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# Synthesis and Properties of (Phthalocyaninato)- and (Tetrabenzoporphyrinato)cobalt(III) Thiocyanate and Isothiocyanate Compounds. Crystal and Molecular Structure of (Phthalocyaninato)(pyridine)(thiocyanato)cobalt(III)

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Dichloro(phthalocyaninato)cobalt(III), $PcCoCl_2$, and potassium thiocyanate react in ethanol with reduction of the macrocycle and ligand exchange to give potassium bis(isothiocyanato)(phthalocyaninato)cobalt(III)–ethanol, $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**). $^1H$ NMR data of **1** in acetone suggest three isomers with respect to the nature of the metal–thiocyanate bond. Monomeric **1** decomposes in the presence of water to form (phthalocyaninato)($\mu$-thiocyanato)cobalt(III), $[PcCoSCN]_n$ (**2**). **2** is also obtained by treating $PcCoCCl_3COO\cdot CCl_3COOH$ with KSCN in ethanol or by reacting $PcCoCl_2$ with KSCN in boiling water. Infrared as well as X-ray powder diffraction data give evidence for the bridged structure of **2**, which exhibits a dc dark conductivity of $\sigma_{RT} = 6 \times 10^{-3}$ S/cm without external doping. $[PcCoSCN]_n$ (**2**) is almost insoluble in noncoordinating solvents; N-donor bases such as pyridine (py) and pyrazine (pyz) decompose the bridged structure to give $PcCo(py)SCN\cdot CHCl_3$ (**3**) and PcCo(pyz)SCN (**4**), respectively. By X-ray analysis **3** was found to be a thiocyanate complex in the solid state. $PcCo(py)SCN\cdot CHCl_3$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 19.381$ (1) Å, $b = 18.316$ (9) Å, $c = 10.115$ (6) Å, $\beta = 90.79$ (5)°, and $Z = 4$. $^1H$ NMR measurements of **3** in $CDCl_3$ give evidence for the existence of both S- and N-bonded isomers in solution. IR data of PcCo(pyz)SCN (**4**) compared to those of $PcCo(py)SCN\cdot CHCl_3$ (**3**) indicate a metal–S bond in PcCo(pyz)SCN (**4**). In contrast to the case for (phthalocyaninato)cobalt, (tetrabenzoporphyrinato)cobalt(III) forms exclusively monomeric isothiocyanate complexes $TBA[(TBP)Co(NCS)_2]$ (**6**) and (TBP)CoNCS (**7**).

## Introduction

Bridged one-dimensional macrocyclic metal complexes $[MacML]_n$[1] containing phthalocyanine,[2-6] tetrabenzoporphyrin,[7] and naphthalocyanine[8,9] as the macrocycle (Mac), a transition-metal atom, e.g. Fe, Ru, Co, and Rh, as the central metal atom M, and a linear bidentate ligand L, e.g. cyanide,[2,3,7] pyrazine,[4,6] tetrazine,[5,9] and 1,4-diisocyanobenzene,[6,8] as bridging ligand, exhibit good semiconducting properties, even without external oxidative doping. In this paper for the first time the thiocyanate-bridged compound $[PcCoSCN]_n$ (**2**)[10] is presented and the bonding mode of the monomeric complexes $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**), $PcCo(py)SCN\cdot CHCl_3$ (**3**), and PcCo(pyz)SCN (**4**) is discussed. In addition the influence of a bridging thiocyanate on the electrical properties of **2** is investigated. The mode of bonding of the ambidentate ligand thiocyanate to transition metals was shown to be influenced by a variety of factors; these include the nature of the metal and its oxidation state,[11-13] the steric and electronic characteristics of other ligands in the coordination sphere,[11,14,15] the nature of the solvent,[16-18] and, in case of anionic complexes, the nature of the counterion.[19] Isomerization reactions with respect to the metal–thiocyanate bond were shown to take place in solution[20] as well as in the solid state.[21]

Recent calculations on $[PcML]_n$ ($L = CN^-$, pyz) compounds[22] give evidence for a mixing of bridging-group $\pi$ and transition-metal d orbitals into the conduction band of the bridged species in contrast to the case for main-group polymers such as $[PcSiO]_n$[23] and $[PcSiC_2]_n$,[22] the conductive behavior of which depends exclusively on the doping level, inter-ring separation, and inter-ring rotation. Polymeric bridged compounds such as $[PcMCN]_n$[2,24] (M = Fe, Co) and $[(TBP)CoCN]_n$[7] are semiconductors with a small band gap that is assumed to be tuned by other ligands while it retains the essential trends of the band structure.

Compared to the interplanar distance in $[PcCoCN]_n$[2] (~500 pm), the one in **2** is estimated to be approximately 290 pm longer.[25] In addition the smaller M–S–C angle[26] (100–110°) in comparison with the almost linear M–C–N arrangement[27] (160–170°) has to be taken into account for the polymer structure.

## Experimental Section

All preparations were carried out under an $N_2$–inert-gas atmosphere. Solvents were distilled from the appropriate drying agents under $N_2$. The

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[1] Abbreviations: Mac = macrocycle, Pc = phthalocyaninato, TBP = tetrabenzoporphyrinato, dmgH = dimethylglyoximato, M = transition metal, L = $\pi$-electron-containing bidentate ligand, py = pyridine, pyz = pyrazine, pip = piperidine, ba = *n*-butylamine, *p*-dib = 1,4-diisocyanobenzene, *m*-dib = 1,3-diisocyanobenzene, CNS = unspecified bonding mode of the thiocyanate ligand, $TBA^+$ = tetrabutylammonium cation, Me = methyl.

