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HIGHLY CONDUCTIVE SINGLE CRYSTALS OF METALLOPHTHALOCYANINE

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Potassium dicyanocobalt(Ⅲ)phthalocyanine was electrolyzed to form large single crystals (>4 mm) of cyanocobalt(Ⅲ)phthalocyanine with interplaner distance of 3.45 Å which showed conductivity of 5.7×10^1 S/cm without doping.

Phthalocyanines are of much interest as new materials for conductor, photoelectric conversion systems, etc. The electrochemical redox behaviours of phthalocyanine complexes have been reported.[1,2] These phthalocyanine complexes have been expected to provide low-dimensional conductive materials.[3,4] In the present paper, we report basic characteristics of the highly conductive single crystals of phthalocyanine complexes obtained through electrolysis.

Potassium dicyanocobalt(Ⅲ)phthalocyanine ($K[PcCo(CN)_2]$) was prepared by the reaction of $PcCoCl_2$ with KCN in boiling ethanol and purified by extraction with acetone.[5] Cyclic voltammogram for 1.5×10^{-4} molar solution of $K[PcCo(CN)_2]$ in acetonitrile

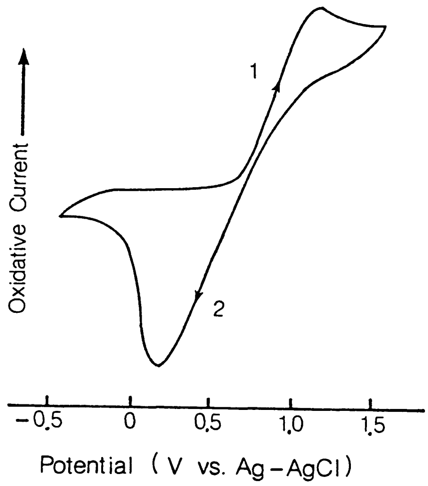

Fig. 1. Cyclic voltammogram for $K[PcCo(CN)_2]$ in acetonitrile. (1.5×10^{-4} mol/dm^3, scan rate 100mV/s)

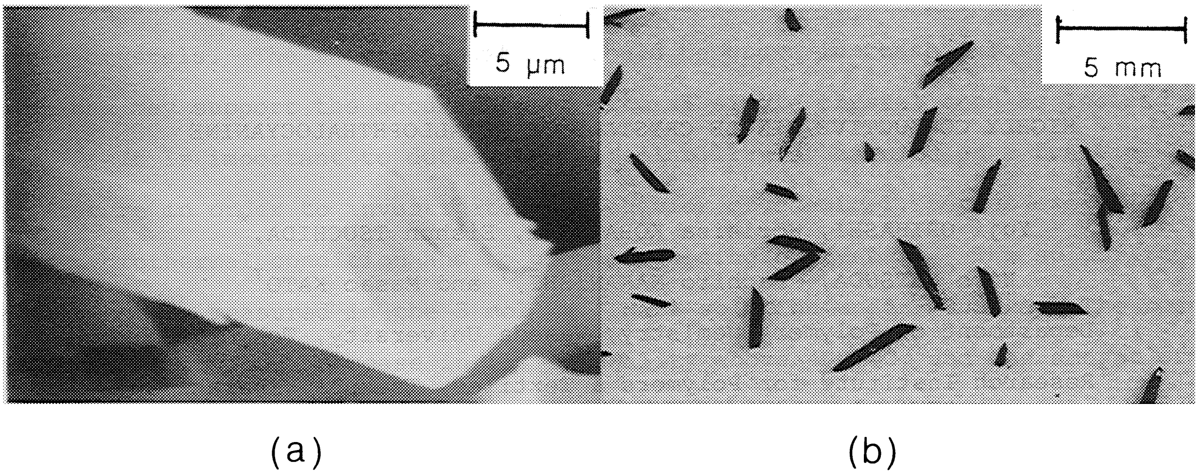

Fig. 2. Photographs of PcCoCN crystals: (a) minuite needle-like crystals grown on the platinum point electrode (b) plate-like crystals grown on the platinum point electrode.

showed the oxidation peak at +1.10 V and that of reductive one at +0.18 V (vs. Ag-AgCl) (Fig. 1). In our standard procedure of electrolysis, 80 cm^3 of $K[PcCo(CN)_2]$ solution was set in 100 cm^3 cell with platinum plate electrodes. No electrolytes were supplied in the solution. When the constant potential around the oxidation peak was applied to the solution for several hours, single crystals were then grown gradually on the anode surface. This crystal growth looked to be independent of the applied potential if it was applied at oxidative condition.

