

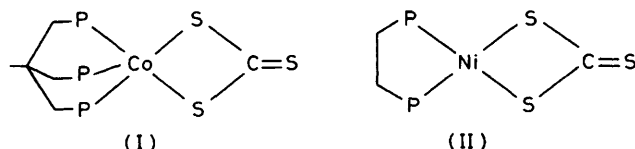
## Cobalt(II) and Nickel(II) Trithiocarbonate Complexes as Nucleophilic Reagents. Reactivity and X-Ray Structure of the Trithiocarbonate Complex $[\text{Co}(\text{tppme})(\text{S}_2\text{CSCH}_3)][\text{BPh}_4] \cdot 1.5\text{thf}^\dagger$

By Claudio Bianchini,\* Carlo Mealli, Andrea Meli, and Giancarlo Scapacci, Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, C.N.R., Via D. Guerrazzi, 27, Florence, Italy

The trithiocarbonate complexes  $[\text{Co}(\text{tppme})(\text{S}_2\text{CS})]$  [ $\text{tppme} = 1,1,1$ -tris(diphenylphosphinomethyl)ethane] and  $[\text{Ni}(\text{dppe})(\text{S}_2\text{CS})]$  [ $\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane] are highly activated toward electrophilic reagents. The unco-ordinated sulphur atom is found to displace the halide ion from alkyl halides or weakly bound ligands from other organometallic derivatives to give sulphur alkylated cations or  $\text{CS}_3$ -bridged binuclear complexes respectively. The crystal and molecular structure of the trithiocarbonate complex  $[\text{Co}(\text{tppme})(\text{S}_2\text{CSCH}_3)][\text{BPh}_4] \cdot 1.5\text{thf}$  has been determined by standard X-ray methods. The compound is monoclinic, space group  $C_{2/c}$ ,  $Z = 8$ ,  $a = 42.420(7)$ ,  $b = 10.221(4)$ ,  $c = 35.449(7)$  Å,  $\beta = 124.93(8)^\circ$ . The complex cation is five-co-ordinated by the three phosphorus of the  $\text{tppme}$  ligand and two sulphur atoms of the trithiocarbonate anion. The latter group can be considered planar, the methyl carbon atom almost lying in the  $\text{CS}_3$  plane. The bonding between the  $\text{Co}(\text{tppme})$  and  $\text{S}_2\text{CS}$  fragments is analysed in terms of qualitative molecular orbital arguments. This trithiocarbonate complex undergoes ligand nucleophilic substitution with diethylamine to form the dithiocarbamate complex  $[\text{Co}(\text{tppme})(\text{S}_2\text{CNEt}_2)][\text{BPh}_4] \cdot 0.5\text{CH}_2\text{Cl}_2$ .

DESPITE their synthetic utility and potential, only a few trithiocarbonate metal complexes have been synthesized and fully characterized.<sup>1</sup> By analogy with  $\pi\text{-CS}_2$  metal complexes,<sup>2,3</sup>  $\eta^2\text{-CS}_3$  complexes have an unco-ordinated sulphur atom, which can be conveniently used as nucleophilic agent.

In a recent communication<sup>4</sup> we described the synthesis of the (trithiocarbonato)cobalt(II) complex  $[\text{Co}(\text{tppme})(\text{S}_2\text{CS})]$  (1), structure (I) [ $\text{tppme} = 1,1,1$ -tris(diphenylphosphinomethyl)ethane] from the reaction of the complex  $[\text{Co}(\text{tppme})(\text{S}_2\text{CPEt}_3)][\text{BPh}_4]_2$  with sodium ethanolate and sulphur. The nickel(II) complex  $[\text{Ni}(\text{dppe})(\text{S}_2\text{CS})]$  (2), structure (II) [ $\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane] can also be obtained by reacting sodium trithiocarbonate with nickel(II) aqua-cations in the presence of  $\text{dppe}$ .