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following methods were used: $^1$H NMR spectra, Bruker WM 400 spectrometer using signals of $CDCl_3$ or acetone-$d_6$ as internal standard; IR spectra, Perkin-Elmer 398 spectrometer as Nujol mulls, with salicylic acid being used for determination of the integrated intensities of the CN stretching frequencies; far-IR spectra, Bruker IFS 114c spectrometer with polyethylene pellets; UV–vis spectra, Perkin-Elmer Lambda 5 spectrometer; magnetic measurements, Gouy balance; EPR spectra, Varian E-12 spectrometer with microcrystalline samples at room temperature; powder diffraction data, Philips K4 spectrometer; thermogravimetrical measurements, Netzsch STA Model 429 instrument under nitrogen at a heating rate of 2 °C/min; C,H,N microanalyses, Carlo Erba Model 1104 Elemental Analyzer; Cl microanalyses, mercurimetric titration; S microanalyses, the method of Wagner;[28] K and Co microanalyses, Pascher Microanalytical Laboratory, Bonn, West Germany; powder dc dark conductivities, four-probe Van der Pauw technique, 1 kbar at room temperature.[29] The activation energies ($E_a$) were determined by temperature-dependent conductivity measurements following the equation $\sigma_{RT} = \sigma_0 e^{-E_a/kT}$.[29]

$PcCoCl_2$,[30] TBA[PcCo(NCS)$_2$],[31] $PcCoCCl_3COO{\cdot}CCl_3COOH$,[31] and (TBP)Co[7] were prepared by reported procedures.

**Preparation of K[PcCo(CNS)$_2$]·$C_2H_5OH$ (1).** $PcCoCl_2$ (300 mg, 0.47 mmol) and a 10-fold excess of KSCN (914 mg, 9.4 mmol) were suspended in 50 mL of ethanol, and the mixture was stirred for 24 h at room temperature, and filtered to yield a green residue containing some amounts of KSCN. Violet rhombic crystals of **1** were obtained by vapor diffusion of diethyl ether into a saturated ethanolic solution of the crude product, yield 210 mg (58%). $^1$H NMR (acetone-$d_6$): $\delta$ 9.68 (m, 8 H), 9.62 (m, 16 H), 9.57 (m, 8 H), 8.33 (m, 8 H), 8.27 (m, 16 H), 8.23 (m, 8 H), 3.61 (q, 8 H), 1.13 (t, 12 H). IR (Nujol mull, cm$^{-1}$): 2095 s. Far-IR (polyethylene, cm$^{-1}$): 302 m, 323 s, 435 s, 518 m, 572 s, 618 w. TG (dissociation range, °C; mass loss calcd, %; mass loss found, %): 90–250; 21; 10 (incomplete distortion, residue contains CN valence frequencies at 2210, 2059, and 2043 cm$^{-1}$). UV–vis (acetone; $\lambda$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)): 660 (138 000), 635 (34 000), 597 (28 000), 330 (42 000). Anal. Calcd for $C_{36}H_{22}CoKN_{10}OS_2$: C, 55.95; H, 2.87; Co, 7.63; K, 5.06; N, 18.12; S, 8.30. Found: C, 56.02; H, 2.63; Co, 7.43; K, 5.77; N, 17.56; S, 8.52.

**Preparation of [PcCoSCN]$_n$ (2). Procedure a.** **1** (154 mg, 0.2 mmol) was powdered and suspended in 50 mL of $H_2O$, and the mixture was stirred for 1 h. **1** decomposed quantitatively, and compound **2** was formed.

**Procedure b.** $PcCoCl_2$ (500 mg, 0.78 mmol) and KSCN (390 mg, 4.0 mmol) were stirred in 75 mL of boiling $H_2O$ for 3 days, the mixture was filtered, and the filtrate was washed with hot water and ethanol. The blue powder **2** was dried at 80 °C under high vacuum; yield 360 mg (73%).

**Procedure c.** $PcCoCCl_3COO{\cdot}CCl_3COOH$ (897 mg, 1.0 mmol) and KSCN (607 mg, 6.0 mmol) were stirred in 200 mL of ethanol for 3 h at room temperature. The reaction mixture was filtered, and the residue was washed several times with ethanol to yield 470 mg (75%) of pure **2**.

IR (Nujol mull, cm$^{-1}$): 2110 m. Far-IR (polyethylene, cm$^{-1}$): 283 w, 300 m, 326 s, 346 vs, 365 w, 406 m, 434 m, 519 m, 571 m, 641 w. TG (dissociation range, °C; mass loss calcd, %; mass loss found, %): 140–350; 9.2; 9.0. Powder diffraction data (2$\theta$, deg): 6.15 w, 8.30 m, 8.70 s, 10.95 s, 11.70 m, 12.87 s, 14.95 w, 15.45 m, 16.73 s, 17.83 m, 19.75 m, 25.55 w, 26.90 w, 27.35 vw, 29.63 w, 31.50 w. Anal. Calcd for $C_{33}H_{16}CoN_9S$: C, 62.96; H, 2.56; N, 20.02; S, 5.10. Found: C, 62.08; H, 2.57; N, 19.53; S, 5.26. Magnetic measurement data ($\chi_g$, cm$^3$ g$^{-1}$): $-3.6 \times 10^{-7}$.

