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A (Trimethylphosphine)cobalt(III) Complex, $Co(NCS)_3(PMe_3)_3$. Synthesis from the Reaction of NO with $Co(NCS)_2(PMe_3)_2$. Crystal and Molecular Structure

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Reaction of NO with $Co(NCS)_2(PMe_3)_2$ has led to a disproportionation reaction giving rise to the synthesis of a Co(III) species containing PMe_3 and having the X_3L_3 donor atom set. Simultaneously, the cobalt complex $[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$, which gave $[Co(NO)_2(PMe_3)_2]BPh_4$ in the presence of $NaBPh_4$, has been obtained. The crystal structure of $Co(NCS)_3(PMe_3)_3$ has been determined. Crystals are monoclinic, space group $P2_1$ with $Z = 4$, in a unit cell of dimensions $a = 15.242$ (2) Å, $b = 9.335$ (1) Å, $c = 16.545$ (2) Å, and $\beta = 108.71°$. The structure was solved by the heavy-atom method and refined to $R = 0.034$ for 2336 independent reflections. Two independent molecules are present in the unit cell. In both, the cobalt is at the center of a distorted octahedron. Only the *mer* isomer is observed.

Introduction

In a continuing effort to understand the properties and to develop the chemistry of Co–NO complexes, we have tried to synthesize the $Co(NCS)_2(NO)(PR_3)_2$ compounds by reacting NO with tetracoordinate low-spin $Co(NCS)_2(PR_3)_2$ species.[1]

Under the experimental conditions that gave rise to $CoX_2(NO)(PR_3)_2$ (X = halide), i.e. methanol or acetone as solvents at 25 °C,[2] $Co(NCS)_2(NO)(PR_3)_2$ is isolated with PEt_3. With PMe_3, a disproportion reaction takes place immediately and two new cobalt complexes are isolated: a Co(III) compound, $Co(NCS)_3(PMe_3)_3$, as red crystals and a green species, which is characterized as $[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$ by analysis, IR and UV spectroscopies, and magnetic studies. We report here the chemical identification of these two complexes, together with the X-ray structure of the Co(III) compound. This new reaction is an unexpected way of synthesizing Co(III)–PMe_3 species. Few examples of Co(III) compounds with tertiary phosphine are known: air oxidation of Co(II) gives phosphine oxide–Co(II) complexes, but five-coordinate $CoX_3(PR_3)_2$ compounds have been obtained by oxidation of $CoX_2(PR_3)_2$ by NOCl at −80 °C.[3] Co(III)–O_2 complexes containing PR_3 have also been characterized.[4] The only reported Co(III)–PMe_3 complex, $Co(CH_3)_3(PMe_3)_3$, has been obtained by reaction of LiMe on $Co(acac)_3$ in presence of PMe_3.[5]

Redox reactions are well-known with cobalt complexes containing phosphite ligands.[6] On the other hand, NO is known to act as a reductive and nitrosylating reactant.[7] Its ability to promote dismutation of the cobalt center and to act simultaneously as a nitrosylating agent has already been reported in two examples: Co(sacsac) (sacsac = dithioacetylacetone)[8] and $[Co(NCS)(P(OR)_3)_4]^+$.[9] In the last compound, the particular influence of the NCS anion has also been emphasized.

Experimental Part

All reactions were performed as previously reported.[2] $Co(NCS)_2(PR_3)_2$ compounds were synthesized by literature methods.[1]

Table I. Summary of Crystal and Intensity Collection Data

formula: $Co(NCS)_3\{P(CH_3)_3\}_3$; $CoS_3P_3N_3C_{12}H_{27}$
fw: 460.93
$a = 15.242$ (2) Å
$b = 9.355$ (1) Å
$c = 16.545$ (2) Å
$V = 2229.7$ Å^3
$\beta = 108.71$ (1)°
$Z = 4$
$F(000) = 960$
$D_c = 1.373$ g/cm^3
space group: C_2^2—$P2_1$
radiation: Mo K$\bar{\alpha}$ from graphite monochromator ($\lambda = 0.71069$ Å)
linear abs coeff: $\mu = 12.5$ cm^{-1}
temp: 20 °C
receiving aperature: 4.0 × 4.0 mm
take-off angle: 2.3°
scan mode: θ–2θ
scan range: $(0.75 + 0.35 \tan \theta)°$
2θ limits: 52°

Syntheses. $Co(NCS)_2(NO)(PEt_3)_2$. NO gas was bubbled through a methanol solution (25 mL) of $Co(NCS)_2(PEt_3)_2$ (4.6 g, 11.4 mmol) for 15 min. The green solution turned brown, and brown crystals precipitated, which were filtered and dried under argon. Anal. Calcd for: $CoN_3S_2OP_2C_8H_{18}$: C, 38.10; H, 6.80; N, 9.52. Found: C, 37.76; H, 6.91; N, 9.38.

