Interactions of metalloporphyrins as donors with the electron acceptors C_{60}, tetracyanoquinomethane (TCNQ) and trinitrofluorenylidenemalonitrile

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Crystals of $C_{60} \cdot Pt^{II}(OEP) \cdot 2(C_6H_6)$, $TCNQ \cdot Cu^{II}(OEP)$, $TCNQ \cdot H_2(OEP)$, $TCNQ \cdot 2Cu^{II}(OEP)$, $TCNQ \cdot 2Zn^{II}(OEP)$ and $TNFM \cdot Co^{II}(OEP)$ [OEP is the dianion of octaethylporphyrin, TCNQ is 7,7,8,8-tetracyanoquinodimethane, TNFM is (2,4,7-trinitrofluorenylidene)malonitrile] have been obtained by diffusion of a solution of the porphyrin as donor into a solution of the respective acceptor molecule. The structure of $C_{60} \cdot Pt^{II}(OEP) \cdot 2(C_6H_6)$ consists of an ordered C_{60} cage nestled against the platinum porphyrin which makes close face-to-face contact with another $Pt^{II}(OEP)$ molecule. In contrast, there are no close face-to-face contacts between porphyrins in the crystal structures of $TCNQ \cdot Cu^{II}(OEP)$, $TCNQ \cdot H_2(OEP)$, and $TNFM \cdot Co^{II}(OEP)$. These compounds consist of classical donor–acceptor stacks of interleaved porphyrin and TCNQ or TNFM molecules with separations of ca. 3.3 Å between adjacent molecules. However with $TCNQ \cdot 2Cu^{II}(OEP)$ and $TCNQ \cdot 2Zn^{II}(OEP)$ the structures involve TCNQ (A) and $M^{II}(OEP)$ (D) molecules that crystallize in stacks with a DDA(DDA)$_n$DDA arrangement. Within these stacks there are pairwise contacts between $M^{II}(OEP)$ molecules and these pairs are compared to those found in $C_{60} \cdot Pt^{II}(OEP) \cdot 2(C_6H_6)$ and related fullerene-containing crystals.

Introduction

Porphyrins have been found to form supramolecular arrays with fullerenes that have unusually close approach of the curved surface of the nearly spherical fullerene to the plane of the porphyrin. Mixing solutions of C_{60} or C_{70} with solutions of metallo-octaethylporphyrin complexes[1,2] or tetraphenyl-porphrins and their metal complexes[3–8] have produced a number of crystalline solids that contain the porphyrin and fullerene components (and usually some solvent molecules).[9] This laboratory previously reported the structures of the isomorphous series, $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$, $C_{60} \cdot 2Zn^{II}(OEP) \cdot CHCl_3$ and $C_{60}O \cdot 2Co^{II}(OEP) \cdot CHCl_3$ and of a second iso-morphous 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 $C_{70} \cdot Cu^{II}(OEP) \cdot C_6H_6 \cdot CHCl_3$.[7] In these crystals, there is close, face-to-face stacking of pairs of $M^{II}(OEP)$ units that is more pronounced than that seen in crystals of the pure metalloporphyrin alone. Thus, in $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ the Co · · · Co separation (3.438 Å) and the mean plane separation (MPS, 3.21 Å) are shorter than they are in $Co^{II}(OEP)$ [10] (Co · · · Co separation, 4.742 Å; MPS, 3.33 Å). In the two series of complexes mentioned above, the eight ethyl groups of each metalloporphyrin are arranged so that they form an octopus-like embrace of the fullerene surface. This orientation of the ethyl groups facilitates the close approach of neighboring porphyrins. However, despite the close approach of the fullerene to the porphyrin, the metal atoms are too far away from the nearest fullerene carbon atoms to engage in conventional covalent bonding with the fullerenes.

The ability to co-crystallize fullerenes with porphyrins to produce solids in which the fullerene component is orien-tationally ordered has proven to be a useful tool for the structural investigation of endohedral fullerenes, fullerenes with atoms trapped inside. Thus, the structures of the fullerene cages and the locations of the interior atoms in a number of endohedral fullerenes including $Sc_3N@C_{80}$,[11] $ErSc_2N@C_{80}$,[12] $Sc_3N@C_{78}$,[13] $Er_2@C_{82}$,[14] and $Kr@C_{60}$[15] have been determined

by co-crystallizing these endohedrals with a suitable metallo-octaethylporphyrin.

