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Synthesis, Characterization, and Conductivity of (μ-Cyano)(phthalocyaninato)cobalt(III)

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Abstract: Evidence for the synthesis of (μ-cyano)(phthalocyaninato)cobalt(III), $[PcCoCN]_n$ (**2**), via splitting off sodium cyanide from sodium dicyano(phthalocyaninato)cobalt(III), $NaPcCo(CN)_2$ (**1a**), is presented. Treatment of $[PcCoCN]_n$ (**2**) with base molecules L like pyridine, 2-methylpyrazine, piperidine, and *n*-butylamine leads to monomeric complexes PcCoCN(L) (**3**). All compounds are characterized by IR, far-IR, UV, and ^1H NMR spectroscopy, thermal and elemental analyses, and partly by FD mass spectroscopy. The infrared data are discussed in detail. The undoped polymer $[PcCoCN]_n$ (**2**) exhibits dc-dark conductivities around 10^{-2} S/cm. When the polymeric structure was decomposed by treatment with a competing ligand, the conductivity was diminished by 6–10 orders of magnitude.

Metal phthalocyanines that are axially bridged to polymers $[R_4PcMX]_n$, where R = H, M = Al, Ga, Cr, and X = F^-, and where R = H, *t*-Bu, M = Si, Ge, Sn, and X = O^{2-}, S^{2-}, exhibit electrical conductivities between 10^{-8} and 10^{-12} S/cm.[1-3] Doping with iodine increases the conductivities by 5–8 orders of magnitude up to 1 S/cm. We now report the synthesis and the conductivity of a corresponding polymer $[PcMCN]_n$ when the cyano group is introduced as a bridging ligand.

Our choice for the central atom of the metal phthalocyanine was determined by the following criteria: (i) ease of synthesis of the PcMCN unit and (ii) the possibility for hexacoordination by means of an additional coordinate bond. Cobalt fulfills both demands.

(Phthalocyaninato)cobalt compounds with trivalent central atoms, containing cyano groups as axial ligands, were produced through air oxidation of PcCo in the presence of cyanide in dimethylacetamide or by the addition of excess cyanide to a solution of $PcCoCH_3$. The complexes so obtained were investigated only as solutions; they were formulated as $PcCo(CN)_2$ and $PcCo(CN)CH_3$.[4,5]

The hydroxyl derivative of the tetrasulfonic acid-substituted phthalocyaninecobalt, $TsPcCoOH(H_2O)$, the corresponding methyl compound, $TsPcCoCH_3$, and the cyanoaquo complex, $TsPcCoCN(H_2O)$, however, were isolated as the tetrasodium salts.[6] In addition to the above-mentioned compounds, a further series of (phthalocyaninato)cobalt(III) organic derivatives is known.[4,7-11] They are diamagnetic and are described by the general formula $Pc^{2-}Co^{3+}X^{1-}(L)$.

Experimental Section

(Phthalocyaninato)cobalt(II) and Dichloro(phthalocyaninato)cobalt(II) were prepared and purified by reported procedures.[12] Routine infrared spectra were recorded on a Pye Unicam SP 1000 and in the CN stretch region on a Beckman IR 12 spectrometer as Nujol mulls. ^1H NMR spectra were obtained on a Bruker HX 90 apparatus. UV–Vis spectra were recorded on a Beckman Acta MVII spectrometer. Mass spectra were obtained on a Varian MAT 711 mass spectrometer by direct inlet and FD technique. Thermogravimetric measurements were carried out on a Netzsch STA Model 429 under nitrogen at a heating rate of 2 °C min^{-1}.

Synthesis of Sodium Dicyano(phthalocyaninato)cobalt(III), $NaPcCo(CN)_2 \cdot 5H_2O$ (1a). Procedure a. Dichloro(phthalocyaninato)cobalt(III) (1.28 g, 2 mmol) and sodium cyanide (1.47 g, 30 mmol) were suspended in 70 mL of ethanol. The mixture was refluxed for 72 h and filtered. The solid residue was washed several times with water. The resulting microcrystalline purple-black powder was dried under high vacuum for 5 h, yielding 1.15 g (78%) of product. This material is sufficiently pure for polymerization. Further purification is possible by dissolving it in dry acetone and subsequent removing of the solvent.

