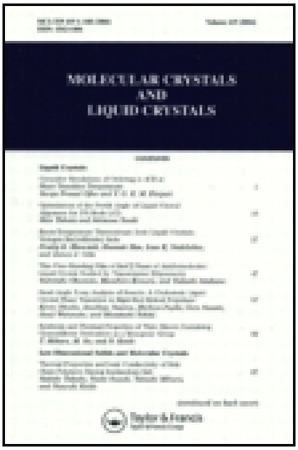

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Molecular Conductors Comprised of Organic Cations and Phthalocyanines

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MOLECULAR CONDUCTORS COMPRISED OF ORGANIC CATIONS AND PHTHALOCYANINES

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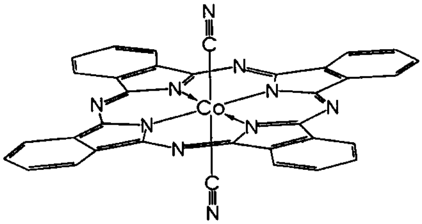
Abstract The axially substituted dicyanophthalocyaninatocobalt(III) anion, $[Co(Pc)(CN)_2]^-$, has been utilized for constructing molecular conductors. Highly conducting partially oxidized salt can be obtained from the combination with a closed-shell cation of $[PPh_4]^+$. The crystal is composed of one-dimensional stacks of partially oxidized phthalocyanine. On the other hand, phthalocyanine is found to be not oxidized in the salts with open-shell cations such as TTF or TMTTF.

INTRODUCTION



In order to construct molecular conductors in which π-electron overlapping is multi-dimensional, we have been utilizing axially substituted metal-phthalocyanine as a component, expecting that steric interactions prevent the molecules forming simple one-dimensional columns. It has actually been found that the electrochemical oxidation of the potassium salt of a cobalt(III)phthalocyanine anion which is axially substituted by two cyano groups, $K^+[Co(Pc)(CN)_2]^-$, yields partially oxidized salt of $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$, in which two-dimensional phthalocyanine sheets are formed.[1-4] Rather large space between the sheets is filled with the potassium ions and the solvent molecules. This crystal is unstable, since some of the solvent molecules are not tightly bound to the other parts of the lattice and easily removed from the lattice. If one intends to obtain the stable crystal which has no solvent molecules in the lattice, one potassium ion and five acetonitrile molecules have to be replaced by a single large cation. Not only the volume but also the shape of the cation must be very important for the arrangement of the Pc units. Fortunately, we have found that the potassium ion in the starting salt can be easily replaced by organic cations by metathesis with the iodides or bromides.[5] Many simple salts of $[Co(Pc)(CN)_2]^-$ with closed-shell organic cations having various shapes have been prepared, and they have been subjected to the electrochemical oxidation to obtain the partially oxidized salts. With this method, we have obtained some conducting crystals. The second method adopted is the electrochemical oxidation of the solution containing $K^+[Co(Pc)(CN)_2]^-$ and organic donor components such as TTF, TMTTF, etc. This method is expected to give crystals comprised of the Pc units and open-shell radical cations. We describe here the structures and the properties of the crystals obtained by these two methods.

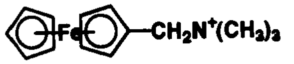
CRYSTALS WITH CLOSED-SHELL CATIONS

More than thirty salts with closed-shell organic cations have been subjected to the electrochemical oxidation. Table 1 lists the salts which gave conducting products; the conductivities are relatively high. The most conductive one, the crystal obtained by the electrochemical oxidation of $5^+[Co(Pc)(CN)_2]^-$ ($[PPh_4][Co(Pc)(CN)_2]$), has sufficient crystal dimensions for X-ray structural study, but others are too thin or too small.

