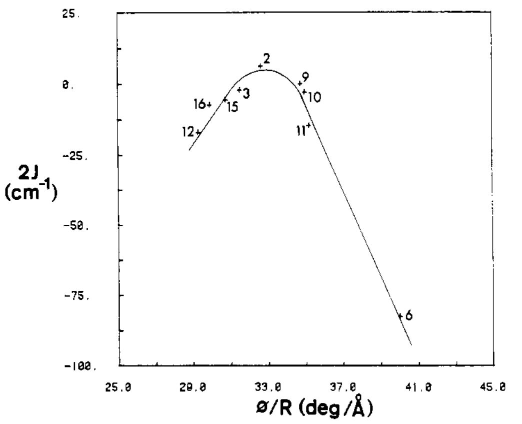

Figure 3. Plot of the singlet–triplet splitting $2J$ as a function of ϕ/R (see text for definitions). The solid line is a guide for the eye. The data are numbered as in Table V.

distance in II. The available $2J$ values (Table V) are plotted as a function of ϕ/R in Figure 3. It is noteworthy that the expected[6,8,12,19,25] behavior of the singlet–triplet splitting is observed in that $2J$ increases with increased ϕ/R until it reaches a maximum value, after which further increase in ϕ/R leads to a reduction in $2J$. Since there are both ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contributions to J, the existence of some values of ϕ/R where these two terms approximately cancel is predicted, and the present observation of $J \approx 0$, therefore, is an expected result. It should be emphasized that while the magnetic data in Figure 2 could be interpreted in terms of two noninteracting copper(II) centers, the correct interpretation (and the only interpretation consistent with the structure) is that of contributions to J of opposite sign that happen to cancel each other.

It is apparent from the plot in Figure 3 that all of the available structural and magnetic data for these structurally related bis(μ-chloro)-bridged dimers fit this gross trend, irrespective of their assignment as structural types I or II. It is important to note that the orbitals involved in the superexchange pathway are fundamentally the same in both cases, although the coefficients of the various orbital functions in the ground-state linear combination vary from complex to complex as a result of the chemical and structural environment of the copper ions. We expect that it will be possible to correlate exchange coupling with these coefficients. It is further expected that there will be a smooth variation of the coefficients with subtle structural changes and that this smooth variation of coefficients provides the basis for the $2J$ vs. ϕ/R correlation. As further data become available, it will be possible to replace the empirical quantity R^{-1} by a more satisfying function such as $\exp(-bR)$ as suggested by Glerup, Hodgson, and Pedersen[9] or, at least, by R^{-n}, but the present data are insufficient to justify this refinement.

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Registry No. $[Cu(Et_3en)Cl_2]_2$, 83897-46-5.

Supplementary Material Available: Tables of anisotropic thermal parameters (U_{ij}), observed and calculated structure factors (electrons × 10), and bond lengths (Table VI) and bond angles (Table VII) in the *N,N,N'*-triethylethylenediamine ligand (16 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica dell'Università di Venezia, 30123 Venice, Italy, and the Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Difrattometrica del CNR, Università di Parma, 43100 Parma, Italy

Synthesis and Characterization of Phosphite-Containing Cobalt(III) Complexes Obtained via Disproportionation Reactions of Pentacoordinate Mononitrosyl Derivatives. Crystal Structure of *trans*-Bis(isothiocyanato)tetrakis(triethyl phosphite)cobalt(III) Tetraphenylborate

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The disproportionation reactions of $Co(SCN)_2$ (in the presence of $P(OMe)_3$) and $[Co(NCS)L_3(NO)]^+$ ($L = P(OEt)_3$ or $PhP(OEt)_2$) species have been examined and have led to the synthesis of the first cobalt(III) complexes with the donor-atom set X_2L_4 (X = pseudohalogen; L = monodentate phosphite). Both the *cis*- and the *trans*-$[Co(NCS)_2L_4]BPh_4$ isomers were isolated and characterized, and the crystal structure of *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$ was determined. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of the following dimensions: $a = 19.05$ (2) Å, $b = 13.25$ (1) Å, $c = 27.46$ (3) Å, $\beta = 109.86$ (7)°. The structure was solved by the heavy-atom method from automated diffractometer data and refined to $R = 0.0935$ for 3199 reflections.

Introduction

Previous reports from our laboratories have dealt with studies of cobalt(II) halide reactions with phosphites and subsequent reactions with nitric oxide.[2] We found that CoX_2 (X = Cl, Br, I) reacts with phosphite to produce $[CoXL_4]^+$ species, which react with nitric oxide to form $[CoXL_3(NO)]^+$ cations. We have extended these studies to include the reactivity of cobalt(II) thiocyanate and found, instead of substitution products, Co(I) and Co(III) complexes. Redox reactions of this type have been only occasionally observed though the properties of cobalt(II) compounds have been extensively investigated.[3] Similar reactivity has been observed only with $Co(ClO_4)_2{\cdot}6H_2O$ in the presence of sterically con-

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strained polynuclear phosphites,[4] $[CoCl(NO)_2]_2$ in molten PPh_3,[5] and the disproportionation of $[Co(NO)(SacSac)_2]$ (SacSac = dithioacetylacetonate).[6] We now report detailed studies of the disproportionation reactions of Co(II) complexes with coordinated thiocyanate along with one of the few X-ray crystal structures of a Co(III) complex with phosphorus donor ligands, *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$.[7]

Experimental Section

Materials. All solvents were purified by standard methods and distilled under a stream of nitrogen just prior to use. $Co(SCN)_2$ (Alfa Inorganics) was used as received. Trimethyl and triethyl phosphites (Baker) were purified by distillation under nitrogen while the diethylphenyl phosphite was prepared by the reported method.[8] Nitric oxide (Baker) was purified by passing it through a −80 °C trap. All other reagents were used as received.

