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A highly conducting partially oxidized salt of axially substituted phthalocyanine. Structure and physical properties of $TPP[Co(Pc)(CN)_2]_2$ {TPP = tetraphenylphosphonium, $[Co(Pc)(CN)_2]$ = dicyano(phthalocyaninato)cobalt(III)}

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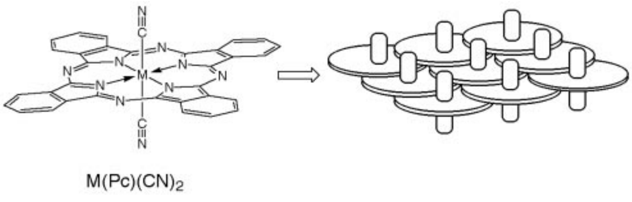
A highly conducting partially oxidized salt of $TPP[Co(Pc)(CN)_2]_2$ can be obtained by electrocrystallization of $TPP[Co(Pc)(CN)_2]$. The crystal is composed of one-dimensional TPP arrays surrounded by slipped-stacked one-dimensional $[Co(Pc)(CN)_2]$ chains. The electrical conductivity at room temperature is quite high, $120\ \Omega^{-1}\ cm^{-1}$, though at low temperature it is weakly semiconducting. The band width for this stacking mode has been estimated from both thermoelectric power measurements and an extended Hückel calculation. The latter suggests that the band width value for the slipped-stacking mode is about 40% of the value for the face-to-face stacking mode. The width estimated from the metallic temperature dependence of the thermoelectric power is actually in excellent agreement with that estimated from the calculation.

Metal phthalocyanines are known to form conducting solids when the π-ligand is oxidized. Partially oxidized salts of M(Pc)X ($M = H_2$, Ni, Cu, *etc.*; X = I, $(BF_4)_{0.33}$, $(SbF_6)_{0.5}$, *etc.*)[1–4] are known as metallic one-dimensional conductors, the crystals of which consist of one-dimensional face-to-face stacking Pc columns and one-dimensional anion chains. On the other hand, we have adopted axially substituted phthalocyanines, $M(Pc)(CN)_2$, as novel components of multi-dimensional π–π overlaps, as shown in Scheme 1. When M is a trivalent metal ion, the starting closed-shell state is monoanionic and the conducting crystals can be obtained from electrochemical oxidation of the starting simple salts. Based on this method with $M = Co^{III}$, we have obtained several conducting neutral radical crystals with a variety of dimensionalities of the electronic structure.[5]

Other target crystals are the partially oxidized salts based on $Co(Pc)(CN)_2$. The first successful example, $K[Co(Pc)(CN)_2]_2{\cdot}5CH_3CN$, was obtained using the potassium salt and acetonitrile as a solvent.[6] The Pc units form a two-dimensional sheet as shown in Scheme 1, and the cation and acetonitrile molecules are packed between the sheets. The crystal is unstable since the crystal solvent is easily removed from the lattice. The conductivity is, however, found to be high (*ca.* $10\ \Omega^{-1}\ cm^{-1}$), though the crystal is far from perfect due to mosaic distortion.

This example of a partially oxidized salt encourages us to investigate the possibility of finding other conducting salts with different counter ions. After trying various organic cations including pyridinium, ammonium, and phosphonium derivatives, we have found that the tetraphenylphosphonium salt gives a highly conducting salt of $TPP[Co(Pc)(CN)_2]_2$ by electrocrystallization. In this crystal, the Pc rings form a slipped-stacked one-dimensional chain. Since the HOMO coefficients at the peripheral benzene rings of Pc are suggested to be much smaller compared with the central tetraazaannulene part, the conductivity is expected to be much smaller than those of face-to-face stacked M(Pc)X type conductors in which the π–π overlap includes mainly the tetraazaannulene part. The conductivity of $TPP[Co(Pc)(CN)_2]_2$ is, however, found to be rather high, *ca.* $120\ \Omega^{-1}\ cm^{-1}$ at room temperature, which is almost comparable to those of M(Pc)X. Though the dimensionality of the electronic system in $TPP[Co(Pc)(CN)_2]_2$ is lower than that we expected, this system provides an opportunity for evaluating the effectiveness of carrier transfer through this stacking mode peculiar to $M(Pc)(CN)_2$.



