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MOLECULAR CONDUCTORS BASED ON AXIALLY SUBSTITUTED PHTHALOCYANINE NEUTRAL RADICALS

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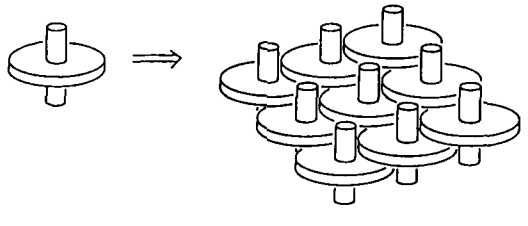
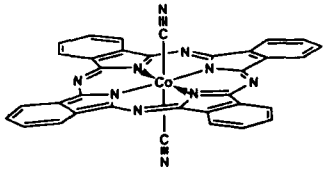
Abstract Electrocrystallization of the dicyanophthalocyaninatocobalt(III) anion, $[Co(Pc)(CN)_2]^-$, gives three kinds of neutral radical crystals which are different in dimensionality. One-dimensional arrays of $Co(Pc)(CN)_2$ are formed in the bromoform containing crystal, $Co(Pc)(CN)_2 \cdot 2CHBr_3$. Two-dimensional sheets of $Co(Pc)(CN)_2$ are formed in a crystal of $Co(Pc)(CN)_2 \cdot 2CHCl_3$. A three-dimensional network of $Co(Pc)(CN)_2$ is formed in $Co(Pc)(CN)_2 \cdot 2H_2O$. The conductivity anisotropy is in good agreement with the dimensionality of the π–π interaction. The conductivity value, which is rather high as neutral radical solids, is systematically increased with increasing the dimensionality, suggesting that the conduction-limiting factor in a neutral radical system, on-site Coulomb repulsion energy, can be reduced by increasing the dimensionality.

INTRODUCTION

Multi-dimensionality is now recognized as being essential for maintaining the metallic state at low temperatures and for achieving a superconducting state. We have approached the construction of multi-dimensional π–π overlapping molecular stacks using an axially substituted phthalocyanines.[1-4] As shown in SCHEME, the axial substituents prevent direct overlap of the molecules; instead, the molecules need to slip a large distance to make contacts between the planar parts. This is expected to make the total overlap multi-dimensional.



SCHEME



$Co(Pc)(CN)_2$

We have already examined this possibility by electrocrystallization of the potassium salt of a phthalocyaninatocobalt(III) anion which is axially substituted by two cyano groups, $K[Co(Pc)(CN)_2]$. The product crystal from the acetonitrile solution is $K[Co^{III}(Pc)(CN)_2]_2 \cdot 5CH_3CN$, in which the Pc ligand is partially oxidized.[1,2] This crystal is composed of two-dimensional sheets of $Co(Pc)(CN)_2$ just like a stacking pattern shown in SCHEME. The cation and acetonitrile molecules are packed between the sheets. Unfortunately, the immediate exclusion of acetonitrile molecules from the lattice makes it impossible to measure the intrinsic electrical properties.

After then, we have been attempting the electrochemical oxidation using different solvents, and using different cations, in order to obtain stable crystals. Among the obtained crystals, we have found that some crystals are constituted with completely oxidized Pc units and solvent molecules. Since the starting Pc unit is monoanion, these crystals are neutral radical solids. In this paper, we describe their rather high conductivity and the relationship between the conductivity and the dimensionality.

EXPERIMENTAL

The starting potassium salt of the dicyanophthalocyaninatocobalt(III) anion was synthesized following a method reported previously.[5] When the electrochemical oxidation (constant current of 0.5 - 2 μA) was carried out using a mixed solvent of bromoform and acetonitrile or acetone, needles (typical size; $0.7 \times 0.05 \times 0.05$ mm^3) with the composition $Co(Pc)(CN)_2 \cdot 2CHBr_3$ were obtained. Crystals of $Co(Pc)(CN)_2 \cdot 2CHCl_3$[6] and $Co(Pc)(CN)_2 \cdot 2H_2O$[2] were obtained as reported before.

The single crystal X-ray structural study of $Co(Pc)(CN)_2 \cdot 2CHBr_3$ was performed with a Rigaku AFC-5R diffractometer. The crystal data are as follows: monoclinic, space group $P2_1/c$, a = 7.938(3), b = 18.066(3), c = 13.020(2) Å, β = 97.23(2)°, V = 1852.3(7) Å^3, Z = 2, and the final R = 0.073 (R_w = 0.082) for 1032 independent reflections ($I_o > 3\sigma(I_o)$).

The electrical conductivity measurements were carried out by a four-probe or two-probe method depending on the size and the resistance of the specimen.