Synthesis of the Complexes. All the preparative work was performed under an inert atmosphere with use of standard Schlenk techniques. Once isolated, the complexes were kept under argon at −30 °C.

$\{Co[P(OMe)_3]_5\}BPh_4$ and *cis*-$\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$. Addition of trimethyl phosphite (50 mmol, 6.2 g) to a solution of cobalt(II) thiocyanate (10 mmol, 1.75 g) in methanol (60 mL) produced a green solution, which turned yellow after 5–10 min. The solution was stirred for 2 h and addition of $NaBPh_4$ (10 mmol, 3.4 g) induced the precipitation of a yellow-orange product containing $\{Co[P(OMe)_3]_5\}BPh_4$ and *cis*-$\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$, which were separated by fractional crystallization. In a typical separation the more soluble Co(I) complex was extracted from 3 g of crude product with three 50-mL portions of warm methanol (40–50 °C), which, when cooled slowly from +4 to −30 °C, produced crystalline $\{Co[P(OMe)_3]_5\}BPh_4$ in 45% yield. Crystals of *cis*-$\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$ were obtained by dissolving the orange residue in a mixture of acetone–methanol (1:3) at room temperature and cooling to −30 °C (yield 40%). The molar ratio of Co(I):Co(III) complex formed in the disproportionation reaction was shown to be about 1:1. Anal. Calcd for $\{Co[P(OMe)_3]_5\}BPh_4$: C, 46.91; H, 6.56. Found: C, 46.75; H, 6.47. Calcd for $\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$: C, 46.07; H, 5.70; N, 2.83. Found: C, 45.81; H, 5.51; N, 2.83.

$\{Co[P(OMe)_3]_5\}_2[Co(NCS)_4]$. Trimethyl phosphite (30 mmol, 3.7 g) was added to a suspension of $Co(SCN)_2$ (10 mmol, 1.75 g) in 50 mL of dichloromethane, and the mixture was stirred for 1 day. The solvent was removed, and the resulting oil was triturated with methanol (20 mL) to give green crystals of the product, which were further purified by recrystallization from methanol (yield ≃30%). Anal. Calcd: C, 24.75; H, 5.50; N, 3.40. Found: C, 24.70; H, 5.43; N, 3.33.

$[Co(NCS)L_4]BPh_4$ (L = $P(OEt)_3$, $PhP(OEt)_2$). These complexes were prepared according to the procedure of Bertacco et al.[9] (yield 80%). Anal. Calcd for $\{Co(NCS)[P(OEt)_3]_4\}BPh_4$: C, 53.45; H, 7.33; N, 1.27. Found: C, 53.18; H, 7.50; N, 1.24. μ_{eff}(solution): 2.07 μ_B ν(CN): (KBr) 2052 cm^{-1}; (CH_2Cl_2) 2055 cm^{-1}; λ_{max} (ϵ) ($ClCH_2CH_2Cl$): 535 (236), 655 nm (176). Anal. Calcd for $\{Co(NCS)[PhP(OEt)_2]_4\}BPh_4$: C, 63.52; H, 6.51; N, 1.14. Found: C, 63.67; H, 6.40; N, 1.10. μ_{eff}(solution): 2.10 μ_B. ν(CN): (KBr) 2060 cm^{-1}; (CH_2Cl_2) 2058 cm^{-1}. λ_{max} (ϵ) ($ClCH_2CH_2Cl$): 585 (301), 675 nm (242).

$\{Co(NCS)_2[PhP(OEt)_2]_3\}$. The complex was prepared according to the reported method.[9] Anal. Calcd: C, 49.93; H, 5.85; N, 3.64. Found: C, 49.77; H, 5.77; N, 3.54. μ_{eff}(solution): 2.10 μ_B. ν(CN): (KBr) 2067 cm^{-1}; ($ClCH_2CH_2Cl$) 2065 cm^{-1}. λ_{max} (ϵ) ($ClCH_2CH_2Cl$): 372 (7.7×10^3), 667 nm (225).

$\{Co[P(OEt)_3]_2(NO)_2\}BPh_4$ and *cis*- and *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$. Nitric oxide was bubbled for 5 min through a stirred solution of $\{Co(NCS)[P(OEt)_3]_4\}BPh_4$ (3.6 mmol, 4 g) in dichloromethane (200 mL). The solvent was removed by evaporation to yield a brown oil, which was stirred with ethanol (20 mL) for 2 h to produce an orange-red product, which was washed with ethanol and diethyl ether and dried under vacuum. The more soluble $[CoL_2(NO)_2]BPh_4$ was extracted from the crude product with 150 mL of warm ethanol (40 °C). The dinitrosyl complex separated as red-brown crystals upon cooling of the solution to −30 °C and was further purified by recrystallization from ethanol (yield ≥50%). The remaining yellow-orange solid was mixed with 50 mL of ethanol and enough acetone (10–15 mL) to produce a homogeneous solution at room temperature. The solution was cooled very slowly to 4 °C to give red crystals of *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$, which were washed with ethanol and diethyl ether and dried under vacuum (yield 10%). Further cooling of the solution to −30 °C precipitated a mixture of the cis and trans isomers, which were removed by filtration. Yellow crystals of *cis*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$ separated upon concentration of the filtrate to 20 mL and were collected, washed with ethanol and diethyl ether, and dried under vacuum (yield ≃20%). The total yield of the Co(III) complexes was about 40%. The molar ratio of $[CoL_2(NO)_2]BPh_4$:Co(III) complex formed in the disproportionation reaction was shown by this separation to be about 1.25:1. That this ratio is greater than 1 may be attributed to the fact that the intermediate pentacoordinate mononitrosyl complex $\{Co(NCS)[P(OEt)_3]_3(NO)\}^+$ can, in parallel to the disproportionation reaction, further react with NO to produce the $[CoL_2(NO)_2]BPh_4$ complex (see Results and Discussion). Anal. Calcd for $\{Co[P(OEt)_3]_2(NO)_2\}BPh_4$: C, 56.12; H, 6.54; N, 3.64. Found: C, 56.10; H, 6.48; N, 3.72. Λ_M (in CH_3NO_2 solution at 25 °C): 55.6 cm^2 M^{-1} Ω^{-1}. ν(NO) (CH_2Cl_2): 1869 s, 1811 s cm^{-1}. Anal. Calcd for *cis*- and *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$: C, 51.81; H, 6.96; N, 2.42. Found (cis isomer): C, 52.12; H, 7.05; N, 2.40. Found: (trans isomer): C, 52.20; H, 7.56; N, 2.38.

