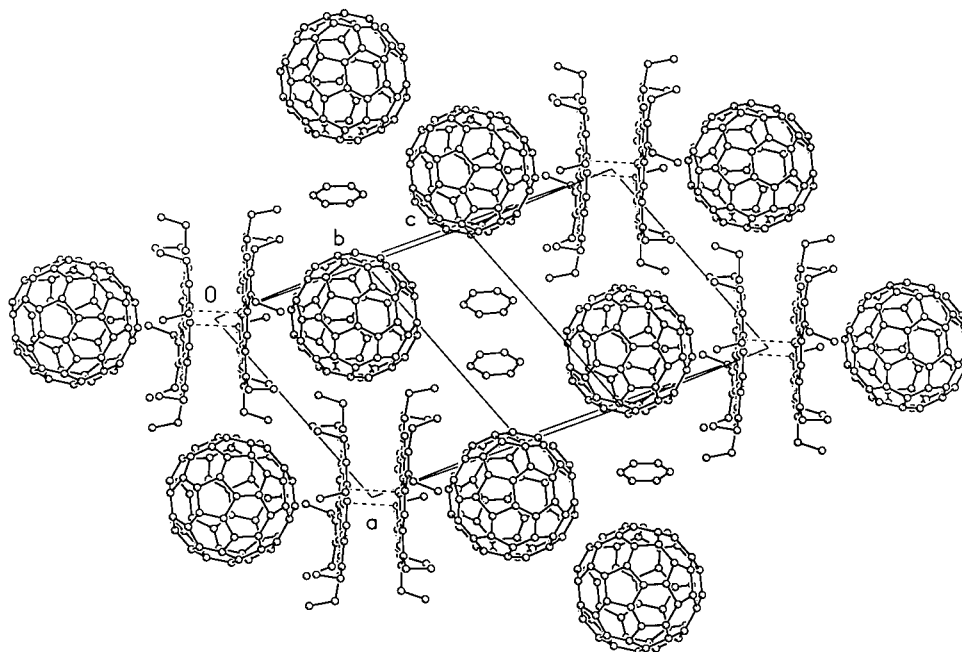


Figure 6. A stereoview of the molecular packing in $C_{70}\cdot Co^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$.

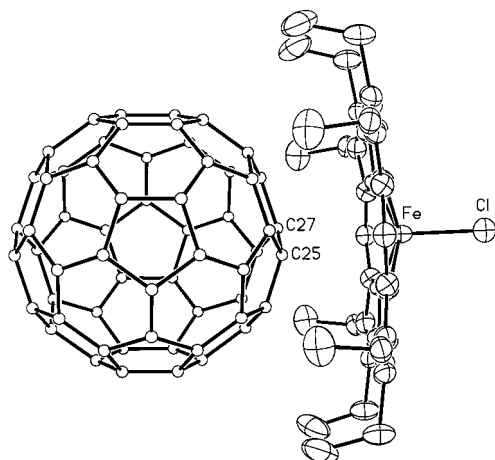


Figure 7. A view of the fullerene/porphyrin units in $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$ with 50% thermal ellipsoids.

like embrace of the fullerene surface. This orientation of the ethyl groups also facilitates the adjoining porphyrin/porphyrin interactions.

For the four-coordinate metalloporphyrins, the face-to-face stacking of pairs of $M^{II}(OEP)$ units is also a prominent feature of the structures with both C_{60} and with C_{70} . Scheidt and Lee have previously classified such interactions as weak when the lateral shift is greater than 4.5 Å, intermediate when the lateral shift is about 3.5 Å, and strong when this shift is about 1.5 Å.¹⁵ In this scheme, the face-to-face interactions of the four-coordinate metalloporphyrins are all strong in the fullerene cocrystals. In contrast, in the porphyrin–porphyrin arrangements in $Co^{II}(OEP)$ itself and in the triclinic B form of $Ni^{II}(OEP)$ they correspond to intermediate face-to-face interactions. However, in five-coordinate $ClFe^{III}(OEP)$ the position of the Fe–Cl bond prohibits such close contact, and consequently in $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$ the face-to-face interaction is weak.