The crystals were black-purple with metallic luster, and insoluble in ordinary organic and inorganic solvents. IR spectrum indicated the existence of phthalocyanine ring and cyano group directly bound to cobalt. The crystals were composed of cyanocobalt(Ⅲ)phthalocyanine (PcCoCN) which was revealed by elementary analysis, found : C, 65.44; H, 3.47; N, 21.18; Co, 9.91%; Calcd for $C_{33}H_{16}N_9Co$: C, 66.34; H, 2.70; N, 21.24; Co, 9.86%. Size and shape of the crystals depended on both the morphology of anode surface and $K[PcCo(CN)_2]$ concentration. For example, minute needle-like crystals were obtained when two platinum electrodes (S=4.0 cm^2) were used for the electrolysis of $K[PcCo(CN)_2]$ with high concentration (1×10^{-3} mol/dm^3), whereas long plate-like crystals, longer than 4 mm, were obtained when platinum point electrode (0.2 cm^2) was used as anode under low concentration (1×10^{-4} mol/dm^3). Typical crystals were shown

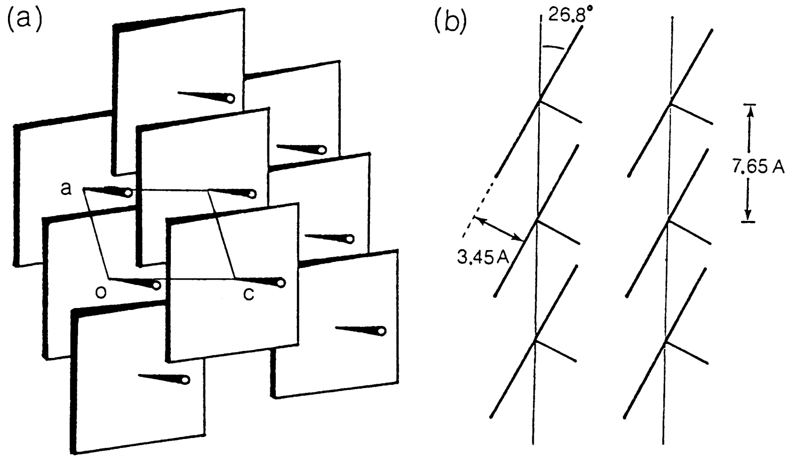

Fig. 3. Schematic drawing of the molecular packing of PcCoCN: (a) projected onto the (101) plane; (b) viewed along the ($\bar{1}$22) plane.

in Fig. 2. The ESR measurements of the obtained crystals revealed that cobalt ion was ESR silent, namely Co(III).

Conductivity of pressed disk at room temperature was evaluated to be 3×10^{-1} S/cm by two-probe method. Activation energy of 0.02 eV was calculated from the temperature dependence of the conductivity. The conductivity of large single crystal was 5.7×10^{1} S/cm obtained along the longer direction of the crystal growth by the four-probe method and this activation energy was 0.04 eV. It should be noted that no decay was found after keeping it under room atmosphere for over a month. Although poly-PcCoCN has already been reported,5) it has a cyano-bridged one dimensional structure and shows the conductivity of 2×10^{-2} S/cm. In order to understand this difference of conductivity, X-ray single crystal diffraction analysis was carried out. The oscillation and Weissenberg photographs of the crystal showed only low angle reflections ($2\theta<60°$) implying that the phthalocyanine rings arranged with long-range order. Cell parameters and intensity data with indexing were derived from the measurements on the four circle diffractometer. This compound was revealed to be crystallized in the triclinic space group P$\bar{1}$, with a=7.65(3), b=9.85(4), c=9.82(3)Å; α=90.8(3) , β=107.3(3) , γ=107.2(3); Fw=597.5, V=670.35 Å^3, Z=1, Dx=1.46, Dm=1.46 Mg/m^3 (by flotation). By taking the intensity orders of strongly reflected planes into account, molecular arrangement of the present crystal was estimated and illustrated in Fig. 3, where phthalocyanine ring is expressed by a rectanglar plane and cyano group by a rod perpendicularly bound to the plane. It turns out that the interplaner distance is about 3.45 Å, i.e., certain amount of π-orbital interaction should be effective. Every plane is overlapped with adjacent six planes, suggesting three-dimensional π-orbital interactions. This may be the reason of high conductivity.

In conclusion, large single crystals of cyanocobalt(Ⅲ)phthalocyanine with three-dimensional π-electron overlapping have been prepared through electrolysis. This methodology should give strong impact on design of organic conductors. The analysis on the reaction mechanism and the application to other derivatives are in progress.

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