With the aim to probe the reactivity toward electrophilic groups of both compounds (1) and (2) we have carried out a systematic work of synthesis and characterization. This involves reactions with complexes containing weakly bound ligands such as the tetrahydrofuran molecule in  $[\text{Cr}(\text{CO})_5(\text{thf})]$  or with alkyl halides such as  $\text{CH}_3\text{I}$ . In the latter case the further reactivity of the reaction product, namely the trithiocarbonate complex  $[\text{Co}(\text{tppme})(\text{S}_2\text{CSCH}_3)][\text{BPh}_4] \cdot 1.5\text{thf}$  (5), toward ligand nucleophilic substitution with diethylamine has been also probed.

In this paper we report in detail all the reactions performed, the chemical and physical properties of the

<sup>†</sup> S-(Methyl trithiocarbonato-S'S'') [1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt tetraphenylborate-tetrahydrofuran (1/1.5).

products, and a complete X-ray structural determination of the above trithiocarbonate complex.

### EXPERIMENTAL

Compound (1),<sup>4</sup>  $\text{tppme}$ ,<sup>5</sup> and  $\text{Na}_2\text{CS}_3 \cdot \text{H}_2\text{O}$ <sup>6</sup> were prepared as previously described. Both  $[\text{Cr}(\text{CO})_6]$  and  $\text{dppe}$  were purchased from Strem Chemicals Inc., Dauvers, Mass., and used without further purification. All other chemicals employed were of reagent grade quality. Reagent grade tetrahydrofuran (thf) was further purified by distillation over  $\text{LiAlH}_4$ . All operations were performed under dry nitrogen using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using samples mullied in Nujol. All other physical measurements were executed by methods previously described.<sup>7</sup> The analytical, magnetic, and conductivity data of the complexes are reported in Table 1. Table 2 lists the electronic spectral data.

**Synthesis of  $[\text{Ni}(\text{dppe})(\text{S}_2\text{CS})]$  (2).**—A solution of  $\text{Na}_2\text{CS}_3 \cdot \text{H}_2\text{O}$  (0.17 g, 1 mmol) in ethanol (15  $\text{cm}^3$ ) was added to a mixture of  $[\text{Ni}(\text{H}_2\text{O})_6][\text{BF}_4]_2$  (0.34 g, 1 mmol) in ethanol (20  $\text{cm}^3$ ) and  $\text{dppe}$  (0.40 g, 1 mmol) in  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ). The resulting red-orange solution was concentrated and the orange crystals, so formed, were washed with ethanol and light petroleum (b.p. 40–70 °C). They were recrystallized from  $\text{CH}_2\text{Cl}_2$ –EtOH; yield 85%.

**Synthesis of  $[(\text{tppme})\text{Co}(\mu\text{-CS}_3)\text{Cr}(\text{CO})_5]$  (3).**—A solution of  $[\text{Cr}(\text{CO})_5(\text{thf})]$  formed by the u.v.-irradiation of the corresponding hexacarbonyl complex<sup>8</sup> (0.15 g, 0.7 mmol) in thf (50  $\text{cm}^3$ ) was added to a suspension of (1) (0.47 g, 0.6 mmol) in thf (250  $\text{cm}^3$ ). Within 3 h the solid dissolved and a red-brown solution was obtained. After evaporation of the solvent at reduced pressure the residue was extracted with  $\text{CH}_2\text{Cl}_2$  (25  $\text{cm}^3$ ). Red-brown crystals were obtained on addition of EtOH (40  $\text{cm}^3$ ) and slow evaporation of the solvent. Recrystallization was from the same solvents; yield 60%.

**Synthesis of  $[(\text{dppe})\text{Ni}(\mu\text{-CS}_3)\text{Cr}(\text{CO})_5]$  (4).**—This red-orange complex was prepared by the same procedure as the above cobalt compound except for the use of complex (2) in place of (1); yield 70%.

