Nearly Isotropic Two-dimensional Sheets in a Partially Oxidized Co(Pc)(CN)$_2$ Salt (Pc = phthalocyaninato)

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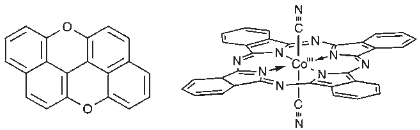
Nearly isotropic two-dimensional sheets of partially oxidized Co(Pc)(CN)$_2$ units were observed to form in a salt with PXX (PXX = *peri*-xanthenoxanthene), [PXX]$_2$[Co(Pc)(CN)$_2$]$\cdot$CH$_3$CN. The crystal is semiconducting under ambient pressure but displays stable metallic behavior under high pressure.

Electrochemical crystallization of the dicyano(phthalocyaninato)cobalt(III) anion ([Co^{III}(Pc)(CN)$_2$]$^-$) has been found to produce a number of neutral radical and partially oxidized salt conductors.[1] The π–π stacking structure varies with solvent species or cationic species incorporated in the lattice. To date, only one-dimensional (1-D) π–π stacking structure has been observed in partially oxidized salts with closed-shell cationic species.[2]

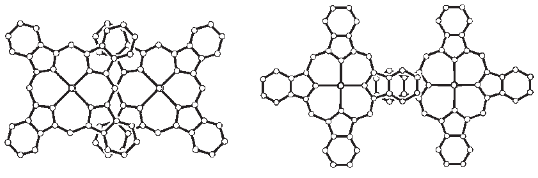


PXX [Co(Pc)(CN)$_2$]$^-$

Chart 1.

On the other hand, an open-shell cationic component of PXX has been found to give two kinds of needle crystals, [PXX][Co(Pc)(CN)$_2$][3] and [PXX]$_2$[Co(Pc)(CN)$_2$].[4] In the former crystal, the Pc units form a ladder chain, while in the latter the Pc units attain a 2-D π–π stacking structure. In both crystals, the formal charge of the [Co(Pc)(CN)$_2$] unit has been elucidated as -0.5 from the PXX geometry. Though 2-D π–π stacking was observed in [PXX]$_2$[Co(Pc)(CN)$_2$] and the crystal showed very high conductivity (1000 S cm^{-1} at room temperature), the electronic system is still found to be anisotropic because of the 2-D interaction involving two uneven overlap modes (Figure 1).

The above crystals were obtained by electrochemical oxidation of an acetonitrile solution containing PXX and [Co^{III}(Pc)(CN)$_2$]$^-$. We have noticed that the same electrolysis frequently yields platelet crystals. The composition of the crystal has been determined as [PXX]$_2$[Co(Pc)(CN)$_2$]$\cdot$CH$_3$CN (**1**) by the structure analysis. Since the platelet crystal was only moderately conducting (10 S cm^{-1} at room temperature), at first we considered that the Pc unit was not oxidized. However, when electrolysis was carried out with addition of chlorobenzene to the solution, different platelet crystals were obtained and determined as [PXX]$_4$[Co(Pc)(CN)$_2$]$\cdot$CH$_3$CN (**2**). A detailed comparison of these two platelet crystals has revealed that the Pc unit in [PXX]$_2$[Co(Pc)(CN)$_2$]$\cdot$CH$_3$CN is partially oxidized, and forms a nearly isotropic double-sheet structure.



Type-A overlap Type-B overlap

Figure 1. Two types of Pc overlaps. The overlap integral for Type-A is 2–5 times greater than for Type-B.