Scheme 1

Experimental

The starting potassium salt, $K[Co(Pc)(CN)_2]$, was synthesized following the method reported.[7] The cation exchange was carried out by metathesis using the potassium salt and tetraphenylphosphonium iodide. An electrocrystallization cell equipped with a glass frit between the two compartments was filled with *ca.* 30 ml of the acetonitrile solution of $TPP[Co(Pc)(CN)_2]$ (0.3–0.4 mmol dm^{-3}). A constant current of typically 1 μA was applied between two platinum electrodes immersed in the solution of each compartment for 1–2 weeks at 20 °C. The needle crystals were grown on the anode surface during the current flow, and harvested by filtration. A single phase crystalline product of $TPP[Co(Pc)(CN)_2]_2$ was obtained even when the current was varied (0.5–2 μA).

An automated Mac Science MXC 18 diffractometer with graphite-monochromatized Mo-Kα radiation was used for data collection at 296 K. The data-collection conditions are summarized in Table 1. Three standard reflections, which were monitored every 100 data measurements, showed no significant deviation in intensities. The structure was solved by a direct method (SHELX-86[8]), and the hydrogen atoms were placed at the calculated ideal positions. A full-matrix least-squares

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Table 1 Data-collection conditions and crystal data of TPP[Co(Pc)(CN)$_2$]$_2$

chemical formula	$C_{92}H_{52}N_{20}PCo_2$
molecular weight	1590.44
crystal size/mm	$0.6 \times 0.1 \times 0.1$
crystal system	tetragonal
space group	$P4_2/n$
a/Å	21.676(8)
c/Å	7.474(4)
V/Å^3	3511(3)
Z	2
D_{calc}/g cm^{-3}	1.50
μ(Mo-Kα)/cm^{-1}	5.590
2θ range/°	$3 < 2\theta < 60$
range of h, k, l	$0 \leqslant h \leqslant 28$, $0 \leqslant k \leqslant 28$, $0 \leqslant l \leqslant 9$
scan width/°	$1.29 + 0.35 \tan\theta$
scan mode	ω–2θ
scan rate/° min^{-1}	8
no. of reflections measured	5969
no. of independent reflections observed [$I > 3\sigma(I)$]	2203
no. of parameters	270
R	0.055
R_w	0.073

technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms (positional parameters are constrained to the attached carbons) was employed for the structure refinement. Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/97.

Electrical conductivity measurements were performed by a four-probe method in the temperature range 2–345 K. The thermoelectric power measurements were carried out using a system similar to that reported by Chaikin and Kwak.[9]

Results and Discussion

The bond lengths and angles of the Pc unit derived from the X-ray structure analysis are within a range of the ordinary Pc structure. Since the bond lengths were found to be rather insensitive to the charge on the Pc ring,[5] the oxidation state is simply estimated from the stoichiometry. This is safely justified from the fact that the oxidation potentials of TPP$^+$, Co^{III}, and CN$^-$ are fairly high compared with the Pc π-system. Since the ratio of cation : Pc units is 1 : 2, the effective charge of one [Co(Pc)(CN)$_2$] unit is -0.5. This gives the effective charge of the Pc ring as -1.5; each Pc ring is formally oxidized by 0.5e from the initial closed-shell Pc^{2-}.

The crystal structure of TPP[Co(Pc)(CN)$_2$]$_2$ is shown in Fig. 1(a). As we expected, the π–π overlap between the Pc rings is partial due to the existence of the axial CN ligands, yet the Pc units form a one-dimensional chain along the c-axis. Even after forming such a one-dimensional chain there still remain planar Pc parts which can overlap with other Pc rings, and therefore two-dimensional π–π overlap is expected to occur when the additional overlap is achieved with the neighboring chains. In fact, the Pc chain has an additional π–π overlap but with the cation instead of the next chain [Fig. 1(b)]. Special symmetry of the cation, $\bar{4}$, induces a tetragonal arrangement of the one-dimensional Pc chains. This makes it difficult for the Pc chains to form a sheet as shown in Scheme 1.

The structure of the one-dimensional chain is shown in Fig. 1(c). The Pc rings which are translationally related along the c-axis are stacked with overlaps at two of the four peripheral benzene rings with interplanar distances of 3.46 and 3.40 Å. The effectiveness of this stacking mode has been evaluated from an extended Hückel calculation based on these structural data. The overlap integral between the Pc rings in a chain is calculated to be 8.5×10^{-3}, which amounts to about 40% of the value estimated for the typical face-to-face stacking M(Pc)X type conductors [22×10^{-3} for Ni(Pc)I].

