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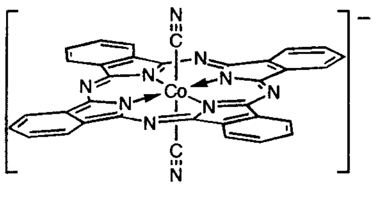
Cyano-bridged cobalt–phthalocyanine dimer: a trapped species by crystallization with a π radical cation

Susumu Takano, Toshio Naito and Tamotsu Inabe*†

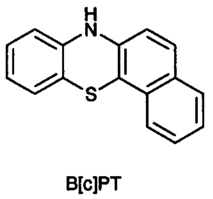
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060, Japan

Electrochemical oxidation of the solution containing benzo[c]phenothiazine (B[c]PT) and dicyanophthalocyaninatocobalt(III) anion, $[Co(Pc)(CN)_2]^-$, gives crystalline solids containing cyano-bridged cobalt–phthalocyanine dimer units. The dimeric species which may exist in equilibrium with the monomer is selectively trapped by crystallization with the B[c]PT cation radical.

Phthalocyanine (Pc) is known as an important industrial product, and its electronic properties also receive attention from the viewpoints of photoconductivity and dark conductivity.[1] Dicyanophthalocyaninatocobalt(III) anion, $[Co(Pc)(CN)_2]^-$, can be a novel component of multi-dimensional conductors,[2] and the neutral radical[3] and partially oxidized conductors[4] have been obtained by electrochemical oxidation of this anion. Combination of $[Co(Pc)(CN)_2]^-$ with π-donor components has yielded non-conducting simple salts,[5] whereas the salts are expected to be conducting when the composition deviates from 1:1. During the study of preparing such salts, we have found that benzo[c]phenothiazine, B[c]PT, can form a 1:1 compound with the dimerized phthalocyanine unit, [(CN)−(Pc)Co−CN−Co(Pc)(CN)] {(μ-cyano-*C*,*N*)bis[cyano(phthalocyaninato)cobalt(III)]}. This CN-bridged metallophthalocyanine dimer is assumed to exist as a minor species of equilibrium in the acetonitrile solution of $[Co(Pc)(CN)_2]^-$, and is selectively trapped and accumulated in the form of a crystal through molecular recognition by the co-existing B[c]PT radical cation.



$[Co(Pc)(CN)_2]^-$



B[c]PT

[B[c]PT][(CN)(Pc)Co−CN−Co(Pc)(CN)] was obtained by an electrochemical oxidation technique. $K[Co(Pc)(CN)_2]$ (20 mg) and B[c]PT (8 mg) was dissolved in acetonitrile (*ca.* 30 ml) and placed in a glass-fritted two-compartment electrochemical cell. A constant current of 1 μA applied between the two platinum electrodes immersed in each compartment for two weeks yielded typically 10 mg of the product crystals.

The molecular structure derived from the X-ray structure analysis‡ is shown in Fig. 1. Since the whole [(CN)(Pc)Co−CN−Co(Pc)(CN)] unit is crystallographically independent, there are two possible orientations for the bridging CN group. When the structure was refined by fixing the orientation, the thermal parameters for C_{bridge} and N_{bridge} were never reasonable; the B_{eq} value for the carbon atom is too small [1.8(2) Å^2 for C_{bridge}−Co(1), 2.1(2) Å^2 for C_{bridge}−Co(46)] and that of the nitrogen atom is too large [3.8(2) and 3.6(2) Å^2, respectively]. The real structure is thus suggested to contain both orientations with equal probability, and the final refinement based on this model gives the improved thermal parameters; B_{eq} of N(44A) is 2.6(2) Å^2 and that of C(45A) is 2.9(2) Å^2.[6] The slightly bending configuration of the Co−CN−Co backbone is also consistent with other cyano-bridged Co^{III} complexes[7] with simpler ligands (NH_3 and CN). Since the structure is an average of the two orientations, the molecule is expected to be symmetrical. Slight deviation from

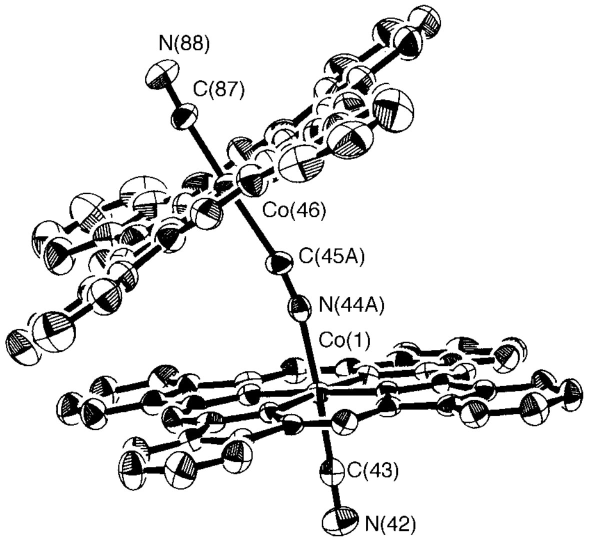


Fig. 1 Perspective view and a part of the atom numbering scheme of the [(CN)(Pc)Co−CN−Co(Pc)(CN)] unit. Selected bond lengths (Å) and angles (°): Co(1)−N(44A) 1.986(7), Co(46)−C(45A) 2.070(7), N(44A)−C(45A) 1.130(8), Co(1)−N(44A)−C(45A) 167.5(7), Co(46)−C(45A)−N(44A) 170.2(7).