Not all porphyrin–fullerene co-crystals of the type $M^{II}(OEP)$ have the ethyl groups arranged so that they surround the neighboring fullerene. Thus, in $C_{60} \cdot Pd^{II}(OEP) \cdot 1.5C_6H_6$, and in the isomorphic pair, $C_{60} \cdot Cu^{II}(OEP) \cdot 2C_6H_6$, and $C_{60} \cdot Ni^{II}(OEP) \cdot 2C_6H_6$, only four of the ethyl groups are directed toward the fullerene, but again pairs of porphyrins make close face-to-face contact. For example in $C_{60} \cdot Ni^{II}(OEP) \cdot 2C_6H_6$ the Ni · · · Ni distance is 4.487 Å and the MPS is 3.517 Å,[14] while in $Ni^{II}(OEP)$ itself the Ni · · · Ni distance is 4.802 Å and the MPS is 3.44 Å.[16]

The fullerene–porphyrin interaction in crystals involves some degree of charge transfer with the fullerene acting in its usual fashion as an electron acceptor while the metalloporphyrin acts as an electron donor along with other factors including electrostatic interactions, coordination effects, and Pauli repulsive interactions between closed shells.[5,7,8,17] Will flat acceptors also induce the close approach of pairs of porphyrins as seen in the crystalline fullerene containing materials such as $C_{60} \cdot 2Co^{II}(OEP) \cdot CHCl_3$ and $C_{60} \cdot Ni^{II}(OEP) \cdot 2C_6H_6$? Athough a number of studies have been made of the interaction of metalloporphyrins with strong organic π-acceptors such as trinitrobenzene in solution, little structural work has been done in this area.[18] Crystalline $TCNQ \cdot Ni^{II}$(tetramethylporphyrin) has been isolated and its structure shown to consist of inter-leaved stacks of the constituent molecules.[19] Consequently, in this material there are no close porphyrin/porphyrin contacts of the type seen in the fullerene–porphyrin co-crystals.

Here we report the preparations of some co-crystals of $M^{II}(OEP)$ and of H_2OEP with conventional flat organic acceptors and with C_{60}, and we compare their structures.
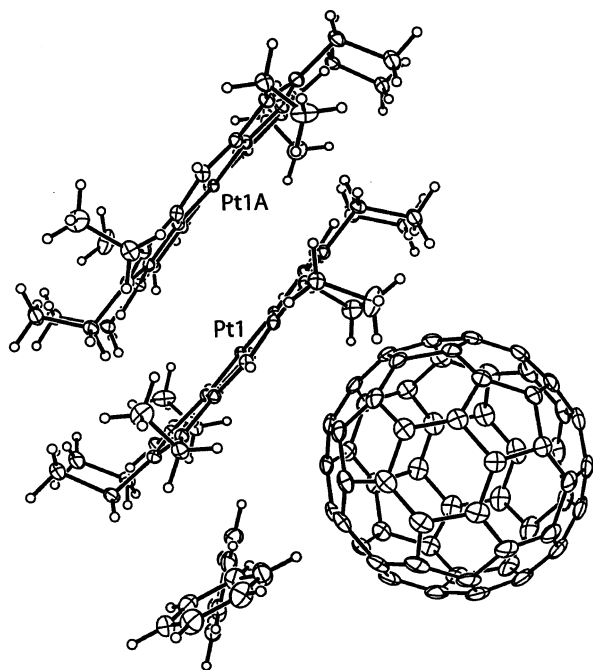
Results

Co-crystallizations of $M^{II}(OEP)$ or H_2OEP with TCNQ, TNFM, and C_{60} were performed by layering saturated solutions

of the two components over one another and allowing the solutions to mix by diffusion. Structures of the classical metal-loprophyrin donors and the flat organic acceptors are shown in Scheme 1. With TCNQ it is possible to obtain crystals with either a 1 : 1 TCNQ : $M^{II}(OEP)$ stoichiometry or a 1 : 2 TCNQ : $M^{II}(OEP)$ stoichiometry. The stoichiometry of the product depends upon the solvents used for crystal growth. Thus for example, dark red needles of TCNQ·$Cu^{II}(OEP)$ were obtained by diffusion of a solution of $Cu^{II}(OEP)$ in chloroform into a solution of TCNQ in acetonitrile, while red rods of TCNQ·$2Cu^{II}(OEP)$ were obtained by diffusion of a solution of $Cu^{II}(OEP)$ in chlorobenzene into a solution of TCNQ in acetonitrile.

Scheme 1
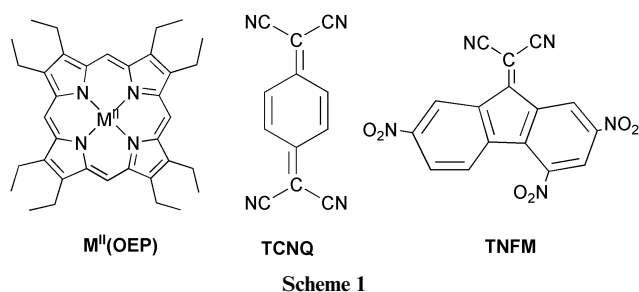
The structure of $C_{60}·Pt^{II}(OEP)·2(C_6H_6)$