Procedure b. (Phthalocyaninato)cobalt(II) (0.57 g, 1 mmol) and sodium cyanide (0.98 g, 20 mmol were suspended in 60 mL of ethanol. Air was bubbled through the refluxing mixture for 72 h. After filtration the solid residue was washed several times with water. $NaPcCo(CN)_2$ was separated from unreacted, insoluble PcCo by Soxhlet extraction with dry acetone.

Infrared spectrum (Nujol mull, cm^{-1}) 2130 w; ^1H NMR (acetone-d_6) 8.2 (m, 8 H), 9.5 (m, 8 H); mass spectrum (inlet temperature 200 °C), *m/e* 26, 27, 52; FD, *m/e* 646; TG (dissociation range °C, mass decrease %) first step, 110–135, 12, second step, 280–310 4. Anal. Calcd for $C_{34}H_{26}N_{10}O_5CoNa$: C, 55.44; H, 3.56; N, 19.01; O, 10.86; Co, 8.00; Na, 3.12. Found: C, 55.32; H, 3.66; N, 18.68; O, 10.7; Co, 7.87; Na, 3.13.

Synthesis of (μ-Cyano)(phthalocyaninato)cobalt(III), $[PcCoCN]_n$ (2). Procedure a. $[PcCoCN]_n$ was prepared by extracting $NaPcCo(CN)_2$ with water 72 h in a Soxhlet extractor. Subsequent extraction with acetone separates unreacted $NaPcCo(CN)_2$, yielding the blue product.

Procedure b. Dichloro(phthalocyaninato)cobalt(III) (1.28 g, 2 mmol) and sodium cyanide 1.47 g, 30 mmol) were suspended in 70 mL of water. The mixture was refluxed for 3 days, filtered, and washed with water. Extraction with acetone left 1 g (83.7%) of a blue powder.

Infrared spectrum (Nujol mull, cm^{-1}) 2158 m; mass spectrum (inlet temperature 200 °C), *m/e* 26, 27, 52; TG (dissociation range °C, mass decrease %) 220–300, 4.7. Anal. Calcd for $C_{33}H_{16}N_9Co$: C, 66.34; H, 2.70; N, 21.10; Co, 9.86. Found: C, 65.80; H, 2.90; N, 20.61; Co, 9.60; Na, <0.1.

Synthesis of Cyano(phthalocyaninato)cobalt(III) Base Adducts, PcCo(CN)L (3a–d). L = pyridine, py; 2-methylpyrazine, mepyz; piperidine, pip; *n*-butylamine, bu. The complexes PcCo(CN)L were prepared by stirring $[PcCoCN]_n$ in the pure ligand L at 50 °C between 2 and 5 days. The blue suspension changed in a green solution, which was cooled and filtered. The resulting powder was dried under vacuum, yielding the products PcCo(CN)L.

Infrared spectrum (Nujol mull, cm^{-1}) 2147 w; thermal decomposition starts at 180 °C. Anal. Calcd for PcCo(CN)py, $C_{38}H_{21}N_{10}Co$: C,

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(1) (a) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. . *J. Am. Chem. Soc.* **1979**, *101*, 7071. (b) Dirk, C. W.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *Org. Coat. Plast. Chem.* **1980**, *43*, 646. (c) Meyer, G.; Wöhrle, D. *Makromol. Chem.* **1974**, *175*, 714. (d) Meyer, G.; Hartmann, M.; Wöhrle, D. *Ibid.* **1975**, *176*, 831, 1919.

