# $C_i$ Symmetric and Non-Centrosymmetric Crystalline Complexes of [60]Fullerene with Octakis(dimethylamino)porphyrazinato-Copper(II) and -Nickel(II)

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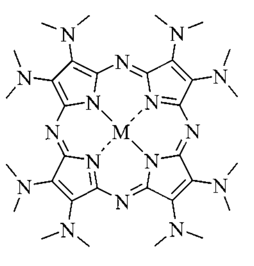
X-ray structural analysis of octakis(dimethylamino)porphyrazinato-metallo(II)·[60]fullerene complexes (M = $Cu^{2+}$ and $Ni^{2+}$) surprisingly revealed two totally different supramolecular structures, the first exhibiting a $C_i$ symmetric sandwich complex of two slightly dished porphyrazine units enclosing one fullerene sphere, the other featuring a noncentrosymmetric 1:1 complex with a strongly warped porphyrazine unit.

## Introduction

In continuation of our previous studies[1] on charge-transfer complexes of porphyrazines we herein report on the syntheses and structures of two donor-acceptor crystals formed from [60]fullerene and metallated porphyrazines. These complexes are considered possible precursors for much sought-after three-dimensional molecular magnets[2] and possible structures with superconducting properties. For structurally related complexes see those of fullerenes with metallated octaethylporphyrines.[3,4]

## Results and Discussion

The syntheses of octakis(dimethylamino)porphyrazinato-metallo(II) (Scheme 1, M-Pz, with M = $Ni^{2+}$, $Cu^{2+}$, $2H^{+}$) and of the $(2H\text{-}Pz)_2\text{-}C_{60}$ complex have been reported previously.[5] The complexes were synthesised by incubation of fullerene and excess of porphyrazine (M-Pz) under an argon atmosphere and subsequent isolation and purification by repeated extraction-evaporation-dissolution cycles. Slow evaporation of the benzene or toluene solution afforded nonconducting black needles which were subsequently handled in air.



Scheme 1. Oktakis(dimethylaminoporphyrazinato)-metal(II), the porphyrazine unit of the fullerene complexes **1**, **2**, and **3**; (M = Ni, Cu, 2H).

## $(CuPz)_2\text{-}C_{60}$ (1)

The X-ray analysis of **1** (see Experimental Section) revealed the formation of a $C_i$ symmetric 2:1 Cu(Pz):$C_{60}$ complex (Figure 1) which at the molecular level is very similar to that formed between 2H-Pz and $C_{60}$ (**3**), though in the latter the symmetry is $C_2$ and crystallisation occurred in a noncentrosymmetric space group. Here in **1**, each $C_{60}$ molecule is sandwiched between pairs of dished Cu(Pz) units (Figure 1), the copper atom lying 0.06 Å out of the $N_4$ coordination plane, and 0.18 and 0.48 Å out of the planes of the four "pyrrole-linking" *meso*-N-atoms, and the eight peripheral dimethylamino N-atoms, respectively. The distance from the centroid of the $C_{60}$ molecule to the $N_4$ coor-

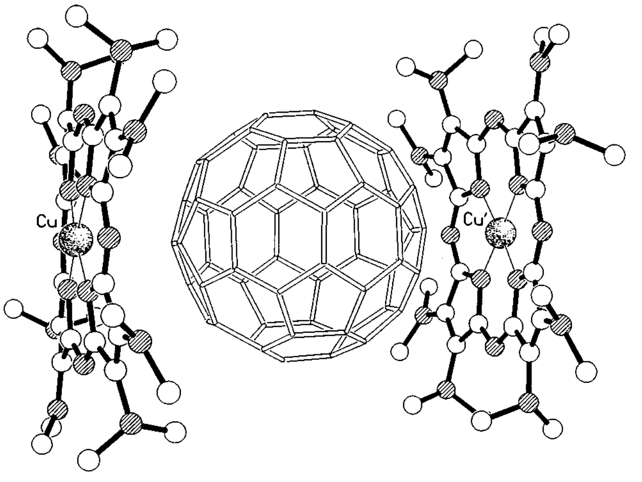


Figure 1. The 2:1 complex **1** formed between Cu(Pz) and $C_{60}$. The Cu–N distances are in the range 1.939(4) to 1.945(4) Å.