$\{Co[PhP(OEt)_2]_2(NO)_2\}BPh_4$ and *trans*-$\{Co(NCS)_2[PhP(OEt)_2]_4\}BPh_4$. These complexes were prepared by following the method reported above; however, only the trans-Co(III) complex was obtained in pure form with a yield of about 20%. Anal. Calcd for $\{Co[PhP(OEt)_2]_2(NO)_2\}BPh_4$: C, 63.32; H, 6.04; N, 3.36. Found: C, 63.12; H, 5.92; N, 3.49. Λ_M (in CH_3NO_2 solution at 25 °C): 53.8 cm^2 M^{-1} Ω^{-1}. ν(NO) (CH_2Cl_2): 1858 s, 1806 s cm^{-1}. Anal. Calcd for *trans*-$\{Co(NCS)_2[PhP(OEt)_2]_4BPh_4$: C, 61.59; H, 6.27; N, 2.18. Found: C, 61.37; H, 6.15; N, 1.93.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 457 infrared spectrophotometer. Solid-state spectra were obtained from KBr pellets while solution spectra were obtained with use of potassium bromide solution cells (path length of 0.5 mm).

Proton magnetic resonance spectra were recorded on a Varian EM 390 instrument with tetramethylsilane as an internal standard.

Electronic spectra were recorded on a Cary 219 and/or Perkin-Elmer Coleman 575 spectrophotometers.

Magnetic susceptibility measurements were performed on powdered samples at ambient temperature with a Cahn Instruments Faraday balance using $Hg[Co(NCS)_4]$ as standard. Solution susceptibilities were determined by the Evans method.[10] The correction for the diamagnetism of the ligands was made with use of the tables given by Figgis and Lewis.[11]

Conductivities of 10^{-3} M solutions of complexes in nitromethane, methanol, and ethanol at 25 °C were measured with an Haloisis bridge.

Gas uptake was measured in a glass vacuum system by following the procedure described previously.[2b]

X-ray Analysis, Data Collection, and Refinement. Initial lattice constants and space group information for *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$ were determined from oscillation and zero- and first-layer Weissenberg photographs obtained with use of an equi-inclination Weissenberg camera. The crystals belong to the monoclinic system, with the systematic absences uniquely indicating the $P2_1/c$ space group. Precise cell dimensions were derived by least-squares refinement of the 2θ values for 22 reflections measured on an automated single-crystal Siemens diffractometer. Crystallographic data are as follows: $a = 19.05$ (2) Å, $b = 13.25$ (1) Å, $c = 27.46$ (3) Å, $\beta = 109.86$ (7)°, $V = 6519$ Å^3, $Z = 4$, $D_c = 1.18$ g cm^{-3}, $F(000) =$

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Table I. Physical Constants and Selected IR and NMR Data for Some Co–Phosphite Complexes

complexes	color	dec pt,[a] °C	Λ_M,[b] cm^2 Ω^{-1} mol^{-1}	ν(CN),[c] cm^{-1}		ν(CS),[c] cm^{-1}		chem shift, τ[d,e] CH$_2$	chem shift, τ[d,e] CH$_3$
cis-$\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$	orange	121	57.9	2110 s (2109) s	2094 s (2091) s	(818) m	(794) m		5.90 m
cis-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$	yellow-orange	111	55.9	2112 s (2112) s	2097 s (2098) s	(785) m	(772) m	5.52 m	8.50 t 8.56 t
trans-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$	red	118	52.5	2104 s (2108) s		(783) m		5.51 m	8.52 t
trans-$\{Co(NCS)_2[PhP(OEt)_2]_4\}BPh_4$	red	113	49.6	2107 s (2100) s		(775) m		6.13 m	8.67 t
$\{Co[P(OMe)_3]_5\}BPh_4$	yellow	121	54.8						6.43 d
$\{Co[P(OMe)_3]_5\}_2[Co(NCS)_4]$	green	123	137.5	2072 s (2070) s					6.30 br 6.31 d[f]

[a] All the decomposition points are uncorrected. [b] Molar conductances (Λ_M) were determined in 10^{-3} M nitromethane solutions at 25 °C. [c] Frequencies in parentheses are from spectra of KBr pellets of complexes in the solid state; all other values are from spectra of CH_2Cl_2 solutions. [d] In $(CD_3)_2CO$. [e] At room temperature. [f] In CD_3OD.

