Multi-Dimensional Stacking Structures in Phthalocyanine-Based Electrical Conductors, K[Co(phthalocyaninato)$(CN)_2]_2 \cdot 5CH_3CN$ and Co(phthalocyaninato)$(CN)_2 \cdot 2H_2O$

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Two kinds of electrically conducting crystals have been obtained by the electrochemical oxidation of potassium dicyanophthalocyaninatocobalt(III), $KCo(Pc)(CN)_2$. Oxidation in acetonitrile gives $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$, in which the phthalocyanine rings are two-dimensionally stacked. Since some of the acetonitrile molecules can be easily removed from the lattice, the crystal is not stable outside of the solution. Mosaically distorted crystals, which are exposed to air, show relatively high conductivities ($\approx 10\ \Omega^{-1}cm^{-1}$ at room temperature). On the other hand, oxidation in benzonitrile in the presence of dibenzo-18-crown-6 yields $Co(Pc)(CN)_2 \cdot 2H_2O$, in which the phthalocyanine rings are three-dimensionally stacked. The water molecules in this crystal form hydrogen bonds, and the crystal is stable against drying. The conductivity of this crystal is $\approx 1\ \Omega^{-1}cm^{-1}$ at room temperature. The multi-dimensionalities observed in these two kinds of crystals arise from a slipped stacking of phthalocyanine, due to steric interactions of the axial substituents.

Up to now, more than twenty organic superconductors have been discovered, and the obtained superconducting transition temperature now exceeds 10 K.[1] Since one-dimensional systems, e.g., typical organic conductors such as TTF-TCNQ,[2] are known to be unstable at low temperatures due to a Peierls distortion arising from an electron-phonon interaction, increasing the dimensionality is now recognized as being essential for maintaining the metallic properties and, consequently, to achieve a superconducting state. From this point of view, a number of molecules which have chalcogen atoms have been synthesized so that they can interact transversely with adjacent molecules (Fig. 1(a)). In fact, all of the organic superconductors so far discovered comprise this type of molecule, i.e., BEDT-TTF,[3] TMTSF,[4] MDT-TTF,[5] DMET,[6] $Ni(dmit)_2$, and $Pd(dmit)_2$.[7] Since chemical modifications by chalcogen atoms are rather limited, another approach to constructing two-dimensional systems is important for extending the varieties of organic superconductors.

Metal phthalocyanines as well as metal-free phthalocyanine are known to form low-dimensional conducting materials upon oxidation.[8] In most cases, oxidation takes place at the ligand site, and conduction occurs through an overlapping of the ligand π-orbitals. One of the advantages of this system is the feasibility of substitution at the axial sites, which is difficult for ordinary conjugation systems. Making use of this advantage, several kinds of co-facial polymers were synthesized as members of a group of conducting polymers (Fig. 1(b)).[9] From a different point of view, axial substituents are expected to be useful in constructing multi-dimensional systems. If a molecule has projections at its center (axial substituents), it cannot be stacked directly above another molecule. Consequently, the molecules form slipped stacks due to a steric interaction of the axial substituents. Regarding such stacking, a two-dimensional molecular arrangement expected is represented schematically in Fig. 1(c). A three-dimensional molecular arrangement (Fig. 1(d)) may be obtained when the counter parts are small enough to fit the space. Taking the size of phthalooyanine into account, intermolecular interactions are expected to be sufficiently effective for electrical conduction, although the overlapping is partial. In order to examine this possibility, electrochemical oxidation was carried out for the dicyano-

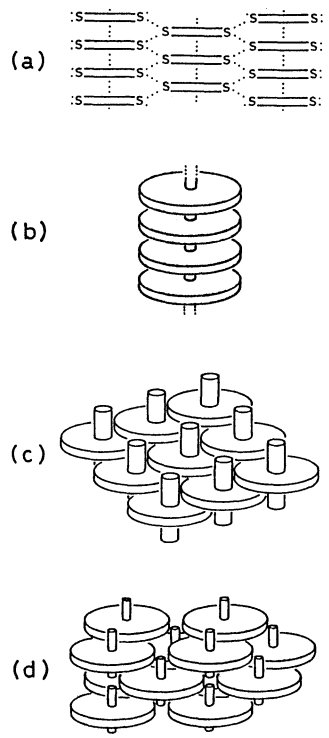

Fig. 1. Schematic representation of molecular arrangement in molecular conductors. Transverse interaction by chalcogen atoms (represented by S) (a) and axially substituted molecules, one-dimensional (b), two-dimensional (c), and three-dimensional (d).

phthalocyaninatocobalt(III) anion, $[Co(Pc)(CN)_2]^-$. Two kinds of products, $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$[10] and $Co(Pc)(CN)_2 \cdot 2H_2O$, were obtained; they were found to have stacking forms corresponding to Figs. 1(c) and (d), respectively. In this paper, the structures and the electrical properties of these two products are presented.

Experimental

Materials. $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ was obtained by the electrocrystallization of $KCo(Pc)(CN)_2$ with a constant current of 2—10 μA in acetonitrile without adding an electrolyte. $KCo(Pc)(CN)_2$ was prepared following a method reported by Metz and Hanack.[11]

When crown ether was added to a $KCo(Pc)(CN)_2$ solution, electrocrystallization yielded different types of crystals. The best crystal quality was obtained when benzonitrile was used as the solvent, although the size was small, i.e., the largest dimension was less than 0.5 mm. The crystals obtained in benzonitrile with an excess amount of dibenzo-18-crown-6 were found to be $Co(Pc)(CN)_2 \cdot 2H_2O$ by X-ray analysis.