$Co(NCS)_3(PMe_3)_3$. Bubbling NO through a methanol solution of $Co(NCS)_2(PMe_3)_2$ (20 mL; 6.9 mmol, 2.25 g) allowed the immediate precipitation of a red microcrystalline powder, together with some green crystals. Filtration and recrystallization from methanol or acetone led to red needles after cooling at −25 °C. They were filtered and dried under argon. Anal. Calcd for $CoN_3S_3P_3C_{12}H_{27}$: C, 31.24; H, 5.85; N, 9.11; P, 20.18; Co, 12.78. Found: C, 30.98; H, 5.88; N, 9.13; Co, 11.70.

$[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$. After filtration of the red powder, the remaining brown solution was concentrated and kept at −25 °C for 12 h. Green needles deposited, which were filtered and dried under argon. Anal. Calcd for $Co_3N_8S_4O_4P_4C_{16}H_{36}$: C, 23.05; H, 4.32; N, 13.43; P, 14.89; Co, 21.23. Found: C, 24.40; H, 4.47; N, 13.12; P, 15.01; Co, 21.27.

$[Co(NO)_2(PMe_3)_2]BPh_4$. A 0.96-mmol (0.8-g) sample of $[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$ dissolved in acetone (20 mL) was treated with $Na[B(C_6H_5)_4]$ (1.9 mmol, 0.6 g), and the mixture was stirred at room temperature. No color change of the green solution was observed. Adding 20 mL of diethyl ether allowed precipitation of a brown powder, which was filtered and dried under argon. Anal. Calcd for $CoN_2O_2P_2BC_{30}H_{38}$: C, 61.05; H, 6.44; N, 4.75. Found: C, 61.43; H, 6.84; N, 4.87.

Collection and Reduction of X-ray Data. A crystal suitable for the X-ray determination was obtained from an acetone solution kept at −25 °C. The crystals belong to the monoclinic system, space group $P2_1$ or $P2_1/m$. The selected crystal was a red needle with boundary planes {010}, {101}, and {$\bar{1}$01}. The distances from these faces to an arbitrary origin were 0.213, 0.05, and 0.025 mm, respectively. The crystal was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data is given in Table I. A total of 4816 independent reflections ($h,k,\pm l$) were

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(1) Rigo, P.; Bressan, M.; Turco, A. *Inorg. Chem.* **1968**, *7*, 1460–1463.
(2) Alnaji, O.; Peres, Y.; Dahan, F.; Dartiguenave, M.; Dartiguenave, Y. *Inorg. Chim. Acta* **1986**, *114*, 151–158.
(3) Jensen, K. A.; Nygaard, B.; Pederson, C. T. *Acta Chem. Scand.* **1963**, *17*, 1126–1132.
(4) Halpern, J.; Goodall, B. L.; Khare, G. P.; Liu, H. S.; Pluth, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 2301–2303. Drago, R. S.; Stahlbush, J. R.; Kitko, D. J.; Breese, J. *J. Am. Chem. Soc.* **1980**, *102*, 1884–1889. Dartiguenave, M., unpublished results.
(5) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 956–966. Komiya, S.; Yamamoto, A.; Yamamoto, T. *Transition Met. Chem.* **1979**, *11*, 343–344.
(6) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1–106. Albright, J. O.; Clardy, J. C.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 1575–1580.
(7) Bressan, M.; Rigo, P. *J. Chem. Soc., Chem. Commun.* **1974**, 553. Gwost, D.; Caulton, K. G. *Inorg. Chem.* **1973**, *12*, 2095–2099. McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53–76.
(8) Hendrickson, A. R.; Ho, R. K. Y.; Martin, R. L. *Inorg. Chem.* **1974**, *13*, 1279–1281.
(9) Albertin, G.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1983**, *22*, 515–520 and references therein.

