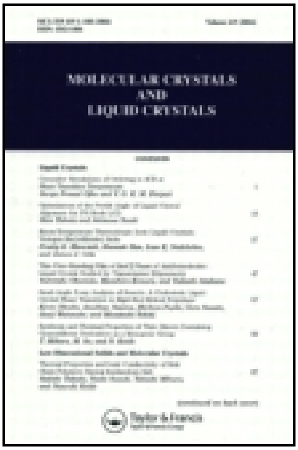

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Two-Dimensional Molecular Arrangement in Phthalocyanine Based Conducting Crystals

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TWO-DIMENSIONAL MOLECULAR ARRANGEMENT IN PHTHALOCYANINE BASED CONDUCTING CRYSTALS

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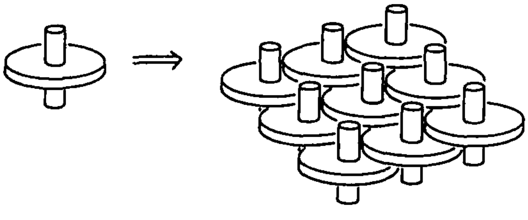
Abstract Molecular arrangements in the crystals composed of the dicyanocobalt(III)phthalocyanine units, $Co(Pc)(CN)_2$, have been examined. When the unit is closed-shell anion, the crystals contain one-dimensional arrays or isolated dimers of the $Co(Pc)(CN)_2$ units. Two-dimensional sheets of $Co(Pc)(CN)_2$, which are similar to those observed for the partially oxidized potassium salt, are formed when the unit is completely oxidized with existence of chloroform. A three-dimensional network of $Co(Pc)(CN)_2$ is also obtained when the unit is oxidized with existence of water. Resultant neutral radical crystals, $Co(Pc)(CN)_2.2CHCl_3$ and $Co(Pc)(CN)_2.2H_2O$, are highly conducting.

INTRODUCTION

Control of the molecular arrangement in the solid state is recognized as important as synthesizing the component molecules for conductors, magnets, and non-linear optical crystals.[1] Especially, for molecular conductors, π–π overlapping is essential for the conduction. Simple one-dimensional π–π stacking is however not enough to maintain the metallic state at low temperatures, and consequently to achieve a superconducting state. Now, it is well recognized that multi-dimensional π–π interaction is necessary to construct molecular superconductors. Introduction of chalcogen atoms at the peripheral positions of π-conjugated molecules may be a promising approach to making molecules interact both along the stacking and side-by-side directions, and many synthesizing efforts are made on this basis. Our proposal stands on a different basis.[2-5] When a planar π-conjugated molecule has projections at the center, the molecule cannot stack directly above another molecule. This situation gives a possibility to form a two-dimensional sheet as shown in SCHEME I. For this purpose,



SCHEME I

phthalocyanines are a desirable candidate, since the existence of the central metal makes it feasible to introduce axial substituents. We have already found that the potassium salt of cobalt(III)phthalocyanine anion which is axially substituted by two cyano groups, $K^+[Co(Pc)(CN)_2]^-$, can be partially oxidized electrochemically in acetonitrile. The crystal, $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$, is not stable in open air, since the solvent molecules included in the crystal are easily removed from the lattice. The crystal structure is, however, prominent. As shown in Fig. 1, the crystal is composed of two-dimensional sheets of phthalocyanines, and the cation and acetonitrile molecules are packed between the sheets. This crystal structure encouraged us, and we have been trying the electrochemical oxidation using different solvents, and using different cations, in order to obtain stable conductors based on this $Co(Pc)(CN)_2$ unit. In this paper, we describe the crystal structures and some electrical properties of the crystals obtained.

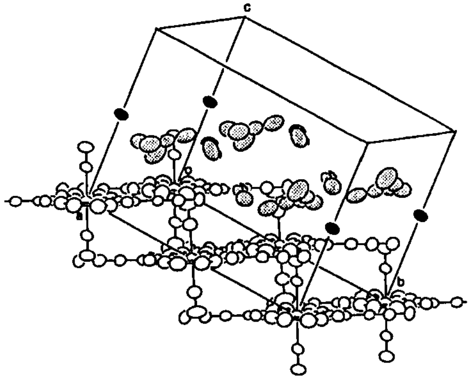


FIGURE 1 Crystal structure of $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$.

