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Multi-dimensional π–π stacking interaction in neutral radical crystals obtained by electrochemical oxidation of $[Co^{III}(2,3\text{-}Nc)(CN)_2]^-$ (2,3-Nc = 2,3-naphthalocyanine)

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Electrochemical oxidation of the dicyano(2,3-naphthalocyanato)cobalt(III) anion ($[Co(2,3\text{-}Nc)(CN)_2]^-$) yields electrically conducting crystals comprised of the $Co(2,3\text{-}Nc)(CN)_2$ neutral radicals and some crystal solvents. The oxidation of the potassium salt in acetonitrile gives $Co(2,3\text{-}Nc)(CN)_2{\cdot}CH_3CN$, while that in a mixed solvent of acetonitrile/*o*-dichlorobenzene (DCB) gives $Co(2,3\text{-}Nc)(CN)_2{\cdot}2DCB$. X-Ray structure analyses show that two- or three-dimensional π–π stacking interactions are achieved in these crystals. Compared with the phthalocyanine (Pc) derivatives this higher-dimensionality in the 2,3-Nc radical crystals, even with a large crystal solvent, arises from the linear extension of the π-conjugation system of Pc.

Ordinary π-conjugated closed-shell organic molecules cannot form conducting solids due to the wide HOMO–LUMO gap. Even for open-shell molecules it is difficult to obtain conducting solids owing to the inevitable on-site Coulombic repulsion, and most organic molecular conductors are designed based on charge-transfer complexes or radical salts. We have recently found that the conductivity of neutral phthalocyanine radical crystals is improved by increasing the dimensionality of the electronic interaction.[1] In this system, a phthalocyanine derivative with two axial ligands, the dicyano(phthalocyaninato)cobalt(III) anion ($[Co(Pc)(CN)_2]^-$), was used as the starting material. This Pc unit is designed to arrange the molecules in the lattice with multi-dimensional π–π stacking interactions. The oxidation of the starting Pc anion yielded a neutral π-radical, and it formed neutral radical crystals with various crystal solvents[2–4] in addition to some partially oxidized salts.[5,6] Interestingly, the dimensionality of the π–π stacking interaction varies depending on the crystal solvent in a range from one to three dimensions.[2–4]

Our strategy to construct a multi-dimensional π–π stacking structure from axially substituted metallomacrocyclic compounds has been proved to be effective. The efficiency is expected to become higher when the macrocyclic π-ligand is larger. A π-extended phthalocyanine derivative, 2,3-naphthalocyanine (2,3-Nc), is considered to be a good candidate to verify such an expectation. Therefore, we have synthesized $[Co(2,3\text{-}Nc)(CN)_2]^-$, and electrochemically oxidized it. As expected, neutral radical crystals have been obtained again with some crystal solvents. In this paper, we describe the crystal structures and some electrical properties of $Co(2,3\text{-}Nc)(CN)_2{\cdot}CH_3CN$ and $Co(2,3\text{-}Nc)(CN)_2{\cdot}2DCB$, focusing on the dimensionality of the π–π interaction achieved in these crystals.

Experimental

Materials

$Co^{II}(2,3\text{-}Nc)$ was synthesized by one of the typical methods for the preparation of phthalocyanines, but our method was slightly different from the reported one.[7] A quinoline solution of 2,3-dicyanonaphthalene and anhydrous $CoCl_2$ was refluxed for 5 hours under a nitrogen atmosphere. After cooling the solution, methanol was added and the solid products were separated by filtration. The solids were washed with methanol, water, and acetone several times each to remove byproducts and unreacted 2,3-dicyanonaphthalene. Isolated $Co^{II}(2,3\text{-}Nc)$ was a dark green powder (yield 41%). The potassium salt of $[Co^{III}(2,3\text{-}Nc)(CN)_2]^-$ was prepared in acetone or n-BuOH following the method reported.[8] The reaction mixture was separated by filtration and washed with water to remove KCN, and $K[Co^{III}(2,3\text{-}Nc)(CN)_2]$ was extracted by acetone using a Soxhlet extractor or dissolving in acetone at room temperature. The solution was condensed to 1/10 in volume and hexane was added. The resultant green powder product was filtered (yield 25%). The IR and UV/VIS spectra are in good agreement with those reported.[8]