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Table II. Fractional Atomic Coordinates with Esd's in Parentheses

	molecule I			molecule II		
atom	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Co	0.63272 (8)	1/4	0.77631 (7)	0.11449 (8)	0.5355 (2)	0.74137 (7)
N(1)	0.5858 (5)	0.2626 (9)	0.8737 (5)	−0.0124 (6)	0.5686 (9)	0.6672 (5)
C(1)	0.5598 (6)	0.2778 (11)	0.9310 (6)	−0.0881 (7)	0.6010 (10)	0.6292 (6)
S(1)	0.5232 (2)	0.3045 (4)	1.0117 (2)	−0.1925 (2)	0.6510 (4)	0.5773 (2)
N(2)	0.5417 (5)	0.3753 (9)	0.7098 (5)	0.1651 (6)	0.6637 (10)	0.6807 (5)
C(2)	0.4945 (7)	0.4593 (13)	0.6653 (6)	0.1862 (6)	0.7496 (13)	0.6408 (6)
S(2)	0.4300 (2)	0.5781 (4)	0.6029 (2)	0.2158 (2)	0.8704 (4)	0.5838 (2)
N(3)	0.7252 (6)	0.1241 (9)	0.8368 (5)	0.0694 (5)	0.4039 (9)	0.8056 (5)
C(3)	0.7756 (6)	0.0329 (12)	0.8648 (5)	0.0517 (6)	0.3143 (11)	0.8449 (6)
S(3)	0.8471 (2)	−0.0987 (3)	0.9063 (2)	0.0284 (2)	0.1826 (3)	0.8986 (2)
P(1)	0.6987 (2)	0.2209 (3)	0.6746 (2)	0.2521 (2)	0.4737 (3)	0.8333 (2)
C(4)	0.7055 (7)	0.0385 (13)	0.6398 (6)	0.2736 (6)	0.5170 (13)	0.9453 (5)
C(5)	0.8208 (6)	0.2668 (14)	0.7036 (5)	0.2687 (7)	0.2813 (11)	0.8457 (6)
C(6)	0.6444 (7)	0.3202 (11)	0.5773 (5)	0.3512 (6)	0.5431 (14)	0.8094 (5)
P(2)	0.7133 (2)	0.4545 (3)	0.8316 (2)	0.1203 (2)	0.3721 (3)	0.6402 (2)
C(7)	0.8265 (7)	0.4285 (13)	0.9065 (7)	0.0720 (9)	0.1980 (13)	0.6506 (8)
C(8)	0.6553 (8)	0.5604 (13)	0.8901 (6)	0.0530 (8)	0.4349 (15)	0.5341 (6)
C(9)	0.7256 (8)	0.5860 (11)	0.7576 (6)	0.2307 (7)	0.3340 (14)	0.6270 (7)
P(3)	0.5255 (2)	0.0702 (3)	0.7268 (2)	0.0947 (2)	0.7339 (3)	0.8150 (2)
C(10)	0.5654 (8)	−0.1100 (12)	0.7569 (8)	0.0509 (7)	0.6690 (12)	0.9032 (6)
C(11)	0.4625 (8)	0.0669 (15)	0.6127 (6)	0.1921 (8)	0.8550 (12)	0.8521 (7)
C(12)	0.4328 (7)	0.0868 (13)	0.7694 (6)	0.0092 (8)	0.8567 (12)	0.7492 (7)

recorded out to $2\theta(\mathrm{Mo}) = 52°$ by procedures described elsewhere.[10] Intensity standards, recorded periodically, showed no fluctuations greater than 1%. Data reduction was then performed, and 2336 independent reflections having $I > 3\sigma(I)$ were corrected for absorption,[11] $T_{\min} = 0.86$, and $T_{\max} = 0.94$.

Solution Structure and Refinement. The structure was solved[12] by the heavy-atom method, in the noncentrosymmetric space group $P2_1$. The origin was fixed at $y = {}^1/_4$ for one Co atom. A subsequent Fourier map phased on Co atoms revealed the positions of all non-hydrogen atoms. There were no correlation matrix elements between parameters of independent molecules in the refinement procedure, confirming the space group choice. All non-hydrogen atoms were refined anisotropically with the atomic scattering factors of Co^{3+}, P, S, N, and C proposed by Cromer and Waber,[13] with anomalous dispersion effects.[14] The hydrogen atoms were located on a difference Fourier map and introduced in calculations in idealized positions (C–H = 0.95 Å; H–C–H = 109.5°) with an isotropic temperature factor $U = 0.08$ Å^2 kept fixed. Their scattering factors were taken from Stewart et al.[15] The two enantiomers were tested ($R_1 = 0.034$ and $R_2 = 0.037$), and the first one was kept. The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum||F_o| - |F_c|/\sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.040$. The weighting scheme was $w = [\sigma^2(F_o) + (0.031F_o)^2]^{-1}$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.2$ with $n = 2336$ observations and $m = 396$ variables. An analysis of variance showed no unusual trends. In the last cycles of refinement, the shifts for all parameters were less than 0.05σ. A final difference Fourier map showed no excursion of electron density greater than 0.4 e/Å^3. The final fractional atomic coordinates are listed in Table II.