SIMPLE SALTS

Simple salts with various types of organic closed-shell cations can be prepared by metathesis of the potassium salt and iodides or bromides of the cation desired. In this case, both cation and anion are closed-shell, and the crystal is electrically insulating. We have examined their crystal structures to see whether the two-dimensional sheet structure obtained for $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ is always dominant for the crystallization of the unit used or it can occur only when the Pc ring is oxidized. Among four simple salts studied (tetra-*n*-heptylammonium, *n*-tetradecylpyridinium, dimethyldiphenylphosphonium, and *p*-dimethylaminophenyl-trimethylammonium salts), none has been found to have the sheet structure. As an example, the crystal structure of (*n*-tetradecylpyridinium)$Co(Pc)(CN)_2 \cdot CH_3CN$ is shown in Fig. 2. In this case, two kinds of crystallographically independent Pc units exist. The Pc unit B forms one-dimensional π–π overlapping with those related by translation along the *c*-axis, but the unit A is rather isolated by the cations. Similarly, only isolated dimers or one-dimensional π–π

overlapping of the Pc units are observed in the crystals of the other salts. One reason why the Pc units do not form two-dimensional sheets in the simple salts is considered to be due to the electrostatic repulsion force operated between the cations and/or between the anions. If the Pc units form two-dimensional sheets, the cations have to arranged in two-dimensional array. This is much more energetically unfavorable compared with the arrays of alternately arranged cations and anions.

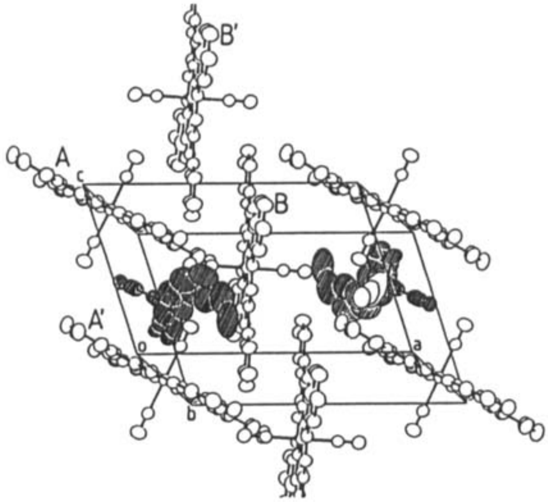


FIGURE 2 Crystal structure of (*n*-tetradecylpyridinium)Co(Pc)$(CN)_2 \cdot CH_3CN$.

NEUTRAL RADICAL CRYSTALS

In order to convert the electrically insulating simple salts to conductive crystals, we have been utilizing a technique of electrochemical oxidation. In some cases, it was found that the crystals obtained are composed of the completely oxidized Pc units and solvents.[6] Since the starting Pc unit is a closed-shell monoanion, the oxidized form is a neutral radical. So far, we have studied two kinds of these crystals; Co(Pc)$(CN)_2 \cdot 2CHCl_3$ and Co(Pc)$(CN)_2 \cdot 2H_2O$.

The crystal structure of Co(Pc)$(CN)_2 \cdot 2CHCl_3$ is shown in Fig. 3. The Pc units

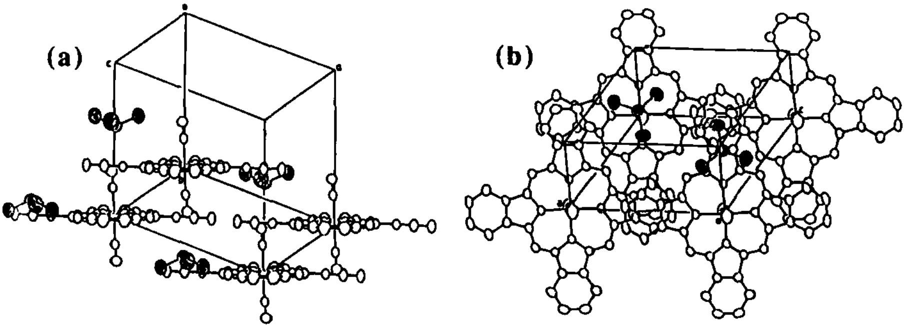


FIGURE 3 Crystal structure of Co(Pc)$(CN)_2 \cdot 2CHCl_3$: (a) view along the Pc plane; (b) view perpendicular to the Pc plane.