X-Ray Structure Analyses. An automated RIGAKU AFC-5R diffractometer with graphite monochromatized Mo$K\alpha$ radiation was used for data collection at room temperature. After exposing crystals of $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ to air, no diffraction peaks could be observed in X-ray measurements. By carefully observing the crystals under a microscope immediately after transferring them from the electrochemical cell onto filter paper, a slight deformation or cracking of the crystals were noticed. Since the crystals were stable in the electrochemical-cell solution, even when exposed to air, they were assumed to be unstable towards drying. It was also found that crystals stored in pure acetonitrile became non-conducting, suggesting the occurrence of a kind of disproportionation. Therefore, X-ray measurements were carried out after shielding the crystal in a Lindemann-glass capillary containing solution from the anode side of the electrochemical cell. Fifty reflections with $25° < 2\theta < 30°$ were used to determine the lattice parameters (Table 1). Intensity data were collected in the region $2\theta < 60°$ ($-21 \leqq h \leqq 21$, $-23 \leqq k < 23$, $0 \leqq l \leqq 14$) in the θ-2θ mode at a scan rate of 5° min^{-1}. The background counts at each end were 4—12.6 sec. The intensities of the three standards used (monitored every 100 data measurements) remained constant within 3%. Of the 10515 unique reflections measured, 4849 independent reflections with $|F_o| > 3\sigma(F_o)$ were used for the structure analysis. The crystal structure was solved by the Patterson method.

A single crystal of $Co(Pc)(CN)_2 \cdot 2H_2O$ was directly mounted on a glass capillary and exposed to air during data collection. Twenty-four reflections with $21° < 2\theta < 30°$ were used to determine the lattice parameters. The crystal data are listed in Table 1. Intensity data were collected in the region $2\theta < 60°$ ($-19 \leqq h \leqq 18$, $0 \leqq k \leqq 20$, $0 \leqq l \leqq 10$) in the θ-2θ mode at a scan rate of 4° min^{-1}. The background counts at each end were 5—15.4 sec. The intensities of the three standards used (monitored every 100 data measurements) remained constant within 3%. Of the 2265 unique reflections measured, 1144 independent reflections with $|F_o| > 3\sigma(F_o)$ were used for the structure analysis. The crystal structure was solved by a direct method.

The positions of the hydrogen atoms were determined from difference synthesis maps, except for those attached to disordered solvent molecules. A block-diagonal least-squares technique (UNICS III[12]) with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms (weighting scheme, $1/\omega = \sigma^2 + (0.015\,|F_o|)^2$) was employed for the structure refinement of both crystals.

Measurements. Electrical conductivity measurements were carried out by a conventional four-probe method, except when the crystal was too small, in which case one contact was shared for the current and voltage probes. Thermoelectric power measurements were performed by a method reported earlier.[13]

Results and Discussion

$K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$. The obtained phthalocyanine structures are shown in Fig. 2; the atomic parameters are listed in Table 2.[14] The crystal struc-

Table 1. Crystal Data

	$K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$	$Co(Pc)(CN)_2 \cdot 2H_2O$
Chemical formula	$C_{78}H_{47}N_{25}Co_2K$	$C_{34}H_{20}N_{10}O_2Co$
Molecular weight	1491.377	659.535
Crystal color	Dark purple	Dark purple
Crystal size/mm	0.5×0.6×0.3	0.4×0.2×0.1
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/m$
a/Å	15.577(3)	14.173(4)
b/Å	16.626(3)	14.250(2)
c/Å	10.645(2)	7.701(2)
α/deg	94.89(2)	90
β/deg	99.22(2)	115.19(2)
γ/deg	138.37(1)	90
V/Å^3	1717.3(7)	1407.3(6)
Z	1	2
D_c/g cm^{-3}	1.442	1.556
μ(Mo$K\alpha$)/cm^{-1}	6.06	6.59
R	0.050	0.070
R_w	0.067	0.067

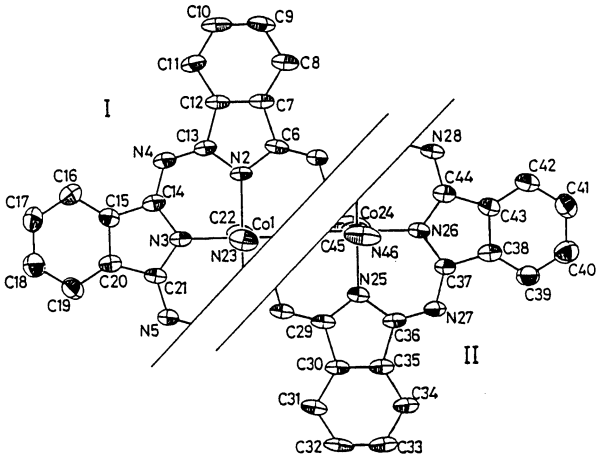

Fig. 2. ORTEP drawing[18] of $[Co(Pc)(CN)_2]^{0.5-}$ in $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ showing the atom numbering scheme; the molecule I is located at (0, 0, 0) and the molecule II is located at (0, 0.5, 0).