**Preparation of PcCo(py)SCN·$CHCl_3$ (3).** **2** (472 mg, 0.75 mmol) was stirred in 100 mL of pyridine for 24 h at room temperature. Excess pyridine was removed, and the green residue was dissolved in $CHCl_3$. If the solvent was allowed to evaporate slowly, dark violet needles of **3** were formed; yield 500 mg (82%). $^1$H NMR ($CDCl_3$): $\delta$ 9.62 (m, 2 H), 9.59 (m, 8 H), 8.26 (m, 2 H), 8.22 (m, 8 H), 7.24 (s, $CHCl_3$), 6.14 (t, 1 H), 6.07 (t, 0.25 H), 5.28 (t, 2 H), 5.17 (t, 0.5 H), 1.92 (d, 2 H); a second doublet due to the N-bonded isomer of **3** was not observed. IR (Nujol mull, cm$^{-1}$): 2105 m. Far-IR (polyethylene, cm$^{-1}$): 279 m, 300 w, 326 s, 435 m, 519 w, 576 m, 638 w. TG (dissociation range, °C; mass loss calcd, %; mass loss found, %): 90–120 ($CHCl_3$), 160–350 (py, SCN); 31.0; 31.2. UV–vis ($CHCl_3$; $\lambda$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)): 669 (165 000), 638 (42 000), 604 (37 000), 349 (58 000), 331 (49 000). Anal. Calcd for $C_{39}H_{22}Cl_3CoN_9S$: C, 56.57; H, 2.68; Cl, 12.84; N, 16.92; S, 3.87. Found: C, 56.32; H, 2.53; Cl, 13.08; N, 16.84; S, 4.03.

**Table I.** Crystal Data, Intensity Data Collection, and Structure Solution for PcCo(py)SCN·$CHCl_3$ (3)

| | |
|---|---|
| formula | $C_{38}H_{21}N_{10}SCo{\cdot}CHCl_3$ |
| cryst color, form | dark purple, needle shaped |
| *a*, Å | 19.381 (14) |
| *b*, Å | 18.316 (9) |
| *c*, Å | 10.115 (6) |
| $\beta$, deg | 90.79 (5) |
| cryst class | monoclinic |
| space group | $P2_1/n$ |
| *V*, Å$^3$ | 3590.3 |
| *d*(calcd), g cm$^{-3}$ | 1.532 |
| *Z* | 4 |
| cryst dimens, mm | $0.2 \times 2.0 \times 0.15$ |
| abs coeff ($\mu$), cm$^{-1}$ | 8.02 |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.710 69) |
| monochromator | graphite |
| temp, °C | 21 |
| range of 2$\theta$, deg | $3.0 \geq 2\theta \geq 55.0$ |
| scan speed, deg min$^{-1}$ | 0.5–29.3 |
| scan range, deg | 1.0 |
| total no. of data | 5342 |
| no. of unique data | 5233 |
| no. of variables | 488 |
| *R* | 0.162 |
| *R*(aniso) | 0.071 |

**Preparation of PcCo(pyz)SCN (4).** In a septum-closed flask **2** (63 mg, 0.1 mmol) was stirred at 70–80 °C for 2 days in a pyrazine melt (320 mg, 4 mmol). Excess pyrazine was removed by sublimation under high vacuum at 50 °C. **4** (68 mg, 96%) was obtained as a green powder. IR (Nujol mull, cm$^{-1}$): 2105 m. Far-IR (polyethylene, cm$^{-1}$): 283 m, 300 w, 325 s, 418 w, 438 s, 476 m, 518 m, 573 s, 643 w. TG (dissociation range, °C; mass loss calcd, %; mass loss found, %): 160–360; 19.5; 17.0. UV–vis ($CHCl_3$; $\lambda$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)): 659 (153 000), 629 (40 000), 596 (34 000), 347 (54 000). Anal. Calcd for $C_{37}H_{20}CoN_9S$: C, 62.62; H, 2.84; N, 17.76; S, 4.52. Found: C, 61.96; H, 2.94; N, 18.31; S, 4.60.

**Preparation of TBA[(TBP)Co(NCS)$_2$] (6).** (TBP)Co (225 mg, 0.4 mmol) and chloroacetic acid (160 mg, 1.6 mmol) were stirred in 50 mL of dichloromethane for 3 h. The solution was filtered and the solvent evaporated at room temperature. The residue and a large excess of (TBA)SCN were taken up in 50 mL of ethanol, and the mixture was stirred for 2 h and filtered. The product **6** was washed with ethanol, water, and ether; yield 160 mg (44%). $^1$H NMR (acetone-$d_6$): $\delta$ 11.33 (s, 4 H), 11.28 (s, 1 H), 9.82 (m, 8 H), 9.77 (m, 2 H), 8.19 (m, 8 H), 8.15 (m, 2 H), 3.27 (t, 10 H), 1.68 (quintet, 10 H), 1.31 (sextet, 10 H), 0.89 (t, 15 H). IR (Nujol mull, cm$^{-1}$): 2115 vs. Far-IR (polyethylene, cm$^{-1}$): 284 m, 315 w, 350 w, 394 m, 414 vs, 510 w, 631 m. TG (dissociation range, °C; mass loss calcd, %; mass loss found, %): 130–350; 39.0; 34.0. Anal. Calcd for $C_{54}H_{56}CoN_7S_2$: C, 70.03; H, 6.09; N, 10.59; S, 6.92. Found: C, 69.72; H, 6.18; N, 10.49; S, 7.30.