The structure of $C_{60}·Pt^{II}(OEP)·2(C_6H_6)$ consists of an ordered fullerene cage which is nestled against a $Pt^{II}(OEP)$ molecule as seen in Fig. 1. As Fig. 1 shows, two $Pt^{II}(OEP)$ molecules make face-to-face contact. Four of the eight ethyl groups are near the fullerene, and the other four point in the opposite direction, toward the neighboring porphyrin. The non-bonded Pt · · · Pt separation is 4.633 Å and the MPS is 3.535 Å. For comparison, in crystalline $Pt^{II}(OEP)$ the non-bonded Pt · · · Pt separation is 8.165 Å and the MPS is 3.442 Å.[20] The closest contact between a fullerene carbon atom and the platinum center in the porphyrin is 3.084 Å. The porphyrin is planar, and the Pt–N distances span a narrow range, 2.0105(13) to 2.0178(12) Å. For comparison the Pt–N distances in simple $Pt^{II}(OEP)$ are 2.012 to 2.013 Å.[20]
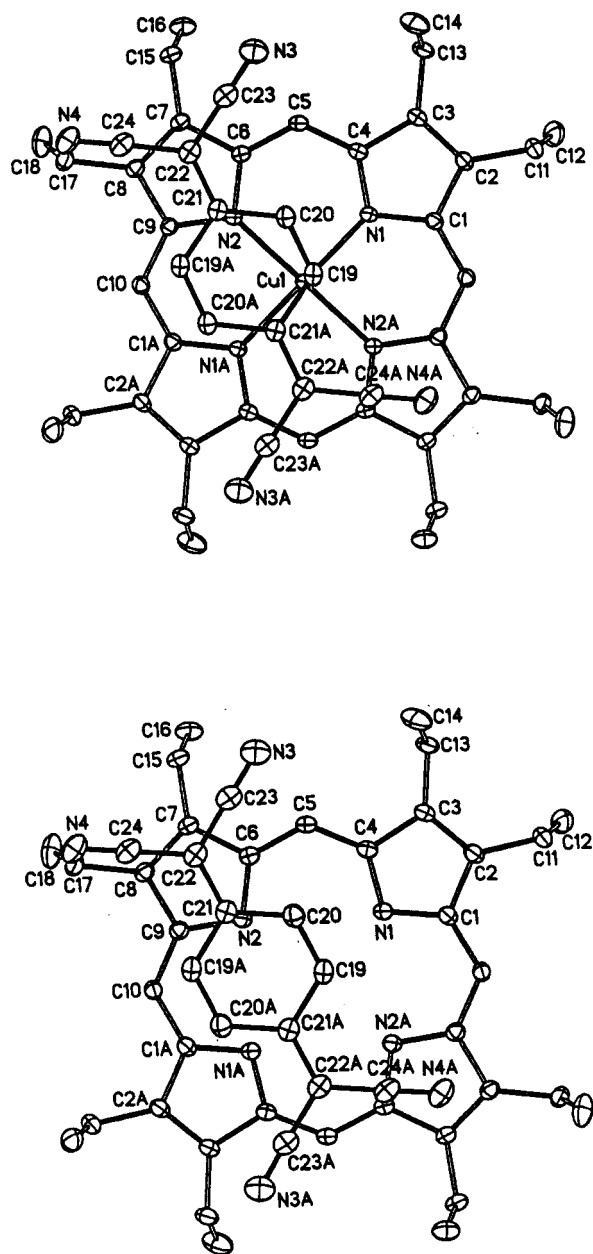
Crystalline $C_{60}·Pt^{II}(OEP)·2(C_6H_6)$ is isomorphous and isostructural with $C_{60}·Ni^{II}(OEP)·2(C_6H_6)$[13] and $C_{60}·Cu^{II}(OEP)·2(C_6H_6)$[2] whose structures have been reported previously. Crystal data for $C_{60}·Pt^{II}(OEP)·2(C_6H_6)$ and the other new compounds reported here are presented in Table 1.

The structure of TCNQ·$Cu^{II}(OEP)$ and TCNQ·$H_2(OEP)$

The structure of TCNQ·$Cu^{II}(OEP)$ consists of columns that contain interleaved molecules of TCNQ and $Cu^{II}(OEP)$ which are stacked along the crystallographic *a* axis. Fig. 2 shows a projection of the structure of a TCNQ molecule onto that of the neighboring molecule of $Cu^{II}(OEP)$. Fig. 3 shows a stereo-scopic view of a column of the interleaved molecules in TCNQ·$Cu^{II}(OEP)$. The copper atom in the $Cu^{II}(OEP)$ molecule lies at a center of symmetry. Similarly, the TCNQ molecule is situated at a different center of symmetry. Each of these two component molecules is nearly planar. The mean deviation of any of

Fig. 1 A drawing of the structure of $C_{60}·Pt^{II}(OEP)·2(C_6H_6)$ showing the interaction between the fullerene and the porphyrin and the face-to-face contact of a pair of porphyrins.

