Ladder-Type Phthalocyanine Conductor, [PXX][Co(Pc)(CN)$_2$] (PXX = *peri*-xanthenoxanthene, Co(Pc)(CN)$_2$ = dicyano(phthalocyaninato)cobalt(III))

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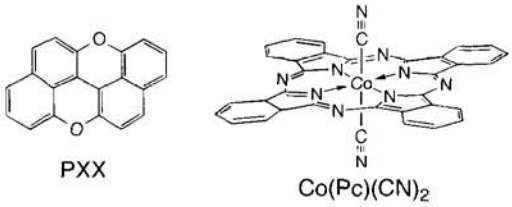
Electrochemical oxidation of PXX and $[Co(Pc)(CN)_2]^-$ in acetonitrile gives a highly conducting crystal containing two-leg ladder chains of the partially oxidized Co(Pc)(CN)$_2$ units. The doubling of the one-dimensional chains makes the electrical properties quite different from those in the single chain conductor.

The ladder-type structure becomes a new target of the lattice architecture, since it is suggested to be a potential superconductor despite its one-dimensional electronic system.[1,2] Indeed, some cuprate which has two-leg ladder chains of copper oxide was found to achieve the superconducting state under pressure.[3] Dicyano(phthalocyaninato)cobalt(III), Co(Pc)(CN)$_2$, which can be a component of two-dimensional conductors,[4] has been found to form ladder chains in the highly conducting crystal of [PXX][Co(Pc)(CN)$_2$]. This is the first example of a metallic molecular ladder conductor.[5-7]



Electrolysis at 20 °C (constant current of 2 μA) of $K^+[Co(Pc)(CN)_2]^-$ (*ca.* 20 mg) under the coexistence with PXX (*ca.* 9 mg) in acetonitrile (*ca.* 30 ml) gave two kinds of crystals, needles and plates,[8] on the anode surface after 8 days. The crystal structure of the needle determined by X-ray analysis is shown in Figure 1.[9] The stoichiometry is found to be 1:1, and both PXX and Co(Pc)(CN)$_2$ individually form one-dimensional chains along the *c*-axis. The chain constructed with slipped stacking of Co(Pc)(CN)$_2$ has an extra overlap with the neighboring Co(Pc)(CN)$_2$ chain, forming a two-leg ladder chain. The effectiveness of the π–π interaction in the ladder chain is evaluated from the extended Hückel calculation; the overlap integral between the Pc rings along the *c*-axis ($s_{//}$, interplanar distance = 3.46 Å) is 6.7×10^{-3}, while that between the chains ($s_{\perp}$, interplanar distance = 3.40 Å) is 2.8×10^{-3}. The value along the chain is nearly the same as that obtained for the one-dimensional single chain conductor of TPP[Co(Pc)(CN)$_2$]$_2$ (TPP = tetraphenylphosphonium).[10] In contrast to the uniform spacing between the Co(Pc)(CN)$_2$ units along the chain, the one-dimensional column formed by PXX is clearly dimerized; there are two kinds of overlap integrals, 4.4×10^{-3} and 1.7×10^{-3}, between PXX's.

The temperature dependence of the electrical conductivity measured by a four-probe method is shown in Figure 2. During the electrochemical oxidation, there could be freedom in distributing the charge on each molecule in the formation of the 1:1 crystal. If only PXX's were oxidized, the conduction would occur only through the open-shell PXX column. Such a material with a half-filled band structure cannot be highly conducting due to the on-site Coulomb repulsion on PXX. The observed high conductivity (160 S cm^{-1} at room temperature) rather suggests that both components are partially oxidized. Since the dimerized one-dimensional column of PXX is not advantageous to electrical conduction even when PXX is partially oxidized, the charge transport must mainly occur in the uniform Co(Pc)(CN)$_2$ ladder chain. The effective charge δ in $[PXX]^{\delta+}[Co(Pc)(CN)_2]^{\delta-}$ is expected to be close to 0.5 because of the dimerized structure observed in the PXX column. The bond lengths in PXX also support this assignment from a comparison with those in PXX^0 and $PXX^{0.5+}$.[8,10] The partially oxidized state for both components is considered to result from the small difference between the redox potentials for the first oxidation; the redox potential of $[Co(Pc)(CN)_2]^-$ is 1.10 V vs. Ag/AgCl in acetonitrile, while it is 0.79 V for PXX. In contrast to the weak temperature dependence of the conductivity in the single chain conductor, TPP[Co(Pc)(CN)$_2$]$_2$, the temperature dependence is clearly metallic above 100 K. Below 100 K, the