**Preparation of (TBP)CoNCS (7).** (TBP)Co (225 mg, 0.4 mmol) and chloroacetic acid (160 mg, 1.6 mmol) were stirred in 50 mL of dichloromethane for 3 h. The solution was filtered and the solvent evaporated at room temperature. The residue and a large excess of KSCN were taken up in 50 mL of ethanol, and the mixture was stirred for 2 h and filtered. The product **7** was washed with ethanol, water, and ether; Yield 90 mg (36%). $^1$H NMR ($CDCl_3$): $\delta$ 10.89 (s, 4 H), 10.81 (s, 2 H), 9.51–9.48 (m, 12 H), 8.17–8.14 (m, 12 H). IR (Nujol mull, cm$^{-1}$): 2112 s. Far-IR (polyethylene, cm$^{-1}$): 215 m, 284 s, 392 vs, 418 w, 437 s, 635 w. TG (dissociation range, °C; mass loss calcd, %; mass loss found, %): 140–240 (SCN); 9.0; 9.0. Anal. Calcd for $C_{37}H_{20}CoN_5S$: C, 71.04; H, 3.22; N, 11.19; S, 5.13. Found: C, 70.98; H, 3.37; N, 11.44; S, 5.31.

**X-ray Data Collection and Reduction.** Dark violet needles of PcCo(py)SCN·$CHCl_3$ (3) were obtained from a $CHCl_3$ solution of **3** by very slow evaporation of the solvent. The orientation matrix and the cell parameters were determined from a crystal of given dimensions on a Syntex P3 four-circle diffractometer. Fifteen reflections were centered and used to determine the monoclinic crystal system. The lattice constants and the symmetry were proved by axial photographs (30°) around each axis. Measurement of intensities: $\omega$ scan, 1° range, Mo K$\alpha$ (graphite monochromatized), 2$\theta$ maximum 55°. The conditions limiting possible reflections were found to be *h*0*l*, $h + l = 2n$, and 0*k*0, $k = 2n$. They are consistent with the space group $P2_1/n$. The intensity of a standard reflection recorded every 50 reflections varied 4.2%. A total of 5233 unique reflections with $F \geq 3\sigma(F)$ were used for the structure determination, with weak reflections suppressed by the data collection routine. A summary of crystal data, intensity collection, and structure

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**Table II.** Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^{-1}$ pm$^2$) for PcCo(py)SCN·$CHCl_3$ (**3**)

| | *x* | *y* | *z* | *U*[a] |
|---|---|---|---|---|
| Co | 2542 (1) | 4055 (1) | 4757 (1) | 43 (1) |
| S | 1819 (1) | 3202 (1) | 5586 (2) | 68 (1) |
| N(1) | 2615 (2) | 3568 (2) | 3075 (4) | 46 (1) |
| C(2) | 2185 (3) | 3662 (3) | 1989 (5) | 48 (2) |
| N(3) | 1651 (2) | 4105 (2) | 1872 (4) | 50 (1) |
| C(4) | 1463 (3) | 4537 (3) | 2857 (5) | 49 (2) |
| N(5) | 1759 (2) | 4597 (2) | 4098 (4) | 46 (1) |
| C(6) | 1366 (3) | 5077 (3) | 4793 (5) | 52 (2) |
| N(7) | 1457 (2) | 5292 (2) | 6033 (4) | 56 (2) |
| C(8) | 1960 (3) | 5029 (3) | 6781 (5) | 55 (2) |
| N(9) | 2447 (2) | 4522 (2) | 6461 (4) | 48 (1) |
| C(10) | 2867 (3) | 4419 (3) | 7548 (5) | 54 (2) |
| N(11) | 3389 (3) | 3956 (3) | 7668 (4) | 60 (2) |
| C(12) | 3576 (3) | 3527 (3) | 6692 (5) | 54 (2) |
| N(13) | 3308 (2) | 3497 (2) | 5438 (4) | 49 (1) |
| C(14) | 3657 (3) | 2967 (3) | 4766 (5) | 52 (2) |
| N(15) | 3557 (2) | 2741 (2) | 3537 (4) | 55 (2) |
| C(16) | 3076 (3) | 3027 (3) | 2783 (5) | 49 (2) |
| C(17) | 2945 (3) | 2772 (3) | 1423 (5) | 53 (2) |
| C(18) | 3264 (3) | 2237 (3) | 672 (6) | 65 (2) |
| C(19) | 3009 (4) | 2120 (3) | −589 (6) | 74 (2) |
| C(20) | 2456 (4) | 2518 (3) | −1094 (6) | 71 (2) |
| C(21) | 2127 (3) | 3054 (3) | −326 (5) | 62 (2) |
| C(22) | 2391 (3) | 3168 (3) | 941 (5) | 53 (2) |
| C(23) | 864 (3) | 5002 (3) | 2758 (6) | 53 (2) |
| C(24) | 397 (3) | 5137 (3) | 1725 (6) | 68 (2) |
| C(25) | −140 (3) | 5613 (4) | 1979 (7) | 79 (3) |
| C(26) | −194 (3) | 5955 (4) | 3198 (8) | 84 (3) |
| C(27) | 273 (3) | 5835 (3) | 4212 (7) | 67 (2) |
| C(28) | 804 (3) | 5348 (3) | 3964 (6) | 54 (2) |
| C(29) | 2072 (3) | 5272 (3) | 8140 (6) | 60 (2) |
| C(30) | 1733 (4) | 5794 (3) | 8891 (6) | 77 (3) |
| C(31) | 2004 (5) | 5904 (4) | 10172 (7) | 90 (3) |
| C(32) | 2566 (5) | 5513 (4) | 10637 (7) | 94 (3) |
| C(33) | 2899 (4) | 4998 (4) | 9891 (6) | 78 (3) |
| C(34) | 2641 (4) | 4887 (3) | 8612 (5) | 64 (2) |
| C(35) | 4130 (3) | 2994 (3) | 6836 (6) | 59 (2) |
| C(36) | 4540 (3) | 2798 (4) | 7916 (6) | 73 (2) |
| C(37) | 5031 (4) | 2259 (4) | 7706 (8) | 90 (3) |
| C(38) | 5097 (4) | 1935 (4) | 6440 (9) | 90 (3) |
| C(39) | 4681 (3) | 2118 (3) | 5428 (7) | 73 (2) |
| C(40) | 4187 (3) | 2654 (3) | 5623 (6) | 59 (2) |
| N(41) | 3189 (2) | 4852 (2) | 4178 (4) | 44 (1) |
| C(42) | 3034 (3) | 5564 (3) | 4349 (5) | 53 (2) |
| C(43) | 3459 (3) | 6119 (3) | 4006 (6) | 62 (2) |
| C(44) | 4083 (3) | 5966 (3) | 3449 (7) | 76 (2) |
| C(45) | 4259 (3) | 5243 (4) | 3265 (7) | 82 (3) |
| C(46) | 3798 (3) | 4711 (3) | 3645 (6) | 65 (2) |
| C(47) | 1722 (3) | 2573 (3) | 4450 (7) | 70 (2) |
| N(48) | 1624 (4) | 2108 (3) | 3702 (7) | 113 (3) |
| C | 646 (5) | 1392 (5) | 6412 (9) | 118 (4) |
| Cl(1) | 1000 (2) | 975 (3) | 7723 (4) | 232 (3) |
| Cl(2) | 235 (3) | 768 (2) | 5473 (4) | 241 (3) |
| Cl(3) | 84 (3) | 2041 (3) | 6782 (5) | 264 (3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