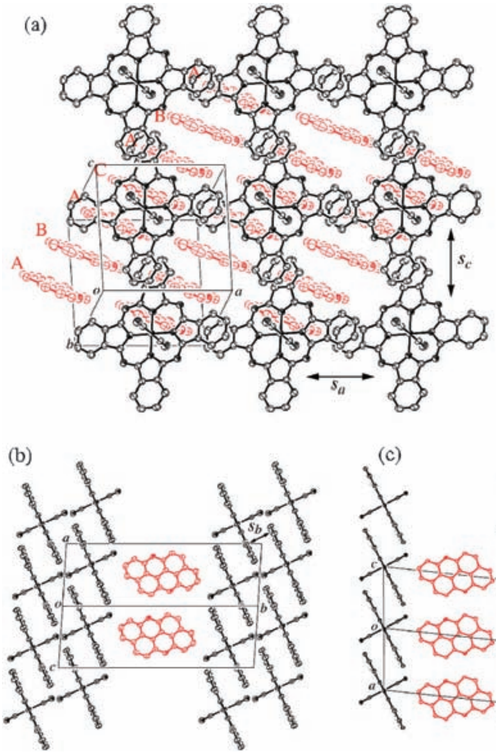


Figure 2. (a) Overall molecular arrangement in **1** (CH$_3$CN is omitted for clarity). The red moieties correspond to PXX. Overlap integrals in the 2-D Pc sheet: $s_a = -1.6 \times 10^{-3}$ and $s_c = -2.3 \times 10^{-3}$. (b) Double-sheet structure of **1**. Overlap integral between the sheets: $s_b = -4.8 \times 10^{-3}$. (c) Single sheet structure of **2**.

As shown in Figure 2a[5] the Pc units in **1** form a 2-D sheet along the *ac* plane, and CH$_3$CN occupies the void. The overlap mode is type B in Figure 1 along both the *a* and *c* axes, and the overlap integrals are nearly equal. This sheet further interacts with another sheet by Type A overlap, forming a double sheet as shown in Figure 2b. PXX forms a 1-D column along the [1 0 1] direction. The whole PXX-A and two halves of PXX-B and -C are crystallographically independent, repeating as an

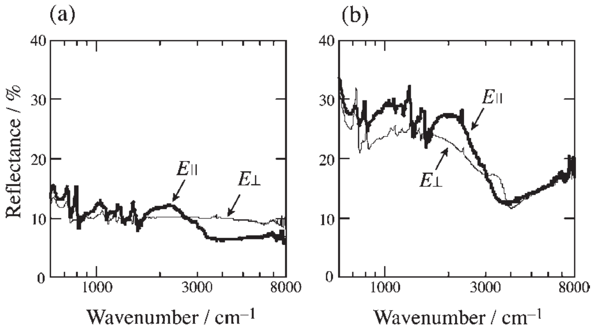


Figure 3. Single-crystal optical reflectance spectra in the *ac* plane of (a) **2** and (b) **1**. In both spectra, $E\|$ is the polarization parallel to the PXX 1-D column and $E\perp$ is the polarization perpendicular to the PXX 1-D column.

ABAC unit. Compared with PXX-A and -C, the thermal ellipsoids of PXX-B are unusually elongated. The difference syntheses indicate that the misoriented PXX moiety overlaps at the PXX-B site.[6] Because of this disorder, the geometry of PXX-B was not determined precisely. On the other hand, from the geometries of PXX-A and PXX-C, the formal charge was estimated[7] as nearly zero and +1, respectively. The charge disproportionation and disorder in the PXX column suggest low conductivity through this column.

The crystal structure of **2** is shown in Figure 2c.[8] In this structure, the Pc units form a 2-D sheet nearly identical with that of **1**. However, in this crystal, each sheet is discrete. PXX also forms a 1-D column and the main features are the same as those in **1**; namely, charge disproportionation of zero (ordered PXX-A′) and +1 (ordered PXX-C′) and disorder for PXX-B′. If the formal charge of the disordered PXX is zero, the formal charge of [Co(Pc)(CN)$_2$] in **2** becomes −1; the Pc ligand is not oxidized. This assumption was supported from the following observations. First, the optical reflectance spectra showed meaningful dispersion corresponding to the electronic transition only along the PXX 1-D column, as shown in Figure 3a. Secondly, the conductivity in **2** was rather low and anisotropic (10^{-4} S cm^{-1} along the PXX 1-D column and 10^{-5} S cm^{-1} perpendicular to the column at room temperature). If PXX-B′ had an open-shell π orbital, strong HOMO–HOMO interaction might be expected to operate between neighboring PXX's and misorientation of PXX-B′ would not occur. Therefore, it is likely that the PXX-B′ sandwiched between the two neutral PXX-A′ molecules is neutral and can be disordered.