Table II. Electronic Absorption Data for Selected Co–Phosphite Complexes

complexes	medium	λ_{max}, nm (ϵ)
cis-$\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$	$ClCH_2CH_2Cl$	310 sh, 408 (3.0×10^3)
cis-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$	$ClCH_2CH_2Cl$	320 sh, 407 (3.1×10^3)
trans-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$	$ClCH_2CH_2Cl$	337 (6.7×10^3), 390 (4.4×10^3), 488 (0.94×10^3)
trans-$\{Co(NCS)_2[PhP(OEt)_2]_4\}BPh_4$	$ClCH_2CH_2Cl$	372 (13.2×10^3), 508 (0.96×10^3)
$\{Co[P(OMe)_3]_5\}BPh_4$	$ClCH_2CH_2Cl$	384 (1.2×10^3)
$\{Co[P(OMe)_3]_5\}_2[Co(NCS)_4]$	$ClCH_2CH_2Cl$	320 (12.9×10^3), 380 (2.48×10^3), 588 sh, 624 (1.9×10^3)
	CH_3OH	380 (2.28×10^3)

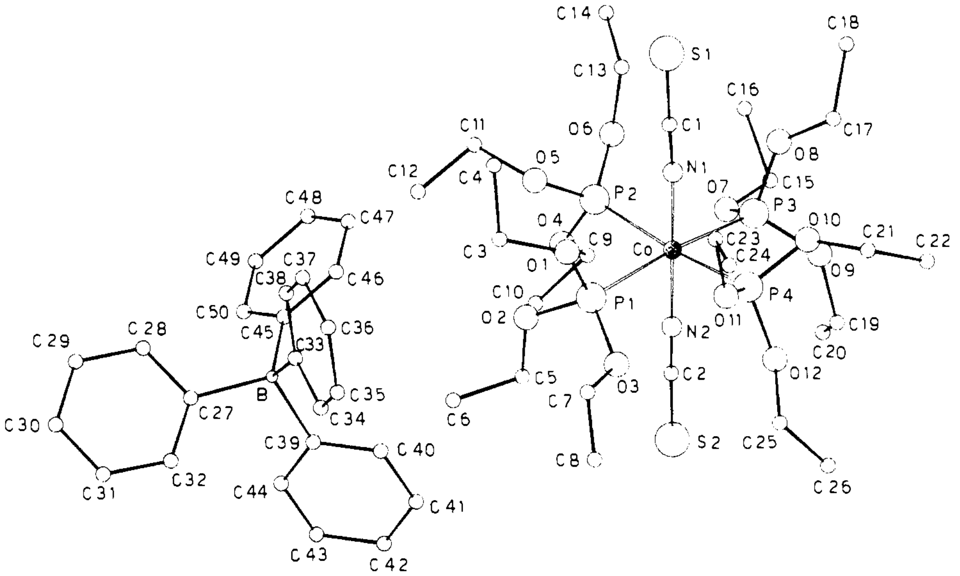

Figure 1. Projection of the structure showing the two coordination polyhedra.

2456. Intensity measurements were made at room temperature with use of a small prismatic crystal sealed in a Lindeman-glass capillary and mounted with the crystallographic *b* axis and the instrument ϕ axis approximately coincident. Data were collected in the scan range 2θ (5.0–43.0°) with the use of Nb-filtered Mo radiation ($\lambda = 0.71069$ Å) by employing the moving-counter–moving-crystal scan technique, the drive speed being related to the number of counts on the peak (lowest speed 2.5° min^{-1}). The pulse height discriminator was set to admit 90% of the Mo Kα peak. In this way a total of 8250 reflections ($+h,+k,+l$) were collected. After systematic absences were deleted, symmetry-equivalent reflections were merged to produce a unique set of 7364 reflections, of which only 3229 (42%) having $I > 2\sigma(I)$ were retained for subsequent calculations. Two check reflections were monitored every 50 measurements to detect long-term drift in the equipment or change in the sample, and their intensities showed no significant variations over the course of the experiment. Data were reduced to structure amplitudes by application of the standard Lorentz and polarization factors. No allowance was made for the small effects of absorption ($\mu = 4.7$ cm^{-1}) or extinction. The structure was solved by conventional Patterson and difference Fourier syntheses. Full-matrix least-squares refinement with isotropic thermal parameters yielded a value of 0.1218 for the R index. Because of storage limitations and the large number of variables, the refinement was carried out by blocking the least-squares matrix (two blocks) and by constraining the carbon atoms of the phenyl rings to the rigid-group approximation. Moreover, only Co, S, P, O, and N, as well as the C atoms of thiocyanate groups, were assigned anisotropic thermal parameters in further refinement, which gave $R = 0.1013$. At this stage, analysis of the agreement between F_o and F_c indicated that a number of reflections should be omitted. Elimination of 30 reflections with subsequent refinement resulted in final values of 0.0935 and 0.0985 for R and R_w. The function minimized was $\sum w|\Delta F^2|$, the weight w being unit at first, while in the final stage of refinement the weighting scheme $w = 1/\sigma^2(F_o) + 0.005F_o^2$, derived from counting statistics, was assumed. Since the crystal diffracted weakly, little reliable data could be collected and this probably accounts for the somewhat large R values. In addition, the number of variable parameters is rather high (356), yielding an observation to parameters ratio of 9.1:1. A final difference Fourier map was devoid of significant features, with the maximal residual electron density being 0.7 e Å^{-3}.