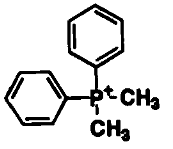
TABLE 1 Electrical conductivity of some electrochemical products

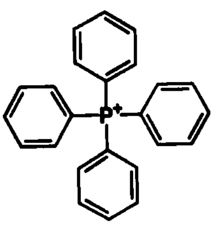
Starting simple salt	Crystal appearance	Conductivity at room temperature[a]/ Ω^{-1} cm^{-1}
$1^+[Co(Pc)(CN)_2]^-$	needle	3.0×10^{-2}
$2^+[Co(Pc)(CN)_2]^-$	needle	2.7×10^{-1}
$3^+[Co(Pc)(CN)_2]^-$	needle	1.6×10^{-1}
$4^+[Co(Pc)(CN)_2]^-$	powder	7.2×10^{-2}
$5^+[Co(Pc)(CN)_2]^-$	needle	1.4×10^{2}*

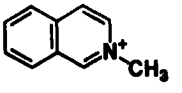
[a]powder compaction. *single crystal.

1^+ =


$4^+ = (CH_3)_4N^+$

2^+ =


5^+ =


3^+ =


The crystal structure of the product from $[PPh_4][Co(Pc)(CN)_2]$ is shown in Fig. 1. The composition was found to be $[PPh_4][Co(Pc)(CN)_2]_2$ and the crystal data are as follows; tetragonal, space group $P4_2/n$, $a = 21.676(8)$, $c = 7.474(4)$ Å, $V = 3511(3)$ Å^3, $Z = 2$, and the final $R = 0.054$. The partially oxidized Pc units (the formal charge of Pc is -1.5 in this salt and the initial closed-shell form is -2) stack regularly along the *c*-axis, forming a one-dimensional chain. Since the Pc units in the neighboring chains are related to each other by the 4_2 axis, the π–π overlaps are not possible between the chains. The PPh_4 cations are packed in the channel surrounded by the Pc chains (one-dimensional chains of the Pc units and of the PPh_4 cations are shown in Fig. 6). Each phenyl plane of PPh_4 is nearly parallel to the Pc plane. A $\bar{4}$ symmetry of PPh_4 is retained in the crystal, and this symmetry makes the Pc chain arrange in the highly symmetric fashion.

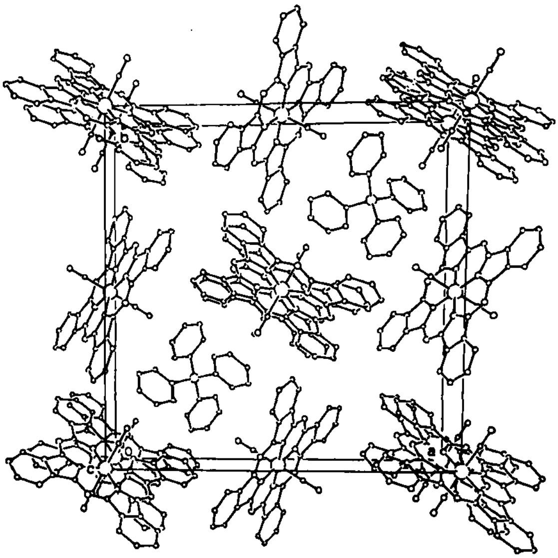


FIGURE 1
Crystal structure of $[PPh_4][Co(Pc)(CN)_2]_2$.

As shown in Table 1, the crystal of $[PPh_4][Co(Pc)(CN)_2]_2$ is highly conducting. The temperature dependence of the electrical resistivity is shown in Fig. 2. At higher temperatures, the resistivity is virtually constant. At low temperatures, the resistivity is steeply increased with decreasing the temperature, showing typical behavior of semiconductors. As suggested from the crystal structure, this crystal is a typical one-dimensional conductor; the anisotropy of conduction, $\sigma_{//c}/\sigma_{\perp c}$, has been found to be about 10^3.

The temperature dependence of the thermoelectric power (TEP) of $[PPh_4][Co(Pc)(CN)_2]_2$ is shown in Fig. 3. The TEP is linearly correlated to the temperature down to 130 K, suggesting the metallic nature of this salt. If this salt is assumed to be one-dimensional metal, the bandwidth is estimated to be about 0.5 eV from the slope. This bandwidth is slightly smaller compared with ordinary organic metals. This may be the reason why the temperature dependence of the resistivity is not clearly metallic.

