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DIMENSIONALITY CONTROL OF PHTHALOCYANINE BASED CONDUCTORS

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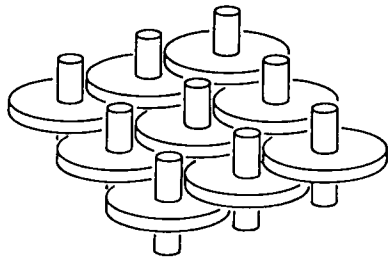
Abstract A wide variety of crystal structures can be obtained by the electrochemical oxidation of the potassium salt of an axially substituted phthalocyanine anion with changing the solvent used. The dimensionality of the π–π interaction and the electronic system can be varied in the range from one-dimensional to three-dimensional. They are relatively conductive despite that phthalocyanine is completely oxidized (neutral radical).

INTRODUCTION

Dimensionality of the electronic system in molecular conductors is determinant of the ground state at low temperatures. This factor is essentially derived from the molecular arrangement in the lattice. For ordinary π-conjugated molecules, one-dimensional columns are preferentially formed, since they have a tendency to crystallize with face-to-face overlaps. Higher dimensionality has been achieved when the molecules are modified with chalcogen atoms at the peripheral positions so that they can interact transversely with adjacent molecules. Our approach to the construction of multi-dimensional systems is slightly different from this ordinary way. If a molecule has projections at its center, it cannot be stacked directly above another molecule. Consequently, the molecules need to slip a large distance to make contacts between the planar parts. This will give a chance of forming two-dimensional sheets.

Metal-phthalocyanines are the desirable component, since it is easy to introduce axial substituents. We have already found that the potassium salt of a cobalt(III)phthalocyanine anion which is axially substituted by two cyano groups, $K^+[Co(Pc)(CN)_2]^-$, can be oxidized electrochemically in acetonitrile, yielding partially oxidized $K[Co(Pc)(CN)_2]_2$-



two-dimensional structure

$5CH_3CN$.[1-4] The crystal is composed of two-dimensional sheets of phthalocyanines as expected. The solvent molecules in the crystal are, however, easily removed from the lattice, resulting in mosaic distortion of the crystal.

In order to obtain stable crystals, we have been attempting the electrochemical oxidation using various solvents. In the course of this research, we have found that a rather wide variety of crystal structures can be obtained by slightly changing the solvent used. In some cases, crystals have been found to be constituted with the completely oxidized (neutral radical) Pc units and solvent molecules. Such neutral radical crystals are expected to be not conductive, but they have been found to be rather conductive. Furthermore, the conductivity has been found to be correlated to the dimensionality of the electronic system. We describe the structures and transport properties of these crystals as well as the properties of some other crystals obtained.

NEUTRAL RADICAL CRYSTALS

$Co(Pc)(CN)_2 \cdot 2CHBr_3$[5]

When the electrochemical oxidation was carried out using a mixed solvent of bromoform and acetnitrile or acetone, $Co(Pc)(CN)_2 \cdot 2CHBr_3$ was obtained. In this crystal, only one-dimensional partial stacking of Pc is formed along the *a*-axis, as shown in Fig. 1.

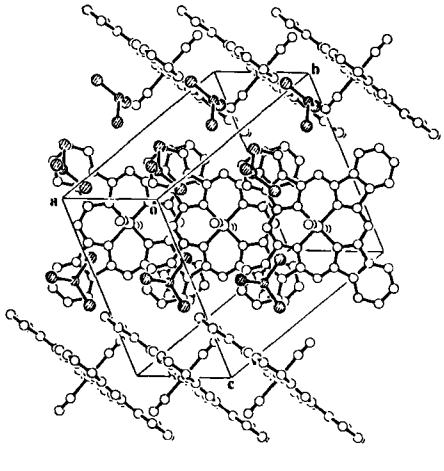


FIGURE 1 Crystal structure of $Co(Pc)(CN)_2 \cdot 2CHBr_3$.

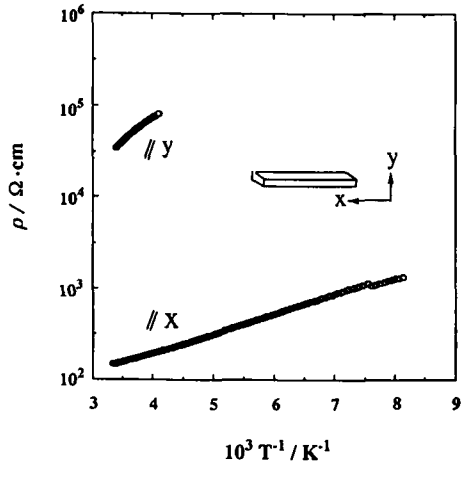


FIGURE 2 Electrical resistivity of $Co(Pc)(CN)_2 \cdot 2CHBr_3$.