Cocrystallization of these fullerenes with the metalloporphyrins by necessity changes the nature of the fullerene/fullerene contacts from those seen in pure crystalline fullerenes. As seen in Figure 2, in the $C_{60}\cdot 2Co^{II}(OEP)\cdot CHCl_3$, $C_{60}\cdot 2Zn^{II}(OEP)\cdot CHCl_3$, and $C_{60}O\cdot 2Co^{II}(OEP)\cdot CHCl_3$ family, the fullerenes are

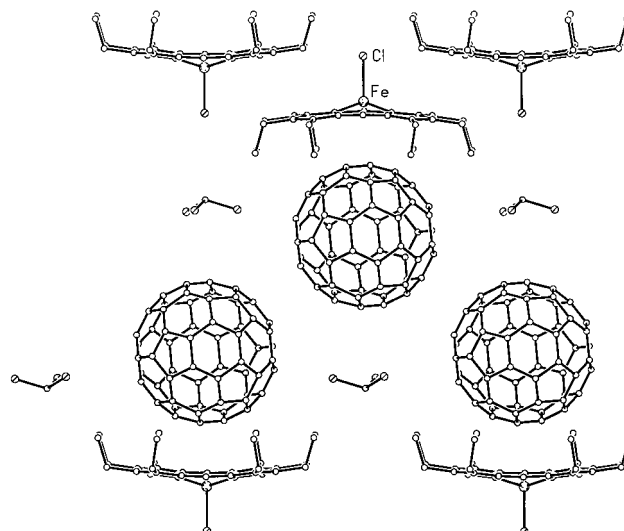


Figure 8. A drawing that shows the molecular packing in $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$.

entirely surrounded by C–H groups from the two $M^{II}(OEP)$ units that encapsulate the fullerene as well as from two adjacent pairs of $M^{II}(OEP)$ units that sit off to the other side of the fullerene. Consequently the center to center distance between the fullerenes in this family is quite large, ca. 13.09 Å. In the series $C_{70}\cdot Co^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$, $C_{70}\cdot Ni^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$, and $C_{70}\cdot Cu^{II}(OEP)\cdot C_6H_6\cdot CHCl_3$, the closest contacts between C_{70} molecules are 3.486, 3.438, and 3.395 Å, respectively. In $C_{60}\cdot ClFe^{III}(OEP)\cdot CHCl_3$ the shortest separation between the centers of the C_{60} molecules that lie in the plane shown in Figure 8 is 9.80 Å, which compares to the spacing of 9.94 Å (at 110 K) that is seen in C_{60} itself.

Examination of the planarity of the MN_4 portion of the metalloporphyrins in the new compounds reported here shows that the metal protrudes only slightly from the plane of the four nitrogen donors. Relevant data, the distances of the metal from the N_4 plane, are given in Table 1 as the M– N_4 plane distances. The deviations are small and range from 0.0114 to 0.1605 Å. Those for the zinc compound are an order of magnitude larger

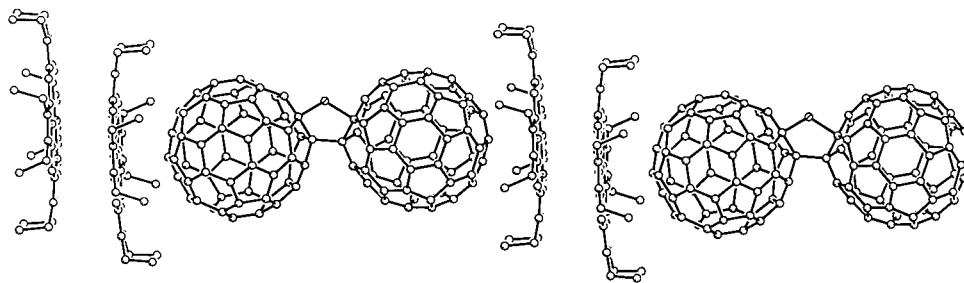


Figure 9. The molecular packing of fullerenes and porphyrins in $C_{120}O \cdot Co^{II}(OEP) \cdot O.4C_6H_6 \cdot 0.6CHCl_3$. Only one set of four orientations of the C_{60} units is shown.