Table III. Fractional Atomic Coordinates ($\times 10^4$)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Co	2569 (1)	8308 (2)	7450 (1)	C16	1257 (11)	9920 (17)	5587 (8)
S1	435 (3)	8976 (5)	7842 (2)	C17	1602 (12)	11164 (19)	7101 (9)
N1	1737 (7)	8605 (11)	7618 (5)	C18	828 (12)	11650 (18)	6799 (9)
C1	1213 (10)	8735 (13)	7709 (6)	C19	3924 (23)	10590 (33)	7104 (17)
S2	4627 (4)	7570 (6)	6989 (4)	C20	3874 (20)	10188 (33)	6711 (16)
N2	3403 (7)	8013 (11)	7260 (5)	C21	3130 (10)	11182 (16)	8414 (7)
C2	3904 (11)	7818 (15)	7146 (8)	C22	3436 (12)	11997 (19)	8144 (8)
P1	2855 (3)	6935 (4)	7954 (2)	C23	2583 (10)	9000 (15)	8879 (7)
P2	1802 (2)	7361 (4)	6806 (2)	C24	2893 (12)	9065 (18)	9435 (9)
P3	2411 (2)	9643 (4)	6922 (2)	C25	4696 (17)	9221 (24)	8665 (12)
P4	3190 (2)	9271 (4)	8132 (2)	C26	5329 (14)	9766 (22)	8646 (10)
O1	2296 (6)	6764 (9)	8240 (4)	B	2786 (10)	1932 (16)	4759 (8)
O2	2885 (6)	5900 (9)	7686 (4)	C27	2785 (7)	673 (7)	4823 (5)
O3	3647 (6)	7052 (9)	8371 (4)	C28	2113 (7)	164 (7)	4589 (5)
O4	2180 (6)	6718 (9)	6496 (4)	C29	2071 (7)	−875 (7)	4657 (5)
O5	1423 (6)	6555 (9)	7053 (4)	C30	2701 (7)	−1405 (7)	4960 (5)
O6	1148 (6)	7862 (10)	6368 (4)	C31	3373 (7)	−896 (7)	5195 (5)
O7	2280 (6)	9255 (9)	6357 (4)	C32	3415 (7)	143 (7)	5126 (5)
O8	1699 (6)	10292 (8)	6853 (4)	C33	2663 (7)	2355 (10)	5292 (4)
O9	3045 (5)	10450 (9)	7052 (4)	C34	3273 (7)	2544 (10)	5739 (4)
O10	2847 (5)	10322 (8)	8042 (4)	C35	3158 (7)	2857 (10)	6192 (4)
O11	3222 (6)	8910 (9)	8691 (4)	C36	2432 (7)	2980 (10)	6198 (4)
O12	4040 (6)	9392 (9)	8212 (4)	C37	1822 (7)	2791 (10)	5751 (4)
C3	1979 (12)	5827 (19)	8338 (8)	C38	1938 (7)	2478 (10)	5299 (4)
C4	1131 (12)	6041 (18)	8258 (8)	C39	3612 (6)	2299 (11)	4704 (5)
C5	3514 (11)	5596 (18)	7517 (8)	C40	3910 (6)	3247 (11)	4879 (5)
C6	3584 (14)	4492 (23)	7582 (10)	C41	4566 (6)	3563 (11)	4805 (5)
C7	3844 (17)	6501 (24)	8855 (12)	C42	4924 (6)	2931 (11)	4556 (5)
C8	4611 (17)	6331 (23)	9124 (12)	C43	4626 (6)	1983 (11)	4380 (5)
C9	2360 (12)	7039 (19)	6048 (9)	C44	3970 (6)	1667 (11)	4455 (5)
C10	2756 (14)	6083 (21)	5895 (10)	C45	2192 (5)	2360 (8)	4225 (3)
C11	882 (11)	5795 (18)	6731 (8)	C46	1855 (5)	3298 (8)	4217 (3)
C12	1233 (12)	4833 (19)	6808 (9)	C47	1342 (5)	3664 (8)	3757 (3)
C13	478 (11)	8268 (15)	6466 (7)	C48	1167 (5)	3094 (8)	3304 (3)
C14	−161 (13)	8252 (19)	5918 (9)	C49	1504 (5)	2156 (8)	3312 (3)
C15	2099 (9)	10010 (14)	5922 (7)	C50	2017 (5)	1790 (8)	3772 (3)

Some C atoms from ethyl groups exhibited high thermal parameters, suggesting that there might be some degree of disorder.

Final atomic coordinates are given in Table III with atoms labeled according to Figure 1. A listing of observed and calculated structure factors is available as supplementary material. Complex neutral-atom scattering factors were employed, and the effects of anomalous dispersion were included in all structure factor calculations. All computations were performed with use of the SHELX-76 system program on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Casalecchio, Bologna, Italy).

Results and Discussion

Reaction of $Co(SCN)_2$ with Phosphites. Cobalt(II) thiocyanate quickly disproportionates in the presence of $P(OMe)_3$ to quantitatively produce $Co[P(OMe)_3]_5^+$ and *cis*-$\{Co(NCS)_2[P(OMe)_3]_4\}^+$ in equivalent amounts according to the stoichiometry[12]

$$2Co(SCN)_2 + 9P(OMe)_3 \rightarrow \{Co[P(OMe)_3]_5\}^+ + cis\text{-}\{Co(NCS)_2[P(OMe)_3]_4\}^+ + 2SCN^- \quad (1)$$

The phosphites $P(OEt)_3$ and $PhP(OEt)_2$ also react quickly with $Co(SCN)_2$ in ethanol at room temperature, but only the simple cobalt(II) complexes $[Co(NCS)_2L_3]$ and/or $[Co(NCS)L_4]^+$ are obtained. The relative amounts of these two complexes depend on the $Co(SCN)_2$:L ratio. In the presence of a large excess of $P(OEt)_3$ a disproportionation reaction does occur and, after 1 week, small amounts of corresponding Co(I) and Co(III) complexes are detected. No Co(III) species, however, is observed after several weeks with the phosphite $PhP(OEt)_2$.

Scheme I

$$[Co(NCS)L_4]^+ \xrightarrow{NO} [Co(NCS)L_3(NO)]^+ \rightarrow [CoL_2(NO)_2]^+ + [Co(NCS)_2L_4]^+$$

The disparate reactivity of the three phosphites $P(OMe)_3$, $P(OEt)_3$, and $PhP(OEt)_2$ toward $Co(SCN)_2$ may be interpreted in terms of steric effects and π-accepting properties of the phosphite ligands. The cone angles of the ligands[13] decrease in the order $PhP(OEt)_2 > P(OEt)_3 > P(OMe)_3$, whereas the π acidity increases in the sequence $PhP(OEt)_2 < P(OEt)_3 < P(OMe)_3$. The rate of the disproportionation reaction, therefore, is enhanced with increasing phosphite π acidity and decreasing cone angle. The products of the disproportionation, $[CoL_5]^+$ and $[Co(NCS)_2L_4]^+$, are stable and can be prepared by an alternative method with all three phosphite ligands (vide infra). Thus, the different steric bulk and π acidity of the ligands do not influence the reaction because of the varying stability of the final products but rather affect the reaction rate and/or the stability of the Co(II) intermediate toward the disproportionation reaction.