Fig. 2 Top: A drawing of the structure of TCNQ·$Cu^{II}(OEP)$ that highlights the overlap of TCNQ (shown with solid lines between atoms) and $Cu^{II}(OEP)$ (shown with open lines between atoms). Bottom: A drawing of the structure of TCNQ·$H_2(OEP)$ that shows the overlap of TCNQ (shown with solid lines between atoms) and $H_2(OEP)$ (shown with open lines between atoms). Both drawings show 50% thermal contours.

	C_{60}·Pt^{II}(OEP)·2(C_6H_6)	TCNQ·Cu^{II}(OEP)	TCNQ·H_2(OEP)
Formula	$C_{108}H_{56}N_4Pt$	$C_{48}H_{48}CuN_8$	$C_{48}H_{50}N_8$
Fw	1604.66	800.48	738.96
a/Å	14.1778(19)	7.0673(6)	7.0582(7)
b/Å	14.4430(14)	25.567(2)	25.645(2)
c/Å	17.1813(17)	11.0938(9)	11.0904(10)
α/°	87.679(7)	90	90(10)
β/°	75.728(6)	94.018(4)	93.752(4)
γ/°	75.512(6)	90	90
V/Å^3	3300.4(6)	1999.6(3)	2003.1(3)
Z	2	2	2
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
T/°C	90(2)	89(2)	90(2)
μ/cm^{-1}	2.191	0.592	0.074
R_1 (obs'd data)	0.021	0.033	0.047
wR_2 (all data, F^2 refinement)	0.054	0.040	0.073
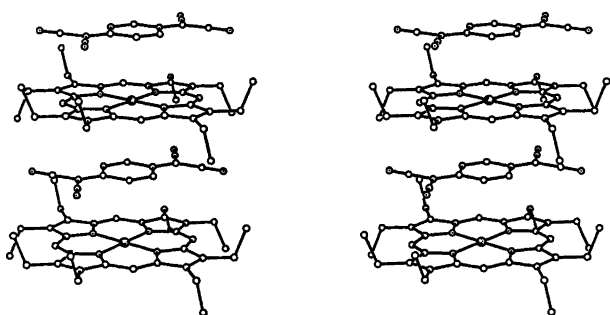
Fig. 3 A stereoscopic drawing of the structure of TCNQ·Cu^{II}(OEP) showing a columnar portion.

the core porphyrin atoms, excluding the ethyl groups, from the plane of this core is only 0.0174 Å. In the TCNQ molecules the mean deviation from the plane for all atoms is only 0.0159 Å. The distance between the plane of the Cu^{II}(OEP) and TCNQ molecules is 3.300 Å. The tilt between the planes of these two molecules is 1°. The closest approach of a neighboring atom in the TCNQ molecule to the copper atom is 3.293 Å (the Cu · · · C19 distance).

The geometry for each of the individual molecular components in TCNQ·Cu^{II}(OEP) is normal. In TCNQ·Cu^{II}(OEP) the Cu–N1 distance is 2.0013(9) and the Cu–N2 distance is 2.0058(9) Å. These distances are similar to those in simple crystalline Cu^{II}(OEP) where the Cu–N distances are 1.996(3) and 1.999(3) Å.[21]

As the data in Table 1 show, crystals of TCNQ·H_2(OEP) are isostructural with those of TCNQ·Cu^{II}(OEP), and thus the solid consists of columns that contain interleaved molecules of H_2(OEP) and TCNQ. The H_2(OEP) and TCNQ molecules are situated at alternating centers of symmetry along the a axis. Each of these two component molecules is nearly planar. The mean deviation of any of the core porphyrin atoms, excluding the ethyl groups, from the plane of this core is only 0.0174 Å. In the TCNQ molecules the mean deviation from the plane for all atoms is only 0.0246 Å.

Fig. 2 shows the overlap of a molecule of TCNQ with the adjoining molecule of H_2(OEP). The distance between the planes of these two molecules is 3.286 Å. The tilt between the planes of these two molecules is 1°. As Fig. 2 shows, the overlappings between the two molecules in TCNQ·H_2(OEP) and in TCNQ·Cu^{II}(OEP) are very similar.

