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Crystal Structure of the Electrochemical Product of Potassium Dicyanophthalocyaninatocobalt(III). Novel Two-Dimensional Stacking Interaction of Phthalocyanine

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The crystal obtained by electrocrystallization of potassium dicyanophthalocyaninatocobalt(III), K[Co(Pc)$(CN)_2$], in acetonitrile has been found to be a cation deficient salt, K[Co(Pc)$(CN)_2]_2(CH_3CN)_5$. The structural study has indicated that partly overlapped phthalocyanine rings form a two-dimensional sheet.

Recently, a highly conductive single crystal was obtained by electrocrystallization of K[Co(Pc)$(CN)_2$] in acetonitrile and its properties were reported.$^{1-3)}$ Although the crystal size was relatively large, the crystal structure was not fully determined due to a mosaic disorder. Since the component molecule has axial substitutents, the molecular overlap is expected not to be the type observed for low-dimensional metals composed of planar phthalocyanines.$^{4)}$ In the present study, in order to elucidate the molecular arrangement in this compound by X-ray analysis, crystal growth was attempted by the reported method.$^{1)}$ However, some deformation of crystals was observed under a microscope immediately after removing the solvent from the crystal surface. Therefore, during the X-ray measurements in this study it was attempted to keep the crystal in the presence of its solution. By this procedure it has become possible to collect the diffraction data, and the crystal structure thus obtained is presented in this letter.

Diffraction data were collected at room temperature using an automated RIGAKU AFC-5R four-circle diffractometer with MoKα radiation. A crystal was sealed in a glass capillary with the anode-side solution in the electrochemical cell used for

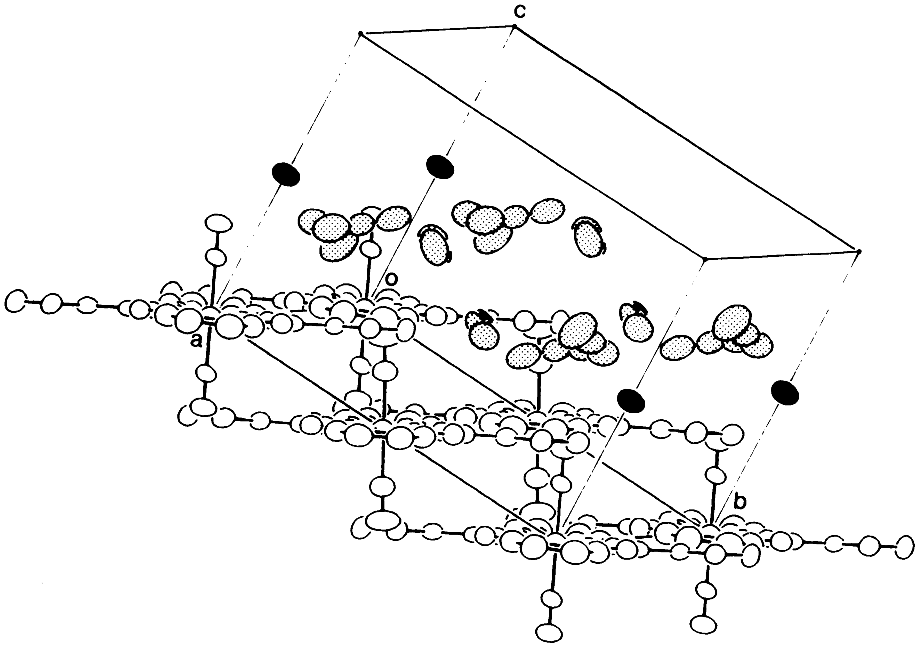

Fig. 1. Crystal structure of $K[Co(Pc)(CN)_2]_2(CH_3CN)_5$; fully and lightly shaded ellipsoids indicate potassium and acetnitrile, respectively.