Neutral radical crystals of $Co(2,3\text{-}Nc)(CN)_2{\cdot}CH_3CN$ and $Co(2,3\text{-}Nc)(CN)_2{\cdot}2DCB$ were grown by electrochemical oxidation of the potassium salt of $[Co(2,3\text{-}Nc)(CN)]^-$ in acetonitrile and in DCB/acetonitrile, respectively. An electrocrystallization cell equipped with a glass frit between the two compartments was filled with about 30 ml of the solution including typically 10 mg of the $[Co(2,3\text{-}Nc)(CN)_2]^-$ salt. A constant current of 0.5–2 μA was applied between two platinum electrodes immersed in the solution of each compartment for 2–4 weeks at 37–40 °C. The crystals were obtained on the anode surfaces.

X-Ray structure analyses

Needle-like single crystals obtained for $Co(2,3\text{-}Nc)(CN)_2{\cdot}CH_3CN$ and $Co(2,3\text{-}Nc)(CN)_2{\cdot}2DCB$ were used for X-ray structure analyses. An automated four-circle Rigaku AFC7R diffractometer ($Co(2,3\text{-}Nc)(CN)_2{\cdot}CH_3CN$) or an imaging plate Rigaku R-axis Rapid diffractometer ($Co(2,3\text{-}Nc)(CN)_2{\cdot}2DCB$) with graphite monochromated Mo-Kα radiation was used for the measurements. The crystal data and data-collection conditions are summarized in Table 1. Owing to the instability of $Co(2,3\text{-}Nc)(CN)_2{\cdot}2DCB$, the measurements were performed at low temperature with a cold nitrogen gas flow equipment. The crystal structures were solved by direct methods (SIR 92[9]), and the hydrogen atoms except for those included in CH_3CN were placed at the calculated ideal positions. A full-matrix least-squares technique (teXsan[10]) with anisotropic thermal parameters for non-hydrogen atoms of $Co(2,3\text{-}Nc)(CN)_2$ and DCB and isotropic for non-hydrogen atoms of CH_3CN and hydrogen atoms (1.2

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Table 1 Crystal data for Co(2,3-Nc)(CN)$_2$·CH$_3$CN and Co(2,3-Nc)(CN)$_2$·2DCB

	Co(2,3-Nc)(CN)$_2$·CH$_3$CN	Co(2,3-Nc)(CN)$_2$·2DCB
Chemical formula	$C_{52}H_{27}N_{11}Co$	$C_{62}H_{32}N_{10}Cl_4Co$
Formula weight	864.79	1117.75
Temperature of data collection/K	293	123
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.864(2)	10.684(1)
b/Å	12.475(4)	15.005(2)
c/Å	8.827(2)	8.068(1)
α/°	107.83(2)	92.37(1)
β/°	93.02(2)	95.72(1)
γ/°	102.30(2)	70.08(1)
V/Å^3	1002.0(6)	1209.9(3)
Z	1	1
μ(Mo-Kα)/cm^{-1}	4.83	6.32
No. of reflections measured	4622	5066
No. of independent reflections observed	2669 [$I > 3\sigma(I)$]	2359 [$I > 3\sigma(I)$]
R_{int}	0.027	0.050
R	0.072	0.064
Rw	0.080	0.045

times that of the attached carbon) was employed for the structure refinement (hydrogens of CH$_3$CN were not included).

CCDC reference number 1145/236. See http://www.rsc.org/suppdata/jm/b0/b004025h/ for crystallographic files in .cif format.

Measurements

Electrical conductivity measurements were performed by a two-probe method using gold paste and gold wires ($\phi = 20$ μm) as probes.