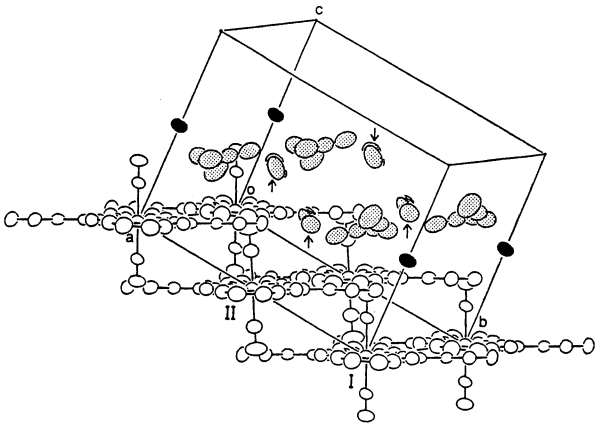

Fig. 3. Crystal structure of $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$; fully and lightly shaded ellipsoids indicate potassium and acetonitrile, respectively. The arrows indicate acetonitrile which does not coordinate to potassium.

ture is shown in Fig. 3. The cobalt atoms and potassium ion are located at the center of the inversion. There are five acetonitrile molecules in the unit cell; four of them coordinate to the potassium ion, in addition to the axial cyano groups, as shown in Fig. 4. The remaining acetonitrile molecule occupies the space centered at (0, 0.5, 0.5), which is positionally and orientationally disordered. Since this molecule has no interaction with the other part of the lattice, a loss of acetonitrile from the lattice is expected to occur easily.

The stacking structure of the phthalocyanine rings is shown in Fig. 5. Phthalocyanine (II) located at (0, 0.5, 1) is crystallographically independent of that (I) located at (0, 0, 1). However, they are almost parallel (angle between the two planes, 0.82°) and equally separated. Thus, the stacking along the *b*-axis can be regarded as uniform. The bond lengths and angles

Table 2. Atomic Parameters for $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ ($\times 10^4$)

	x	*y*	*z*	B_{eq}/Å^{2} [a]
Co 1	0(—)	0(—)	0(—)	2.5
N 2	1645(3)	524(3)	468(3)	2.7
N 3	1017(3)	1626(3)	1147(3)	2.8
N 4	3297(3)	2675(3)	1942(3)	3.3
N 5	−772(3)	1348(3)	850(3)	3.1
C 6	1740(4)	−195(4)	−19(4)	2.9
C 7	3179(4)	583(4)	535(4)	3.2
C 8	3793(4)	288(5)	342(5)	4.2
C 9	5211(5)	1266(5)	961(5)	4.8
C10	5955(4)	2451(5)	1734(5)	4.8
C11	5327(4)	2722(4)	1942(4)	4.0
C12	3910(4)	1752(4)	1306(4)	3.2
C13	2924(4)	1693(4)	1268(4)	2.9
C14	2387(4)	2619(4)	1882(4)	3.0
C15	2776(4)	3679(4)	2645(4)	2.9
C16	4007(4)	4861(4)	3540(4)	3.8
C17	4000(5)	5639(4)	4112(5)	4.4
C18	2816(5)	5254(4)	3785(5)	4.4
C19	1580(5)	4070(4)	2892(5)	3.8
C20	1581(4)	3286(4)	2320(4)	3.0
C21	511(4)	2010(4)	1378(4)	2.8
C22	−477(4)	−707(4)	1464(4)	2.8
N23	−777(4)	−1131(4)	2313(4)	4.3
Co24	0(—)	5000(—)	0(—)	2.7
N25	1617(3)	5491(3)	456(3)	2.9
N26	1038(3)	6609(3)	1213(3)	3.0
N27	3303(3)	7632(3)	1997(3)	3.4
N28	−732(3)	6369(3)	947(3)	3.2
C29	1707(4)	4787(4)	−84(4)	3.0
C30	3128(4)	5524(4)	448(4)	3.1
C31	3746(4)	5232(4)	214(5)	3.8
C32	5154(5)	6203(5)	871(5)	4.5
C33	5903(4)	7368(5)	1724(5)	4.5
C34	5284(4)	7642(4)	1970(5)	4.0
C35	3874(4)	6685(4)	1294(4)	3.2
C36	2907(4)	6656(4)	1293(4)	3.1
C37	2406(4)	7581(4)	1943(4)	3.0
C38	2827(4)	8656(4)	2710(4)	3.4
C39	4073(4)	9849(4)	3574(5)	4.0
C40	4115(5)	10663(4)	4145(5)	4.4
C41	2934(5)	10296(4)	3841(5)	4.2
C42	1684(4)	9107(4)	2952(4)	3.8
C43	1647(4)	8286(4)	2396(4)	3.2
C44	549(4)	7007(4)	1461(4)	3.2
C45	−578(4)	4185(4)	1371(4)	3.6
N46	−988(4)	3648(5)	2141(4)	5.9
K47	0(—)	0(—)	5000(—)	5.6
N48	−999(5)	830(5)	3936(5)	7.8
C49	−1541(6)	1040(6)	3717(6)	7.1
C50	−2275(8)	1201(8)	3425(9)	10.6
N51	2468(5)	2383(5)	5070(6)	10.1
C52	2462(5)	2969(5)	5665(5)	6.6
C53	2305(7)	3565(6)	6344(7)	10.1
N54[b]	796(18)	4284(20)	5861(19)	7.7
N55[b]	−2172(18)	3189(19)	5216(18)	6.3
C56[c]	3(13)	4078(13)	5629(11)	8.0
C57[c]	−1230(12)	3700(12)	5369(10)	8.0

a) $B_{eq}=4/3\sum_i\sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) Occupancy=1/4. c) Occupancy=1/2.

