

Solid-State Structures

Packing Motifs in Porphyrazine Macrocycles Carrying Peripherally Annulated Thiadiazole Rings: Crystal Growths of Metal-Free and Cobalt Tetrakis(1,2,5-thiadiazole)porphyrazines**

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Phthalocyanine compounds have received extensive attention in the last three decades because of their commercial applications as dyes and catalysts, as well as because of their interesting electrooptical and magnetic properties.^[1–3] Various chemical modifications have been carried out, mainly on the benzo ring in phthalocyanine, to modify the physical properties.^[4–6] Recently Ercolani and co-workers synthesized tetrakis(thiadiazole)porphyrazine (TTDPzH₂) and the corresponding metal(II) derivatives (TTDPzM; M = Mg, Cu, Mn, Fe, Co, Ni, and Zn).^[7,8] While intermolecular interactions of the thiadiazole ring in symmetrical macrocycles are expected in the solid state, no structural data have been reported so far, although structural studies on the related low-symmetry macrocycles have recently appeared in the literature.^[9,10]

Herein we consider the crystal growths of TTDPzH₂ and TTDPzCo as well as magnetic measurements on the latter compound. We report polymeric structures of these two compounds, which are completely different from the structures of phthalocyanines.

The materials TTDPzH₂ and TTDPzCo were prepared by literature methods.^[7,8] Single crystals of the compounds were obtained by sublimation under a reduced pressure (a few mbar) with a continuous flow of N₂ (30 mL min^{−1}). The conditions were optimized so that the sublimation temperatures for TTDPzH₂ and TTDPzCo were 500 and 550 °C, respectively. It is notable that crystals, which were suitable for X-ray crystal analyses, were not grown without the gas flow.

TTDPzH₂ crystallized in a monoclinic *P*2₁/*n* space group with half of the molecule crystallographically asymmetric.^[11] The molecules form a layered structure (Figure 1). The layer is formed by a 2D hexagonal close packing of TTDPzH₂ with very short S⋯N contacts of 2.948(2) and 3.245(2) Å. In addition, the layers are stacked along the *c* axis by π – π interactions, with an interlayer distance of 3.45 Å. One molecule interacts with four molecules in adjacent layers.

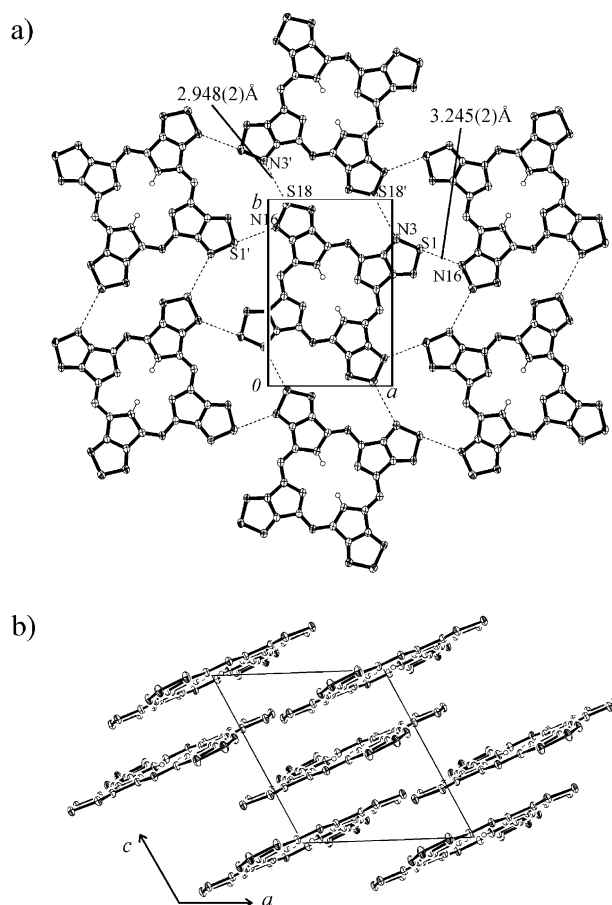


Figure 1. Top (a) and side (b) views of the layered crystal structure in TTDPzH₂.