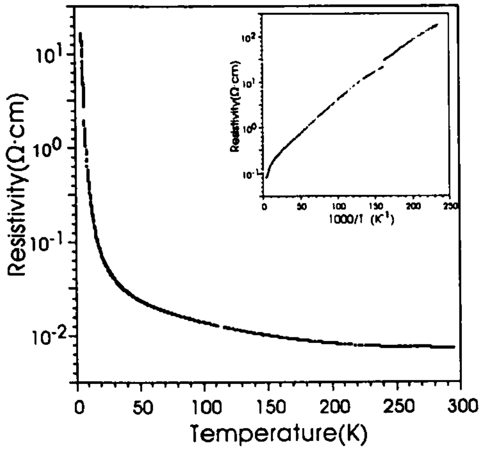


FIGURE 2 Electrical resistivity of $[PPh_4][Co(Pc)(CN)_2]_2$.

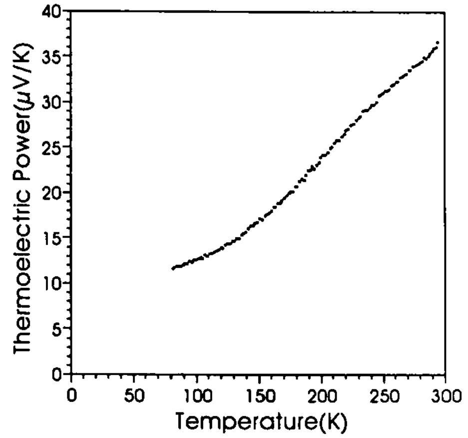


FIGURE 3 Thermoelectric power of $[PPh_4][Co(Pc)(CN)_2]_2$.

CRYSTALS WITH OPEN-SHELL CATIONS

Donor components used for the electrochemical oxidation were those for typical organic conductors, namely, TTF, TMTTF, BEDT-TTF, TMTSF, etc. During the electrocrystallization, oxidation can be occurred on donors or on both donors and the Pc units. Even when only one component is oxidized, deviation from the 1:1 stoichiometry is expected to give conductors. Among various donors tried, the combination with TMTTF or TTF gave single crystals with sufficient dimensions for X-ray structural analysis.

The crystal obtained from the combination with TMTTF has been found to be $[TMTTF][Co(Pc)(CN)_2]\cdot 2CH_3CN$. The crystal structure is shown in Fig. 4, and the crystal data are as follows; triclinic, space group $P\bar{1}$, a = 11.343(5), b = 12.153(4), c = 8.714(3) Å, α = 108.98(3), β = 104.68(3), γ = 82.02(3)°, V = 1097(1) Å^3, Z = 1, and the final R = 0.047. The Pc units form one-dimensional chains along the c-axis. The TMTTF molecule is surrounded by the Pc chains and acetonitrile molecules, and completely isolated from each other. The oxidation state of TMTTF estimated from the bond lengths is +1, and no oxidation of the Pc unit has been confirmed by the infrared spectrum. Consequently, this salt comprises radical cations of TMTTF and closed-shell anions of the Pc unit, and actually this crystal is an insulator.

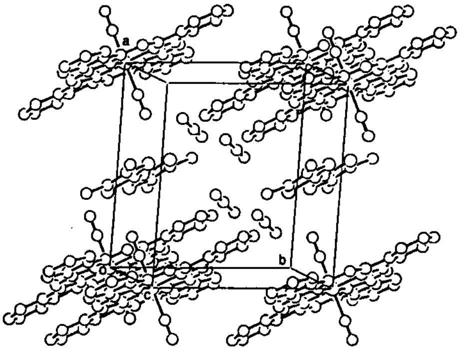


FIGURE 4 Crystal structure of [TMTTF][Co(Pc)(CN)$_2$]·2CH$_3$CN.

When TTF is combined with the Pc unit, the 1:1 salt is also obtained. As shown in Fig. 5, the crystal structure is very similar to that of [PPh$_4$][Co(Pc)(CN)$_2$]$_2$, and the crystal data are as follows; tetragonal, space group $P4_2/n$, a = 21.440(5), c = 7.488(2) Å, V = 3442(1) Å^3, Z = 4, and the final R = 0.050. This crystal structure is obtained by replacing one PPh$_4$ cation in [PPh$_4$][Co(Pc)(CN)$_2$]$_2$ by two TTF. Therefore, both the TTF molecules and the Pc units stack one-dimensionally, as shown in Fig. 6. The oxidation state of TTF has been found to be +1, and again the Pc unit is a closed-shell anion. Since the TTF radical cations interact with each other along the c-axis, this crystal becomes moderately conductive (10^{-4} Ω^{-1} cm^{-1} at room temperature).