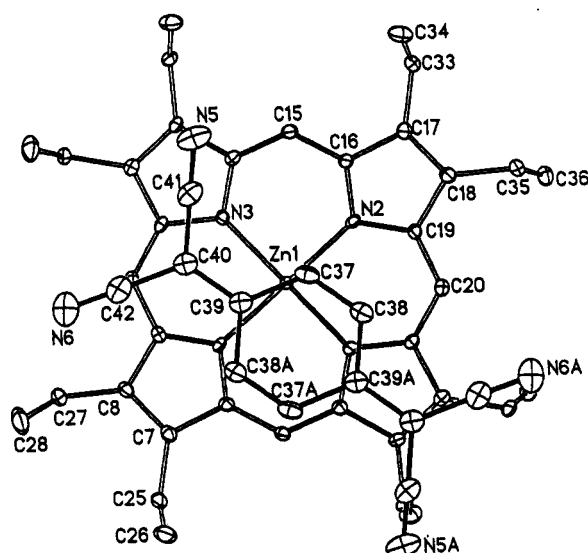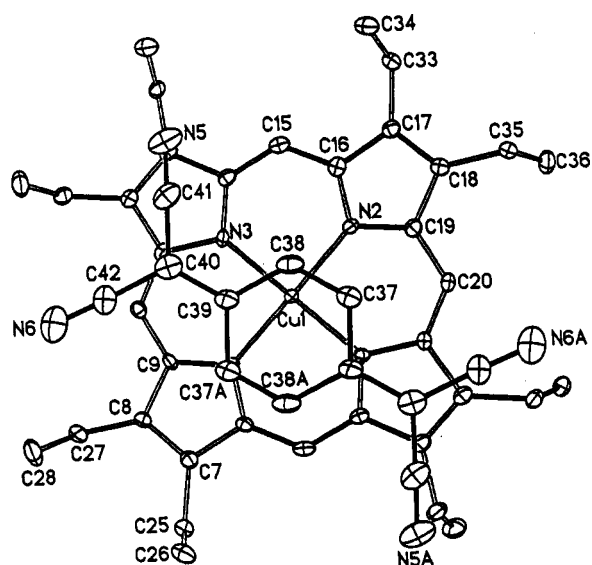### The structure of TCNQ·2Cu^{II}(OEP) and TCNQ·2Zn^{II}(OEP)

This isostructural pair of compounds crystallize with one molecule of the metalloporphyrin and a half molecule of TCNQ in the asymmetric unit. The other half of the TCNQ molecule is generated by inversion through a crystallographic center of symmetry. Within the individual molecules, the structural parameters fall within normal ranges. For example, in TCNQ·2Cu^{II}(OEP) the Cu–N distances (2.017(4) to N1, 2.001(4) to N2, 2.005(4) to N3, and 2.011(4) to N4) are similar to those in pristine Cu^{II}(OEP) (1.996(3) and 1.999(3) Å). In TCNQ·2Zn^{II}(OEP) the Zn–N distances (2.0370(18) to N1, 2.028(2) to N2, 2.0384(19) to N3, and 2.040(2) to N4) are similar to those in C_{60}·2Zn^{II}(OEP)·CHCl$_3$ where they range from 2.030(4) to 2.089(4) Å.[1]

The structures of TCNQ·2Cu^{II}(OEP) and TCNQ·2Zn^{II}(OEP) involve TCNQ (A) and M^{II}(OEP) (D) molecules that crystallize in stacks with a DDA(DDA)$_n$DDA arrangement as seen in the stereoscopic drawing shown in Fig. 4. Within these stacks the TCNQ and M^{II}(OEP) molecules make close face-to-face contact that is shown in Fig. 5. In TCNQ·2Cu^{II}(OEP) the mean plane separation between the porphyrin and the TCNQ molecules is 3.19 Å and the tilt between these planes is 1.9°. In TCNQ·2Zn^{II}(OEP) the analogous parameters are similar, 3.16 Å and 2.3°. The closest contact between Cu in TCNQ·2Cu^{II}(OEP) and the nearest atom in the adjacent TCNQ is 3.290 Å to C38. In TCNQ·2Zn^{II}(OEP) the closest Zn · · · C distance is 3.308 Å and involves C37A. As seen in Fig. 5, the position of the TCNQ molecule is shifted slightly with respect to the M^{II}(OEP) unit in the copper and zinc structures.
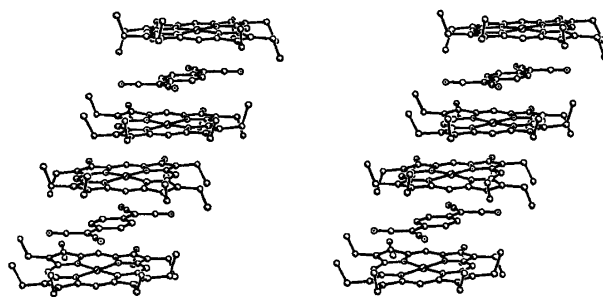
Fig. 4 A stereoscopic drawing of the structure of TCNQ·2Cu^{II}(OEP) showing the columnar portion with the DADDA arrangement of moelcules.

As seen in Fig. 6, pairs of Zn^{II}(OEP) molecules in TCNQ·2Zn^{II}(OEP) pack about a center of symmetry so that they make face-to-face contact. Within the pair, five of the ethyl groups on each porphyrin are directed away from the adjacent porphyrin, while three point in the direction of the neighboring porphyrin. The non-bonded Zn · · · Zn separation is 4.553 Å and the MPS is 3.18 Å. However, in C_{60}·2Zn^{II}(OEP)·CHCl$_3$ the Zn · · · Zn separation is significantly shorter, 3.166 Å, but the MPS is similar, 3.21 Å.[1]