Bromoform molecules located between the Pc chains are tightly bound with the cyano groups, which makes inter-chain overlap impossible. The electrical resistivity at room temperature (Fig. 2) along the *a*-axis is about 10^2 Ω cm, while that perpendicular to the *a*-axis is more than two orders higher.

Co(Pc)(CN)$_2$·2CHCl$_3$[6]

When a mixed solvent of chloroform and acetonitrile was used for the electrocrystallization, platelet crystals of Co(Pc)(CN)$_2$·2CHCl$_3$ were obtained. In the crystal, the Pc units form a two-dimensional sheet parallel to the *ac*-plane (Fig. 3). Chloroform molecules are packed between the two-dimensional Pc sheets. The electrical resistivity is, as expected from the structure, clearly anisotropic; the resistivities along the directions parallel to the two-dimensional Pc sheet (//*x* and //*z* in Fig. 4) are more than two orders lower than that perpendicular to the sheet (//*y*).

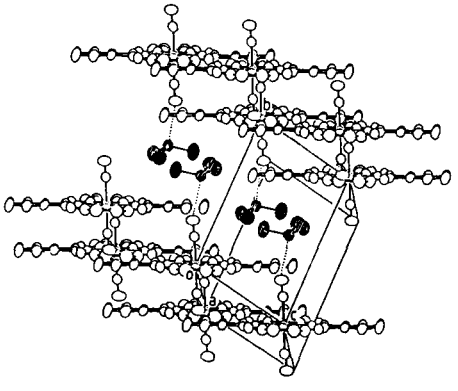


FIGURE 3 Crystal structure of Co(Pc)(CN)$_2$·2CHCl$_3$.

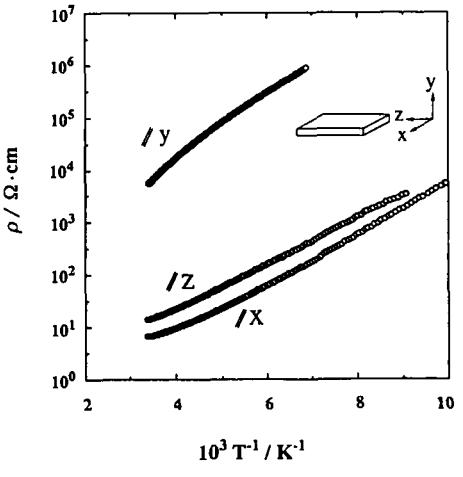


FIGURE 4 Electrical resistivity of Co(Pc)(CN)$_2$·2CHCl$_3$.

Co(Pc)(CN)$_2$·2H$_2$O[6]

The H_2O containing crystal, Co(Pc)(CN)$_2$·2H_2O, was obtained by using a mixed solvent of H_2O and benzonitrile or acetonitrile. In the crystal, a rather complicated three-dimensional network of Pc is formed; one Pc unit interacts with two adjacent Pc units along the *c*-axis, two adjacent Pc units along the [112] direction, and two adjacent Pc units along the [1$\bar{1}$2] direction (Fig. 5). This three-dimensional π–π interaction is

clearly demonstrated by the isotropic conductivity; the resistivity of the powder compacted sample is only slightly larger than that of the single crystal, as shown in Fig. 6.

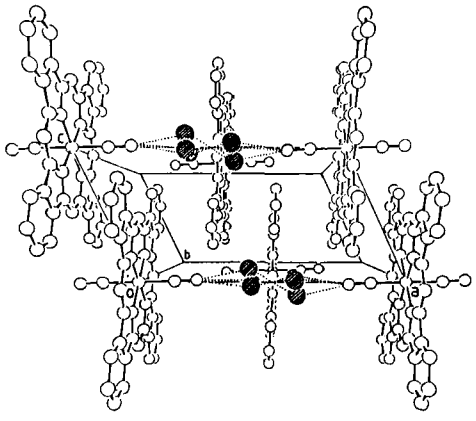


FIGURE 5 Crystal structure of $Co(Pc)(CN)_2 \cdot 2H_2O$.

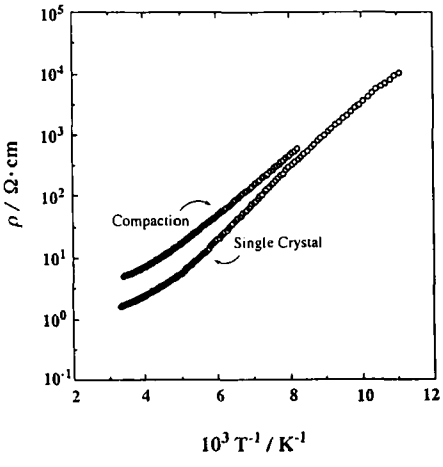


FIGURE 6 Electrical resistivity of $Co(Pc)(CN)_2 \cdot 2H_2O$.