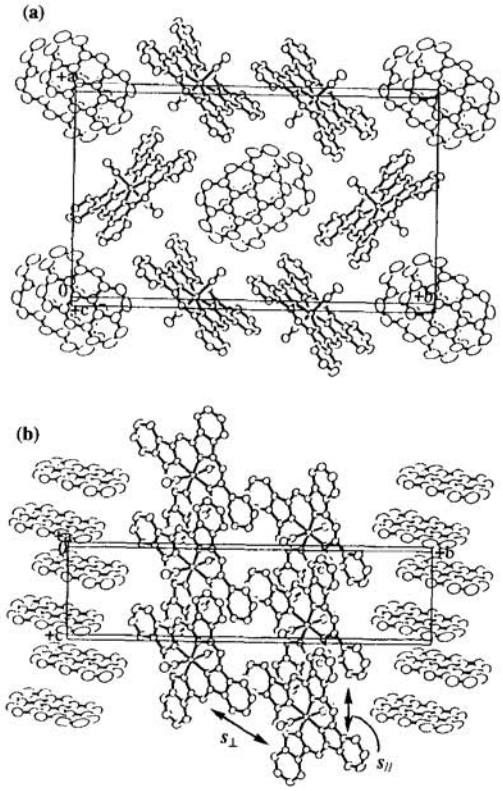


Figure 1. Perspective view normal to the *ab* plane of the unit cell of [PXX][Co(Pc)(CN)$_2$] (a), and the molecular arrangement in the *bc* plane (b).

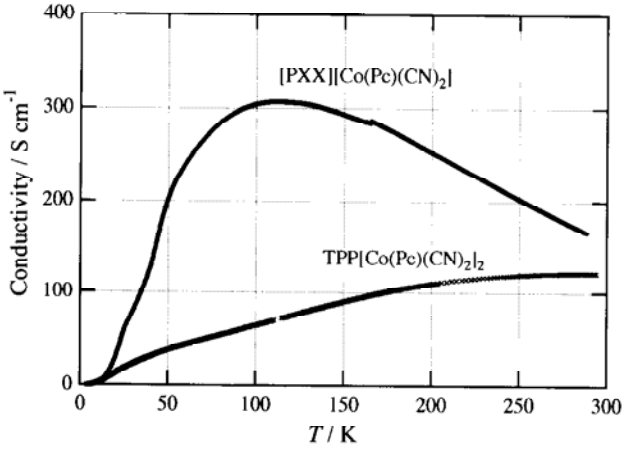


Figure 2. Temperature dependence of the electrical conductivity along the *c*-axis (needle axis) of $[PXX][Co(Pc)(CN)_2]$ and $TPP[Co(Pc)(CN)_2]_2$.

conductivity decreases gradually, suggesting that some insulating state appears.