Fig. 5 Top: A drawing of the structure of TCNQ·2Cu^{II}(OEP) that shows the overlap of TCNQ (shown with solid lines between atoms) and Cu^{II}(OEP) (shown with open lines between atoms). D. A drawing of the structure of TCNQ·2Zn^{II}(OEP) that shows the overlap of TCNQ (shown with solid lines between atoms) and Zn^{II}(OEP) (shown with open lines between atoms). Both drawings show 50% thermal contours.
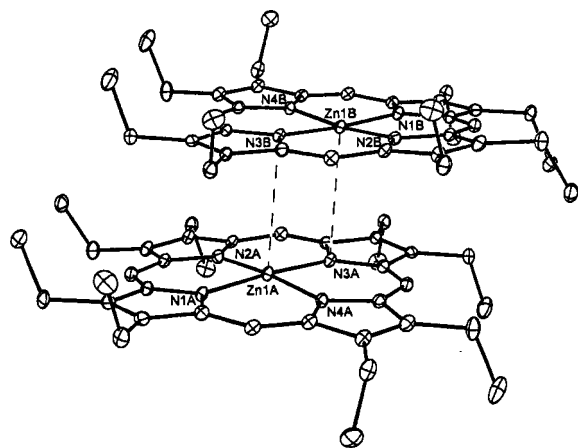
Fig. 6 A view of the face-to-face contact between a pair of Zn^{II}(OEP) molecules in TCNQ·2Zn^{I}(OEP).

In TCNQ·2Cu^{II}(OEP) the relationship between the pairs of porphyrins is similar. The non-bonded Cu · · · Cu separation is 4.705 Å and the MPS is 3.20 Å. For comparison, in C$_{70}$· 2Cu^{II}(OEP)·C$_6$H$_6$·CHCl$_3$ the Cu · · · Cu separation is much shorter, 3.407 Å, while the MPS is just slightly greater, 3.26 Å.[1] The Cu · · · Cu separation in TCNQ·2Cu^{II}(OEP) is just slightly shorter than that (4.805 Å) in pristine Cu^{II}(OEP),[21] but the MPS in pristine Cu^{II}(OEP) is longer, 3.43 Å, than it is in TCNQ·2Cu^{II}(OEP).

The structure of TNFM·Co^{II}(OEP)

The structure of TNFM·Co^{II}(OEP) also involves columns that contain alternating molecules of TCNQ and Co^{II}(OEP) that are stacked along the crystallographic *a* axis. There are two independent half molecules of Co^{II}(OEP) and one whole molecule of TNFM in the asymmetric unit. The cobalt atoms in the Co^{II}(OEP) molecules lie at centers of symmetry along the *a* axis. The two molecules are nearly planar. The mean deviation of any of the core porphyrin atoms, excluding the ethyl groups, from the plane of this core is only 0.008 Å for the molecules containing Co1 and 0.025 Å for the molecule containing Co2. The angle between the planes of these two porphyrins is 0.5°. The TNFM molecule has no crystallographically imposed symmetry. There is disorder in the position of the nitro group involving N5, O1 and O2 with a major site with occupancy 0.592(3) attached to C37 and a minor site attached to C40 with occupancy 0.408(3). In the TNFM molecule the mean deviation from the plane for all atoms is only 0.025 Å. Fig. 7 shows the overlaps of the TNFM molecule and two different Co^{II}(OEP) molecules in Co^{II}(OEP)·TNFM. The closest approaches of atoms in TNFM to the cobalt atoms of the two porphyrins are 3.333 Å for Co1 · · · C43 and 3.372 for Co2 · · · C43.

Fig. 8 shows a stereoscopic drawing of the columnar part of the structure of TNFM·Co^{II}(OEP).

There are no unusual distortions of the geometry of the individual molecular components in TNFM·Co^{II}(OEP). In TNFM·Co^{II}(OEP) the Co–N distances are 1.969(2) Å for Co1–N1, 1.970(2) Å for Co1–N2, 1.966(2) Å for Co2–N3, and 1.966(2) Å for Co–N4. For comparison, in crystalline Co^{II}(OEP) itself, the Co–N distances are similar: 1.967(3) and 1.975(2) Å.[22]

Discussion

The structural studies reported here emphasize the differences between fullerenes as electron acceptors and conventional, flat organic acceptors. In C$_{60}$·Pt^{II}(OEP)·2(C$_6$H$_6$) as in other fullerene/M^{II}(OEP) assemblies,[1,2,8] the pairs of porphyrins make close face-to-face contact. This sort of face-to-face contact is absent in the structures of the 1 : 1 adducts of M^{II}(OEP) or H$_2$(OEP) with flat organic acceptors. In these cases, the donors and acceptors are interleaved into stacks, and consequently there are no direct porphyrin/porphyrin contacts. Additionally, carbon atoms of the fullerenes are closer to the metal centers in the fullerene/M^{II}(OEP) co-crystals than are the carbon atoms of the conventional, flat organic acceptors in the acceptor/ M^{II}(OEP) crystals.