(2) (a) Kuznesof, P. M.; Wynne, K. J.; Nohr, R. S.; Kenney, M. E. *J. Chem. Soc., Chem. Commun.* **1980**, 121. (b) Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Siebenmann, P. G. *J. Am. Chem. Soc.* **1981**, *103*, 4371. (c) Nohr, R. S.; Wynne, K. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1210. (d) Nohr, R. S.; Wynne, K. J.; Kenney, M. E. Second Chemical Congress of the North American Continent, San Francisco, CA, August, 1980; American Chemical Society: Washington, D.C.; Abstr. INOR 161.

(3) (a) Hanack, M.; Metz, J.; Pawlowski, G. *Chem. Ber.* **1982**, *115*, 2836. (b) Metz, J.; Pawlowski, G.; Hanack, M., applied for German patent. (c) Schneider, O.; Metz, J.; Hanack, M. *Mol. Cryst. Liq. Cryst.* **1982**, *81*, 273. (d) Hanack, M.; Fischer, K. *Chem. Ber.*, in press. (e) Metz, J.; Pawlowski, G.; Hanack, M. *Angew. Chem.*, in press.

(4) Day, P.; Hill, H. A. O.; Price, M. G. *J. Chem. Soc. A* **1968**, 90.

(5) Stillman, M. J.; Thomson, A. J. *J. Chem. Soc., Faraday Trans. 2*, **1974**, 790.

(6) Weber J. H.; Busch, D. H. *Inorg. Chem.* **1965**, *4*, 472.

(7) Eckert, H.; Lagerlund, I.; Ugi, I. *Tetrahedron* **1977**, *33*, 2243.

(8) Taube, R.; Drews, H.; Duc-Hiep, T. *Z. Chem.* **1969**, *9*, 115.

(9) Volpin, M. E.; Taube, R.; Drews, H.; Volkara, L. G.; Levctin, Y. Am.; Usuakova, T. M. *J. Organomet. Chem.* **1972**, *39*, C79.

(10) Eckert, H.; Schier, A. *Angew. Chem.* **1979**, *91*, 841.

(11) Taube, R.; Drews, H.; Marx, G. *Z. Anorg. Allg. Chem.* **1977**, *436*, 5.

(12) (a) Myers, J. F.; Rayner Canham, G. W.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461. (b) Ugi, I.; Eckert, H. *Liebigs Ann. Chem.* **1979**, 278.

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Table I. Infrared, ^{1}H NMR, and Conductivity Data of PcCo(III) Derivatives 1, 2, 3

	ν_{CN}, cm^{-1} [a]	^{1}H NMR, δ	σ_{RT}, S/cm
$NaPcCo(CN)_2$	2130	8.2 m (aromatic H), 9.5 m (aromatic H)	
PcCo(bu)CN	2142	*b*	3×10^{-12}
PcCo(pip)CN	2145	−5 s (pip N-*H*), −2.8 m (pip C_α-H), −1.3 to −0.3 m (pip C_β-H, C_δ-H), 8.3 m (aromatic H), 9.5 M (aromatic H)	3×10^{-8}
PcCo(py)CN	2147	*b*	3×10^{-12}
PcCo(mepyz)CN	2148	*b*	8×10^{-11}
$[PcCoCN]_n$	2158	*c*	2×10^{-2}

[a] Nujol mull. [b] Not sufficiently soluble. [c] Insoluble in uncoordinating solvents.

67.46; H, 3.13; N, 20.70. Found; C, 67.25; H, 3.56; N, 20.70.

Infrared spectrum (Nujol mull, cm^{-1}) 2148 m; thermal decomposition starts at 180 °C. Anal. Calcd for PcCo(CN)mepyz, $C_{38}H_{22}N_{11}Co$: C, 66.00; H, 3.20; N, 22.28. Found: C, 66.05; H, 3.29; N, 22.33.