Results

1. Reaction of NO with $Co(NCS)_2(PEt_3)_2$. Bubbling NO through a methanol solution of the cobalt(II) complex $Co(NCS)_2(PEt_3)_2$ (ν(NC) = 2030 cm^{-1}; ν(CS) = 820 cm^{-1}) is followed immediately by a color change from red to brown, and storage of this solution at −25 °C overnight allows precipitation of brown crystals of $Co(NCS)_2(NO)(PEt_3)_2$. Its IR spectrum shows the presence of only one ν(NC) at 2030 cm^{-1}, one ν(CS) at 810 cm^{-1}, and δ(NCS) at 470 cm^{-1}, with one ν(NO) at 1770 cm^{-1} and a shoulder at 1680 cm^{-1}. This is indicative of a trigonal-bipyramidal structure with linear Co–NO as was reported for $CoI_2(NO)(PMe_3)_2$.[2]

Table III. Infrared Bands of NCS and NO in the Complexes (cm^{-1}) as Nujol Mulls

complex	ν(NC)	ν(NS)	δ(NCS)	δ(NO)
$Co(NCS)_2(PEt_3)_2$	2030	820	470	
$Co(NCS)_2(NO)(PEt_3)_2$	2020	810	470	1770 1680
$Co(NCS)_2(PMe_3)_2$	2020	830		
$Co(NCS)_2(NO)(PMe_3)_2$				1760^a
$Co(NCS)_3(PMe_3)_3$	2100	750	470	
$[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$	2060	...	475	1840, 1790
$[Co(NO)_2(PMe_3)_2]BPh_4$				1840, 1775

^{a}Only in MeOH solution.

2. Reaction of NO with $Co(NCS)_2(PMe_3)_2$. $Co(NCS)_3(PMe_3)_3$. We have followed by infrared spectroscopy the reaction of NO gas with $Co(NCS)_2(PMe_3)_2$ (ν(CN) = 2030 cm^{-1}; ν(CS) = 820 cm^{-1}) in methanol. Formation of $Co(NO)(NCS)_2(PMe_3)_2$ is deduced from the presence of one ν(NO) at 1760 cm^{-1}, but this complex has not been isolated. The impure red solid that precipitates gives rise to diamagnetic needles of $Co(NCS)_3(PMe_3)_3$ by recrystallization in methanol. No ν(NO) is apparent in the IR spectrum. The isothiocyanato groups are characterized by a broad ν(CN) band at 2100 cm^{-1} (Table III), which rules out the presence of a bridging NCS ligand and δ(NCS) at 470 cm^{-1}. ν(CS) appears at 750 cm^{-1}, which is in the range of the C=S vibrations reported in Co(III) complexes.[16] The complex is non-conducting in acetone. No supplementary structural information can be obtained from the $^{31}P\{^1H\}$ NMR since only one broad singlet with two shoulders is present at 12 ppm (CD_2Cl_2/CH_2Cl_2) at −85 °C. The solutions are air-stable. ^{1}H NMR demonstrates that the *mer* isomer is only present in dichloromethane solution by observation of a methyl "virtual" coupling triplet for the two trans PMe_3 groups at 1.75 ppm (J_{HP} = 4.5 Hz) and a doublet corresponding to the third PMe_3 at 1.57 ppm (J_{HP} = 11 Hz). The intensity ratio of these two peaks is 2/1.[21]

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(10) Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639–2644.

(11) Coppens, P.; Leiserowitz, L.; Rabinovitch, D. *Acta Crystallogr.* **1965**, *18*, 1035–1038.

(12) Sheldrick, G. M. *SHELX76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(13) Cromer, D. T.; Waber, J. T. *"International Tables for X-ray Crystallography"*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99–101.

(14) Cromer, D. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1, p 149.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(16) Chamberlain, M. M.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 6412–6415. Baldwin, M. E. *J. Chem. Soc. 1961*, 471–479. Gutterman, D. F., Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3364–3371.