The thermoelectric power (TEP) shown in Figure 3 clearly obeys a metallic behavior. It is reasonable to assume that the TEP values reflect the transport properties in the most highly conducting $Co(Pc)(CN)_2$ ladder chain; the positive values are consistent with the hole conduction in the partially oxidized Pc π-system. The values and the slope are much smaller than those of the single chain conductor, $TPP[Co(Pc)(CN)_2]_2$, in which the band width is estimated to be ~0.5 eV.[11] The energy dispersion in the band structure for the two-leg ladder chain is expressed as two overlapping one-dimensional bands (ε_+ and ε_-, Figure 4); $\varepsilon_\pm = -|2t_{//} \cos(k) \pm t_\perp|$, where $t_{//}$ and $t_\perp$ are the transfer integrals along the one-dimensional chain and between the chains, respectively, and k is the wave vector. The transport properties,

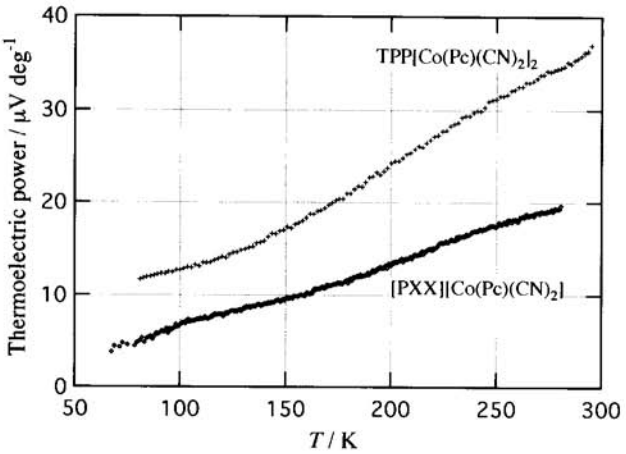


Figure 3. Temperature dependence of the thermoelectric power along the *c*-axis of $[PXX][Co(Pc)(CN)_2]$ and $TPP[Co(Pc)(CN)_2]_2$.

thus, strongly depend on the position of the Fermi energy. If the Fermi level lies in either of the two bands, the transport properties are governed by the single band and must be similar to those in the single chain conductor. The smaller TEP values and slope compared with $TPP[Co(Pc)(CN)_2]_2$ suggest that the Fermi level lies in both ε_+ and ε_-.

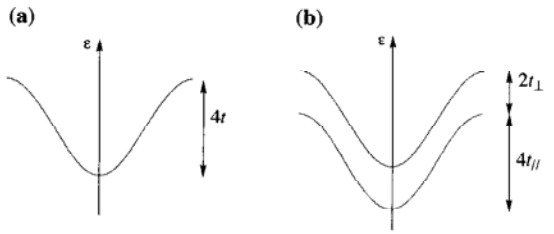


Figure 4. Schematic representation of the one-dimensional single chain band (a) and two-leg ladder band (b).

In conclusion, the crystal of $[PXX][Co(Pc)(CN)_2]$ has been found to contain metallic two-leg ladder chains of $Co(Pc)(CN)_2$. The transport properties are significantly modified from the case of the single chain conductor, revealing characteristics of the ladder electronic system. The nature of the insulating state observed and the transition mechanism inherent in a ladder system may be an interesting subject. The conductivity measurements under high pressure and the study on the structural and physical properties at low temperature are now under way.

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References and Notes

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8 The plates have been found to be $[PXX]_2[Co(Pc)(CN)_2]\cdot CH_3CN$ in which only PXX is partially oxidized.
9 Crystal data for $[PXX][Co(Pc)(CN)_2]$: $C_{54}H_{26}N_{10}O_2Co$, monoclinic, space group $P2_1/a$, a = 17.743(2) Å, b = 29.344(3) Å, c = 7.678(3) Å, β = 102.36(2)°, V = 3904(1) Å^3, Z = 4, d_{calc} = 1.541 g cm^{-3}. The intensity data were collected on a RIGAKU AFC-7R diffractometer using $\omega/2\theta$ scan mode at 293 K with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71069 Å). A purplish black needle with dimensions of 0.1 × 0.1 × 0.6 mm^3, μ(Mo-$K\alpha$) = 0.503 mm^{-1}, 9789 reflections measured, 9128 unique reflections, 5933 reflections with $I > 2.5\sigma(I)$, R = 0.057, Rw = 0.062 (604 variables).
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