Finally, it should be noted that CoX_2 (X = Cl, Br, I) reacts with all the phosphites to produce only $[CoX_2L_3]$ and/or $[CoXL_4]^+$ species[2] and no evidence of Co(III) species has ever been observed. Therefore, the presence of the SCN moiety plays an essential role in the disproportionation reaction.

Reactions with Nitric Oxide. At room temperature $[Co(NCS)L_4]^+$ (L = $P(OEt)_3$ or $PhP(OEt)_2$) take up NO to give the pentacoordinate mononitrosyl cations of the type [Co-

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(12) When the reaction is run with the L:$Co(SCN)_2$ molar ratio maintained less than 3, one observes the precipitation of a green paramagnetic product, which was isolated and characterized as $\{Co[P(OMe)_3]_5\}_2[Co(NCS)_4]$. The same complex was also obtained with use of dichloromethane as solvent. A methanolic solution of the $[Co(NCS)_4]^{2-}$ anion in the presence of $P(OMe)_3$ disproportionates to give $Co[P(OMe)_3]_5^+$ and *cis*-$\{Co(NCS)_2[P(OMe)_3]_4\}^+$ as final products.

(13) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table IV. Structural Parameters (Distances in Å, Angles in deg) Involving the Co-N-C-S Fragment in Some Octahedral Co^{III} Complexes

compd[a]	Co-N	N-C	C-S	Co-N-C	N-C-S
I	1.974 (18)	1.174 (29)	1.629 (18)	170.7 (10)	177.5 (12)
II	1.93 (1), 1.92 (1)	1.16 (2), 1.15 (2)	1.61 (2), 1.60 (2)	175.6 (12), 161.1 (13)	178.8 (13), 178.8 (13)
III	1.922 (7)	1.141 (11)	1.633 (8)	175.3 (6)	179.3 (7)
IV	1.89 (1), 1.88 (1)	1.17 (2), 1.13 (2)	1.58 (2), 1.64 (2)	172.1 (13), 172.3 (14)	178.2 (14), 178.7 (14)
V	1.903 (9)	1.15 (1)	1.62 (1)	175.8 (9)	178.3 (10)
VI	1.928 (9)	1.18 (1)	1.61 (1)	170.1 (7)	176.3 (8)
VII	1.922 (11)	1.16 (2)	1.62 (1)	173.8 (9)	176.3 (10)
VIII	1.909 (16)	1.20 (2)	1.64 (2)	176.0 (12)	178.2 (14)
IX	1.838 (15), 1.874 (15)	1.12 (3), 1.13 (3)	1.67 (2), 1.61 (2)	176.1 (15), 178.8 (16)	177.8 (17), 178.4 (19)

[a] Legend: I, *trans*-(sulfito)(isothiocyanato)bis(ethylenediamine)cobalt dihydrate;[23a] II, (2,2′,2″-triaminotriethylamine)bis(isothiocyanato)cobalt thiocyanate monohydrate;[23b] III, bis(ethylenediamine)(isothiocyanato)nitrocobalt thiocyanate;[23c] IV, *trans*-bis(isothiocyanato)(*rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradec-4,11-diene)cobalt thiocyanate hydrate;[23d] V, *trans*-bis(ethylenediamine)(isothiocyanato)nitrocobalt iodide;[23e] VI, *trans*-bis(ethylenediamine)(isothiocyanato)(nitrito)cobalt iodide;[23e] VII, *trans*-bis(ethylenediamine)(isothiocyanato)nitrocobalt perchlorate;[23e] VIII, *trans*-bis(ethylenediamine)(isothiocyanato)(nitrito)cobalt perchlorate;[23e] IX, title complex.

$(NCS)L_3(NO)]^+$, which then disproportionate to produce formal cobalt(I), $[CoL_2(NO)_2]^+$, and cobalt(III), $[Co(NCS)_2L_4]^+$, complexes as shown in Scheme I.[14]

Several lines of evidence suggest the stoichiometry in reaction 2. When the $[Co(NCS)L_4]^+$:NO molar ratio is unity,

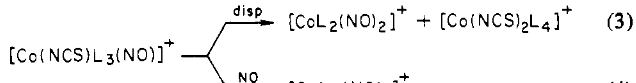
$$2[Co(NCS)L_4]^+ + 2NO \rightarrow [CoL_2(NO)_2]^+ + [Co(NCS)_2L_4]^+ + 2L \quad (2)$$

the two final products, $[CoL_2(NO)_2]^+$ and $[Co(NCS)_2L_4]^+$, are formed in equivalent amounts and can be recovered in quantitative yields. The diamagnetism of the final reaction mixture indicates the complete reaction of $[Co(NCS)L_4]^+$ and the absence of Co(II) products. Gas chromatographic analysis of the final solution and corresponding vapor phase does not show any N_2O, precluding NO oxidation of Co(II).