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dination planes is 6.32 Å, (this parameter, and others given in this communication, refer to the low temperature structural determinations) a value identical to that observed in **3**. The copper atom lies 0.18 and 0.48 Å out of the planes of the four "pyrrole-linking" N-atoms, and the eight peripheral dimethylamino N-atoms, respectively. A feature of particular interest is a short approach of 2.89 Å between the copper and one of the $C_{60}$ carbon atoms, the carbon being positioned almost directly above the centre of the copper coordination plane. Although, as in **3**, the crystals contain aromatic solvent molecules (S) positioned between $C_{60}$ units, the overall supramolecular structure is distinctly different. The pattern of -Pz-$C_{60}$-Pz-Pz-$C_{60}$-Pz- and -$C_{60}$-S-$C_{60}$-S- sandwiches is retained (Figure 2), but in the third direction (into the plane of the paper in Figure 2) adjacent sheets are offset so that the linear -$C_{60}$-$C_{60}$-$C_{60}$- sequence seen (Figure 3) running horizontally in **3** is no longer present. The shortest inter-sheet $C_{60}\cdots C_{60}$ separation is 13.9 Å.

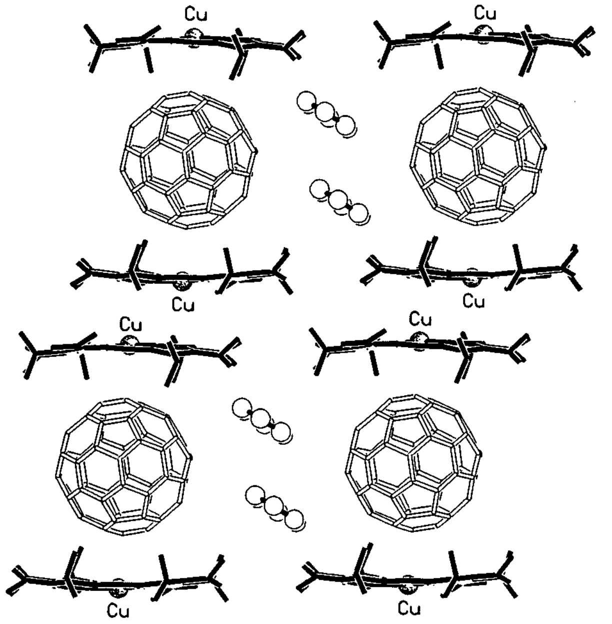

Figure 2. Part of one of the 2D sheets of $C_{60}$, Cu(Pz) and benzene solvent molecules in the structure of **1**. The back-to-back Cu···Cu separation is 4.67 Å, the lateral displacement being 3.31 Å. The interplanar separation between the Cu(Pz) units is ca. 3.4 Å. The lateral $C_{60}\cdots C_{60}$ distance is 15.1 Å.