solution is given in Table I. For the absorption correction a $\psi$ scan was applied using only reflections with $\chi$ between 40 and 90° as well as $\theta$ between 3 and 15°.

**Structure Solution and Refinement.** Atomic scattering factors were taken from ref 32. For the evaluation the SHELXTL[33] system on an Eclipse S/250 computer was employed to solve the structure by direct-phase determination. The parameters of the complete structure could be refined by anisotropic least-squares cycles to $R = 0.071$. The positions of the hydrogen atoms are calculated geometrically and considered isotropically in all refinements. Positional and isotropic thermal parameters are listed in Table II. Selected bond lengths and angles are given in Table III.

**Table III.** Selected Bond Distances (pm) and Angles (deg) for PcCo(py)SCN·$CHCl_3$ (**3**)

| | | | |
|---|---|---|---|
| Co–S | 226.9 (2) | Co–N(1) | 192.8 (4) |
| S–C(47) | 163.6 (6) | Co–N(9) | 193.6 (4) |
| C(47)–N(48) | 115.2 (9) | Co–N(5) | 192.5 (4) |
| Co–N(41) | 201.6 (4) | Co–N(13) | 192.2 (4) |

| | | | |
|---|---|---|---|
| Co–S–C(47) | 106.9 (2) | N(1)–Co–N(9) | 178.2 (2) |
| S–C(47)–N(48) | 175.6 (6) | N(5)–Co–N(13) | 178.5 (2) |
| S–Co–N(1) | 93.5 (1) | S–Co–N(41) | 175.0 (1) |
| S–Co–N(5) | 89.7 (1) | N(1)–Co–N(41) | 91.5 (2) |
| S–Co–N(9) | 84.7 (1) | N(5)–Co–N(41) | 91.0 (2) |
| S–Co–N(13) | 88.8 (1) | N(9)–Co–N(41) | 90.3 (2) |
| N(1)–Co–N(5) | 90.0 (2) | N(13)–Co–N(41) | 90.5 (2) |
| N(5)–Co–N(9) | 89.8 (2) | Co–N(41)–C(42) | 121.5 (3) |
| N(9)–Co–N(13) | 89.9 (2) | Co–N(41)–C(46) | 122.3 (3) |
| N(1)–Co–N(13) | 90.3 (2) | C(42)–N(41)–C(46) | 116.2 (4) |

## Results and Discussion

In contrast to the case for (phthalocyaninato)cobalt(III) cyanide compounds[2] (phthalocyaninato)cobalt(III) thiocyanate and isothiocyanate complexes are not available by air oxidation of $PcCo^{II}$[2] in the presence of the anion. Thiocyanate groups can only be introduced by ligand exchange if the starting material contains cobalt in the oxidation state III.

$PcCoCl_2$[30] and KSCN react in ethanol with reduction of the phthalocyanine ring system to form the monomeric complex $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**), which decomposes in the presence of water to form the bridged compound $[PcCoSCN]_n$ (**2**). By exchange of $K^+$ in **1** with $TBA^+$ the monomeric complex TBA-$[PcCo(NCS)_2]$ (**5**) is formed as previously reported.[31] **5** is stable in water and cannot be converted to the bridged species **2**.

$[PcCoSCN]_n$ (**2**) is also obtained by heating $PcCoCl_2$ and KSCN in water or by reacting $PcCoCCl_3COO\cdot CCl_3COOH$[31] with KSCN in ethanol at room temperature. Small crystals of $[PcCoSCN]_n$ (**2**) are formed by a very slow polymerization of **1** and simultaneous crystallization on an activated surface.[34] **2** is almost insoluble in noncoordinating solvents but reacts with N-donor bases (L) to yield PcCo(L)SCN, $PcCoL_2$, or PcCoL. While with an excess of pyridine and pyrazine PcCo(py)SCN (**3**) and PcCo(pyz)SCN (**4**) respectively are formed, reactions with piperidine and *n*-butylamine lead to the reduced (phthalocyaninato)cobalt(II) compounds $PcCo(pip)_2$[35] and PcCo(ba).[35] In pure dimethylformamide the bridged structure of **2** remains. Whereas PcCo(py)SCN·$CHCl_3$ (**3**) can be crystallized from $CHCl_3$, PcCo(pyz)SCN (**4**) is almost insoluble in organic solvents.