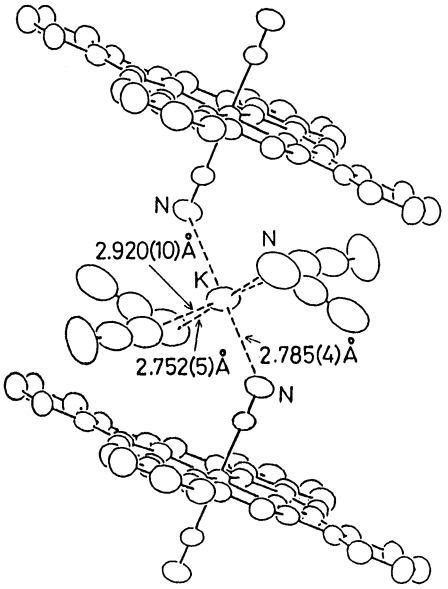

Fig. 4. Geometry of coordination of the potassium ion.

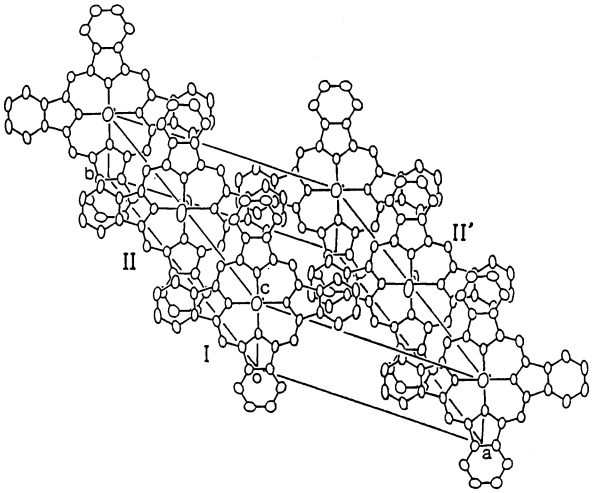

Fig. 5. Molecular overlap in the two-dimensional phthalocyanine sheet in $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$; viewed perpendicular to the molecular plane. The molecule II′ is translationally related to the molecule II along the *a*-axis.

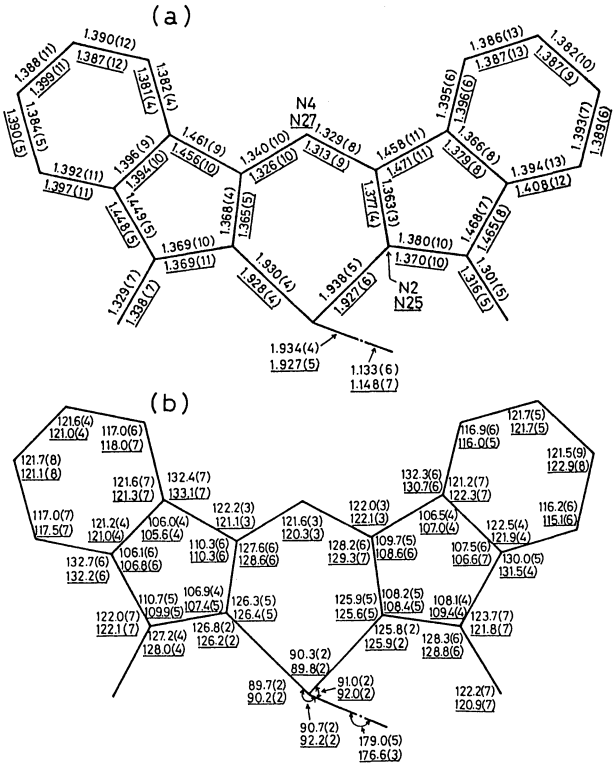

Fig. 6. Bond lengths (Å) and angles (degree) of $[Co(Pc)(CN)_2]^{0.5-}$ in $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$; the values for the molecule II are underlined.