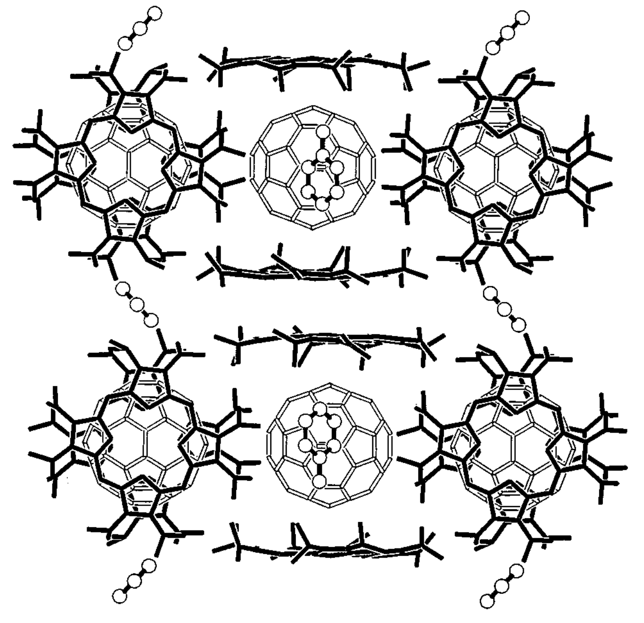

Figure 3. Part of the 3D network of Pz, $C_{60}$ and toluene (S) molecules present in the structure of **3**. The centroids of the back-to-back Pz molecules are laterally displaced by 1.14 Å. The horizontal $C_{60}\cdots C_{60}$ centroid···centroid separation is 10.5 Å and the vertical and out of the plane $C_{60}\cdots S\cdots C_{60}$ distances are 15.9 Å.

## NiPz-$C_{60}$ (2)

Crystals of the complex formed between Ni(Pz) and $C_{60}$ (**2**) (for crystal data see in the Experimental Section) were found to have a 1:1 stoichiometry and a totally different supramolecular structure. The Ni(Pz) unit has a distinctly warped conformation with the plane of diametrically opposite pyrrole rings being rotated by ca. 30° with respect to each other about their N···N vectors; the nickel and the four coordinated nitrogen atoms are coplanar to within 0.006 Å. In this complex each $C_{60}$ unit lies within a cleft formed by

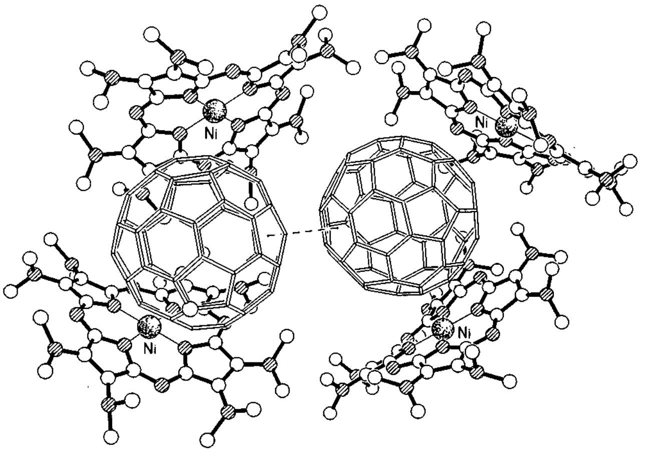

Figure 4. The partial encapsulation of a pair of π-stacked $C_{60}$ units in the 1:1 Ni(Pz):$C_{60}$ complex **2**. The Ni–N distances are in the range 1.859(4) to 1.870(4) Å. The $N_4$ plane···$C_{60}$ centroid distances are 6.31 and 6.40 Å, and the $C_{60}\cdots C_{60}$ centroid···centroid separation is 9.95 Å.

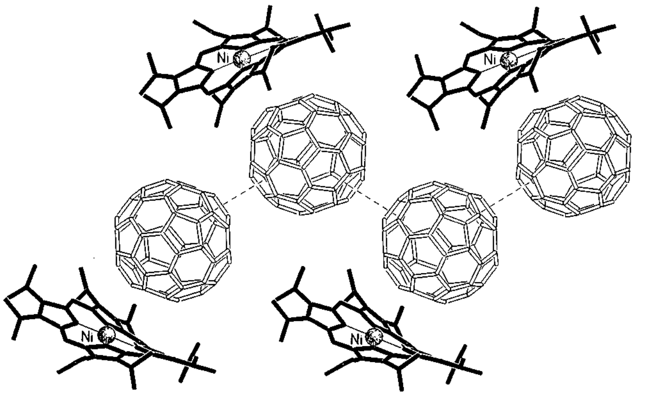

Figure 5. Part of one of the continuous zigzag chains of π-stacked, $2_1$ screw related, $C_{60}$ units in the structure of **2**. The $C_{60}\cdots C_{60}$ face-to-face and centroid···centroid separations are 3.39 and 9.95 Å respectively.