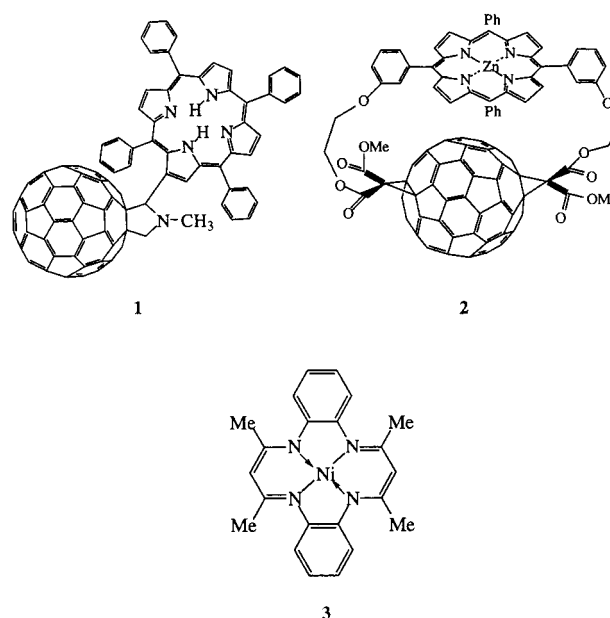
than those of the corresponding cobalt complexes. In all cases the metal ions are displaced from the N_4 plane in such a fashion that they are closer to the immediately adjacent porphyrin and further from the neighboring fullerene.

The cocrystallizations reported here may be facilitated by charge-transfer interactions between the porphyrin and the fullerene, with the fullerene acting as an acceptor and the metalloporphyrin as a donor. A number of studies have been made of the interaction of metalloporphyrins with strong organic π -acceptors such as trinitrobenzene.³² The acceptor properties of the fullerenes are a consequence of their ease of reduction.³³

Chromatographic materials with appended porphyrins have been developed for the separation of fullerenes.³⁴ The porphyrin/fullerene interactions seen in these cocrystallized materials provide a model for the porphyrin/fullerene interactions that occur during chromatography. Interactions of fullerenes with one or two porphyrin units have been considered as part of the chromatographic process.

Other cases are known where fullerenes and related large flat molecules are found in close proximity. Crystalline $C_{60} \cdot 2$ octakis-(dimethylamino)porphyrazine $\cdot C_6H_5CH_3$ has a structure similar to that of $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ with two of the macrocycles cupping the fullerene.³⁵ However, in this structure the fullerene portion is disordered over several orientations. The planar porphyrazine molecules are arranged in a face-to-face fashion. The pyrrolidine-linked tetraphenylporphyrin/ C_{60} dyad, **1**, crystallizes in a fashion that places the fullerene of one molecule in close proximity to the porphyrin plane of another.³⁶ An unusual donor/acceptor relationship, in which the fullerene acts as a donor and the porphyrin acts as the acceptor, was proposed for the intermolecular interactions in crystalline **1**. The C_{60} /porphyrin dyad, **2**, was synthesized with covalent links that enforce proximity of the porphyrin and fullerene.³⁷ Evidence of π - π stacking of the two components comes from the bathochromic shift of the Soret and Q-bands of the zinc porphyrin in the dyad relative to the free porphyrin and the

complete quenching of the expected porphyrin fluorescence at 500 nm. Another set of covalently linked dyads containing C_{60} and porphyrins have been reported.³⁸ A variety of metal-free tetra(substituted-aryl)porphyrins have also been found to form cocrystals with C_{60} .³⁹



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C_{60} as well as the cage molecules, 1,2-dicarbododecaborane and P_4S_3 , have also been found to cocrystallize with the nickel complex, **3**.⁴⁰ In these crystals each side of the saddle-shaped nickel complex interacts with a fullerene molecule. It remains to be seen whether porphyrins that have saddle shapes due to steric encumbrances on the periphery can cocrystallize with fullerenes. However, in that context it is interesting to note that $Ni^{II}(OEP)$, which does crystallize in both planar and saddle-shaped modifications, assumes a planar geometry when it cocrystallizes with C_{70} .