The molecular structure of the tetrabenzoporphyrin macrocycle is comparable to that of the phthalocyanine ring system. The methine bridges of the TBP molecule, however, change its electronic structure at the central metal atom and therefore cause a different metal–ligand complexation behavior.

$(TBP)Co^{III}$ compounds react in $CHCl_3$ in the presence of (TBA)SCN to form the monomeric complex TBA[(TBP)Co-$(NCS)_2$] (**6**). A compound with a 1:1 ratio of (tetrabenzoporphyrinato)cobalt(III) and thiocyanate is formed by using the potassium salt KSCN. In contrast to the case for $[PcCoSCN]_n$ (**2**) (TBP)CoNCS (**7**) is shown to be a pentacoordinated monomeric complex.

Various infrared criteria have been developed to establish the bonding type for thiocyanate complexes.[36,37] In general the CN valence frequency of thiocyanate compounds increases from free thiocyanate to metal–N, metal–S, and bridged species. However, in the case of Co(III) compounds exceptions were found.[38–40]

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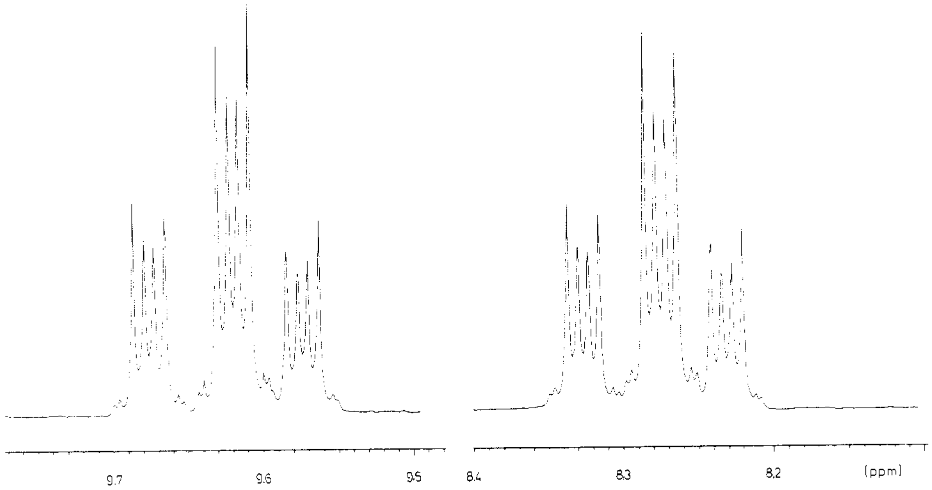

**Figure 1.** $^1H$ NMR spectrum of **1** in acetone-$d_6$.

**Table IV.** Internal Standard Ratios ($R$) of Compounds **1–7** in the Solid State

| compd | $\nu_{CN}$, $cm^{-1\,a}$ | $R^c$ | mode of bonding |
|---|---|---|---|
| $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**) | 2095 | 0.6 | ? |
| $[PcCoSCN]_n$ (**2**) | 2110 | 0.2 | M–SCN–M |
| $PcCo(py)SCN\cdot CHCl_3$ (**3**) | 2105 | 0.1 | M–S |
| PcCo(pyz)SCN (**4**) | 2105 | 0.1 | M–S |
| $TBA[PcCo(NCS)_2]$ (**5**) | $2097^b$ | 2.2 | M–N |
| $TBA[(TBP)Co(NCS)_2]$ (**6**) | 2115 | 1.5 | M–N |
| (TBP)CoNCS (**7**) | 2112 | 1.0 | M–N |

[a] Nujol mull. [b] In ref 31 $\nu_{CN}$ was measured to be 2102 $cm^{-1}$. [c] Salicylic acid was used as internal standard; see ref 42 for an explanation of the ratio.

**Table V.** Powder Dc Dark Conductivities (Activation Energy) of Compounds **1–4** and **7**

| compd | $\sigma_{RT}$, S/cm ($E_a$, eV) |
|---|---|
| $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**) | $2 \times 10^{-6\,b}$ |
| $[PcCoSCN]_n$ (**2**) | $6 \times 10^{-3\,a}$ (0.22) |
| $PcCo(py)SCN\cdot CHCl_3$ (**3**) | $1 \times 10^{-7\,b}$ |
| PcCo(pyz)SCN (**4**) | $3 \times 10^{-7\,b}$ |
| (TBP)CoNCS (**7**) | $6 \times 10^{-5\,b}$ |

[a] Four-probe technique. [b] Two-probe technique.

Therefore, the CN valence frequencies of compounds **1–7** are not suitable for determining the bonding modes. The bonding modes can also not be determined from the CS valence frequencies, as these cannot be observed.

Another approach for estimating the type of metal–thiocyanate bonding is calculating the integrated intensity of the CN valence frequency, which is broad and strong in metal–N-bonded compounds but weak and sharp in metal–S-bonded compounds.[41,42] The determination of the integrated intensity is possible in solution[41] as well as in the solid state.[42] Due to the low solubility of compounds **2** and **4** the solid-state method was preferred (see Table IV). The $R$ values in Table IV indicate different bonding modes in the complexes $TBA[PcCo(NCS)_2]$ (**5**) and PcCo(L)SCN (L = py (**3**), pyz (**4**)). **5** is assumed to be an isothiocyanate compound whereas the internal standard ratios of **3** and **4** give evidence for a metal–S-coordination. The bonding mode of $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**), however, cannot be determined unambiguously from the IR data (Table IV). In comparison with the CN valence frequency of $TBA[PcCo(NCS)_2]$ (**5**) the $R$ value of **1** indicates the same type of bonding.