Results and discussion

Electrochemical oxidation of [Co^{III}(2,3-Nc)(CN)$_2$]$^-$

Owing to the linear extension of the Pc π-system the solubility of [Co^{III}(2,3-Nc)(CN)$_2$]$^-$ becomes lower than that of the corresponding Pc derivative. The electrocrystallization succeeded when it was performed at relatively high temperature compared with the Pc case (typically at 20 °C). Since the ionization potential of the 2,3-Nc ring[11] is much lower than those of Co^{III} and CN$^-$, the oxidation process exclusively involves the 2,3-Nc π-system. As found from the X-ray structure analyses, the crystals obtained contain the neutral π-radical, Co^{III}(2,3-Nc$^{-}\cdot$)(CN$^-$)$_2$. The molecular geometry change upon the π-radical formation has been examined by comparing the 2,3-Nc framework in these crystals with that of Cu^{II}(2,3-Nc).[12] As was suggested for the Pc π-radicals,[3] this kind of macrocyclic π-ligand is relatively insensitive to the charge on the molecule, and indeed little change was detected in the present 2,3-Nc π-radicals (maximum difference $< 3\sigma$ for the bond lengths in the 2,3-Nc framework).

Crystal structure of Co(2,3-Nc)(CN)$_2$·CH$_3$CN

Fig. 1(a) shows the overview of the molecular packing in the crystal. In the lattice, CH$_3$CN is trapped between the 2,3-Nc radicals. This site is close to the inversion center, and CH$_3$CN is positionally and orientationally disordered. Though there is no specific interaction between CH$_3$CN and the Co(2,3-Nc)(CN)$_2$ radicals, this encapsulation is complete enough to make the crystal stable in the open air.

The central Co atom is located at the inversion center, and all the 2,3-Nc planes are parallel to each other. There are complicated π–π overlaps between the 2,3-Nc planes. Figs. 1(b)–(d) indicate each overlap mode. Along the c-axis two naphthalene rings are overlapped, and the π–π stacking between the 2,3-Nc radicals at (0, 0, 0) and (0, 0, 1) is shown in Fig. 1(b) (interplanar distance; 3.36 Å). The 2,3-Nc radical located at (0, 0, 0) has also the π–π stacking interaction with those at (1, 0, 1) (interplanar distance; 3.48 Å) and at (0, 1, 1) (interplanar distance; 3.45 Å), as shown in Figs. 1(c) and (d). Along these directions, only one naphthalene ring participates in the π–π interaction. Since these three directions are not coplanar, the total π–π stacking interaction results in a three-dimensional network.

Crystal structure of Co(2,3-Nc)(CN)$_2$·2DCB

An overview of the crystal structure is shown in Fig. 2(a). The crystal solvent molecules, DCB, are now arranged in a sheet parallel to the ac plane. Again, there is no specific interaction between DCB and the Co(2,3-Nc)(CN)$_2$ radicals. Owing to this open sheet structure, the crystal is extremely unstable in the open air.

The Co atom in this crystal is also located at the inversion center. Along the c-axis, a two-naphthalene ring overlap which is similar to the π–π stacking along the c-axis in Co(2,3-Nc)(CN)$_2$·CH$_3$CN exists. The interplanar distance is 3.34 Å, and the overlap mode is shown in Fig. 2(b). The Nc radical at (0, 0, 0) has also the π–π stacking interaction with that at (1, 0, 1) (Fig. 2(c), interplanar distance; 3.37 Å). The stacking pattern is similar to that observed along [1 0 1] in Co(2,3-Nc)(CN)$_2$·CH$_3$CN; a one-naphthalene ring overlap. Consequently, the Nc radicals form a two-dimensional sheet parallel to the ac plane. Compared with the π–π overlaps in the ac plane in Co(2,3-Nc)(CN)$_2$·CH$_3$CN, those in Co(2,3-Nc)(CN)$_2$·2DCB are slightly shifted. This arises from the difference in the cell parameters of the ac plane (a, c, and β). Indeed, the area of the ac plane is nearly the same (85.77 Å^2 in Co(2,3-Nc)(CN)$_2$·2DCB *vs.* 86.95 Å^2 in Co(2,3-Nc)(CN)$_2$·CH$_3$CN) and the angle between the 2,3-Nc molecular plane and the ac plane is almost the same (46.5 Å in Co(2,3-Nc)(CN)$_2$·2DCB and 50.9 Å in Co(2,3-Nc)(CN)$_2$·CH$_3$CN).