The progress of the reaction between $[Co(NCS)L_4]^+$ (L = $P(OEt)_3$, $PhP(OEt)_2$) and NO is conveniently followed by IR spectra of the mixture since well-separated bands appear in the coordinated NCS and NO stretching region. The reaction does not depend on the nature of the phosphite ligand, and we therefore limit the following discussion to the slower reacting $\{Co(NCS)[P(OEt)_3]_4\}^+$ derivative. Introduction of NO (in either stoichiometric or excess amount) to a $\{Co(NCS)[P(OEt)_3]_4\}^+$ solution shifts the 2055-cm^{-1} $\nu(CN)$ band to 2065 cm^{-1}, and an intense band appears in the NO stretching region at 1785 cm^{-1}. These bands can be attributed to the mononitrosyl $\{Co(NCS)[P(OEt)_3]_3(NO)\}^+$ complex. The assignment is supported by the infrared spectra of $[CoXL_3(NO)]^+$ (X = Cl, Br, I; L = $P(OEt)_3$, $PhP(OEt)_2$) ions,[2c] which exhibit intense $\nu(NO)$ bands in the 1780–1802-cm^{-1} range.[15]

After the rapid uptake of 1 mol of NO/mol of cobalt(II) complex to form the $\{Co(NCS)[P(OEt)_3]_3(NO)\}^+$ intermediate, the IR bands at 2065 and 1785 cm^{-1} are gradually replaced by the absorptions at 2112 and 2097 cm^{-1} of *cis*-$\{Co(NCS)_2[P(OEt)_3]_4\}^+$ and at 1869 and 1811 cm^{-1} of $\{Co[P(OEt)_3]_2(NO)_2\}^+$. The Co(I) and Co(III) products are isolated in a 1:1 ratio and quantitative yield when excess NO is pumped off the reaction mixture immediately following the formation of the mononitrosyl intermediate. In contrast, if excess nitric oxide is kept in the presence of the mononitrosyl intermediate, the product ratio of $[CoL_2(NO)_2]^+$:*cis*-$[Co(NCS)_2L_4]^+$ is greater than unity. Under these conditions, gas-uptake experiments show that 1.2–1.3 mol of NO is absorbed per mole of $[Co(NCS)L_4]^+$. These results exclude the participation of gaseous NO in the disproportionation reaction and demonstrate that reaction 4[16] proceeds in parallel to the disproportionation as illustrated in Scheme II. The presence of an NCS ligand is essential for the disproportionation reaction since pentacoordinate $[CoX_2L_2(NO)]$ and $[CoXL'_3(NO)]^+$ (X = Cl, Br, I; L = tertiary phosphine; L′ = phosphite)[2c,17] complexes have been obtained in pure form and are stable in solution.[18]

Scheme II



Characterization of New Co(III) Complexes. The disproportionation reactions described above have led to the preparation of the first Co(III) complexes containing the donor atom set P_4X_2 (X = NCS) in which the phosphite ligands are monodentate.[19] The properties of the cobalt(III) complexes (as well as the $Co[P(OMe)_3]_5^+$ cations[20]) obtained by the disproportionation reactions are reported in Tables I and II. The new cobalt(III) $[Co(NCS)_2L_4]^+$ complexes are stable in the solid state and in polar organic solvents. Solids and solutions of these Co(III) species are diamagnetic, and the conductivity values are in agreement with those reported for 1:1 electrolytes.[21] In addition, the elemental analysis and IR, ^1H NMR, and UV spectra are consistent with our structural assignments. The infrared spectra in the $\nu(NC)$ and $\nu(CS)$ regions of the NCS ligand permit discrimination between the

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(14) The reaction of $[Co(NCS)_2L_3]$ (L = $PhP(OEt)_2$) and NO also leads to the formation of the pentacoordinated mononitrosyl complex $[Co(NCS)L_3(NO)]^+$, which then disproportionates according to Scheme I.

(15) A hexacoordinate complex such as $[Co(NCS)L_4(NO)]^+$ may be excluded since a change in the stereochemistry about the metal from penta- to hexacoordinate generally changes the MNO coordination geometry from linear to bent with a lowering of $\nu(NO)$ by 100–200 cm^{-1} as previously observed for the $[Co(das)_2(NO)]^{2+}$ and $[CoX(das)_2(NO)]^+$ (X = Br, NCS; das = diarsine) derivatives (Enemark, J. H.; Feltham, R. D.; Riker-Nappier, J.; Bizot, K. F. *Inorg. Chem.* **1975**, *14*, 624).

(16) Analogous reactions have been observed between NO and $[CoXL_3(NO)]^+$ (X = Cl, Br, I; L = phosphite) ions.[2c]

(17) Dolcetti, G.; Hoffman, N. W.; Collman, J. P. *Inorg. Chim. Acta* **1972**, *6*, 531 and references therein.

(18) The important role of the NCS ion compared to that of the halogen in determining the stability of pentacoordinate $[CoX_2L_3]$ (X = halogen; L = tertiary or secondary phosphine) in comparison to that of tetracoordinate $[CoX_2L_2]$ derivatives has already been observed (Rigo, P.; Bressan, M.; Turco, A. *Inorg. Chem.* **1968**, *7*, 1460).

(19) Except for the $[CoL_6](ClO_4)_3$ (L = polycyclic phosphite ligands of the type $P(OCH_2)_3CCH_3$) complexes obtained by disproportionation,[4] the previously reported cobalt(III) derivatives containing bi- and polydentate phosphite or arsine ligands have been prepared by oxidation of the corresponding cobalt(II) derivatives: Levason, W.; McAuliffe, C. A. *Coord. Chem. Rev.* **1974**, *12*, 151. Cloyd, J. C., Jr.; Meek, D. W. *Inorg. Chim. Acta* **1972**, *6*, 40. Hartley, J. G.; Kerfoot, D. G. E.; Venanzi, L. M. *Ibid.* **1967**, *1*, 145.

(20) The tetraphenylborate salt of this cation has been prepared by alternative procedures: Glosser, L. W.; Parshall, G. W. *Inorg. Chem.* **1974**, *13*, 1947. Attali, S.; Poilblanc, R. *Inorg. Chim. Acta* **1972**, *6*, 475.