The $^1H$ NMR spectrum of the monomeric complex **1** (Figure 1) shows the typical multiplets of three aromatic AA′XX′ phthalocyanine ring systems. This is assumed to originate in the existence of three metal–N- and metal–S-bonded isomers (**1a–c**) in acetone solution:

$$\underset{\mathbf{1a}}{[PcCo(NCS)_2]^-} \quad \underset{\mathbf{1b}}{[PcCo(NCS)(SCN)]^-} \quad \underset{\mathbf{1c}}{[PcCo(SCN)_2]^-}$$

Analogous results have been found in other Co(III)–thiocyanate complexes;[20,40] e.g., $^1H$ NMR investigations of the isomers $Co(dmgH)_2(py)SCN$ and $Co(dmgH)_2(py)NCS$[40] demonstrate that the methyl groups of the dimethylglyoximato ligand are particularly sensitive to changes in the axial groups in similar compounds. The chemical shifts of the methyl groups of those linkage isomers differ by about 0.05 ppm whereby the signal of the isothiocyanate complex is shifted to lower field compared to that of the thiocyanate complex.

Another explanation for the signals of three AA′XX′ spin systems in the $^1H$ NMR spectrum of $K[PcCo(CNS)_2]\cdot C_2H_5OH$ (**1**) could be the formation of soluble dimers and trimers because of a beginning polymerization as observed in the $^1H$ NMR spectra of $PcFe(Me_4\text{-}p\text{-}dib)_2$[43] and $PcRu(Me_4\text{-}p\text{-}dib)_2$.[43]

The above explanation is not valid in this case since $TBA[PcCo(NCS)_2]$ (**5**) shows a $^1H$ NMR spectrum between 8.2 and 9.7 ppm almost identical with that of **1**. Compound **5** is proved to be stable in the presence of water and cannot be converted into the polymeric compound $[PcCoSCN]_n$ (**2**). Therefore, a polymerization of **1** does not take place here. Whereas the cations $K^+$ and $TBA^+$ in **1** and **5** do not influence the bonding mode in acetone solution, they might be the reason for the different $R$ values in the solid state (Table IV). $TBA^+$ is known to promote the formation of metal–isothiocyanate complexes, in contrast to the case for $K^+$, which supports the formation of metal–thiocyanate complexes as was observed in the compounds $(TBA)_3[Co(CN)_5NCS]$ and $K_3[Co(CN)_5SCN]$.[19]

Compound **2** is diamagnetic and has the stoichiometry PcCoSCN. The integrated intensity of the CN valence frequency (Table IV) suggests a metal–S-bonded species and is also typical for bridged thiocyanate compounds.[42] Evidence for the bridged structure in $[PcCoSCN]_n$ (**2**) is given by the increase of the CN valence frequency from monomeric N-bonded $TBA[PcCo(NCS)_2]$ (**5**) via monomeric S-bonded $PcCo(py)SCN\cdot CHCl_3$ (**3**) and PcCo(pyz)SCN (**4**) to the bridged $[PcCoSCN]_n$ (**2**) as was in general expected[36,37] and also found in (phthalocyaninato)- and (tetrabenzoporphyrinato)cobalt(III) cyanide complexes.[2,7] In contrast to these observations the corresponding (tetrabenzoporphyrinato)cobalt(III) isothiocyanate complexes $TBA[(TBP)Co(NCS)_2]$ (**6**) and (TBP)CoNCS (**7**) show similar CN

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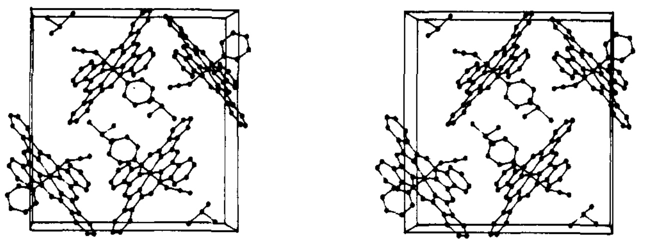

Figure 2. Stereoview of the unit cell of PcCo(py)SCN·$CHCl_3$ (3).

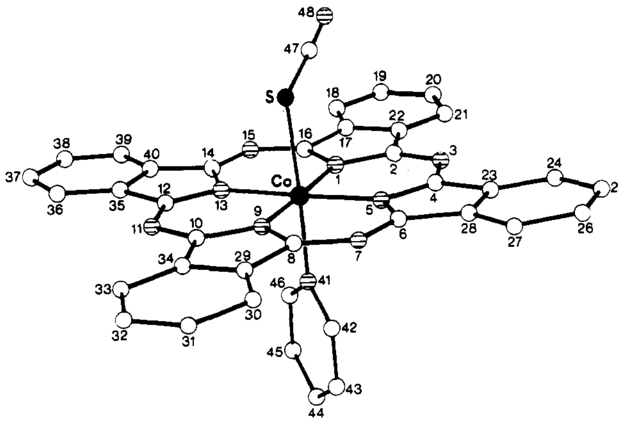

Figure 3. Molecular structure and atom-labeling scheme of PcCo(py)-SCN·$CHCl_3$ (3).

valence frequencies due to their monomeric metal–N-bonded structure (Table IV).