RESULTS AND DISCUSSION

$Co(Pc)(CN)_2 \cdot 2CHBr_3$

The molecular structure of the Pc unit derived from the X-ray structure analysis is practically the same as those in $Co(Pc)(CN)_2 \cdot 2CHCl_3$[6] and $Co(Pc)(CN)_2 \cdot 2H_2O$.[2] The phthalocyaninato skeleton is not so sensitive to the charge on the molecule as suggested

before.[6] In the crystal, the arrangement of Pc is different from that expected; only one-dimensional partial stacking of Pc is formed along the *a*-axis, as shown in Fig. 1.

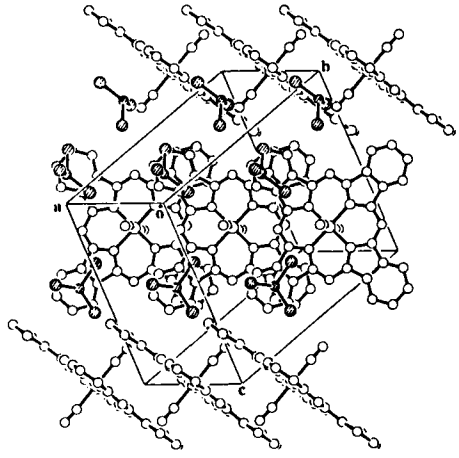


FIGURE 1 Crystal structure of $Co(Pc)(CN)_2 \cdot 2CHBr_3$.

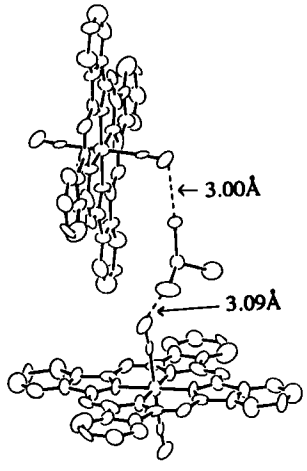


FIGURE 2 Interaction between $CHBr_3$ and $Co(Pc)(CN)_2$ in $Co(Pc)(CN)_2 \cdot 2CHBr_3$.

Bromoform molecules are located between the Pc chains so that the electronic interaction between them is prevented. There is a specific interaction between the cyano group of the Pc unit and the bromoform molecule; as shown in Fig. 2, very short contacts are formed between the Br and N atoms, 3.00 and 3.09 Å. These distances are much shorter compared with the sum of the van der Waals radii (3.4 Å). Similar intermolecular contacts were noted in 4-halobenzonitrile crystals[7] and substituted 2,3-dicyano-5,6-dichlorobenzen crystals.[8] Since two Pc units, which are almost

perpendicular to each other, are bound by one bromoform molecule, inter-chain stacking necessary for higher dimensionality becomes impossible.

The temperature dependence of the electrical resistivity of single crystal $Co(Pc)(CN)_2 \cdot 2CHBr_3$ is shown in Fig. 3. The resistivity along the *a*-axis at room temperature is about 10^2 Ω cm. The resistivity perpendicular to the *a*-axis is more than two orders higher.

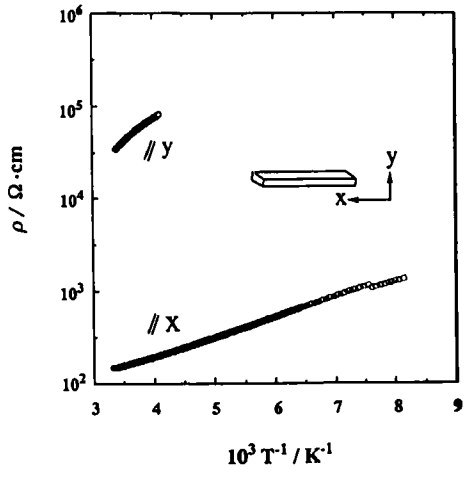


FIGURE 3 Temperature dependence of the resistivity of $Co(Pc)(CN)_2 \cdot 2CHBr_3$.

$Co(Pc)(CN)_2 \cdot 2CHCl_3$[6]

The crystal structure is shown in Fig. 4. The crystal data are as follows: triclinic, space group $P\bar{1}$, a = 10.771(5), b = 11.008(5), c = 8.431(4) Å, α = 96.89(4), β = 108.87(3), γ = 107.95(3)°, V = 872.7(8) Å^3, Z = 1, and R = 0.063 for 2989 independent reflections ($F_o > 3\sigma(F_o)$). In this case, the Pc units form a two-dimensional sheet parallel to the *ac*-plane, which is similar to that observed for the partially oxidized $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ salt. Two benzene rings in phthalocyanine overlap along the *c*-axis and one benzene ring overlap occurs along the *a*-axis. Chloroform molecules are packed between the two-dimensional Pc sheets. There is a very short contact between the carbon atom in the chloroform and the nitrogen atom in the cyano group, 3.07 Å. This distance is short enough to recognize that a hydrogen bond is formed between the C-H group in chloroform and the C≡N group in the Pc unit. The existence of chloroform produces a wide gap in the π–π interaction between the two-dimensional Pc sheets.