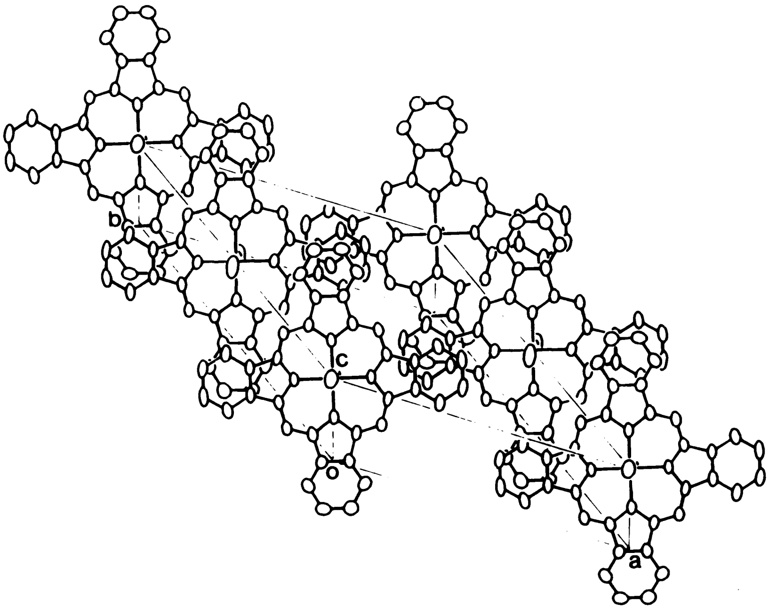

Fig. 2. Molecular overlap in the two-dimensional phthalocyanine sheet; viewed along the direction perpendicular to the molecular plane.

electrocrystallization. Crystal data; triclinic, space group $P\bar{1}$, a=15.577(3), b=16.626(3), c=10.645(2) Å, α=94.89(2), β=99.22(2), γ=138.37(1)°, V=1717.3(7) Å^3, Z=1. 4849 independent reflections with $|F_o|>3\sigma(|F_o|)$ were used for a structure analysis. The composition of this material was found to be $K[Co(Pc)(CN)_2]_2(CH_3CN)_5$ (one unit in the unit cell); an anisotropic block-diagonal least-squares refinement for non-hydrogen atoms with isotropic hydrogen atoms gave final R value of 0.050.

The crystal structure is shown in Fig. 1. It can be seen that cobalt and potassium atoms are located at the center of inversion. Two axial cyano groups are bound to the cobalt atom. Figure 2 shows the crystal structure viewed along the direction perpendicular to the phthalocyanine plane. Planar phthalocyanine rings form a slipped stack due to the axial substituents along the b-axis. In addition to this stacking structure, a partial overlap between phthalocyanine rings can be seen along the [210] direction. Consequently, phthalocyanine rings form a two-dimensional sheet in the ab plane. Distances between the overlapped benzene rings are in the range between 3.45 and 3.57 Å. Potassium ions and acetonitrile molecules are located between the sheets composed of phthalocyanine rings. Therefore, there is no direct interaction between the two-dimensional sheets. The situation of the potassium ion is shown in Fig. 3. The potassium ion is surrounded by two nitrogen atoms of the axial cyano groups and four nitrogen atoms of acetonitrile molecules. The other acetonitrile molecules which do not coordinate to the potassium ion occupy the remaining space and are positionally and orientationally disordered. The structural transformation during the drying process has been confirmed by the powder diffraction pattern of the dried material, which is not consistent with the structure solved

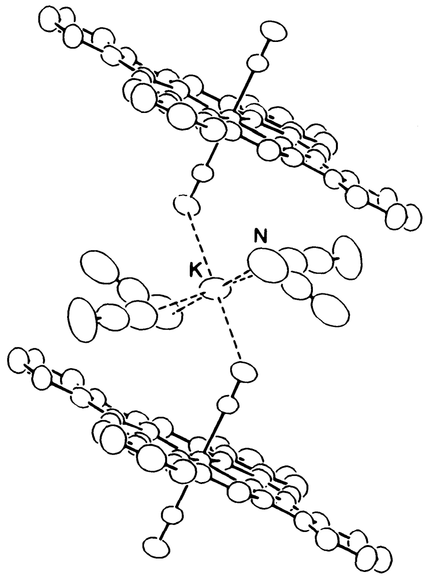

Fig. 3. Geometry of coordination of the potassium ion.

in this study. This transformation may be related to the exclusion of acetonitrile molecules from the lattice. Although the mosaic distortion occurs in this crystal, the electrical conductivity of the dried material is high ($\sim 10\ \Omega^{-1}\mathrm{cm}^{-1}$ at room temperature). This fact is consistent with that the phthalocyanine ring is partially oxidized in this material.

In conclusion, this study has indicated that the product which we obtained by electrocrystallization of $\mathrm{K[Co(Pc)(CN)_2]}$ is a cation deficient salt, $\mathrm{K[Co(Pc)(CN)_2]_2(CH_3CN)_5}$. The lattice is constructed of two-dimensional phthalocyanine sheets and potassium ions which are surrounded by acetonitrile molecules and the axial CN groups. The axial substituents are responsible for the two-dimensional stacking of the phthalocyanine rings.

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