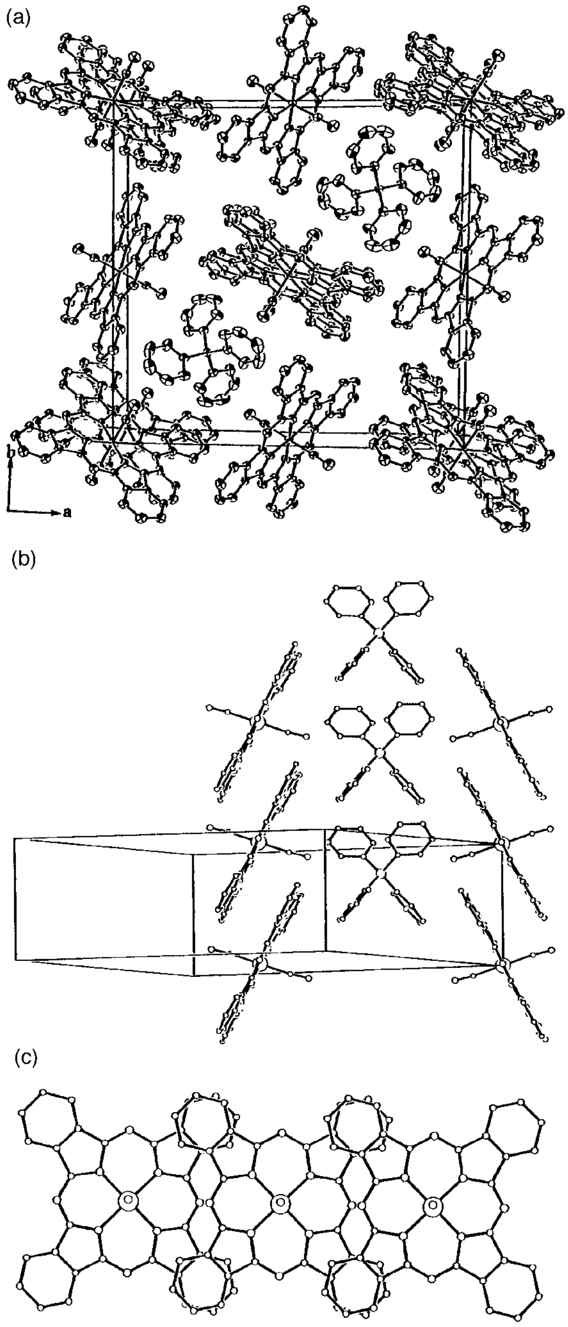

Fig. 1 Crystal structure of TPP[Co(Pc)(CN)$_2$]$_2$; view along the c-axis (a), arrangement of TPP and the Pc chains (b), and molecular stacking in the Pc chain (c)

The temperature dependence of the resistivity along the c-axis is shown in Fig. 2. The value at room temperature is 8.2×10^{-3} Ω cm. This is nearly comparable to that of Ni(Pc)I, 1.8×10^{-3} Ω cm.[1] The marked difference lies in its temperature dependence. Metallic behavior is observed only above 300 K [Fig. 2(b)]. The resistivity around room temperature is nearly temperature independent, and then gradually increases with decreasing temperature. This weak semiconducting behavior contrasts to the metallic behaviour observed for the M(Pc)X type conductors. As shown in the inset, there are three regions of semiconducting behavior. The activation energy above *ca.* 250 K is 0.0024 eV, and that below *ca.* 80 K is 0.0027 eV. The

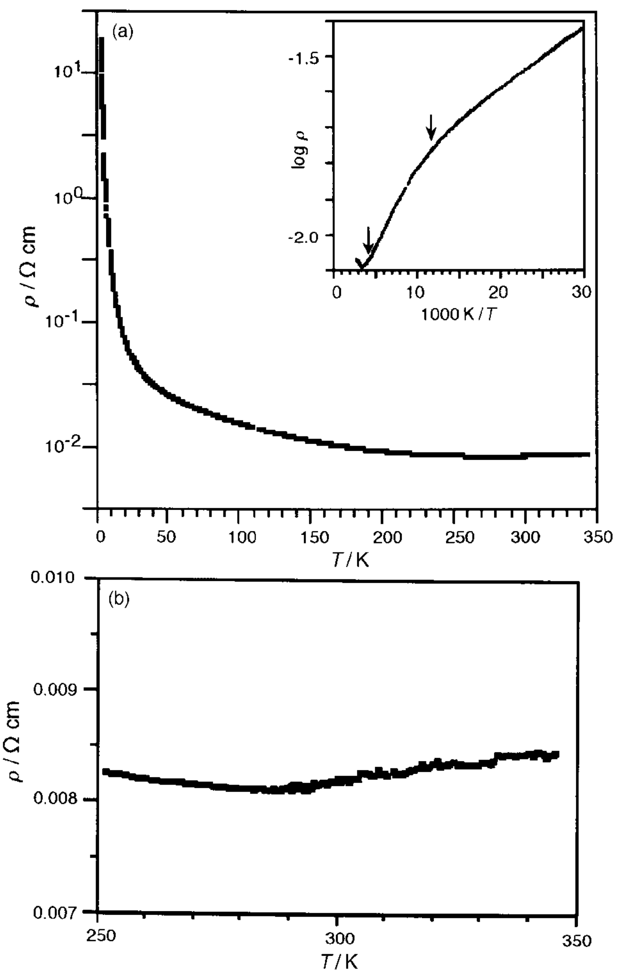

Fig. 2 Temperature dependence of the resistivity of TPP$[Co(Pc)(CN)_2]_2$; in the whole temperature region (a) and the high temperature region (b). Inset in (a) is a plot *vs.* inverse temperature; the arrows indicate the temperatures at which the activation energy changes (250 K and 80 K)