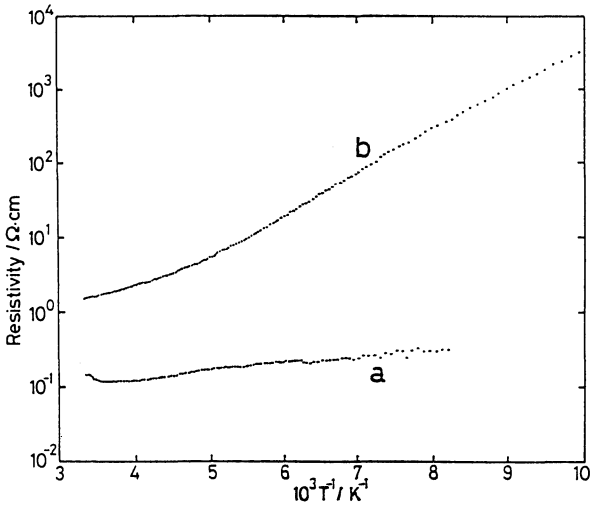

Fig. 7. Electrical resistivities of the dried $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ crystal, **a**, and the $Co(Pc)(CN)_2 \cdot 2H_2O$ crystal, **b**.

shown in Fig. 6 also indicate that there are no large differences between the two molecules. In addition to this stacking, there exists a partial overlap between the phthalocyanine rings along the [2 0 1] direction. The distances between the overlapping benzene rings are 3.45 and 3.57 Å between molecules I and II, and 3.51 Å between molecules I and II′ in Fig. 5. This stacking pattern is the same as that shown in Fig. 1(c), in which the molecules form a two-dimensional network.

Compared with the oxidation potential of the Pc ring, those of the potassium ion, cobalt(III), and the coordinated cyano groups are too high to be oxidized under the present electrochemical conditions. Therefore, the anode removes an electron exclusively from the HOMO level of the Pc ring.[15] Since the potassium-to-phthalocyanine ratio in this material is 1 : 2, the phthalocyanine ring (formal charge of the unoxidized closed-shell structure is Pc^{2-}) is partially oxidized to $Pc^{1.5-}$. For such partially oxidized uniform stacking, a partially filled band (i.e., a metallic state) is expected. Unfortunately, the crystal is not

stable outside of the solution, as mentioned above. This makes it extremely difficult to measure its intrinsic electrical properties. Although the crystals lose any long-range order after drying, most of them retain their shape. Thus, the electrical properties of this dried material were measured to permit speculation about the intrinsic properties. Figure 7 shows the temperature dependence of the resistivity observed for one of the crystals. The value and the temperature dependence vary from crystal to crystal, i.e., they depend on the sample history and size. The typical conductivity at room temperature is $\approx 10\ \Omega^{-1}\ cm^{-1}$. All samples show semiconducting behavior; the activation energy value, which depends on the sample and the number of heat cycles, lies in the range 0.01—0.05 eV. Since these results strongly suggest that the observed properties are dominated by the grain boundaries produced by the drying process, the intrinsic character of this material is probably metallic. The temperature dependence of the thermoelectric power was again not very reproducible. The typical value at room temperature is about $+20\ \mu V\ deg^{-1}$, which is consistent with the hole conduction in the partially oxidized phthalocyanine stacks.

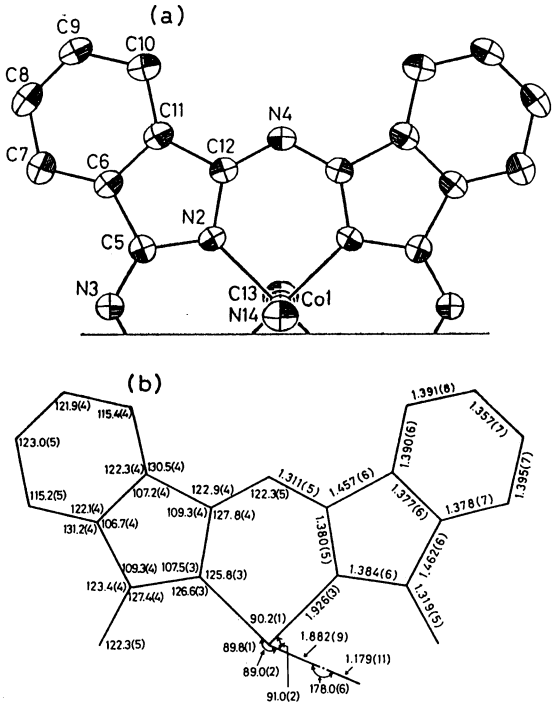

Fig. 8. ORTEP drawing of $Co(Pc)(CN)_2$ in $Co(Pc)(CN)_2 \cdot 2H_2O$ showing the atom numbering scheme (a) and bond lengths (Å) and angles (degree) (b).

Table 3. Atomic Parameters for $Co(Pc)(CN)_2 \cdot 2H_2O$ ($\times 10^4$)

	x	y	z	$B_{eq}/Å^{2a)}$
Co 1	0(—)	0(—)	0(—)	3.0
N 2	452(3)	958(2)	1951(4)	2.9
N 3	0(—)	2365(4)	0(—)	4.0
N 4	1173(5)	0(—)	4811(7)	3.6
C 5	397(4)	1918(3)	1657(6)	3.3
C 6	860(4)	2396(3)	3512(6)	3.5
C 7	981(5)	3336(4)	3970(7)	4.7
C 8	1495(5)	3537(4)	5925(7)	5.2
C 9	1826(5)	2862(4)	7298(7)	5.0
C10	1700(4)	1912(4)	6842(6)	4.0
C11	1193(4)	1706(3)	4896(6)	3.2
C12	947(4)	806(3)	3904(6)	3.0
C13	1343(6)	0(—)	66(9)	3.6
N14	2196(5)	0(—)	166(8)	4.5
O15[a)]	4128(14)	422(12)	−237(28)	14.0
O16[a)]	4323(21)	0(—)	990(36)	12.7

a) Occupancy=1/3.