Infrared spectrum (Nujol mull, cm^{-1}) 2145 w; thermal decomposition starts at 155 °C. ^{1}H NMR ($CDCl_3$) −5.0 (s, 1 H), −2.8 (m, 4 H), −0.3 to −1.3 (m, 6 H), 8.3 (m, 8 H), 9.5 (m, 8 H). Anal. Calcd for PcCo(CN)pip, $C_{38}H_{27}N_{10}Co$: C, 66.86; H, 3.98; N, 20.52. Found: C, 65.36; H, 4.07; N, 20.67.

Infrared spectrum (Nujol mull cm^{-1}) 2142 w; thermal decomposition starts at 160 °C. Anal. Calcd for PcCo(CN)bu, $C_{37}H_{27}N_{10}Co$: C, 66.27; H, 4.05 N, 20.9. Found: C, 65.92; H, 4.21; N, 21.27.

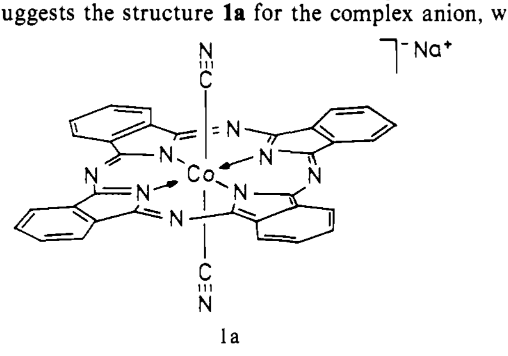
Results and Discussion

If one oxidizes PcCo with thionyl chloride in nitrobenzene, one obtains a paramagnetic complex with the stoichiometry of $PcCoCl_2$, whose investigation with ESR spectrometry requires formulation of the macrocycle as a radical cation $Pc^{1-}Co^{3+}Cl_2$.[12a] When $PcCoCl_2$ is heated for 3 days under reflux in ethanol with an excess of sodium or potassium cyanide, it is converted to a compound with the composition (by elemental analysis) $MPcCo(CN)_2 \cdot 5H_2O$ (M = Na, K) (**1**). Compound **1** can also be prepared by passing air through a suspension of PcCo and alkali cyanide in boiling ethanol;[6,8] (**1**) dissolves in acetone to give a green solution and thus can be separated from the unreacted, insoluble $PcCoCl_2$ or PcCo.

The complex $NaPcCo(CN)_2 \cdot 5H_2O$ (**1a**) was characterized through IR, far-IR, UV, and NMR spectroscopy, thermal and elemental analyses and FD mass spectroscopy (see Table I).

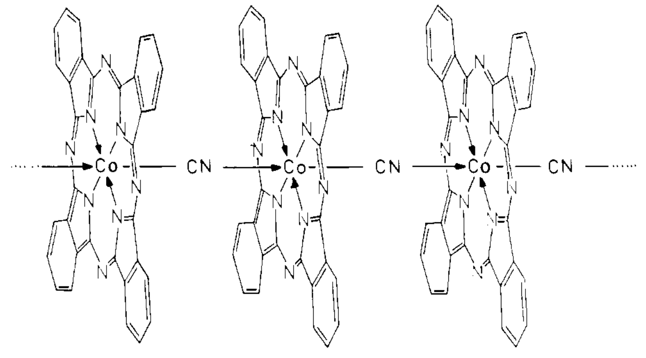
The UV-Vis data for **1** in DMF are identical with the spectrum given in ref 8 for $PcCo(CN)_2$.[13] The IR spectrum of **1a** exhibits a CN valence frequency at 2130 cm^{-1}, which is in the anticipated region for Co(III)-bound terminal cyano groups.[14]