However, in the adducts with a 1 : 2 TCNQ : M^{II}(OEP) stoichiometry, there are direct porphyrin/porphyrin contacts. In these cases the interaction of the two porphyrins, as measured by the non-bonded M · · · M separations, are less than the corresponding interactions found in cases where the analogous metalloporphyrins co-crystallize with fullerenes.

The structures of TCNQ·Cu^{II}(OEP) and TCNQ·H$_2$(OEP) are similar to that of TCNQ·Ni^{II}(tetramethylporphyrin).[19] In TCNQ·Ni^{II}(tetramethylporphyrin) the interplanar spacing between the two components is 3.30 Å, while in TCNQ· Cu^{II}(OEP) it is also 3.30 Å and in TCNQ·H$_2$(OEP) it is 3.29 Å. The degree of overlap between the donor and acceptor are

A

B
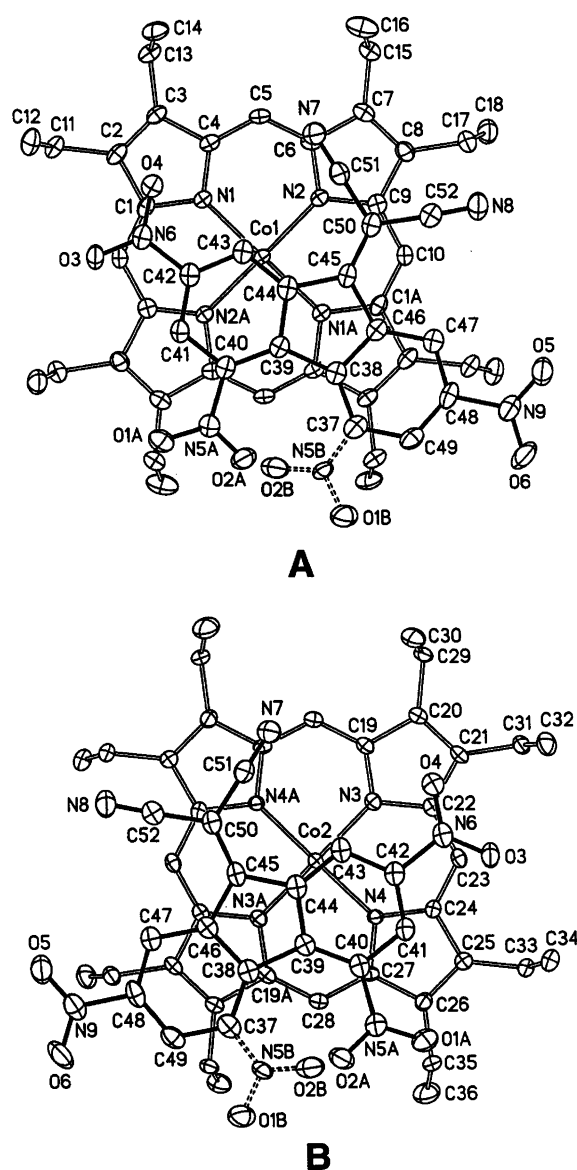
Fig. 7 A drawing of the structure of TNFM·Co^{II}(OEP) that shows the overlap of TNFM (shown with solid lines between atoms) and Co^{II}(OEP) (shown with open lines between atoms) with 50% thermal contours. (**A**) shows the overlap between TNFM and molecule A of Co^{II}(OEP) while (**B**) shows the overlap between TNFM and molecule B of Co^{II}(OEP). There is disorder in the position of the nitro group involving N5, O1 and O2. The solid lines show the major site with occupancy 0.592(3); the dotted lines show the minor site with occupancy 0.408(3).
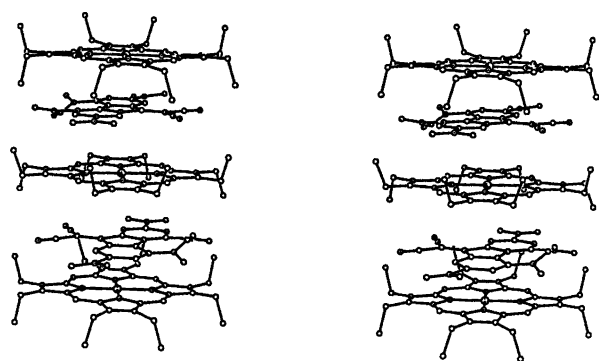
Fig. 8 A stereoscopic drawing of the columns within the structure of TNFM·Co^{II}(OEP). Only the major site of the nitro group involving N5, O1, and O2 is shown.