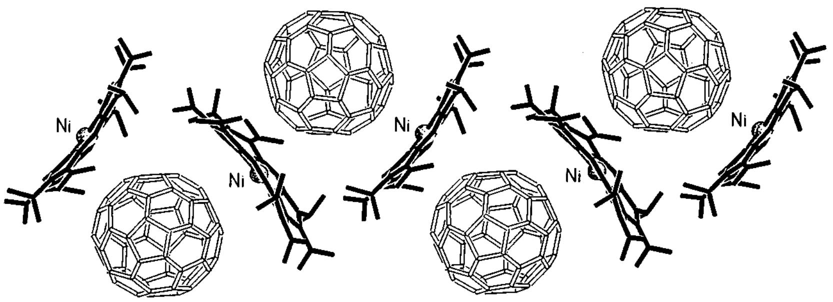

Figure 6. Part of one of the -$C_{60}$-Pz-$C_{60}$-Pz- zigzag chains in the structure of **2**.

two steeply inclined (by ca. 72°) Ni(Pz) molecules (Figure 4), the shortest Ni···C($C_{60}$) distances being 3.29 and 3.64 Å. Two supramolecular features predominate; i) the formation in one direction of continuous zigzag chains of π-stacked, $2_1$ screw related, $C_{60}$ units (Figure 5) with a $C_5$···$C_6$ ring centroid···ring centroid separation of 3.39 Å, and ii) the formation in another direction of continuous -$C_{60}$-Pz-$C_{60}$-Pz- zigzag sandwiches (Figure 6). Perhaps the most important feature of interest of this 1:1 complex **2** is that, like **3**, crystallisation occurs in a noncentrosymmetric space group, thereby offering the potential for the complex to exhibit nonlinear optical properties.

## Electron Paramagnetic Resonance

The electron paramagnetic resonance spectra at 77 K of the solid compound (**1**), and of the parent Cu(Pz) in dichloromethane solution are shown in Figure 7. The spectrum of this parent porphyrazine is characteristic of a monomeric square-planar Cu$^{II}$ complex with axial $g$ tensor ($g_{\|} = 2.15$, $g_{\perp} = 2.05$) and with $^{63,65}$Cu hyperfine coupling of $A_{\|} = 210$ G.[6,7] Further hyperfine splittings from the four equivalent ligating $^{14}$N are also resolvable both at $g_{\|}$ and $g_{\perp}$. The spectrum of **1** (Figure 7, inset) is characteristic of a binuclear triplet state ($S = 1$) species,[8,9] associated with the "back-to-back" Cu(Pz) pairs. The separation of the center fields of the two most intense peaks corresponding to $g_{\perp}$ in Figure 7 is 414 G and corresponds to $D_{\perp}$, the standard zero-field splitting parameter. Copper hyperfine splitting ($A_{\|}/2$) for the porphyrazine pairs is resolved for $g_{\|}$ as a seven-line pattern with a splitting half that for the porphyrazine monomer, which indicates that exchange coupling is larger than the Larmor energy. The expected "$\Delta M = 2$" transition at half field also is observed (not shown). If the system is treated with the point dipole model,[10,11] the Cu–Cu distances may be estimated as $R = (0.650g_{\perp}^2/D_{\perp}\ [\mathrm{cm}^{-1}])^{1/3}$. The measured $D_{\perp}$ for the Cu(Pz)–$C_{60}$ (**1**) complex gives $R =$ 4.3 Å. This approximates the crystal X-ray data of 4.78, the deviation likely arises from other contributions to $D_{\perp}$.[2]