activation energy between these two regions is slightly larger, 0.0099 eV at *ca.* 150 K. Since the values are too small compared with the thermal energy, it is not likely that this apparent activation energy is due to gap formation at the Fermi energy. This is supported by the fact that the one-dimensional Pc chain has no distortion at room temperature. The apparent weak semiconducting behavior rather suggests some anomalous metallic state unique to the one-dimensional system. Its nearly pure one-dimensionality has been confirmed by the anisotropy of the resistivity: $\rho_{\perp c}/\rho_{//c}$ amounts to 10^3.

Fig. 3 shows the temperature dependence of the thermoelectric power. The positive values are consistent with the carrier being hole generated by oxidation of the Pc π-electrons. In contrast to the conductivity behavior, the thermoelectric power shows clear metallic behavior above 150 K. Since thermoelectric power is a transport quantity measured under zero-current conditions, it may be more insensitive to the extrinsic scattering process than in the resistivity measurements. With assuming a one-dimensional tight-binding band structure, the band width is estimated to be *ca.* 0.5 eV from the slope above 150 K. Considering that the band width for the M(Pc)X type conductors, which is typically 1.0–1.2 eV,[1–3] the value for TPP$[Co(Pc)(CN)_2]_2$ obtained from the thermoelectric power is reduced to 40–50%, which is in excellent agreement with the calculation. Even when the band width is reduced to 0.5 eV, it could be still large enough to achieve a superconducting state, when the electronic structure becomes two-dimensional.[10]

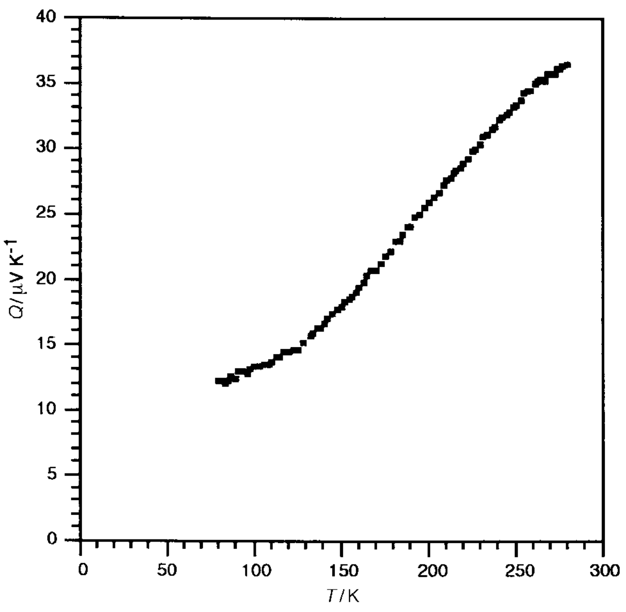

Fig. 3 Temperature dependence of the thermoelectric power (Q) of TPP$[Co(Pc)(CN)_2]_2$

In conclusion, we have found that the electrocrystallization of TPP$[Co(Pc)(CN)_2]$ yields a partially oxidized salt of TPP$[Co(Pc)(CN)_2]_2$. In the crystal, the Pc units form a one-dimensional chain with slipped stacking of the Pc rings. This partially oxidized salt crystal is highly conducting at room temperature, and the thermoelectric power shows its metallic property with moderate band width. The preliminary magnetic measurement shows temperature-independent Pauli-like susceptibility, which is consistent with its metallic nature. The apparent semiconducting behavior observed in the wide temperature range in the conductivity measurements reminds us of the anomalous metallic state of some one-dimensional cuprates.[11] The one-dimensional metallic state is believed to be a non-Fermi liquid and is often regarded as a Luttinger liquid.[12] Whether this salt is a Luttinger liquid or not, the transport properties of a one-dimensional system are very sensitive to perturbations such as high-pressure or impurities that would lead to various ground states, and often involve large quantum fluctuations which would manifest intriguing physics. Further study, including resistivity measurements under high pressures, and synthesis of the corresponding $Fe(Pc)(CN)_2$ salt, is now under way.

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