Powder diffraction data of **2** and $[PcMSCN]_n$ (M = Fe,[44] Mn[45]), which were shown to exhibit a bridged structure, are almost identical and give evidence for an isostructural lattice. The EPR spectrum of $[PcCoSCN]_n$ (**2**) shows no Co(II) absorption.

The dc dark powder conductivities of compounds **1**–**4** and **7** are given in Table V. The conductivity of $[PcCoSCN]_n$ (**2**) is only slightly lower than the value of $[PcCoCN]_n$ ($\sigma_{RT} = 2 \times 10^{-2}$ S/cm)[2]. A similar observation was made in the $[PcFeL]_n$ series (L = CN, SCN).[24,44] The reason for that slight decrease could be the larger interplanar distance of the phthalocyanine ring systems or a more angular polymer chain in $[PcCoSCN]_n$ (**2**) in comparison with that of $[PcCoCN]_n$[2] because of the electron configuration of the sulfur atom. The influence of the linearity of the polymer chain on the conductive behavior was shown recently in the case of $[PcRu(p\text{-dib})]_n$[6] and $[PcRu(m\text{-dib})]_n$.[29] The conductivity of $[PcRu(m\text{-dib})]_n$ is 1 order of magnitude lower than that of $[PcRu(p\text{-dib})]_n$.

As in the case of **1** and **5**, the $^1H$ NMR spectra of PcCo(py)SCN·$CHCl_3$ (**3**), TBA[(TBP)Co$(NCS)_2$] (**6**), and (TBP)-CoNCS (**7**) give evidence for two isomeric complexes in solution. In the case of **3** the metal–S-bonded species predominates; the ratio of isothiocyanate to thiocyanate complex is about 1:4. The AA′XX′ spin system and the signals of the pyridine ligand of each isomer have slightly different chemical shifts. The spectra of **6** and **7** show a higher concentration of the metal–N-bonded isomers.

In the solid state only the S-bonded isomer of **3** is observed. The conclusion drawn from the IR data was proven to be correct by X-ray analysis of PcCo(py)SCN·$CHCl_3$ (**3**) (Figures 2 and 3).

According to X-ray data the central Co atom lies slightly above the almost planar Pc ring system in the direction of the pyridine ligand. The Co–S distance of 226.9 (2) pm and the Co–S–C angle of 106.9 (2)° are in the range of those observed in other Co(III)–S-bonded species.[46] The thiocyanate group is oriented in the direction of an isoindole ring, while the plane of the pyridine ligand is perpendicular to the phthalocyanine core, passing through the aza bridges of the macrocycle[47] (Figure 3).

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**Registry No.** K-**1a**, 108853-66-3; K-**1b**, 109089-06-7; K-**1c**, 109089-07-8; **2**, 99596-81-3; **3**, 109089-01-2; **4**, 109089-02-3; **6**, 109089-04-5; **7**, 109089-05-6; (TBP)Co, 58482-09-0; $PcCoCl_2$, 35141-17-4; $PcCoCCl_3CO_2$, 94288-71-8; PcCo(py)(NCS), 109089-08-9; TBA-[(TBP)Co$(SCN)_2$], 109089-10-3; (TBP)CoSCN, 109089-11-4.

**Supplementary Material Available:** Table SI (extended table of bond lengths), Table SII (extended table of bond angles), Table SIII (anisotropic thermal parameters), and Table SIV (H atom coordinates) (4 pages); Table SV (table of *hkl*, $F_o$, and $F_c$) (33 pages). Ordering information is given on any current masthead page.

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# Steric Control of Electronic Effects in Diacetylated Nickel(II) Schiff Base Complexes

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X-ray structural analysis, electrochemistry, $^{13}C$ NMR spectroscopy, and infrared spectroscopy of the diacetylated Schiff base complexes $[Ni(Me_2Ac_2H_2malen)]$ and $[Ni(Me_2Ac_2Me_2malen)]$ are reported. Differences in the number of methyl groups on the chelate backbone (two for $[Ni(Me_2Ac_2H_2malen)]$, four for $[Ni(Me_2Ac_2Me_2malen)]$) cause the acetyl groups to be rotated out of the $NiN_2O_2$ plane by 16.8 and 58.2°, respectively. Electrochemical measurements on the diacetylated and analogous deacetylated complexes show that delocalization effects from the acetyl groups have been decreased by the rotating of the acetyl groups out of the chelate plane. This interpretation is supported by $^{13}C$ NMR and infrared spectroscopic measurements. As such, the use of steric effects to regulate electronic effects has been demonstrated. $[Ni(Me_2Ac_2H_2malen)]$ crystallized in the monoclinic system ($P2_1/c$) with unit cell dimensions $a$ = 14.686 (2) Å, $b$ = 17.734 (3) Å, $c$ = 11.412 (1) Å, $\beta$ = 101.16 (1)°, and $Z$ = 8; $R$ = 0.049 and $R_w$ = 0.054 for 2730 observed reflections. $[Ni(Me_2Ac_2Me_2malen)]$ crystallized in the monoclinic system ($C2/c$) with unit cell dimensions $a$ = 7.689 (2) Å, $b$ = 8.686 (2) Å, $c$ = 25.579 (9) Å, $\beta$ = 103.84 (3)°, and $Z$ = 4; $R$ = 0.042 and $R_w$ = 0.042 for 1370 observed reflections.

## Introduction

We have previously reported the reversible binding of dioxygen to a new family of cobalt(II) and iron(II) lacunar complexes based on the cyclidene macrocycle.[1-3] The precursor macrocycle, which was first synthesized by Jager,[4] is formed in a template reaction between a nickel(II) complex of the linear tetradentate ligand

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