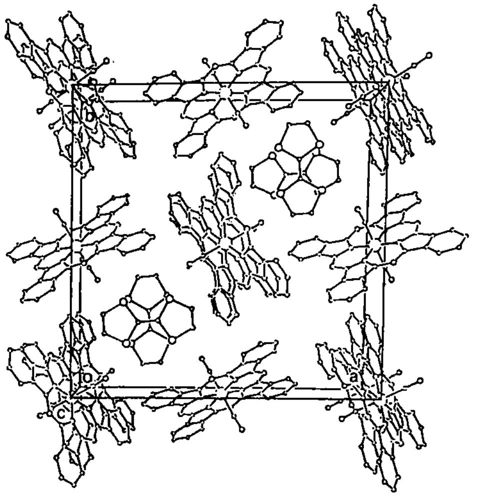


FIGURE 5 Crystal structure of [TTF][Co(Pc)(CN)$_2$]

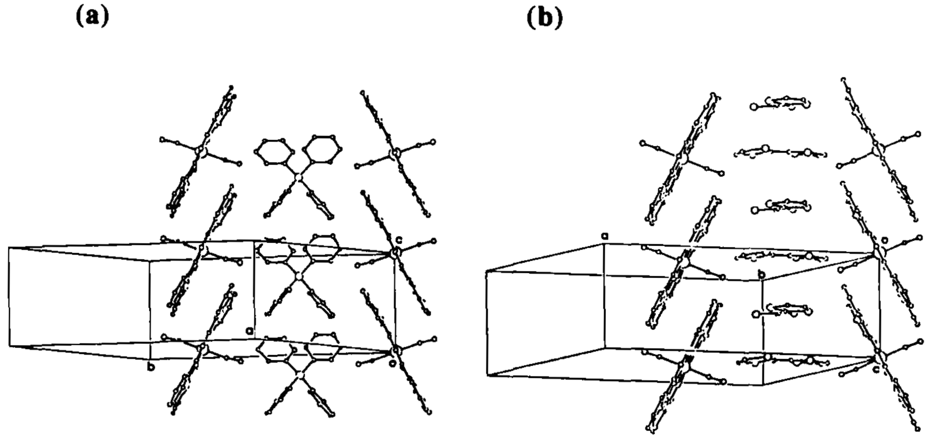


FIGURE 6 One-dimensional chains in $[\mathrm{PPh_4}][\mathrm{Co(Pc)(CN)_2}]_2$ (**a**) and in $[\mathrm{TTF}][\mathrm{Co(Pc)(CN)_2}]$ (**b**).

In conclusion, we have succeeded in the construction of the crystals composed of the axially substituted phthalocyanines and organic closed-shell or open-shell cations. The crystals so far obtained are stable, but the crystal structures are different from that expected. Control of the crystal structure is a very difficult but very important subject in current chemistry. Since there still remain many other possible combinations, the systematic study is necessary for the elucidation of the factors dominating the molecular arrangement in the lattice.

ACKNOWLEDGEMENT

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REFERENCES

1. T. Inabe and Y. Maruyama, *Chem. Lett.*, **1989**, 55.
2. T. Inabe and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, **63**, 2273 (1990).
3. T. Inabe, T. Mitsuhashi, and Y. Maruyama, in "The Physics and Chemistry of Organic Superconductors" edited by G. Saito and S. Kagoshima (Springer-Verlag, 1990), pp.408-411.
4. T. Inabe, Y. Maruyama, and T. Mitsuhashi, *Synth. Metals*, **41-43**, 2629 (1991).
5. T. Inabe, K. Morimoto, H. Hasegawa, and N. Miyajima, *Mol. Cryst. Liq. Cryst.*, in press.