These three neutral radical crystals have an interesting feature. By changing the solvent included in the lattice, the pattern of the π–π interaction is systematically changed; one-dimensional for $CHBr_3$, two-dimensional for $CHCl_3$, and three-dimensional for H_2O. The measurements of the anisotropy of the electrical conductivity have confirmed that the dimensionality of the electronic system follows the dimensionality of the π–π interaction. Furthermore, it has been found that the resistivity value at room temperature is also systematically changed; 10^2 Ω cm for one-dimensional $Co(Pc)(CN)_2 \cdot 2CHBr_3$, 10^1 Ω cm for two-dimensional $Co(Pc)(CN)_2 \cdot 2CHCl_3$, and 10^0 Ω cm for three-dimensional $Co(Pc)(CN)_2 \cdot 2H_2O$. This suggests that the conduction

limiting factor for neutral radical solids, i.e., on-site Coulomb repulsion energy, is reduced when the dimensionality of the electronic system is increased.

CRYSTALS OBTAINED FROM OTHER SOLVENTS

Among various solvents used for the electrocrystallization, following solvents gave single crystals; methanol, suberonitrile, DMSO, and a mixed solvent of benzene and acetonitrile. Their electrical resistivities are relatively low (Fig. 7). Especially the resistivity of the crystal obtained from methanol is quite low ($\sim 10^{-1}$ Ω cm at room temperature). This suggests that the crystal is composed of the partially oxidized Pc units. Unfortunately, all the crystals shown here are not large enough to determine the crystal structure by X-ray diffraction technique.

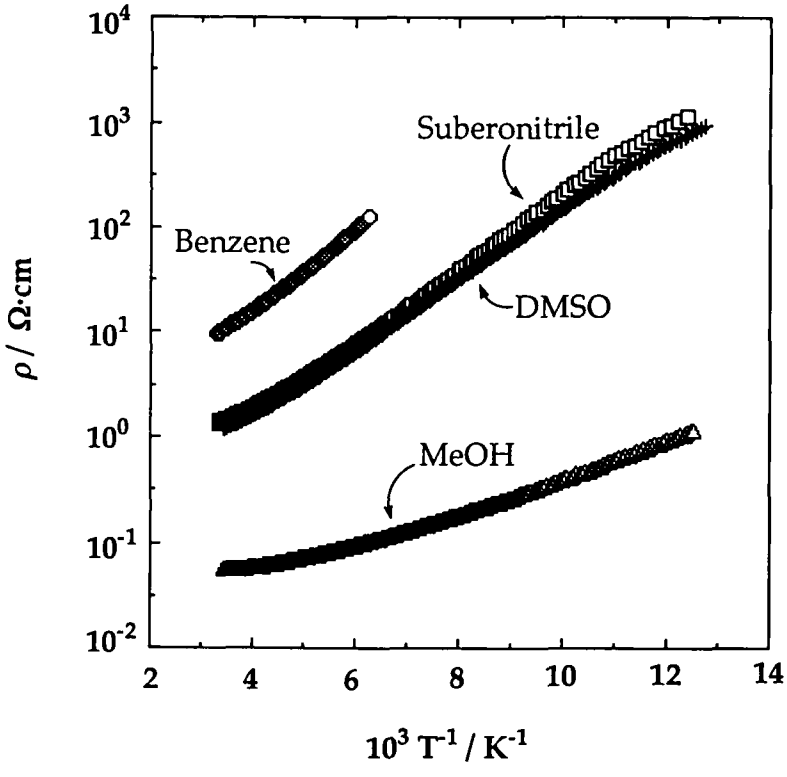


FIGURE 7 Electrical resistivity of the single crystals obtained electrochemically from the solutions of methanol, suberonitrile, DMSO, and (a mixed solvent of acetonitrile and) benzene.

In conclusion, the electrochemical oxidation of K·Co(Pc)$(CN)_2$ has been found to give conducting crystals with a wide variety of crystal structures depending on the solvent used. The solvent molecules are incorporated in the lattice, and the interaction between the solvent molecules and the Pc units dominates the molecular packing and the π–π interaction between the Pc units in the crystal. With utilizing this feature, the dimensionality of the electronic system in the neutral Pc radical crystals has been found to be controlled by changing the solvent molecules included in the lattice.

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