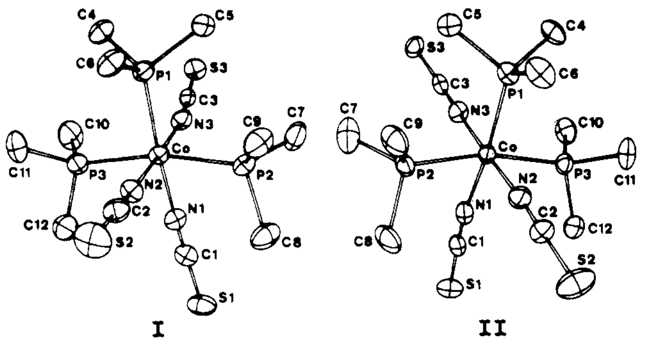

Figure 1. Perspective view of the two independent $Co(NCS)_3(PMe_3)_3$ molecules. (Ellipsoids are drawn at the 30% probability level.)

Thus, these results indicate the formation of a monomeric molecular hexacoordinate Co(III) complex. In order to determine which isomer (*mer* or *fac*) is present in the solid state and since the Co(III) PR_3 complexes are rare, we have grown single crystals for an X-ray structural determination.

X-ray Structure of $Co(NCS)_3(PMe_3)_3$. The crystal structure shows the presence of two independent molecules in the unit cell. A perspective view of these molecules is represented in Figure 1. Selected interatomic distances and angles are reported in Table IV.

In the two molecules the cobalt is at the center of a distorted octahedron, and the ligands are in the *mer* conformation. The bond distance and angle values are not significantly different (Table IV). The cobalt atom is approximately located in the N(1),N(2),N(3),P(1) plane: 0.0038 (8) Å above the plane in complex I and 0.018 (2) Å below the plane in complex II (Figure 1). Thus three of the equatorial positions of the octahedron are spanned by the NCS ligands, which are N bonded. The basal plane is completed by one phosphorus atom P(1). The Co–P(1) distance is significantly shorter than the two others: 2.237 (3) Å compared to 2.294 (3) Å (av), a result which may be related to the trans effect of the NCS^- ligand. Consequently, the Co–N(1) bond distance of the NCS ligand trans to PMe_3 is significantly longer than the two others (1.960 (9) Å compared to 1.877 (9) Å (av)), but still in the range of Co(III)–NCS distances.[9]

The bond angles Co–N–C–S and N–C–S are normal and so are the distances and angles of the PMe_3 ligands.

$[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$. After elimination of $Co(NCS)_3(PMe_3)_3$ by filtration, the brown solution darkens and after overnight cooling at −25 °C deposits green needle-shaped crystals, which are amorphous. They analyze as $Co_3(NCS)_4(NO)_4(PMe_3)_4$. They are soluble in acetone and dichloromethane, giving green solutions, and in methanol, giving a red-brown solution. The molar conductance of a green acetone solution at 20 °C for a concentration $c = 1.25 \times 10^{-3}$ M is 123 $\Omega^{-1}\cdot mol^{-1}\cdot cm^{-3}$, slightly higher than a 1/1 electrolyte (NBu_4Cl: $c = 0.9\ 10^{-3}$ mol/L; $\Lambda = 95$ $\Omega^{-1}\cdot mol^{-1}\cdot cm^{-3}$) but lower than a 2/1 electrolyte. In methanol, the molar conductance of the red solution at 20 °C for a concentration of 10^{-3} mol/L is 219 $\Omega^{-1}\cdot mol^{-1}\cdot cm^{-3}$, i.e. in the range expected for a 2/1 electrolyte.[17] The electronic spectrum of the acetone solution shows the characteristic spectrum of the tetrahedral $[Co(NCS)_4]^{2-}$ species (ν_3 transition as a multiplet with a maximum at 16 080 cm^{-1}), while in methanol the spectrum is representative of the presence of an octahedral Co(II) species (band at about 19 600 cm^{-1}). This indicates the presence of the $[Co(NCS)_4]^{2-}$ anion, which is known to be very sensitive to the solvent environment.[18] The IR spectrum (Nujol mull or solution) shows two ν(NO) at 1840 and 1775 cm^{-1} and two ν(M–N–O) at 640 and 550 cm^{-1}, bands that are characteristic of the $[Co(NO)_2(PMe_3)_2]^+$ entity. Only one ν(CN) is present at 2060 cm^{-1}, and ν(NCS) is at 475 cm^{-1}. ν(CS) is of low intensity and cannot be assigned without ambiguity in the 730 or 850 cm^{-1} region due to the absorption bands typical of the PMe_3 ligands. Thus, equivalent NCS ligands are present in this complex, and their IR vibrational frequencies are directly comparable to those of $(NH_4)_2Co(NCS)_4$ (ν(NC) = 2065 cm^{-1}; ν(CS) = 844, 838 cm^{-1}; δ(NCS) = 418 cm^{-1}) and $K_2Co(NCS)_4$ (ν(NC) = 2085, 2067 cm^{-1}; ν(CS) = 844, 838 cm^{-1}; δ(NCS) = 478 cm^{-1}).[19] Addition of $NaBPh_4$ to the methanol or acetone solution generates the precipitation of a red diamagnetic complex, which analyzes as $[Co(NO)_2(PMe_3)_2]BPh_4$ (ν(NO) at 1775 and 1840 cm^{-1}). All these experiments allow the formulation of the green complex as $[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$, i.e. a diamagnetic cation $[Co(NO)_2(PMe_3)_2]^+$ (a Co^- species if NO is as NO^+) and the paramagnetic anion $[Co(NCS)_4]^{2-}$ (Co^{2+} species). This agrees with the magnetic moment value of 3.12 μ_B at 20 °C, calculated assuming the formula $Co_3(NO)_4(NCS)_4(PMe_3)_4$. This moment follows the Curie–Weiss law $\chi_A(T + 6.43) = 2.52$, between 90 and 300 K. Calculation of the moment for the $[Co(NCS)_4]^{2-}$ anion gives 4.49 μ_B, which compares satisfactorily with the 4.40 ± 0.05 μ_B value determined for $K_2[Co(NCS)_4]\cdot 4H_2O$.[17] The $\langle g \rangle$ value of 3.5 obtained at −166 °C on a powdered sample is also in the range for T_d Co(II) complexes.[20]