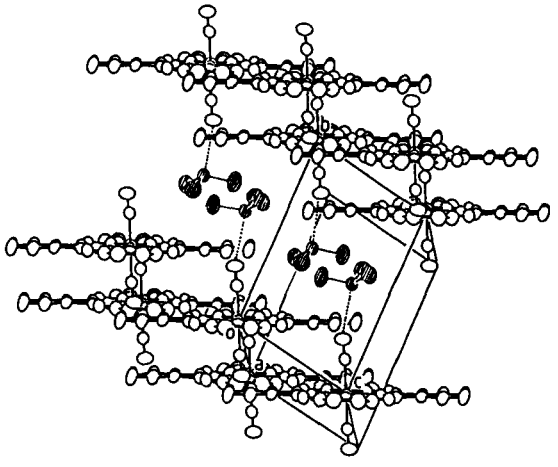


FIGURE 4 Crystal structure of $Co(Pc)(CN)_2 \cdot 2CHCl_3$.

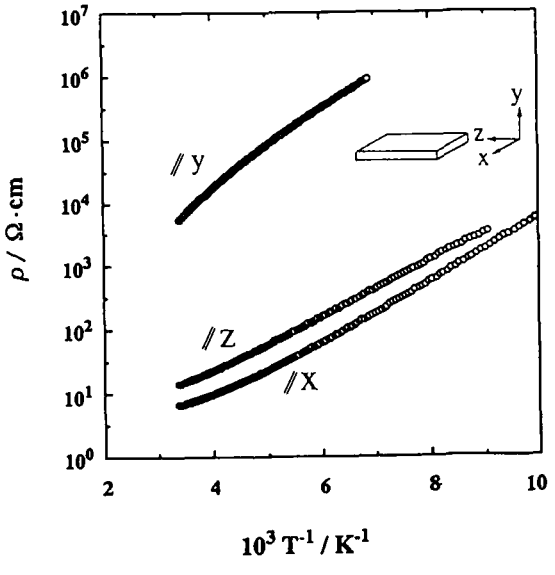


FIGURE 5 Resistivity anisotropy of $Co(Pc)(CN)_2 \cdot 2CHCl_3$.

The electrical resistivity is, as expected from the structure, clearly anisotropic. As shown in Fig. 5, the resistivities along the directions parallel to the two-dimensional Pc sheet (//*x* and //*z*) are more than two orders of magnitude lower than that along the direction perpendicular to the sheet (//*y*).

$Co(Pc)(CN)_2 \cdot 2H_2O$[2,6]

The crystal structure is shown in Fig. 6. The crystal data are as follows: monoclinic, space group $C2/m$, a = 14.173(4), b = 14.250(2), c = 7.701(2) Å, β = 115.19(2)°, V = 1407.3(6) Å^3, Z = 2, and R = 0.070 for 1144 independent reflections ($F_o > 3\sigma(F_o)$). The water molecules in the crystal act as bridges between the Pc units which are translationally related along the a-axis. Since the water molecules are aligned linearly with the axial substituents and the distance between the rings is nearly four times the thickness of aromatic rings, three other Pc rings can be incorporated between those Pc rings. Thus, a two benzene ring overlap exists along the c-axis and a one benzene ring overlap along the [112] and [1$\bar{1}$2] directions. The overall π–π interaction is completely three-dimensional.

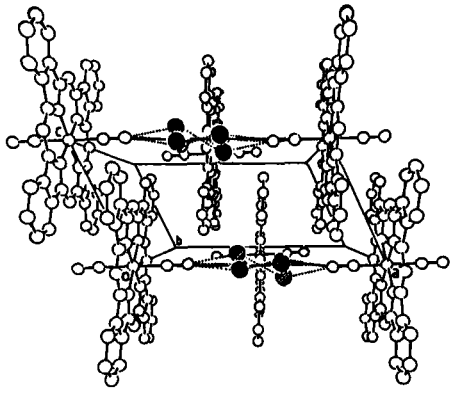


FIGURE 6 Crystal structure of $Co(Pc)(CN)_2 \cdot 2H_2O$.