(21) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

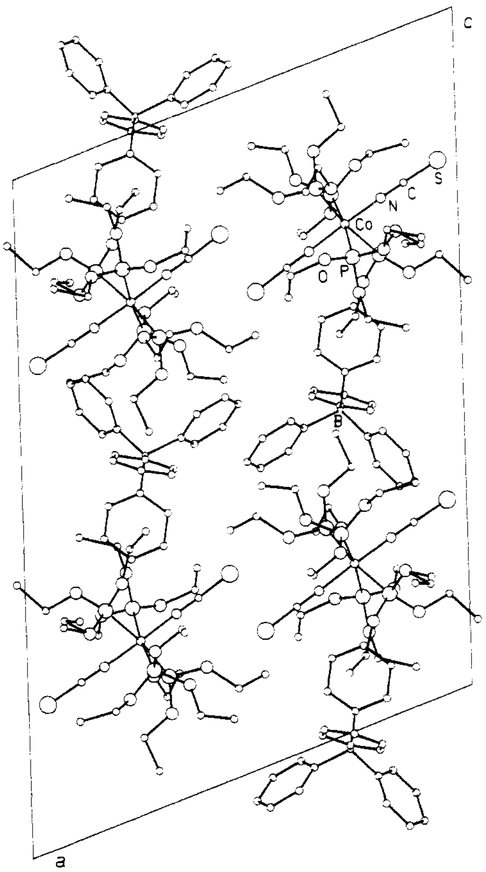

Figure 2. Molecular packing as viewed along [010].

cis and trans isomers (Table I), and the ν(CS) bands in the 772–818-cm^{-1} range indicate an N-bonded thiocyanate group.[22]

Both the cis and the trans isomers of $\{Co(NCS)_2[P(OEt)_3]_4\}^+$ are obtained in pure form; however, only the cis isomer forms with the $P(OMe)_3$ ligand and only the trans isomer results with the $PhP(OEt)_2$ ligand. The cis forms of the Co(III) complexes isomerize at room temperature in dichloromethane or alcohol solution to give the trans derivatives. The course of the reaction is easily monitored via IR or UV spectroscopy. The $P(OMe)_3$ derivative isomerizes with a half-life of 1 day.

The molecular structure of one of the new Co(III) complexes, *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$ is illustrated in Figure 1, and fractional atomic coordinates are listed in Table III. The cobalt cations adopt an essentially octahedral geometry, the coordination sites being occupied by four P atoms from the triethyl phosphite ligands and by two N atoms from the thiocyanate ions. The Co–P bonds (in Å) are all nearly equivalent (Co–P1, 2.238 (6); Co–P2, 2.254 (5); Co–P3, 2.242 (6); Co–P4, 2.243 (6)), and the four P atoms are not coplanar but tetrahedrally distorted within ±0.15 Å, with the Co atom displaced 0.03 Å out of their mean least-squares plane. The two thiocyanate ions coordinate the metal atom through their nitrogen atoms in a trans arrangement, with nearly linear Co–N–C–S fragments. The Co–N bond lengths are slightly shorter than those usually found in octahedral Co(III) isothiocyanate complexes (Table IV).[23] The crystal packing is shown in Figure 2. There are no abnormally short intermolecular contacts, the smallest distance being 3.57 (3) Å for C16···C29 (x, $1 + y$, z).

Conclusions

The influence of the thiocyanate ion in the formation of cobalt(I) and cobalt(III) complexes via disproportionation reactions has been demonstrated by employing phosphites as ligands. Trimethyl phosphite reacts with $Co(SCN)_2$ to give quantitative amounts of the $\{Co[P(OMe)_3]_5\}^+$ and the *cis*-$\{Co(NCS)_2[P(OMe)_3]\}^+$ complexes in a 1:1 ratio. Reaction of $P(OEt)_3$ and $PhP(OEt)_2$ with $Co(SCN)_2$ gives the simple Co(II) derivatives $[Co(NCS)_2L_3]$ and/or $[Co(NCS)L_4]^+$. The difference in behavior has been tentatively explained in terms of both steric and π-accepting properties of the three phosphite ligands. Furthermore, the $[Co(NCS)L_4]^+$ complexes ($L = P(OEt)_3$, $PhP(OEt)_2$) react with nitric oxide to give intermediate pentacoordinate mononitrosyl complexes, $[Co(NCS)L_3(NO)]^+$, which disproportionate to produce $[CoL_2(NO)_2]^+$ and $[Co(NCS)_2L_4]^+$ as final products. The novel disproportionation reactivity exhibited by the Co(II) species described above appears to be due to the presence of coordinated isothiocyanate, and this reactivity may find application in both synthetic and mechanistic investigations.

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Registry No. $\{Co[P(OMe)_3]_5\}BPh_4$, 53701-74-9; *cis*-$\{Co(NCS)_2[P(OMe)_3]_4\}BPh_4$, 83927-92-8; $\{Co[P(OMe)_3]_5\}_2[Co(NCS)_4]$, 83927-93-9; $\{Co(NCS)[P(OEt)_3]_4\}BPh_4$, 83927-95-1; $\{Co(NCS)[PhP(OEt)_2]_4\}BPh_4$, 38890-13-0; $Co(NCS)_2[PhP(OEt)_2]_3$, 38549-36-9; $\{Co[P(OEt)_3]_2(NO)_2\}BPh_4$, 73169-82-1; *cis*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$, 83927-97-3; *trans*-$\{Co(NCS)_2[P(OEt)_3]_4\}BPh_4$, 83997-27-7; $\{Co[PhP(OEt)_2]_2(NO)_2\}BPh_4$, 73169-62-7; *trans*-$\{Co(NCS)_2[PhP(OEt)_2]_4\}BPh_4$, 83927-99-5.

Supplementary Material Available: A listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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