If the electronic state of the PXX column in **1** is the same as that in **2**, the formal charge of [Co(Pc)(CN)$_2$] in **1** should be −0.5; the Pc ligand is partially oxidized. Indeed, the conductivity in **1** was much higher than in **2** and nearly isotropic in the *ac* plane. The isotropic feature in the *ac* plane was also clearly indicated in the reflectance spectra of **1**, as shown in Figure 3b. In contrast to the spectra of **2**, the spectrum of **1** with the polarization perpendicular to the PXX 1-D column has meaningful dispersion corresponding to the intermolecular electronic transition in the Pc sheet. The spectrum with the polarization parallel to the PXX 1-D column may be considered as a combination of the contribution from the Pc sheet and that from the PXX column as seen in the spectrum of **2**. Though the reflectance of **1** was not so high, its nearly isotropic dispersion in the infrared region clearly indicated that the electronic transition involves open-shell Pc π ligands in the sheet.

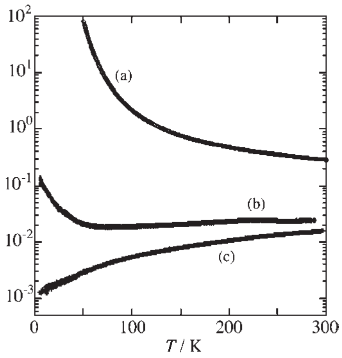


Figure 4. Temperature dependence of the resistivity of **1** under pressure; (a) 1 bar, (b) 0.6 GPa, and (c) 1.2 GPa.

Though the conductivity of **1** was only moderately high under ambient pressure, the above observations indicated that the Pc sheet is nearly isotropic and in a partially oxidized state. We thought that perhaps the localized character of the charge carriers could be mobilized by applying pressure. The pressure dependence was found to be significant, and as shown in Figure 4, the behavior is metallic down to 5 K under pressures above ca. 1 GPa.

In summary, we have identified the first Pc conductor having a nearly isotropic 2-D Pc sheet. The crystal showed stable metallic behavior under high pressure. Detailed study of the electronic structure and magnetic and transport properties of this conductor is now in progress.

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References and Notes

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5 Crystal data for **1**: $C_{76}H_{39}O_4N_{11}Co$, triclinic, space group $P\bar{1}$, $a = 10.712(4)$ Å, $b = 24.531(9)$ Å, $c = 10.555(3)$ Å, $\alpha = 100.53(3)°$, $\beta = 93.30(3)°$, $\gamma = 95.39(3)°$, $V = 2706(1)$ Å^3, $Z = 2$, $D_{\rm calcd} = 1.508$ g cm^{-3}, Rigaku R-AXIS Rapid-imaging plate diffractometer at 298 K, Mo Kα, μ(Mo Kα) = 3.88 cm^{-1}, 12428 reflections measured, 9473 reflections with $I > 3\sigma(I)$, $R = 0.056$, $R_{\rm w} = 0.047$ (829 variables). CCDC-271322.
6 Refinement with two different orientations did not give satisfactory results, since the population of the misoriented PXX was rather small.
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8 Crystal data for **2**: $C_{116}H_{59}O_8N_{11}Co$, triclinic, space group $P\bar{1}$, $a = 10.683(1)$ Å, $b = 17.775(1)$ Å, $c = 10.406(1)$ Å, $\alpha = 99.74(1)°$, $\beta = 93.06(1)°$, $\gamma = 90.99(1)°$, $V = 1943.9(2)$ Å^3, $Z = 1$, $D_{\rm calcd} = 1.532$ g cm^{-3}, Rigaku R-AXIS Rapid-imaging plate diffractometer at 120 K, Mo Kα, μ(Mo Kα) = 3.01 cm^{-1}, 15946 reflections measured, 6957 reflections with $I > 2\sigma(I)$, $R = 0.096$, $R_{\rm w} = 0.114$ (604 variables). CCDC-271323.

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