$Co(Pc)(CN)_2 \cdot 2H_2O$. The molecular structure in this crystal is shown in Fig. 8; the atomic parameters are listed in Table 3.[14] In this crystal, as well as in the $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ crystal, the cobalt atom is coordinated by two axial cyano groups. It is not likely that one of the cyano groups leaves when the phthalocyanine ring is oxidized, as speculated by Orihashi et al.[16]

As shown in Fig. 9, the cobalt atom is located at the center of the inversion. A $2/m$ symmetry element is located on the phthalocyanine molecule. Since the sodium salt of the starting material has been reported

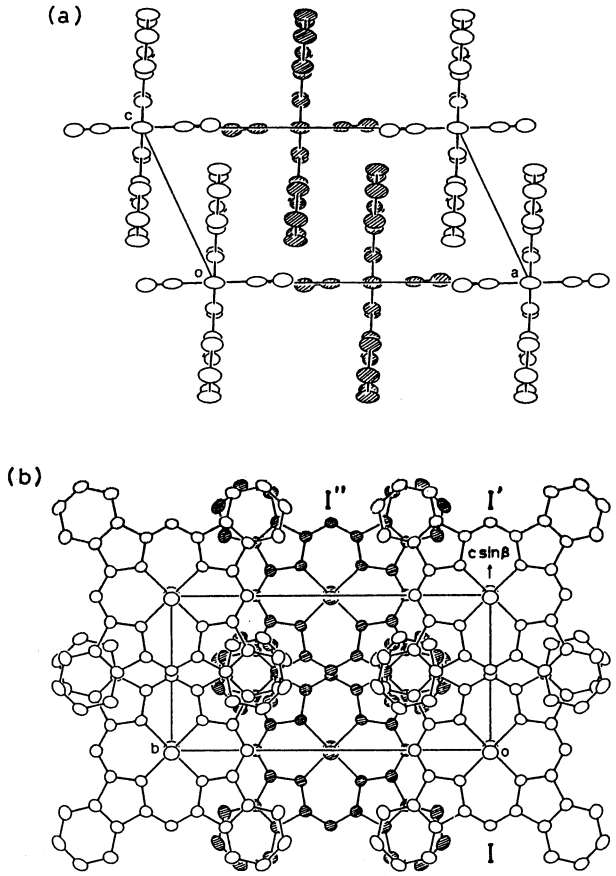

Fig. 9. Crystal structure of $Co(Pc)(CN)_2 \cdot 2H_2O$; projections along the b-axis (a) and along the a-axis (b); I (0, 0, 0), I′ (0, 0, 1), I″ (1/2, 1/2, 1). The water molecules are not presented for clarity.

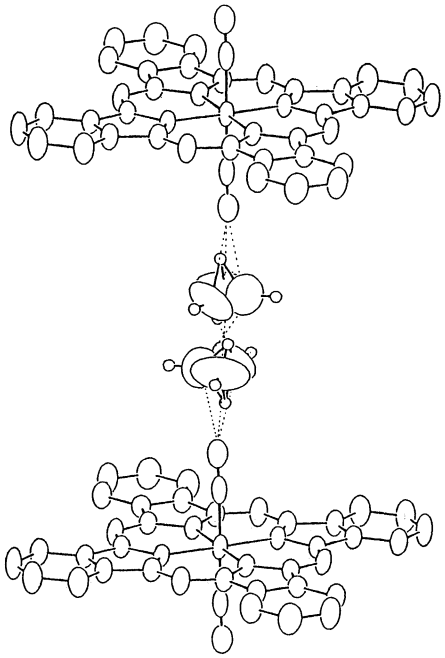

Fig. 10. Hydrogen-bonds between the water molecules and $Co(Pc)(CN)_2$.

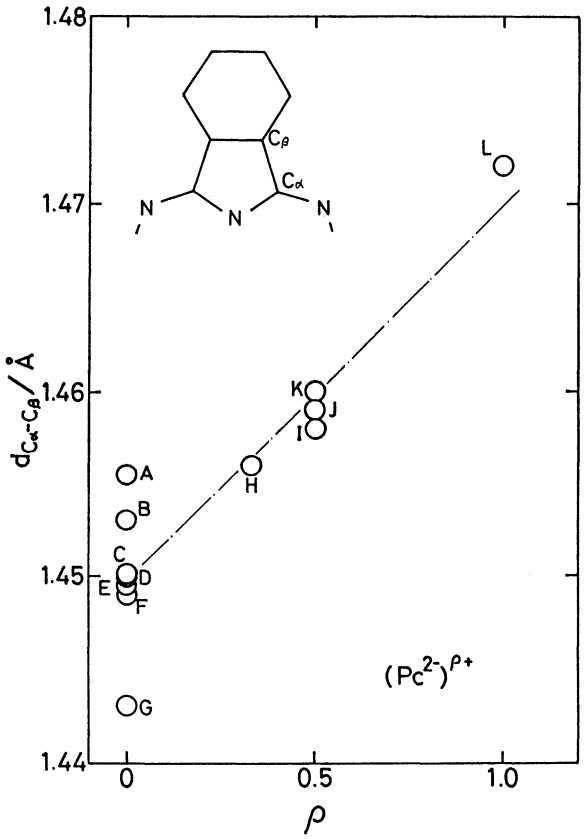

Fig. 11. Correlation between the averaged C_α-C_β distances and the charge on the phthalocyanine skeleton; A: Zn(Pc),[19] B: Cu(Pc),[20] C: Fe(Pc),[21] D: Co(Pc),[22] E: Mn(Pc),[21] F: $Si(Pc)(OSiMe_3)_2$,[23] G: Mn(Pc),[22] H: Ni(Pc)I,[24] I: $[Ni(Pc)]_2(SbF_6)$,[25] J,K: $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$, L: Li(Pc).[26]