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† E-mail: inabe@rigaku1.science.hokudai.ac.jp

‡ *Crystal data*: A prism-like single crystal with dimensions of 0.70 × 0.35 × 0.05 mm^3 was used for X-ray structure analysis. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (293 K). $C_{83}H_{43}N_{20}Co_2S$, $M = 1470.31$, monoclinic, space group $P2_1/a$, $a = 17.680(4)$, $b = 20.692(4)$, $c = 17.599(3)$ Å, $\beta = 96.31(2)°$, $V = 6399(1)$ Å^3, $Z = 4$, and μ(Mo-Kα) = 6.21 cm^{-1}. Of 15 571 reflections measured, 6703 independent reflections with $I > 3.0\sigma(I)$ were used for the refinement. The final R is 0.072 and R_w is 0.058 (955 variables). Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/74.

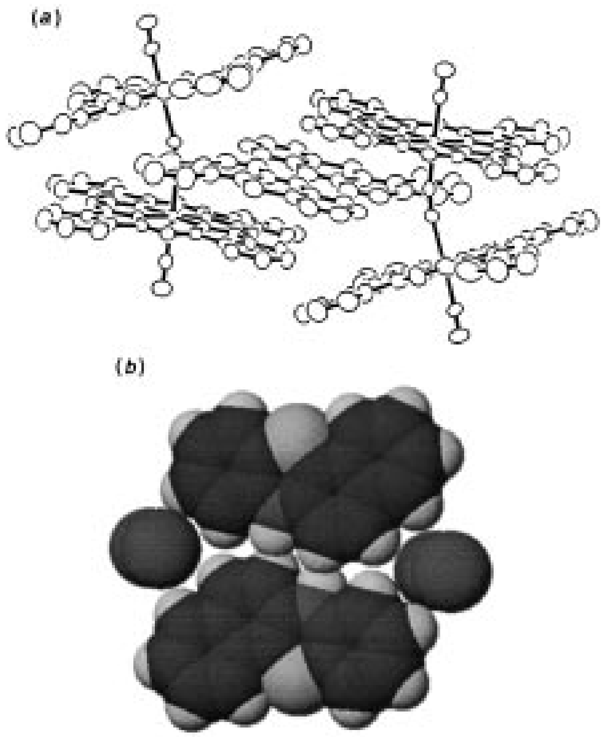
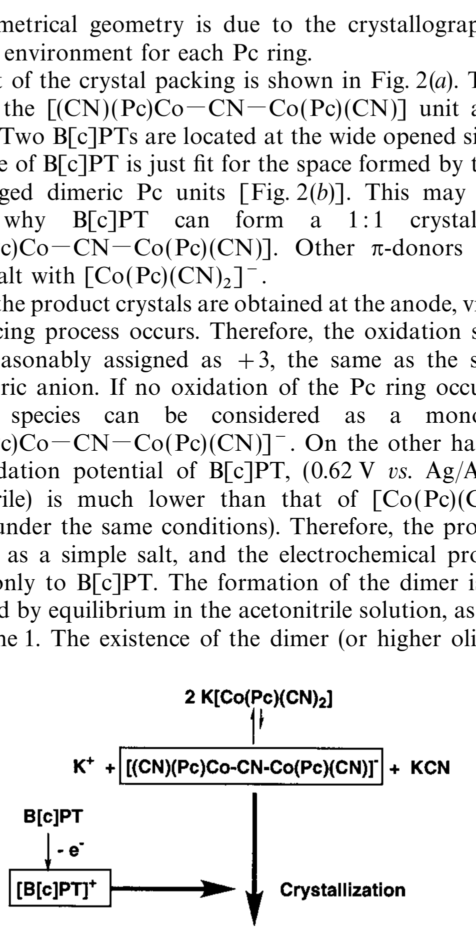


Fig. 2 Crystal packing of the $[B[c]PT]_2[(CN)(Pc)Co-CN-Co(Pc)(CN)]_2$ unit (*a*) and two B[c]PT sandwiched by the two $[(CN)(Pc)Co-CN-Co(Pc)(CN)]$ units represented by the van der Waals radii (*b*); for the latter only the Co—CN—Co fragments are shown

the symmetrical geometry is due to the crystallographically different environment for each Pc ring.

A part of the crystal packing is shown in Fig. 2(*a*). Two Pc rings in the $[(CN)(Pc)Co-CN-Co(Pc)(CN)]$ unit are not parallel. Two B[c]PTs are located at the wide opened site, and the shape of B[c]PT is just fit for the space formed by the two CN-bridged dimeric Pc units [Fig. 2(*b*)]. This may be the reason why B[c]PT can form a 1:1 crystal with $[(CN)(Pc)Co-CN-Co(Pc)(CN)]$. Other π-donors always form a salt with $[Co(Pc)(CN)_2]^-$.