form two-dimensional sheets just as seen in $K[Co(Pc)(CN)_2]_2{\cdot}5CH_3CN$. Two of the four benzene rings of Pc are overlapped with each other along the *c*-axis, and one benzene ring overlapping exists along the *a*-axis. The chloroform molecules which interact with the axial cyano group by weak hydrogen bond are packed between the two-dimensional sheets.

The crystal structure of $Co(Pc)(CN)_2{\cdot}2H_2O$ is shown in Fig. 4. The space group is *C2/m*, and interactions between the Pc units are rather complicated. Two benzene ring overlapping exists along the *c*-axis and one benzene ring overlapping does along the [112] and $[1\bar{1}2]$ directions. The total π–π interaction is, therefore, three-dimensional. The water molecules are hydrogen bonded with the axial cyano group and with each other, and act as a bridge between the Pc units which are translationally related along the *a*-axis.

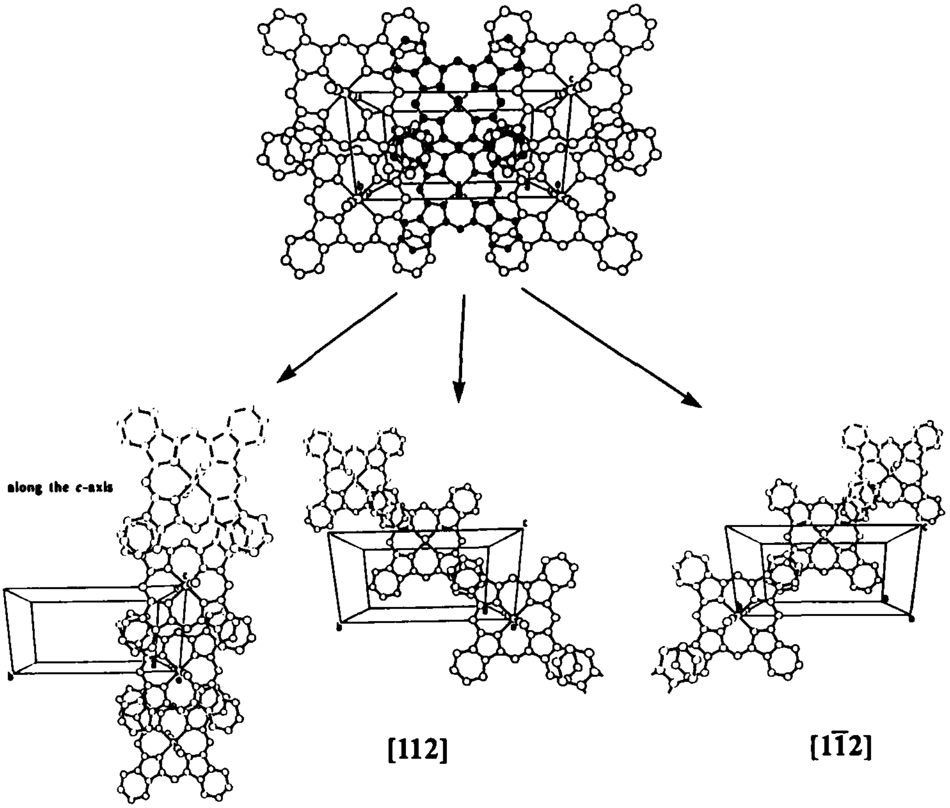


FIGURE 4 Crystal structure of $Co(Pc)(CN)_2{\cdot}2H_2O$. Interactions along the three directions are extracted.