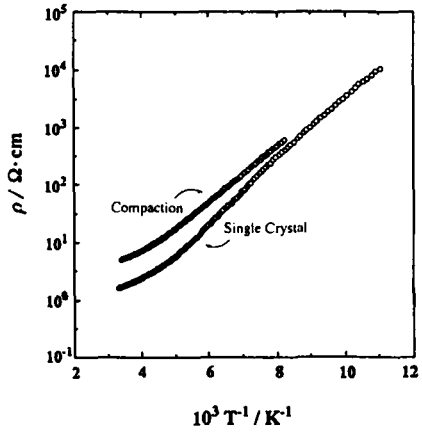


FIGURE 7 Temperature dependence of the resistivity of $Co(Pc)(CN)_2 \cdot 2H_2O$; single crystal and powder compaction.

The temperature dependence of the electrical resistivity is shown in Fig. 7. Since the crystals obtained so far have been small, we have not been able to determine the anisotropy of conduction from the single-crystal measurements. However, nearly isotropic conduction is suggested from the resistivity of the powder compacted sample; it is only slightly larger than that of the single crystal. The resistivity of the compacted sample includes the resistivities along all the directions and the contact resistance between the particles. The small difference observed is therefore indicative of the isotropic character of $Co(Pc)(CN)_2 \cdot 2H_2O$.

General Remarks

A systematic comparison between these three neutral radical crystals may give important information about this system. From a structural point of view, a common feature is the pattern of the molecular overlap; the existence of the axial cyano groups makes the π–π overlap only a part of the whole π-conjugated system. The total π–π interaction in the crystal is, however, considerably different from each other.

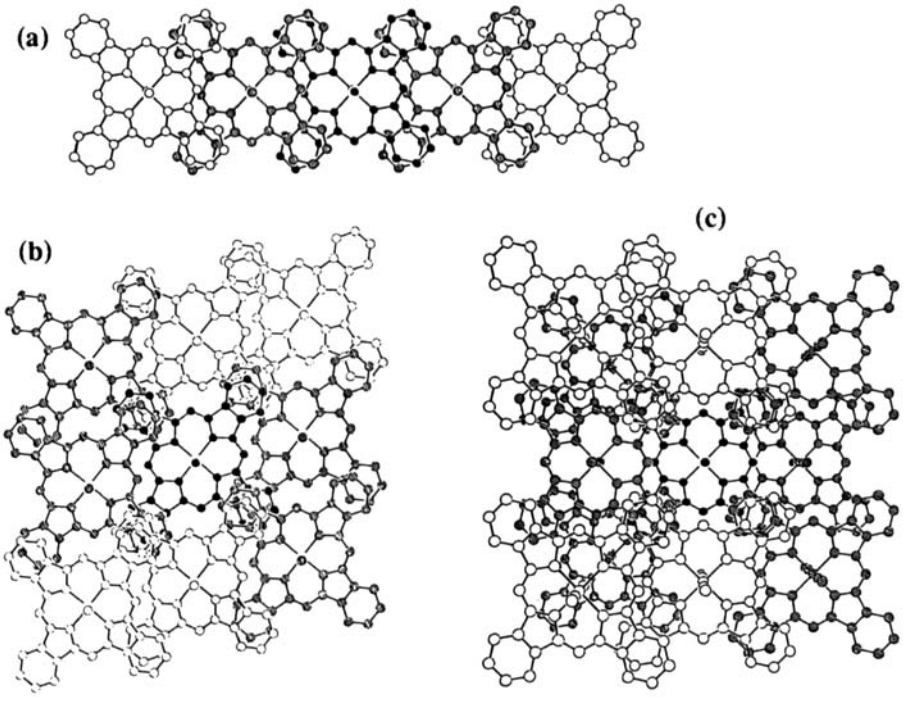


FIGURE 8 Three patterns of the Pc unit stacking; one-dimensional (**a**), two-dimensional (**b**), and three-dimensional (**c**). Hatched molecules have a π–π interaction with the central molecule.

The three interaction patterns are summarized in Fig. 8. In $Co(Pc)(CN)_2 \cdot 2CHBr_3$, the bromoform molecules incorporated isolate individual one-dimensional Pc chains; one Pc ring interacts only with two neighbors. In $Co(Pc)(CN)_2 \cdot 2CHCl_3$, the chloroform molecules do not prevent the additional overlap between the one-dimensional Pc chains; one Pc ring interacts with four neighbors, two above and two below, forming a sheet. In $Co(Pc)(CN)_2 \cdot 2H_2O$, further interaction between the Pc sheets becomes possible; one Pc ring now interacts with six neighbors, three above and three below. One-dimensionality of $Co(Pc)(CN)_2 \cdot 2CHBr_3$, two-dimensionality of $Co(Pc)(CN)_2 \cdot 2CHCl_3$, and three-dimensionality of $Co(Pc)(CN)_2 \cdot 2H_2O$ in the electronic system are consistent with the conductivity anisotropy observed.