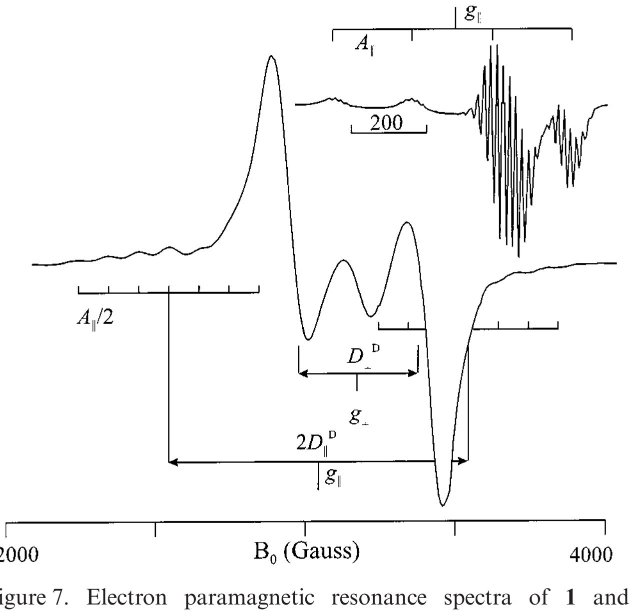

Figure 7. Electron paramagnetic resonance spectra of **1** and Cu(Pz).

## Magnetic Properties

To determine the exchange coupling within the Cu "back to back" porphyrazine pairs, the molar magnetic susceptibility, $\chi_m$, for **1** was measured over the temperature range of 2–300 K. Figure 8 plots $\chi_m T$ versus $T$ with a plot of $\chi_m$ versus $T$ as the inset. The value $\chi_m T = 0.71$–$0.73$ emu mol$^{-1}$ K observed between 300 K and 10 K is expected from the Curie law for two uncoupled Cu porphyrazine pairs per mol of **1** (S = 1/2). The rapid decrease in $\chi_m T$ at temperatures below 10 K reflects antiferromagnetic coupling within the dimer. A least squares fit of the data

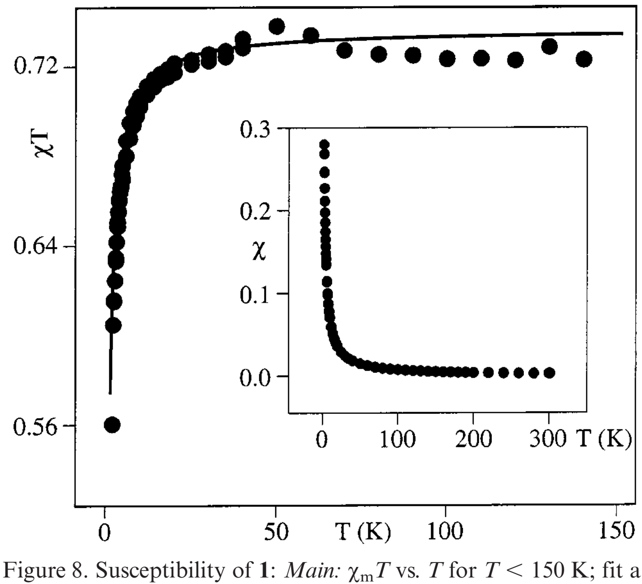

Figure 8. Susceptibility of **1**: *Main:* $\chi_m T$ vs. $T$ for $T < 150$ K; fit as described in text with inclusion of 9.7% monomer. *Inset:* $\chi_m$ vs. $T$

to the Van Vleck Equation [$\chi_m T = [(2Ng^2\beta^2/3k)(3e^{-Jk/T}/(1+3e^{-J/kT})]$ for the thermally excited triplet state gave an exchange coupling of $J = 1.61$ cm$^{-1}$, such a small value being expected from the noncovalent nature of the intradimer interaction.

## Conclusion

Two new octakis(dimethylaminoporphyrazinato)metal(II) fullerene complexes have been synthesised, their interesting different supramolecular structures have been investigated by X-ray crystallography, and the electromagnetic properties of the copper derivative have been characterised by EPR and SQUID measurements. Further investigations on the potential of the nonlinear optical properties of the nickel(porphyrazine) fullerene complex are being carried out.

## Experimental Section

A toluene solution of three equivalents of M-Pz and one equivalent of [60]fullerene was incubated under argon in a sealed tube for 24 h at 130 °C. After evaporation of toluene the excess of M-Pz was washed out with pentane and the complex subsequently extracted with small amounts of benzene. After evaporation, the pentane-benzene extraction cycle was repeated three times. Slow evaporation of the benzene or toluene solution, respectively, afforded nonconducting black needles which were subsequently handled in air.