As mentioned in the previous section, when the Pc unit is not oxidized, the two-dimensional sheet structure has not been obtained. When the Pc unit is oxidized, it becomes a neutral radical and electrostatic repulsion between them is no longer operated in the crystal. This makes the Pc units close enough to form two-dimensional sheets or a three-dimensional network of $\pi-\pi$ overlapping. Furthermore, if the transfer integral in the HOMO-HOMO overlapping is large, these two- and three-dimensional structures are further stabilized. Actually, this is supported by their low electrical resistivity. As shown in Fig. 5, these two neutral radical crystals are unusually conductive. In general, neutral radical crystals are not conductive because of the on-site Coulomb repulsion. The higher dimensionality of these crystals could reduce the on-site Coulomb repulsion.

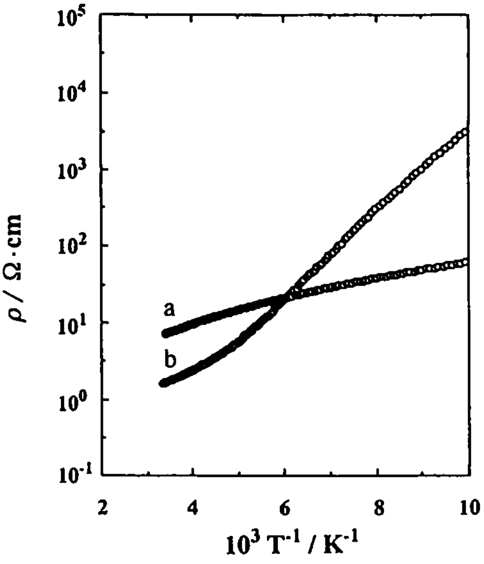


FIGURE 5 Electrical resistivity of $Co(Pc)(CN)_2 \cdot 2CHCl_3$ (a) and $Co(Pc)(CN)_2 \cdot 2H_2O$ (b).

OTHER OXIDIZED CRYSTALS

Attempts have been made to obtain partially oxidized crystals by using different solvents and different cations. Some of the electrochemical products are crystalline, but they are too thin or too small to perform X-ray structure analysis. The conductivity values are summarized in Table 1. The compositions of these products are not clear at the present stage, and some of them could be a neutral radical crystal. Some crystals may also include crystal solvents.

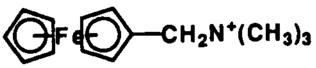
Solvents and cations are needed to be designed to be perfectly fitted to the space made between the two-dimensional sheets of $Co(Pc)(CN)_2$. At the present stage, we have no rationalized direction for the choice of solvents and cations. The sheet structure so far found is only one type, in which the units are rather tightly packed. However, there might be another type of two-dimensional sheet structure in which the $Co(Pc)(CN)_2$ units are rather loosely packed. The axial substituents, the central metal, and the π-ligand itself can be replaced by some other components. These extension will give useful information about the molecular packing of this type of component molecules.

TABLE 1 Electrical conductivity of some electrochemical products

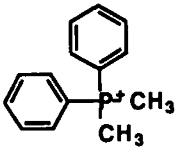
Starting simple salt	Solvent	Crystal appearance	Conductivity at room temperature$^{a)}$ / Ω^{-1} cm^{-1}
$K^+[Co(Pc)(CN)_2]^-$	MeOH	needle	$1.8 \times 10^{1*}$
$1^+[Co(Pc)(CN)_2]^-$	CH_3CN	needle	3.0×10^{-2}
$2^+[Co(Pc)(CN)_2]^-$	CH_3CN	needle	2.7×10^{-1}
$3^+[Co(Pc)(CN)_2]^-$	CH_3CN	needle	1.6×10^{-1}
$4^+[Co(Pc)(CN)_2]^-$	CH_3CN	powder	7.2×10^{-2}
$5^+[Co(Pc)(CN)_2]^-$	CH_3CN	plate	$7.5 \times 10^{-3*}$

$^{a)}$powder compaction. *single crystal.

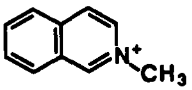
1^+ =



2^+ =

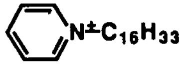


3^+ =



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

5^+ =



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