also similar in these three structures. Other neutral tetra-azamacrocyclic complexes of nickel(II) also form adducts with TCNQ in which the components are interleaved as seen

here.[23,24] In none of the donor/acceptor adducts discussed here is there any σ-coordination of the metal centers by the nitrile groups, a feature which is encountered in some adducts of TCNQ.[25] In the metalloporphyrin adducts with conventional organic acceptors, the stoichiometry of donor to acceptor can be either 1 to 1 or 2 to 1. Likewise, in the adducts of fullerenes with metalloporphyrins, the stoichiometry can either be 1 to 1 as it is in the C$_{60}$·M^{II}(OEP)·2(C$_6$H$_6$) (M = Ni, Cu, or Pt) family of compounds and in the C$_{70}$·Co^{II}(OEP)·C$_6$H$_6$·CHCl$_3$ (M = Co, Ni, or Cu) family or it can be 1 to 2 as it is in the C$_{60}$· 2M^{II}(OEP)·CHCl$_3$ (M = Co or Zn) family.[1,2,8]

The donor/acceptor contacts seen here in TCNQ·Cu^{II}(OEP), TCNQ·H$_2$(OEP), and TNFM·Co^{II}(OEP) can also be compared to previously reported cases where arene molecules interact with metalloporphyrins. For example, in Mn^{II}(TPP)·(CH$_3$C$_6$H$_5$) 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.[26] In (ClO$_4$)-Fe^{III}(TPP)·0.5(m-(CH$_3$)$_2$C$_6$H$_4$), a similar situation occurs with porphyrin mean plane to m-xylene carbon atom distances ranging from 3.32 to 3.66 Å.[27] Much closer arene to metallo-porphyrin contacts are seen in [Fe(TTP)][Ag(Br$_6$CB$_{11}$H$_6$)$_2$]· 4(p-xylene) where two p-xylene molecules make face-to-face contact with the center of the porphyrin.[28] The closest distance between a xylene carbon atom and the porphyrin mean plane is 2.89 Å, and the [Fe(TPP)]$^+$ unit is tightly solvated by these xylene molecules, which are much closer than any of the new co-crystalline materials reported here. In this case the cationic [Fe(TPP)]$^+$ must be acting as the electron acceptor, while the flat organic neighbors act as the donor.

Experimental

Materials

TCNQ and TNM were purchased from Aldrich or Acros, respectively, and used as received.

Crystal growth

Black blocks of C$_{60}$·Pt^{II}(OEP)·2(C$_6$H$_6$) were obtained by diffusion of a saturated solution of C$_{60}$ in benzene into a satur-ated solution of Pt^{II}(OEP) in benzene. Dark red needles of TCNQ·Cu^{II}(OEP) were obtained by diffusion of a saturated solution of Cu^{II}(OEP) in chloroform into a saturated solution of TCNQ in acetonitrile. Dark brown needles of TCNQ· H$_2$(OEP) were obtained from the green solution obtained by diffusion of a saturated solution of H$_2$(OEP) in chloroform into a saturated solution of TCNQ in acetonitrile. Red rods of TCNQ·2Cu^{II}(OEP) and TCNQ·2Zn^{II}(OEP) were obtained by diffusion of a saturated solution of Cu^{II}(OEP) or Zn^{II}(OEP) in chlorobenzene into a saturated solution of TCNQ in acetonitrile. Black needles of TNFM·Co^{II}(OEP) were obtained by diffusion of a solution of Co^{II}(OEP) in chloroform into a solution of TNFM in benzene.

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 were collected on a Brucker SMART CCD with graphite monochromated MoKα radiation. No decay was observed in 50 duplicate frames at the end of each data collection. A semi-empirical absorption correction utilizing equivalents was employed.[29] Crystal data are given in Table 1 and Table 2.

Solution and structure refinement

Calculations for the structures were performed using SHELXS-97 and SHELXL-97.[30] Tables of neutral atom scattering factors,

Table 2 Crystallographic data

	TCNQ·2Cu^{II}(OEP)	TCNQ·2Zn^{II}(OEP)	TNFM·Co^{II}(OEP)
Formula	$C_{84}H_{92}Cu_2N_{12}$	$C_{84}H_{92}N_{12}Zn_2$	$C_{52}H_{48}CoN_9O_6$
Fw	1396.78	1400.44	953.92
a/Å	11.343(2)	11.241(8)	13.2190(10)
b/Å	14.142(4)	14.168(7)	22.5632(17)
c/Å	21.723(9)	21.651(12)	15.0954(11)
a/°	90	90	90
β/°	91.01(2)	90.31(2)	101.873(2)
γ/°	90	90	90
V/Å^3	3484.0(18)	3448(4)	4406.1(6)
Z	2	2	4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2$_1$/c	P2$_1$/c	P2$_1$/c
T/°C	93(2)	90(2)	91(2)
μ/cm^{-1}	0.667	0.753	0.455
R_1 (obs'd data)	0.063	0.032	0.050
wR_2 (all data, F^2 refinement)	0.165	0.091	0.128

f' and f'', and absorption coefficients are from a standard source.[31] The structures were all solved *via* direct methods. All atoms except hydrogen atoms were refined anisotropically. All hydrogen atoms were located in difference Fourier maps and included through the use of a riding model.

CCDC reference numbers 198536–198539 and 213236–213237.

See http://www.rsc.org/suppdata/dt/b3/b306714a/ for crystallographic data in CIF or other electronic format.

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