This suggests the structure **1a** for the complex anion, which is confirmed by the NMR spectrum (Table I).[15] In the FD mass spectrum the peak of highest mass (*m/e* 646) can be ascribed to $[NaPcCo(CN)_2]^+$.[16] The elemental analysis of **1a** corresponds to the correct stoichiometry. A sample of **1a** which had been dried at room temperature under high vacuum contained 12% water, which was removed endothermically between 110 and 135 °C during a simultaneous TG/DTA measurement. A further endothermic weight loss (maximum 300 °C) corresponds to the loss of a cyanide group. At an inlet temperature of 200 °C, mass spectrum peaks for *m/e* 26 [CN], 27 [HCN], and 52 [$(CN)_2$] appeared. The IR spectrum of the solid residue remaining after the second step of thermal analysis showed, in addition to the characteristic bands for PcCo, an absorption at 2230 cm^{-1}, which is evidence for a carbon-bound cyano group. This band remains even after several extractions with water and ether and disappears only after the substance is heated to 490 °C, that is, to a temperature which is usual for splitting off peripheral phthalocyaninato substituents.[19]



1a

Formally, $[PcCoCN]_n$ (**2**) is available through loss of NaCN from **1a**. When **1a** is heated in water in an inert atmosphere for 3 days under reflux and then filtered, cyanide is present in the filtrate. The residue **2** is diamagnetic, in contrast to **1a**, is not soluble in acetone, and corresponds stoichiometrically to the formula PcCoCN. During thermal analysis the weight loss between 220 and 300 °C corresponds to a cyano group, but there is no ring substitution. One can obtain the same compound when $PcCoCl_2$ is treated with sodium cyanide in water. An attempted in situ oxidation of PcCo by air was unsuccessful. The CN valence frequency of **2** appears at 2158 cm^{-1}, and compared with **1a** and similar compounds containing terminal CN groups, is shifted about 30 cm^{-1} to higher energies. If we compare these values with the increase in CN valence frequency in (μ-cyano)bis(glyoximato)cobalt(III) derivatives with respect to complexes with terminal CN group,[21] then the presence of a cyano bridge in **2** is obvious.



2

When **2** is treated with bases (L) such as pyridine (py), 2-methylpyrazine (mepyz), piperidine (pip), and *n*-butylamine (bu), monomeric complexes are obtained with the composition PcCo(CN)L (**3**).

These compounds were characterized through IR and mass spectroscopy as well as by elemental and thermal analyses. The NMR spectrum of **3b** confirms its structure (see Table I). Thermal decomposition of the complexes (**3**) sets in at 155 °C for L = pip and at 180 °C for L = py.

The IR data for **3** shown in Table I exhibit a slight increase of the CN valence frequency with decreasing σ-donor and in-

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(13) Compound $PcCo(CN)_2$ was obtained by oxidation of PcCo in the presence of cyanide. The complex was reported diamagnetic. This does not agree with the given formula and argues for a solution of 1.

(14) (a) Crumbliss A. L.; Gaus, P. L. *Inorg. Chem.* **1976**, *15*, 737. (b) Dows, D. D.; Haim, A.; Wilmarth, W. K. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33. (c) Chadwick, B. M.; Sharp, A. G. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 83.

(15) Kane, A. R. Dissertation, Case Western Reserve University, 1969.

(16) FD MS measurements of ionic organometallic compounds usually show the mass of the complex anion or cation.[17] Nevertheless, the same technique lead to the detection of the mass of Na^+ adducts of organic macromolecules.[18]

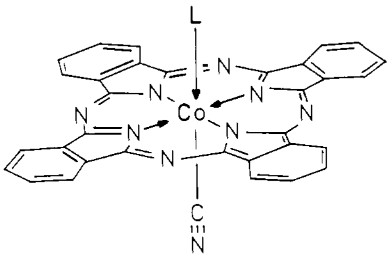
(17) Henis, N. B. H.; Lamana, W.; Humphrey, M. B.; Bursey, M. M.; Brookhart, M. S. *Inorg. Chim. Acta* **1981**, *54*, L11.

(18) Schulten, H. R.; Mahnig, M. *Forschung (Mitteilungen der DFG)* **1981**, *4*, 10.