Epitaxial growths of phthalocyanines have been extensively studied on various surfaces, and it was recognized that the surface interactions seriously affected the solid-state structures of phthalocyanines.^[12] TTDPzH₂ can potentially self-assemble into a planar 2D network in which the molecular planes are all parallel, thus it could have an application in the preparation of oriented thin films.

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TTDPzCo crystallized into a monoclinic $P2_1/c$ space group, in which one molecule was crystallographically independent.^[13] The TTDPzCo molecules form a 1D coordination polymer along the b axis (Figure 2a). A nitrogen atom on the thiadiazole ring occupies the axial position around the Co ion in the neighboring molecule at a distance of 2.300(2) Å. The two molecules are related by a twofold screw axis parallel to the b axis, with a dihedral angle of 82.96(1)°. A similar edge to face interaction was observed for the Zn species containing 3,4-annulated pyridine units.^[14] Furthermore, the coordination chains of TTDPzCo are stacked in the bc plane, thus forming face-to-face π dimers (Figure 2b). Figure 2c shows a projection of the dimer onto the molecular plane. The axial position around the cobalt ion is occupied by the nitrogen atom of the pyrrole ring in the neighboring molecule at a distance of 3.401(2) Å. The intradimer Co...Co distance is 4.0252(6) Å, which is much shorter than the shortest Co...Co

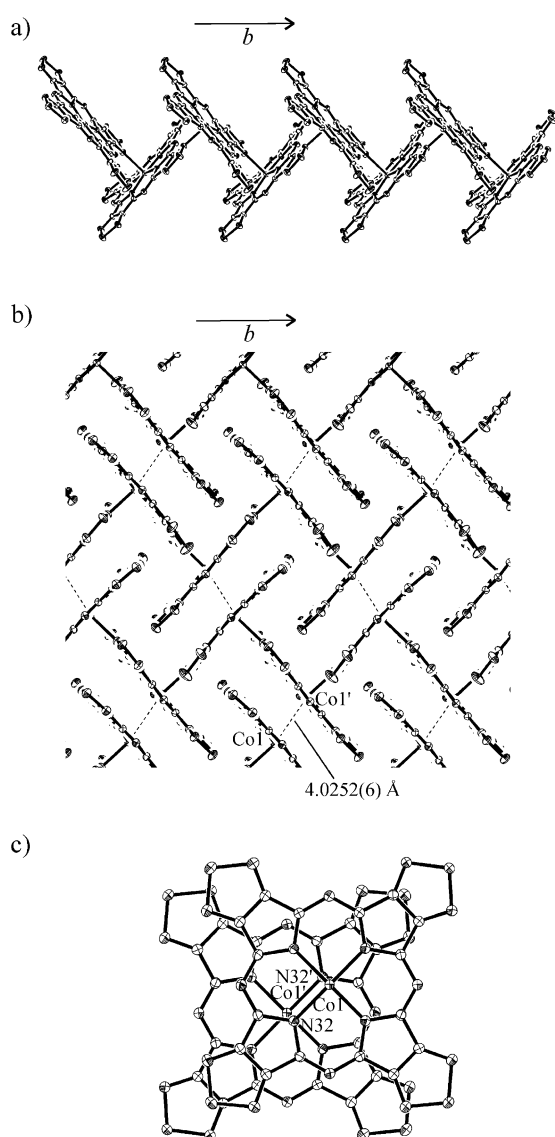


Figure 2. Views of the crystal structure in TTDPzCo; a) coordination polymer along the b axis; b) a projection onto the bc plane; c) face-to-face π dimer in the interchain arrangement.

distance in the coordination chain (7.3535(5) Å). A super-exchange magnetic interaction is expected in the dimer through the Co-N...Co pathway.

It is well known that the structures of metal-containing and metal-free phthalocyanines are nearly identical in either the α or β forms.^[15,16] Their structures are governed by the condensation energy associated with the π - π interaction of the planar molecules. In contrast the structures of TTDPzH₂ and TTDPzCo are completely different, although they have a common feature; the interactions of the thiadiazole ring play an essential role in their solid-state structure: the electrostatic interaction between the thiadiazole rings is responsible for the 2D close packing in TTDPzH₂, while the coordination bond between the ring and the cobalt ion results in the chain structure in TTDPzCo.