Table IV. Selected Interatomic Distances (Å) and Angles (deg) in $Co(NCS)_3(PMe_3)_3$

	I	II
Cobalt Environment		
Co–N(1)	1.965 (9)	1.955 (8)
Co–N(2)	1.877 (7)	1.879 (9)
Co–N(3)	1.861 (8)	1.891 (9)
Co–P(1)	2.237 (3)	2.236 (3)
Co–P(2)	2.296 (3)	2.288 (3)
Co–P(3)	2.303 (3)	2.290 (3)
N(1)–Co–N(2)	92.8 (3)	93.2 (3)
N(1)–Co–N(3)	90.5 (4)	89.5 (3)
N(1)–Co–P(1)	173.7 (2)	172.5 (3)
N(1)–Co–P(2)	85.0 (2)	84.7 (3)
N(1)–Co–P(3)	86.1 (2)	86.2 (3)
N(2)–Co–N(3)	176.7 (4)	177.3 (3)
N(2)–Co–P(1)	93.5 (3)	94.1 (2)
N(2)–Co–P(2)	85.2 (2)	85.1 (3)
N(2)–Co–P(3)	86.5 (3)	85.2 (3)
N(3)–Co–P(1)	83.2 (3)	83.2 (2)
N(3)–Co–P(2)	95.5 (2)	94.8 (3)
N(3)–Co–P(3)	93.4 (3)	95.3 (3)
P(1)–Co–P(2)	95.1 (1)	94.4 (1)
P(1)–Co–P(3)	94.8 (1)	95.9 (1)
P(2)–Co–P(3)	167.5 (1)	166.3 (1)
Thiocyanate Ligands		
N(1)–C(1)	1.147 (14)	1.162 (12)
C(1)–S(1)	1.624 (12)	1.616 (9)
N(2)–C(2)	1.156 (13)	1.148 (15)
C(2)–S(2)	1.616 (11)	1.624 (12)
N(3)–C(3)	1.142 (12)	1.144 (13)
C(3)–S(3)	1.639 (10)	1.622 (10)
Co–N(1)–C(1)	176.2 (8)	172.3 (8)
N(1)–C(1)–S(1)	178.3 (9)	178.2 (4)
Co–N(2)–C(2)	171.3 (9)	172.1 (8)
N(2)–C(2)–S(2)	179.0 (11)	179.6 (10)
Co–N(3)–C(3)	170.1 (7)	171.5 (8)
N(3)–C(3)–S(3)	179.0 (10)	177.6 (10)

Thus NO reacts with $Co(NCS)_2(PMe_3)_2$ by disproportionating the Co(II) center

$$Co(NCS)_2(PMe_3)_2 + NO \rightarrow Co(NCS)_2(NO)(PMe_3)_2$$

$$5Co(NCS)_2(NO)(PMe_3)_2 + NO \rightarrow [Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4] + 2Co(NCS)_3(PMe_3)_3$$

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[17] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

[18] Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M.; Sacco, A. *J. Am. Chem. Soc.* **1961**, *83*, 4157–4161. Cotton, F. A.; Holm, R. H. *J. Am. Chem. Soc.* **1960**, *82*, 2983–2986.