In the case of Co(2,3-Nc)(CN)$_2$·CH$_3$CN, additional sufficient π–π stacking interaction is possible along the [0 1 1] direction. On the other hand, the existence of the DCB sheet prevents the π–π stacking interaction between the 2,3-Nc radical sheets in Co(2,3-Nc)(CN)$_2$·2DCB. Only a weak contact exists along the [0 $\bar{1}$ 1] direction; overlap between the peripheral C–C bonds. This π–π stacking interaction is negligibly small (*vide infra*).

Electrical conductivity

Since these crystals are composed of π-radicals with sufficient π–π stacking interaction, they are expected to be electrical

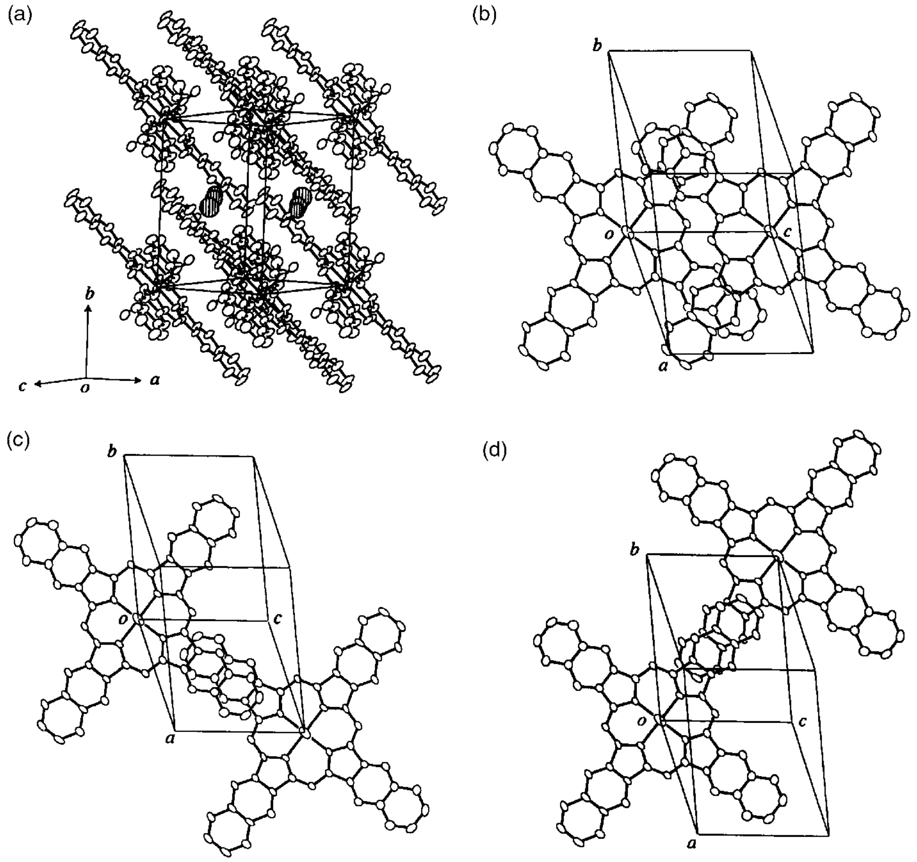

Fig. 1 Crystal structure of Co(2,3-Nc)$(CN)_2$·CH_3CN (a) and the two overlapped units; stacking along [0 0 1] (b), stacking along [1 0 1] (c), and stacking along [0 1 1] (d). Only one-half of the disordered CH_3CN molecules are shown (hatched molecules in (a)).