Tetra(aryl)porphyrins and their metal complexes are known to act as "porphyrin sponges" in which they cocrystallize with hundreds of foreign guest molecules.⁴¹ That behavior is distinct from what we report here. The porphyrin sponges generally

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Table 2

empirical formula	$C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$	$C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$	$C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$	$C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$	$C_{70} \cdot Cu^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$	$C_{60} \cdot ClFe^{III}(OEP) \cdot CHCl_3$	$(C_{120}O) \cdot Co^{II}(OEP) \cdot 0.4C_6H_6 \cdot 0.6CHCl_3$
fw	2023.33	2036.21	1628.85	1628.63	1633.46	1464.02	1423.15
color, habitat	dark purple, needle	dark red, parallelepiped	dark red, plate	black, plate	deep red, needle	black, obelisk	black, parallelepiped
crystal system	orthorhombic	orthorhombic	triclinic	triclinic	triclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P1$	$P1$	$P1$	$C2/m$	$C2/m$
$a, \text{Å}$	14.841(8)	14.833(4)	14.3590(2)	14.412(2)	14.402(6)	18.951(4)	24.271(5)
$b, \text{Å}$	21.06(2)	20.936(5)	14.6280(2)	14.723(2)	14.654(7)	20.784(4)	15.199(2)
$c, \text{Å}$	29.31(2)	29.515(9)	18.7817(2)	18.882(2)	18.836(11)	15.810(3)	17.270(2)
$\alpha, \text{Å}$	90	90	89.8790(10)	89.579(11)	90.088(10)	90	90
$\beta, \text{Å}$	90	90	87.4520(10)	86.987(10)	87.45(10)	90	108.974(11)
$\gamma, \text{Å}$	90	90	61.0970(10)	60.562(10)	61.38(7)	90	90
$V, \text{Å}^3$	9158(10)	9166(4)	3449.32(8)	3484(2)	3485(3)	6227(2)	6024.7(16)
Z	4	4	2	2	2	4	4
radiation ($\lambda, \text{Å}$)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)	Cu K α (1.54178)	Mo K α (0.71073)	Cu K α (1.54178)	Cu K α (1.54178)
T, K	154(2)	156(2)	156(2)	130(2)	156(2)	130(2)	130(2)
$\rho, g/cm^3$	1.467	1.467	1.568	1.553	1.557	1.562	1.569
μ, mm^{-1}	0.515	0.676	0.432	1.973	0.49	4.008	3.479
max/min Transm	0.98–0.95	0.97–0.81	0.98–0.87	0.94–0.65	0.97–0.83	0.73–0.50	0.79–0.64
R_1^a (obsd data)	0.082	0.069	0.069	0.099	0.126	0.126	0.151
wR_2^a	0.197	0.148	0.310	0.306	0.383	0.344	0.455
indep reflects	14298	16154	11915	9191	9080	1643	3980
obs reflects (>2 σ)	9646	5476	6904	5385	4462	1347	2119
parameters	1325	1316	1082	1082	1082	177	241
restraints	648	392	1648	1333	1993	3	29

$$^a R_1 = \sum ||F_o - F_c|| / \sum |F_o|, \quad ^b wR_2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right]^{1/2}$$

involve intercalation of guests into channels that occur between tightly packed porphyrin stacks. The close approach of the fullerene to the porphyrin which characterizes the solids described here is not a prominent feature in the structures of the porphyrin sponges.

Experimental Section

Preparation of Crystals. $C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$. A 0.0005 g (0.0006 mmol) sample of C_{70} was dissolved in a minimum volume of benzene, and the solution was filtered and then carefully layered over a filtered solution of 0.006 g (0.001 mmol) of $Ni^{II}(OEP)$ dissolved in a minimum volume of chloroform in a 5 mm o.d. glass tube. The resultant mixture was allowed to stand for 6–8 days during which dark crystals of the product formed. These were collected by decantation of the solvent to yield 0.0015 g (37%) of product. The other cocrystallized samples were prepared by a similar procedure from their respective components.

X-ray Data Collection. All crystals were coated with a light hydrocarbon oil and mounted on a glass fiber in the cold dinitrogen stream of the diffractometer. Data for $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{60} \cdot ClFe^{III}(OEP) \cdot CHCl_3$, $C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, and $C_{120}O \cdot Co^{II}(OEP) \cdot 0.4C_6H_6 \cdot 0.6CHCl_3$ were collected on a Siemens P4 diffractometer with nickel-filtered Cu K α ($\lambda = 1.54178 \text{ Å}$) radiation from a rotating anode source, while data for $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$, $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, and $C_{70} \cdot Cu^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$ were collected on a Siemens SMART CCD with graphite-monochromated Mo K α radiation. Lorentz and polarization corrections were applied. Check reflections were stable throughout data collection. Crystal data are given in Table 2.