**Crystal Data for 1 (173 K):** $(C_{32}H_{48}N_{16}Cu)_2\cdot C_{60}\cdot 2\,PhH$, $M = 2317.6$, triclinic $P\bar{1}$ 1, (no. 2), $a = 13.892(2)$, $b = 14.229(2)$, $c = 15.840(2)$ Å, $\alpha = 67.01(1)$, $\beta = 83.60(1)$, $\gamma = 65.08(1)°$, $V = 2608.6(6)$ Å$^3$, $Z = 1$ ($C_i$ symmetry), $D_c = 1.475$ g cm$^{-3}$, $\mu$(Cu-$K_\alpha$) = 11.0 cm$^{-1}$, $F(000) = 1206$; 7948 independent reflections, $F^2$ refinement, $R_1 = 0.068$, $wR_2 = 0.171$, 6912 absorption corrected reflections with $|F_o| > 4\sigma(|F_o|)$, $2\theta \le 124°$, 891 parameters. CCDC 135910.

**Data for 1 (293 K):** Triclinic $P\bar{1}$, (no. 2), $a = 13.957(2)$, $b = 14.320(1)$, $c = 15.955(1)$ Å, $\alpha = 67.37(1)$, $\beta = 83.75(1)$, $\gamma = 65.03(1)°$, $V = 2662.7(4)$ Å$^3$, $Z = 1$ ($C_i$ symmetry), $D_c = 1.445$ g cm$^{-3}$, $\mu$(Cu-$K_\alpha$) = 10.8 cm$^{-1}$, $F(000) = 1206$; 7972 independent reflections, $F^2$ refinement, $R_1 = 0.054$, $wR_2 = 0.148$, 6743 absorption corrected reflections with $|F_o| > 4\sigma(|F_o|)$, $2\theta \le 124°$, 1041 parameters.

**Crystal Data for 2 (123 K):** $C_{32}H_{48}N_{16}Ni\cdot C_{60}$, $M = 1436.2$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 15.413(1)$, $b = 18.337(1)$, $c = 21.855(1)$ Å, $V = 6177.0(6)$ Å$^3$, $Z = 4$, $D_c = 1.544$ g cm$^{-3}$, $\mu$(Cu-$K_\alpha$) = 10.3 cm$^{-1}$, $F(000) = 2960$; 6599 independent reflections, $F^2$ refinement, $R_1 = 0.056$, $wR_2 = 0.154$, 6154 absorption corrected reflections with $|F_o| > 4\sigma(|F_o|)$, $2\theta \le 128°$, 999 parameters. The absolute structure was unambiguously determined by a combination of $R$ factor tests [$R_1^+ = 0.0563$, $R_1^- = 0.0589$] and by use of the Flack parameter [$x^+ = 0.00(4)$, $x^- = 1.00(4)$].

**Data for 2 (293 K):** Orthorhombic, $P2_12_12_1$ (no. 19), $a = 15.480(2)$, $b = 18.604(1)$, $c = 22.025(1)$ Å, $V = 6343.0(8)$ Å$^3$, $Z = 4$, $D_c = 1.504$ g cm$^{-3}$, $\mu$(Cu-$K_\alpha$) = 10.0 cm$^{-1}$, $F(000) = 2960$; 5791 independent reflections, $F^2$ refinement, $R_1 = 0.061$, $wR_2 = 0.161$, 4950 independent observed absorption corrected reflections with $|F_o| > 4\sigma(|F_o|)$, $2\theta \le 128°$, 1000 parameters, $R_1^+ = 0.0610$, $R_1^- = 0.0631$, $x^+ = -0.01(5)$, $x^- = +1.01(5)$.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135910 and -135912 (**1**), CCDC-135911 and -135913 (**2**). Copies of the data can be obtained free of charge on applicaton to The Director, CCDC, 12 Union Road,m Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (1223) 336-033; E-mail: deposit@ccdc.cam.ac.uk].

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