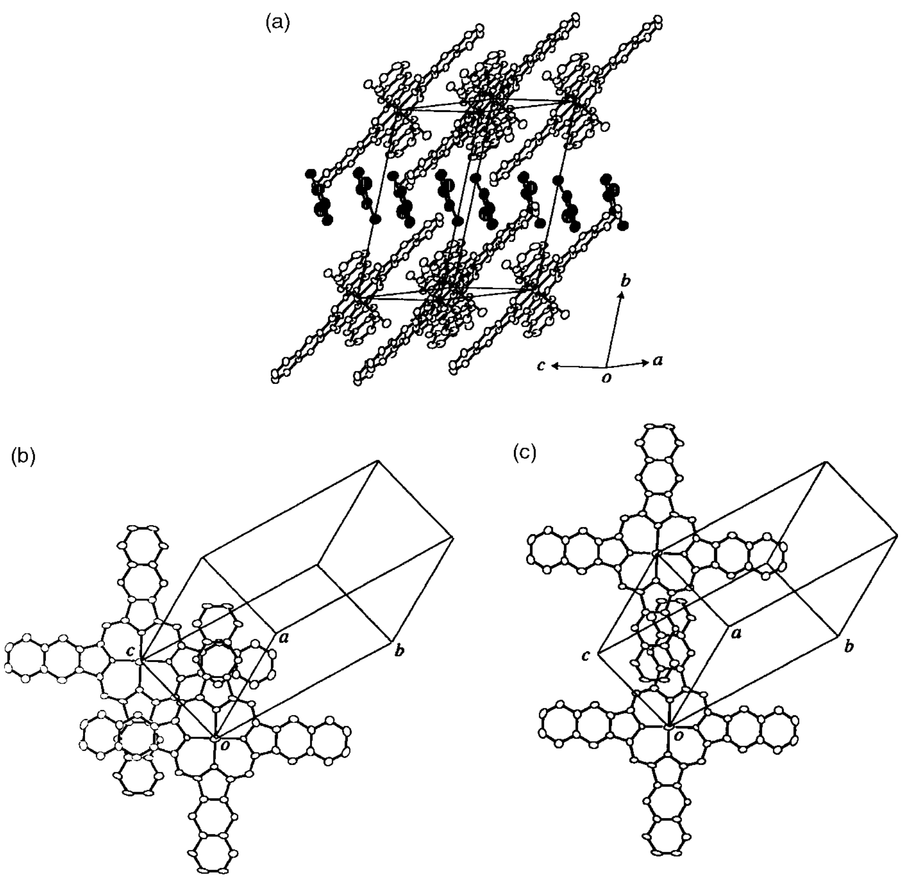

Fig. 2 Crystal structure of Co(2,3-Nc)$(CN)_2$·2DCB (a) and the two overlapped units; stacking along [0 0 1] (b) and stacking along [1 0 1] (c). Hatched molecules in (a) are DCB.

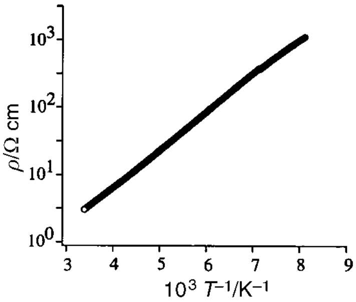

Fig. 3 Temperature dependence of the single-crystal resistivity (*//c*) of Co(2,3-Nc)$(CN)_2$·CH_3CN.

conductors. Unfortunately, the single crystal of Co(2,3-Nc)$(CN)_2$·2DCB is not stable enough for its conductivity to be measured. The compacted powder, during compaction of which some of the crystal solvents are inevitably lost, is still conductive. The conductivity at room temperature is 3×10^{-2} S cm^{-1}, and its temperature dependence is semiconductive with an activation energy of 0.12 eV. On the other hand, the single crystal of Co(2,3-Nc)$(CN)_2$·CH_3CN is stable, and its resistivity was measured using a single crystal. As shown in Fig. 3, the temperature dependence of the resisitivity is semiconductive with an activation energy of 0.11 eV. The conductivity at room temperature along the *c*-axis, 0.3 S cm^{-1}, is relatively high for neutral radicals. This value is comparable to that of the phthalocyanine neutral radical crystal with three-dimensional π–π stacking interactions, namely, Co(Pc)$(CN)_2$·$2H_2O$.[2] The values observed for the 2,3-Nc neutral radical crystals are also comparable to that observed for the CN bridged Co(2,3-Nc) polymer (0.1 S cm^{-1}).[8]