Solution and Structure Refinement. Calculations for the structures were performed using SHELXS-97 and SHELXL-97. Tables of neutral atom scattering factors, f' and f'' , and absorption coefficients are from a standard source.⁴² The structures were all solved by direct methods. All atoms except disordered atoms and hydrogen atoms were refined anisotropically. Hydrogen atoms were included through the use of a riding model. For $C_{60} \cdot ClFe^{III}(OEP) \cdot CHCl_3$, an empirical absorption correction was used,⁴³ while for $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$, and $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$ a semiempirical method utilizing equivalents was employed.⁴⁴ Absorption corrections were not applied to the structures of $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, and $C_{120}O \cdot Co^{II}(OEP) \cdot 0.4C_6H_6 \cdot 0.6CHCl_3$.

The structures of $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$, and $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ were refined as racemic twins with the twin parameters refining to 0.48(2), 0.49(2), and 0.531(9), respectively. For $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, $C_{70} \cdot Ni^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, and $C_{70} \cdot Cu^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, the structure of the C_{70} molecule was constrained to D_{5h} symmetry by the application of same-distance restraints (SADI 0.01) to equivalent distances about the 5-fold axis. In addition, the nine parallel layers of carbon atoms within the C_{70} molecules were restrained to be flat (FLAT 0.001). For anisotropic refinement of the fullerene molecule in $C_{70} \cdot Co^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$, a restraint (DELU 0.001) was applied to the components of the tensor along the C–C bonds. There is large thermal motion of the fullerene in this structure, but there is no apparent disorder. Two different sites are disordered with respect to occupation by both benzene and chloroform. Identification of the individual components was possible, and they were modeled as follows. Site 1 contained 0.50 benzene (C71–C76 as an idealized hexagon) and 0.50 chloroform (C1S, H1S, C11, C12, C13). Site 2 contained 0.50 benzene (C77–C82 as an idealized hexagon), 0.30 chloroform (C2S, H2S, C14A, C15A, C16A), and 0.20 chloroform (C2T, H2T, C14B, C15B, C16B) with the chloroform molecules refined as rigid groups.

The structure of $C_{60} \cdot ClFe^{III}(OEP) \cdot CHCl_3$ was refined using a rigid group for the C_{60} molecule with an occupancy of 0.25 to coincide with the mm symmetry of the site. The C_{60} molecule itself does not reside

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exactly on the *mm* site but is slightly shifted and rotated away from it. The refinement is more stable in the space group *Cmcm* than in *Cmc2₁*.

Although the porphyrin portion of the structure of $C_{120}O \cdot Co^{II}(OEP) \cdot 0.4C_6H_6 \cdot 0.6CHCl_3$ refined normally, the fullerene portion is highly disordered and required special treatment. The point symmetry of the $C_{120}O$ molecule is *2/m*. Rigid body refinement of the C_{60} portion in the asymmetric unit revealed a second molecule of C_{60} unit which was rotated approximately by 30° with respect to a 3-fold axis of the first. The two balls were refined with sufficient restraints to individually describe the icosohedral symmetry but with looser restraints in the region of bonding to the bridging oxygen atom. The occupancies of each were allowed to refine as *x* and 0.5 - *x*, and converged to approximately 0.333/0.167 for the two balls {C1-C60} and {C1B-C60B}. Subsequent refinement was carried out with each ball treated as a rigid group, their group thermal parameters refining. For {C1-C60} the thermal parameter was 0.083(4), and for {C1B-C60B} it was 0.091(2). Occupancies were fixed as previously determined. The unique oxygen atom was refined at 0.25 occupancy, and its thermal parameter converged at 0.071(10). A very weak restraint of 1.60(5) Å for the O-C distances that are nearest to each other was also applied.

However, due to the complex disorder, the actual connectivity of the oxygen atom to the fullerenes cannot be stated with certainty. The structure also contains disorder in the solvent region, where a benzene molecule and a chloroform molecule share a site with mirror symmetry. Using restraints and the site symmetry, relative occupancies were determined by refinement and subsequently fixed. The final refinement placed the occupancy of benzene at 40% and of chloroform at 60%. Hydrogen atoms on the porphyrin were refined using a riding model, while hydrogen atoms on the disordered benzene and chloroform molecules were placed at calculated positions and subsequently fixed. Anisotropic thermal parameters were utilized only for the porphyrin.

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Supporting Information Available: Tables of crystal data (PDF). X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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