to be hydrated,[11] it is likely that the potassium salt contains water in the lattice. The water molecules in this product are, thus, assumed to result from them; they are positionally disordered, i.e., one molecule can occupy any one of three positions (Fig. 10). They form hydrogen-bonds with the axial cyano groups and with each other. These bonds act as a bridge between the phthalocyanine molecules along the *a*-axis. The hydrogen-bonds are assumed to be effective in retaining the water molecules in the lattice after drying the crystals.

The overlap between the phthalocyanine rings along the *c*-axis is the same type as that observed in $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ along the *b*-axis, i.e., two benzene rings overlapping. The other overlap which is similar to that observed along the [2 0 1] direction in $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ (one benzene ring overlapping) exists along the [1 1 2] and [1 $\bar{1}$ 2] directions in $Co(Pc)(CN)_2 \cdot 2H_2O$. Consequently, one phthalocyanine ring interacts with six phthalocyanine rings, so that the total intermolecular interaction becomes three-dimensional. The interplanar distances between the overlapped benzene rings are 3.51 Å between molecules I and I′, and 3.58 Å between molecules I and I″ in Fig. 9.

From the stoichiometry of $Co(Pc)(CN)_2 \cdot 2H_2O$, the phthalocyanine ring is known to be oxidized to Pc^{1-}. The conductivity data are shown in Fig. 7; the reproducibility of independent runs is good. The value at room temperature, $\approx 1\ \Omega^{-1}cm^{-1}$, seems to be a little high for a fully oxidized material. Also, the observed activation energy (0.06—0.11 eV) is too small to consider that the gap is due to the on-site Coulomb repulsion.[17] Since the form of the water molecules in the lattice is $HOH\cdots OH_2$, there might be some contributions from the protonated form, $[H_2OH\cdots OH_2]^+$. It is not possible to estimate the protonated form distribution from an X-ray analysis. Another method to estimate such a contribution is to compare the molecular geometries of the phthalocyanine ring. Considering the π-electron structure of Pc^{2-}, in order to satisfy the 18π-electron system for the tetraazaporphyrine skeleton, two of the eight C_α-C_β bonds (insertion in Fig. 11) have a double-bond character in any one resonance structure. Thus, one of the terminal benzene rings must have a quinonoid structure. When the phthalocyanine ring is oxidized, the 18π-electron system is assumed to no longer be satisfied. Thus, for the total system, recovering the aromaticity for all of the terminal benzene rings may be energetically favorable. For such an electronic structure, all of the C_α-C_β bonds are expected to have a single-bond character. This tendency is summarized in Fig. 11; data are collected only for planar metal phthalocyanines. Assuming a linear correlation, a positive slope can be obtained (the chain-dotted line in Fig. 11). Since the double-bond character is diluted by

1/4 in the phthalocyanine system, the bond-length change by charge is much less pronounced compared with TTF or TCNQ. Although the data chosen in Fig. 11 are highly reliable, this feature makes the error for each data point rather large. Although it should be critical to estimate the oxidation number quantitatively, this relationship indicates that the oxidation number of Pc in $Co(Pc)(CN)_2 \cdot 2H_2O$ (averaged C_α-C_β distance, 1.460 Å) is less than one. This result, as well as the conductivity data, suggests that the composition of this material is $Co^{3+}(Pc)^{(1+x)-}(CN^-)_2(H_3O^+)_x(H_2O)_{2-x}$.

General Remarks

In both $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ and $Co(Pc)(CN)_2 \cdot 2H_2O$ the intermolecular interaction is not one-dimensional, but two-dimensional and three-dimensional, respectively. These multi-dimensionalities arise from a steric effect of the axial substituents. Accurate conductivity anisotropies have not been measured due to both the instability of the crystals for $K[Co(Pc)(CN)_2]_2 \cdot 5CH_3CN$ and the small crystal size for $Co(Pc)(CN)_2 \cdot 2H_2O$. A rough estimation of the anisotropy in $Co(Pc)(CN)_2 \cdot 2H_2O$ has been made by measuring the conductivities along the *c*-axis and perpendicular to the *c*-axis with two contacts (each contact serving as both a voltage and current probe). These measurements indicate that the anisotropy of the conductivity, $\sigma_{//c}/\sigma_{\perp c}$, is 3—10, which is consistent with the three-dimensional stacking form in this material. Our approach to designing multi-dimensional systems, by using axially substituted phthalocyanines as the first step, seems to be successful. The molecular shape can be varied by changing the substituents, the central metals, and the π-ligands. This feature may be useful for the rationalized design of more conducting systems for further progress.

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References

1) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, **1988**, 55.

2) TTF: tetrathiafulvalene, TCNQ: tetracyanoquinodimethane; J. P. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).

3) BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene; H. Inokuchi, *Angew. Chem., Int. Ed. Engl.*, **27**, 1747 (1988), and references therein.

4) TMTSF: tetramethyltetraselenafulvalene; J. M. Williams and K. Carneiro, *Adv. Inorg. Chem. Radiochem.*, **29**, 249 (1989), and references therein.

5) MDT-TTF: methylenedithiotetrathiafulvalene; G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer, and J. Pfeiffer, *Synth. Met.*, **27**, B379 (1988).

6) DMET: dimethyl(ethylenedithio)diselenadithiafulvalene; K. Kikuchi, K. Murata, Y. Honda, T. Namiki, K. Saito, T. Ishiguro, K. Kobayashi, and I. Ikemoto, *J. Phys. Soc. Jpn.*, **56**, 3436 (1987).

7) dmit: 4,5-dimercapto-1,3-dithiole-2-thione; M. Bousseau, L. Valade, J. Legros, P. Cassoux, M. Garbauskas, and L. V. Interrante, *J. Am. Chem. Soc.*, **107**, 1908 (1986); A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, *Chem. Lett.*, **1987**, 1819; L. Brossard, H. Hurdequint, M. Ribault, L. Valade, J. P. Legros, and P. Cassoux, *Synth. Met.*, **27**, B157 (1988).

8) J. L. Petersen, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, and T. J. Marks, *J. Am. Chem. Soc.*, **99**, 286 (1977); T. Inabe, T. J. Marks, R. L. Burton, J. W. Lyding, W. J. McCarthy, C. R. Kannewurf, G. M. Reisner, and F. H. Herbstein, *Solid State Commun.*, **54**, 501 (1985); T. Inabe, S. Nakamura, W-B. Liang, T. J. Marks, R. L. Burton, C. R. Kannewurf, and K. Imaeda, *J. Am. Chem. Soc.*, **107**, 7224 (1985); K. Yakushi, M. Sakuda, I. Hamada, H. Kuroda, A. Kawamoto, J. Tanaka, T. Sugano, and M. Kinoshita, *Synth. Met.*, **19**, 769 (1987).

9) C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1539 (1983); M. Hanack, A. Datz, R. Fay, K. Fischer, U. Keppeler, J. Koch, J. Metz, M. Mezger, O. Schneider, and H. -J. Schulze, "Handbook of Conducting Polymers," ed by T. A. Skotheim, M. Dekker, New York (1987); M. Hanack, S. Deger and A. Lange, *Coord. Chem. Rev.* **83**, 115 (1988); R. S. Nohr, P. M. Kuznesof, K. J. Wynne, M. E. Kenney, and P. G. Siebenman, *J. Am. Chem. Soc.*, **103**, 4371 (1981).

10) T. Inabe and Y. Maruyama, *Chem. Lett.*, **1989**, 55.

11) J. Metz and M. Hanack, *J. Am. Chem. Soc.*, **105**, 828 (1983); M. Hanack and X. Münz, *Synth. Met.*, **10**, 357 (1985); X. Münz and M. Hanack, *Chem. Ber.*, **121**, 235 (1988); C. Hedtmann-Rein, M. Hanack, K. Peters, E. -M. Peters, and H. G. von Schnering, *Inorg. Chem.*, **26**, 2647 (1987).

12) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1979).

13) T. Inabe, T. Mitsuhashi, and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, **61**, 4215 (1988).

14) The lists of structure factors and anisotropic thermal parameters for non-hydrogen atoms are deposited as Document No. 8933 at the Office of the Editor of Bull. Chem. Soc. Jpn.

15) R. Behnisch and M. Hanack, submitted to *Synth. Met.*

16) Y. Orihashi, N. Kobayashi, E. Tsuchida, H. Matsuda, H. Nakanishi, and M. Kato, *Chem. Lett.*, **1985**, 1617; Y. Orihashi, H. Ohno, E. Tsuchida, H. Matsuda, H. Nakanishi, and M. Kato, *Mol. Cryst. Liq. Cryst.*, **160**, 139 (1988).

17) The large *U* (on-site Coulomb repulsion) of phthalocyanines was noted by the magnetic susceptibility measurements; Ref. 8.

18) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee (1976).

19) W. R. Scheidt and W. Dow, *J. Am. Chem. Soc.*, **99**,

1101 (1977).
20) C. J. Brown, *J. Chem. Soc. (A)*, **1968**, 2488.
21) J. F. Kirner, W. Dow, and W. R. Scheidt, *Inorg. Chem.*, **15**, 1685 (1976).
22) R. Mason, G. A. Williams, and P. E. Fielding, *J. Chem. Soc., Dalton Trans.*, **1979**, 676.
23) J. R. Mooney, C. K. Choy, K. Knox, and M. E. Kenney, *J. Am. Chem. Soc.*, **97**, 3033 (1975).
24) C. J. Schramm, R. P. Scaringe, D. J. Stojakovic, B. M. Hoffman, J. A. Ibers, and T. J. Marks, *J. Am. Chem. Soc.*, **102**, 6702 (1980).
25) K. Yakushi, M. Sakuda, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, **1986**, 1161.
26) H. Masuda, submitted to *J. Chem. Soc., Dalton Trans.*