[19] Sabatini, A.; Bertini, I. *Inorg. Chem.* **1965**, *7*, 959–961.

[20] Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1979**, *18*, 2137–2140.

[21] We thank a reviewer for suggesting the use of ^1H NMR to determine the structure in solution: Jenkins, J. M., Shaw, B. L. *J. Chem. Soc. A* **1966**, 770–775, 1407–1409. Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 597–602.

The existence of $Co(NCS)_2(NO)(PMe_3)_2$ as an intermediate is substantiated by the presence in the IR spectrum of the solution of ν(NO) at 1760 cm^{-1} together with the two ν(NO) vibrations of the dinitrosyl cation, which indicates a mechanism similar to the one proposed for Co–phosphite complexes.[9] In this case, a strong field stabilization effect resulting from the electronegative phosphite ligands able to stabilize a Co(III) species cannot be invoked, since PMe_3 is known as a good σ-donor ligand. Thus, the peculiar role of the NCS anion, not yet clear, has to be emphasized.

Conclusion

The redox reaction of NO with $Co(NCS)_2(PMe_3)_2$ occurs through the formation of $Co(NCS)_2(NO)(PMe_3)_2$ as an unstable intermediate. It has been observed in solution and characterized by its ν(NO) but isolated only as the PEt_3 complex.

This complex dismutates to give a Co^-, Co^{2+}, and Co^{3+} species (formally if NO coordinates as NO^+), following a mechanism probably similar to the one observed in Co(NO)(sacsac) and $[Co(NCS)(NO)(P(OR)_3)_4]^+$, that is, in complexes where hard donor ligands (O, N) are present. Although the use of NO as an oxidizing agent is known, its ability to readily produce a Co(III)–PMe_3 complex in good yield under mild conditions was unexpected.

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Registry No. $Co(NCS)_2(NO)(PEt_3)_2$, 101011-29-4; $Co(NCS)_3(PMe_3)_3$, 101011-30-7; $[Co(NO)_2(PMe_3)_2]_2[Co(NCS)_4]$, 101011-32-9; $[Co(NO)_2(PMe_3)_2]BPh_4$, 101011-33-0; $Co(NCS)_2(PEt_3)_2$, 14916-34-8; NO, 10102-43-9.

Supplementary Material Available: Listings of X-ray crystallographic data for $Co(NCS)_3(PMe_3)_3$, including structure factors, anisotropic thermal parameters, hydrogen parameters, and equations for least-squares planes (15 pages). Ordering information is given on any current masthead page.

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A Strongly Chelating Bidentate ClO_4. New Synthesis Route and Crystal Structure Determination of $Ti(ClO_4)_4$

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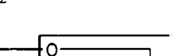
Reaction of Cl_2O_6 with $TiCl_4$ leads to $Ti(ClO_4)_4 \cdot xCl_2O_6$. When this complex is warmed to 42–55 °C under dynamic vacuum (1.33 Pa), colorless single crystals of $Ti(ClO_4)_4$ sublime. This compound crystallizes in the monoclinic system ($C2/c$): $Z = 4$, $a = 12.451$ (3) Å, $b = 7.814$ (1) Å, $c = 12.826$ (3) Å, $\alpha = 108.13$ (3)°, $V = 1186$ (3) Å^3 at −100 °C. The structure was solved by direct methods and refined by full-matrix least squares to a final $R(F) = 0.051$ for 96 variables and 909 reflections. The asymmetric unit contains one independent molecule. The metal center is strongly chelated by four perchlorato ligands (mean Ti–O distance d(Ti–O) = 2.069 Å). The eight oxygen atoms adopt a slightly flattened dodecahedral arrangement with C_2 symmetry. The ClO_4 ligands are distorted with mean observed Cl–O distances $d(Cl–O_b) = 1.51$ Å and $d(Cl–O_t) = 1.39$ Å and angles $O_bClO_b = 97.2°$ and $O_tClO_t = 115.4°$ (O_b is bonded oxygen; O_t is free oxygen). Vibrational spectroscopic data are consistent with the crystal structure and the molecular shape of $Ti(ClO_4)_4$.