Dimensionality of the π–π stacking interaction

In both crystal lattices of the 2,3-Nc radical, more than one π–π stacking interaction exists. The dimensionality of the electronic interaction has therefore been evaluated from the overlap integral values between the HOMOs of 2,3-Nc, in which the unpaired electron is accommodated. The HOMO coefficients were calculated by the extended Hückel method based on the molecular geometry determined by X-ray structure analyses. The overlap integral values for each π–π stacking interaction are summarized in Table 2. In Co(2,3-Nc)$(CN)_2$·CH_3CN, all of the three π–π stacking interactions have appreciable values, though they are slightly anisotropic. On the other hand, the values are highly anisotropic in Co(2,3-Nc)$(CN)_2$·2DCB; the value along [0 $\bar{1}$ 1], between the two-dimensional 2,3-Nc sheets, is only a hundredth of those in the two-dimensional sheet. Therefore, the dimensionality of the electronic interaction may be categorized as two-dimensional for Co(2,3-Nc)$(CN)_2$·2DCB and as three-dimensional for Co(2,3-Nc)$(CN)_2$·CH_3CN. Though a precise comparison of the conductivity was not possible for the present 2,3-Nc radical crystals owing to their small size and instability, the highly conducting nature of three-dimensional Co(2,3-Nc)$(CN)_2$·CH_3CN is consistent with the tendency found for the Pc neutral radical crystals.[2]

Table 2 Overlap integral (*S*) for each π–π overlap in the 2,3-Nc radical crystals

Crystal	Direction of π–π overlap	*S* ($\times10^{-3}$)
Co(2,3-Nc)$(CN)_2$·CH_3CN	[0 0 1]	−3.6
	[1 0 1]	1.3
	[0 1 1]	0.84
Co(2,3-Nc)$(CN)_2$·2DCB	[0 0 1]	−1.34
	[1 0 1]	−0.62
	[0 $\bar{1}$ 1]	−0.018

In general, the electrical properties of neutral radical crystals are closely related to the on-site Coulombic repulsion. If this energy is large, the effect may be clearly observed in the energy gap between the valence (lower Hubbard) and conduction (upper Hubbard) bands. Thus, in this case the thermal activation for charge carrier generation may be the main origin of the semiconducting property. When the on-site Coulombic repulsion energy is not so large, both carrier generation and hopping probability, which is also expected to be thermally activated, may become determinants of the electrical property. At the present stage, the effective on-site Coulombic repulsion energy in these neutral radical crystals is unknown. Considering their relatively high conductivities, increased dimensionality is assumed to decrease the on-site Coulombic repulsion energy and to increase the hopping probability.

Another interesting point in the present system compared with the Pc system is the solvent species which can be accommodated in the lattice. In the Pc neutral radical crystals, relatively small molecules such as $CHBr_3$,[3] $CHCl_3$,[2] DMSO,[4] and H_2O[1,2] can be a second component of the lattice. Compared with them, DCB is significantly larger. The notable point is that the 2,3-Nc neutral radicals can still form a two-dimensional sheet even for such a large crystal solvent. For a smaller crystal solvent such as CH_3CN, the 2,3-Nc radical can interact with six neighbors, resulting in a three-dimensional π–π stacking network. This may be the main feature of the 2,3-Nc system as a result of the linear extension of the Pc π-conjugation.

In conclusion, we have succeeded in growing neutral radical crystals of Co(2,3-Nc)$(CN)_2$. The crystals are conductive, and the π–π stacking network is extended to being two-dimensional in Co(2,3-Nc)$(CN)_2$·2DCB and three-dimensional in Co(2,3-Nc)$(CN)_2$·CH_3CN. The feature that the 2,3-Nc unit can crystallize with a large second component while keeping the two-dimensional π–π stacking network may be promising for construction of two-dimensional partially oxidized conductors based on the Co(2,3-Nc)$(CN)_2$ unit.

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