Since the product crystals are obtained at the anode, virtually no reducing process occurs. Therefore, the oxidation state of Co is reasonably assigned as +3, the same as the starting monomeric anion. If no oxidation of the Pc ring occurs, the dimeric species can be considered as a monoanion, $[(CN)(Pc)Co-CN-Co(Pc)(CN)]^-$. On the other hand, the first oxidation potential of B[c]PT, (0.62 V *vs.* Ag/AgCl in acetonitrile) is much lower than that of $[Co(Pc)(CN)_2]^-$ (1.05 V under the same conditions). Therefore, the product is assigned as a simple salt, and the electrochemical process is related only to B[c]PT. The formation of the dimer is, thus, generated by equilibrium in the acetonitrile solution, as shown in Scheme 1. The existence of the dimer (or higher oligomer) by equilibrium in the solution of $[Co(Pc)(CN)_2]^-$ is also supported by the fact that the formation of the cyano-bridged polymer, $[Co(Pc)(CN)]_n$, was achieved by simply refluxing $Na[Co(Pc)(CN)_2]$ in water.[8] In this situation, dissociated NaCN preferentially stays in the liquid phase, so that the equilibrium moves toward promoting the polymerization.



Scheme 1 Proposed mechanism for the formation of $[B[c]PT][(CN)(Pc)Co-CN-Co(Pc)(CN)]$

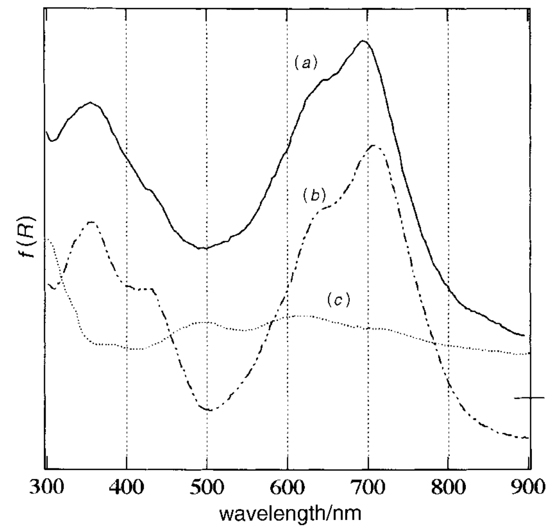


Fig. 3 Diffuse reflectance spectra of $[B[c]PT][(CN)(Pc)Co-CN-Co(Pc)(CN)]$ (*a*), $K[Co(Pc)(CN)_2]$ (*b*), and $B[c]PT\cdot Br$ (*c*). $f(R)$ is the Kubelka–Munk function which corresponds to the absorption. Background level for $[B[c]PT][(CN)(Pc)Co-CN-Co(Pc)(CN)]$ is shifted to the marker at the right vertical axis.

The electrical conductivity of $[B[c]PT][(CN)(Pc)Co-CN-Co(Pc)(CN)]$ is very poor, $<10^{-8}\ \Omega^{-1}\ cm^{-1}$. This is to be expected, since the crystal consists of open-shell cations enclosed by discrete closed-shell anions. Conduction through the overlap between Pc and B[c]PT is not likely owing to the large difference between their ionization potentials.

On the other hand the cyano-bridged metallophthalocyanine polymers are known to be conducting without doping with oxidizing agents,[8–10] while it is not clear why they are conducting. Considering the Co—CN—Co distance (5.186 Å), it is possible for only some of the Pc rings in neighboring polymer chains to be interleaved with each other. Though it was suggested that π–π overlap still plays some role in charge transfer,[9] the conduction through the $-Co-(C{\equiv}N-Co-)_n$ backbone may not be ruled out.

The optical spectroscopic measurements were carried out using powder samples. Fig. 3 shows the diffuse reflectance spectrum of $[B[c]PT][(CN)(Pc)Co-CN-Co(Pc)(CN)]$. Since the absorption by $[B[c]PT]^+$ in the visible region is relatively weak, the Q-band of Pc is clearly seen in the spectrum. The band shape is practically unchanged compared with the spectrum of $K^+[Co(Pc)(CN)_2]^-$, though a slight blue-shift (*ca.* 10 nm) can be seen. These data also suggest that the π–π interaction between the Pc rings is negligibly small. The CN stretching mode in the FTIR spectra using a KBr disc specimen was so weak that it is not detectable with a reliable S/N ratio.

In conclusion, we have found that $[(CN)(Pc)Co-CN-Co(Pc)(CN)]^-$ can selectively be trapped and accumulated in the form of a crystal by co-existence of the B[c]PT radical cation. Since it is extremely difficult to synthesize this type of dimer with high purity, the crystal growth based on molecular recognition by a gradually produced counter ion is an advantageous method for the isolation of such a chemical species.

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