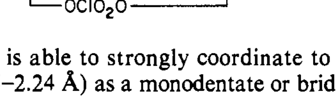
In the last 15 years, the knowledge of perchlorato complexes has expanded with the discovery of convenient syntheses[1] and the systematic studies of their molecular structures using vibrational[2] and more recently EXAFS[3] spectroscopies; on the other hand, the X-ray structural approach has been less successful. Up to now, generally, it has been believed that the low basicity of the ligand ClO_4 would allow only weak coordination[5] (or semicoordination in reference to Hathaway[4]) to metal centers; nevertheless, it has recently been possible to isolate and characterize a few perchlorato complexes with strong metal–ClO_4 interactions.[6] In some of these complexes, this type of coordination is greatly aided by the presence of porphyrin ligands.[6a–d]

In $Sb_2Cl_6(O)(OH)(ClO_4)$[6f]



$Cl_3SbOClO_2OSbCl_3$

and $[Sn_3O_2Cl_4(ClO_4)_4]_2$[6e]



$(Cl_2SnOClO_2OSn(Cl)OClO_2OSn(Cl)OClO_3)_2$

the ClO_4 ligand is able to strongly coordinate to metal centers (d(M–O) = 1.95–2.24 Å) as a monodentate or bridging bidentate group, without the help of electron-draining coligands such as porphyrin rings.

Some recent structural EXAFS investigations on $Cu(ClO_4)_2$[3a] and $M(ClO_4)_n$ ($n = 2$, M = Ni, Co,[3b] Zn;[3c] $n = 3$, M = Ga, In[3c]) have revealed strongly coordinated ClO_4 groups acting between

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(1) (a) Pascal, J.-L.; Potier, J.; Zhang, C. S. *J. Chem. Soc., Dalton Trans.* **1985**, 297 and references therein. (b) Nikitina, Z.; Karelin, A. I.; Rosolovskii, V. Ya. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 71. (c) Schack, C. J.; Pilipovich, D.; Christe, K. O. *J. Inorg. Nucl. Chem. Suppl.* **1976**, *76*, 207.

(2) (a) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091. (b) Chausse, T.; Pascal, J.-L.; Potier, A.; Potier, J. *Nouv. J. Chim.* **1981**, *5*, 261. (c) Zhang, C. S. Thesis, Université des Sciences et Techniques du Languedoc, Montpellier, France, 1984, and references therein.

(3) (a) Pascal, J.-L.; Potier, J.; Jones, D. J.; Rozière, J.; Michalowicz, A. *Inorg. Chem.* **1984**, *23*, 2068. (b) *Ibid.* **1985**, *24*, 238. (c) Pascal, J.-L.; Potier, J.; Seigneurin, A.; Jones, D. J.; Rozière, J., paper presented at the Conference on Progress in X-ray by Synchrotron Radiations, Strasbourg, France, April 1985; *Nouv. J. Chim.*, in press.

(4) (a) Hathaway, B. J. *Oxyanions as Ligands in Comprehensive Coordination Chemistry*; Pergamon: London, in press. (b) Procter, I. M.; Hathaway, B. J.; Nicholls, P. *J. Chem. Soc.* **1968**, 1768.

(5) Gowda, N. M. N.; Naikar, S. B.; Reddy, G. K. N. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 255.

(6) (a) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. U. *J. Am. Chem. Soc.* **1974**, *96*, 972. (b) Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z. I.; Ogoski, H. *Inorg. Chem.* **1980**, *19*, 950 and references therein. (c) Barkigia, K. M.; Spauling, L. D.; Fayer, J. *Ibid.* **1983**, *22*, 349. (d) Klaenh, D. O.; Paulus, H.; Greeve, R.; Elias, H. *Ibid.* **1984**, *23*, 483. (e) Belin, C.; Chaabouni, M.; Pascal, J.-L.; Potier, J.; Rozière, J. *J. Chem. Soc., Chem. Commun.* **1980**, 105. (f) Belin, C.; Chaabouni, M.; Pascal, J.-L.; Potier, J. *Inorg. Chem.* **1982**, *21*, 3557. (g) Genkina, E. A.; Babaeva, V. P.; Rosolovskii, V. Ya. *Koord. Khim.* **1984**, *10*, 1415.

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