(19) The simultaneous TG/DTA measurement of $PcCoCl_2$ exhibits two endothermic steps whose weight losses each correspond to a Cl atom. In the first step, therefore, Cl_2 is split out, which chlorinates the ring and produces ClPcCo. The same reaction can be performed in molten anthracene, which traps the halogen. The yield of PcCo is quantitative. The peripheral Cl atom of ClPcCo is lost at 500 °C.[20]

(20) Metz, J.; Hanack, M., unpublished.

(21) Gauss, P. L.; Crumbliss, A. L. *Inorg. Chem.* **1976**, *15*, 2081.



3a, L = py
b, L = pip
c, L = Bu
d, L = mepyz

creasing π-acceptor abilities of the ligands which are trans to the cyano groups. This tendency is comparable[21] with that of analogous compounds of the cyanobis(glyoximato)cobalt(III) series and runs parallel with the thermal stabilities of the observed complexes. The explanation for this behavior derives from a combination of the Co–C and C–N bond strengths.[22] The strength of the Co–C bond is determined almost exclusively by the σ-donor abilities of the cyano ligands,[21] so that a stronger σ-donor ligand (for example, bu) trans to the cyano group reduces the (Lewis) acidity of the central atom and thus, in comparison with a weaker σ-donor ligand with π acid properties (e.g., py, mepyz) which increase the acidity, brings about a lower CN valence frequency.

The increased valence frequency of **2**, the thermal stability, and the stoichiometry, together with the pronounced tendency of cobalt(III) for octahedral coordination, suggest the formulation of this compound as a cyano-bridged polymer, which is shown schematically in structure **2**.

A monomeric unit of composition PcCoCN, in which the sixth coordination position on the central atom is satisfied by pseudocoordination of an aza-bridging nitrogen from the neighboring phthalocyaninato ring, seems unrealistic, since the cyano nitrogen approaches a ligand strength comparable with ammonia.[23]

The previously investigated (by X-ray analysis) CN-bridged Co(III) complexes are binuclear structures and show a nonlinear Co–CN–Co arrangement.[24] Nevertheless, the additional coordination of the cyanide nitrogen leads to an increase in the CN valence frequency up to 2200 cm^{-1}. Formula **2**, therefore, is given only to illustrate the structural principle and contains no structural details.

The dc-dark conductivity of **2** was determined with an apparatus[25] for the measurement of powder conductivities according to the four-probe van der Pauw technique under 1 kbar of pressure and at room temp.[26] Measurements of the complexes **3** were carried out in the usual two-probe manner.

The dc-dark conductivity of $NaPcCo(CN)_2$ could not be measured because of electrochemical decomposition. The *undoped* complex $[PcCoCN]_n$ (**2**) exhibits electrical conductivities around 10^{-2} S/cm (Table I), which are comparable with values obtained for doped samples of known μ-oxo and μ-fluoro polymers. When the polymeric structure was decomposed by treatment with a competing ligand, e.g., py, pip, bu, mepyz, to form PcCo(CN)L, the conductivity was diminished by 6–10 orders of magnitude (Table I).

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Registry No. 1a, 84279-51-6; **2**, 84279-53-8; **3a**, 84279-54-9; **3b**, 84279-56-1; **3c**, 84303-13-9; **3d**, 84279-55-0; $PcCoCl_2$, 47838-42-6; NaCN, 143-33-9; PcCo, 3317-67-7.

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[22] Purcell, K. F. *J. Am. Chem. Soc.* **1967**, *89*, 248.

[23] Shriver, D. F.; Shriver, S. A.; Anderson, S. E. *Inorg. Chem.* **1965**, *4*, 725.

[24] (a) Fronczek, F. R.; Schaefer, W. P. *Inorg. Chem.* **1974**, *13*, 727. (b) Wang, B. Ch.; Schaefer, W. P.; Marsh, R. E. *Ibid.* **1971**, *10*, 1492.

[25] Hanack, M.; Kobel, W.; Schneider, O.; Selig, K., unpublished.

[26] Measurements of the temperature-dependent conductivities, activation energies, and microwave conductivities are underway and will be published elsewhere.