The distance between the overlapped rings is not very short; in the range of 3.5-3.6 Å for all the $Co(Pc)(CN)_2$ neutral radical crystals. This is because the molecular framework is inappropriate for stacking by a ring-over-bond type overlap. However, the conductivity data indicate that the π–π interaction is sufficient. As a matter of fact, their conductivities are much higher than that expected for neutral radical crystals. In general, it is rather difficult to make a conducting neutral radical crystal because of the effects of on-site Coulomb repulsion. The lowest resistivity value reported so far for neutral radical solids is *ca.* $10^2\ \Omega$ cm for a powder compact.[9] The resistivity data for the $Co(Pc)(CN)_2$ radical crystals are summarized in Fig. 9.

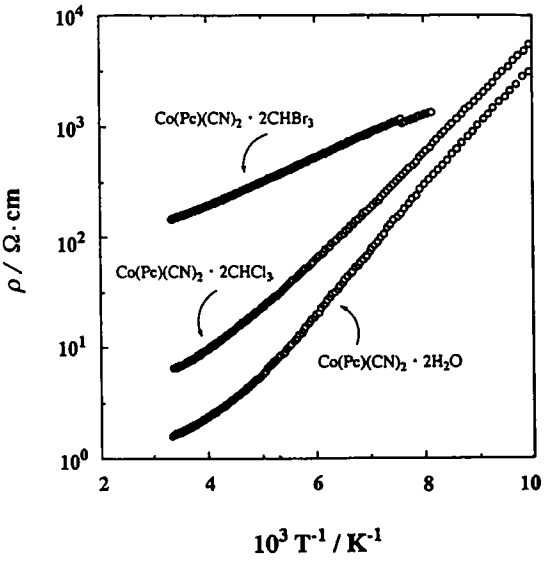


FIGURE 9 Resistivities of the three $Co(Pc)(CN)_2$ neutral radical crystals.

It can be noticed that the resistivity values at room temperature for $Co(Pc)(CN)_2 \cdot 2CHCl_3$ and $Co(Pc)(CN)_2 \cdot 2H_2O$ are lower than the lowest value reported before for neutral radical crystals. It is also notable that the resistivity decreases with increasing the dimensionality. This fact strongly suggests that the conduction-limiting factor, on-site Coulomb repulsion energy, may depend on the dimensionality of the electronic system.

Finally, the possibility of extrinsic conduction in these crystals has been checked by thermoelectric power measurements. One of the results for $Co(Pc)(CN)_2 \cdot 2CHCl_3$ is shown in Fig. 10. The thermoelectric power is linearly correlated to T^{-1}, indicating that the semiconduction in this crystal is intrinsic in origin. Using the conductivity data, the electron to hole mobility ratio, μ_e/μ_h, is obtained as 1.09; both electrons and holes contribute to the transport. Similar results have been obtained for $Co(Pc)(CN)_2 \cdot 2CHBr_3$.

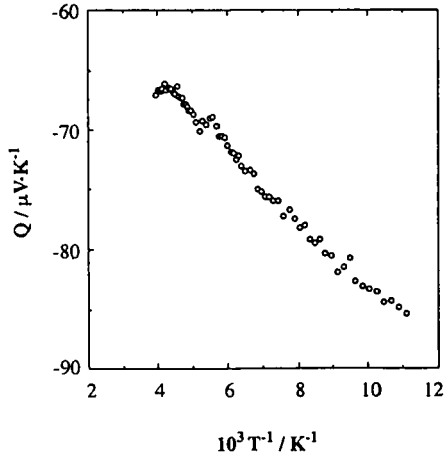


FIGURE 10 Temperature dependence of the thermoelectric power of $Co(Pc)(CN)_2 \cdot 2CHCl_3$.

In conclusion, we have found highly conducting neutral radical crystals based on the $Co(Pc)(CN)_2$ neutral radical. Their resistivities are lower than those for other neutral radical solids, especially the value for $Co(Pc)(CN)_2 \cdot 2H_2O$, 10^0 Ω cm at room temperature, is the lowest so far reported. The resistivity value is found to depend on the dimensionality of the electronic system, suggesting that the on-site Coulomb repulsion energy decreases with increasing the dimensionality.

ACKNOWLEDGEMENT

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