Figure 3 depicts the temperature dependence of the paramagnetic susceptibility χ_p for TTDPzCo.^[17] The values of χ_p show a gradual increase as the temperature decreases down to 12 K, and, after reaching a rather sharp maximum at

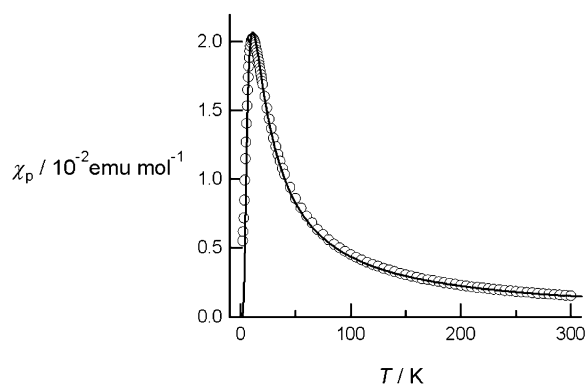


Figure 3. Temperature dependence of the paramagnetic susceptibility χ_p for TTDPzCo. The solid curve is the theoretical best fit of the dimer model.

12 K, the χ_p value exhibits a quick decrease down to zero. The data were interpreted in terms of the antiferromagnetic dimer model.^[18] The solid curve shows the theoretical best fit of this model obtained with $g = 2.21$ and $2J/k_B = -17.8$ K, where g is the g factor, J is the intradimer coupling constant, and k_B is the Boltzmann constant. The experimental data were in good agreement with the dimer model, but could not be explained in terms of a 1D antiferromagnetic chain. Thus, the result is in agreement with the structure.

In conclusion, single crystals of TTDPzH₂ and TTDPzCo were grown by vacuum sublimation under a reduced pressure with a continuous gas flow. While TTDPzH₂ adopts a 2D hexagonal close packing, which could have an application in self-assembling films, TTDPzCo crystallizes into a coordination polymer even though the intrachain magnetic exchange interaction is weaker than the interchain interaction. Highly conductive phthalocyanines have recently attracted much interest,^[19] and the network structures in the present materials could have application in obtaining 3D molecular conductors.

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- [11] X-ray diffraction data were collected with graphite-monochromated MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation on an imaging plate system (Mac Science DIP-3200). The absorption collection was applied by integration using the crystal shape. The structures were solved by a direct method (SHELXS-97). A full-matrix least-squares method on F^2 with anisotropic thermal parameters was employed for the structural refinements (SHELXL-97). Hydrogen atoms were found by the difference Fourier syntheses and they were refined. Crystal data for TTDPzH $_2$: C $_{16}$ H $_2$ N $_6$ S $_4$ ($M_r = 546.58$), red block, $0.10 \times 0.20 \times 0.2 \text{ mm}$, monoclinic, space group $P2_1/n$ $a = 8.9250(3)$, $b = 12.0340(5)$, $c = 9.8650(4) \text{ \AA}$, $\beta = 116.500(2)^\circ$, $V = 948.21(6) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.914 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $2\theta_{\text{max}} = 59.76^\circ$, $F(000) = 548$, reflections collected/unique 10020/2715 ($R_{\text{int}} = 0.032$), parameters 167. Final R indices $R1(I > 2\sigma(I)) = 0.0419$, $wR2 = 0.1019$ (all data), $S = 1.101$ (all data).
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- [13] Crystal data for TTDPzCo: C $_{16}$ N $_6$ S $_4$ Co ($M_r = 603.49$), purple block, $0.10 \times 0.15 \times 0.20 \text{ mm}$, monoclinic, space group $P2_1/c$, $a = 13.2660(4)$, $b = 9.1170(3)$, $c = 18.5140(5) \text{ \AA}$, $\beta = 122.382(2)^\circ$, $V = 1890.99(10) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.120 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $2\theta_{\text{max}} = 59.80^\circ$, $F(000) = 1196$, reflections collected/unique 18880/5194 ($R_{\text{int}} = 0.033$), parameters 334. Final R indices $R1(I > 2\sigma(I)) = 0.0392$, $wR2 = 0.1024$ (all data), $S = 1.042$ (all data). CCDC 216083 (for TTDPzH $_2$) and -216084 (for TTDPzCo) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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