*Synthesis of* [Co(tppmc)(S<sub>2</sub>CSCH<sub>3</sub>)] [BPh<sub>4</sub>]·1.5thf (5).—A suspension of (1) (0.39 g, 0.5 mmol) in thf (40 cm<sup>3</sup>) was allowed to react with a large excess of CH<sub>3</sub>I and NaBPh<sub>4</sub>. Within 30 min the suspended solid dissolved giving a greenish red solution. On addition of n-butyl alcohol and slow evaporation of the solvent green crystals were formed which were separated by filtration and washed with n-butyl alcohol and light petroleum (b.p. 40–70 °C). They were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–thf–ethanol; yield 60%.

each side of the scan. 9 230 Unique reflections were measured up to  $2\theta = 45^\circ$ , 3 263 of which were considered observed having  $I \geq 3\sigma(I)$ . The  $\sigma$  values were calculated as described previously<sup>9</sup> with a value of 0.03 for the instability factor. The intensities of the standard reflections were monitored every 120 min and were subsequently used to establish all the reflections on a common scale. An absorption correction was applied by using the proper routine of the SHELX 76 system of programs.<sup>10</sup> The

TABLE 1  
Analytical and physical data for the complexes

Complex	Analysis <sup>a</sup> (%)			$\mu_{\text{eff}}$ /B.M. (293 K)	$\Lambda$ <sup>b</sup> / $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	C	H	M		
(2) [Ni(dppe)(S <sub>2</sub> CS)]	57.4 (57.35)	4.4 (4.3)	9.95 (10.4)		
(3) [(tppmc)Co(μ-CS <sub>2</sub> )Cr(CO) <sub>2</sub> ] <sup>c</sup>	57.6 (57.35)	3.85 (4.0)	5.9 (6.0)	2.13	
(4) [(dppe)Ni(μ-CS <sub>2</sub> )Cr(CO) <sub>2</sub> ] <sup>d</sup>	50.85 (50.75)	3.25 (3.2)	7.65 (7.75)		
(5) [Co(tppmc)(S <sub>2</sub> CSCH <sub>3</sub> )] [BPh <sub>4</sub> ]·1.5thf <sup>e</sup>	70.85 (71.05)	5.85 (6.05)	4.75 (4.75)	2.09	45
(6) [Co(tppmc)(S <sub>2</sub> CNET <sub>2</sub> )] [BPh <sub>4</sub> ]·0.5CH <sub>2</sub> Cl <sub>2</sub> <sup>f</sup>	70.05 (70.95)	6.15 (5.9)	4.85 (4.95)	1.96	48

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> Molar conductance values for ca. 10<sup>-3</sup> mol dm<sup>-3</sup> nitroethane solutions at 20 °C. <sup>c</sup> Cr, 5.15 (5.3)%; S, 9.7 (9.8)%. <sup>d</sup> Cr, 6.7 (6.85)%. <sup>e</sup> S, 7.7 (7.8)%. <sup>f</sup> N, 1.05 (1.15)%.

*Synthesis of* [Co(tppmc)(S<sub>2</sub>CNET<sub>2</sub>)] [BPh<sub>4</sub>]·0.5CH<sub>2</sub>Cl<sub>2</sub> (6).—A solution of (1) (0.39 g, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>) was treated with an excess of NHET<sub>2</sub> (5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Within few minutes a yellow-green solution was obtained. On addition of NaBPh<sub>4</sub> (0.34 g, 1 mmol) in ethanol (30 cm<sup>3</sup>) and slow evaporation of the solvent, yellow-green crystals were obtained which were washed with ethanol and light petroleum (b.p. 40–70 °C); yield 50%.

*Crystal Data for* [Co(tppmc)(S<sub>2</sub>CSCH<sub>3</sub>)] [BPh<sub>4</sub>]·1.5thf.—C<sub>73</sub>H<sub>74</sub>BCoO<sub>1.5</sub>P<sub>3</sub>S<sub>3</sub>,  $M = 1234.1$ , Monoclinic,  $a = 42.420(7)$ ,  $b = 10.221(4)$ ,  $c = 35.449(7)$  Å,  $\beta = 124.93(8)^\circ$ ,  $U = 12600.9$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.301$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.71069$  Å,  $\mu(\text{Mo-K}\alpha) = 4.85$  cm<sup>-1</sup>, space group  $C_{2/c}$ .

TABLE 2  
Electronic spectral data <sup>a</sup> for the complexes

Complex	$\lambda_{\text{max}}$ /cm <sup>-1</sup>
(2)	20 850 (sh), 23 800 (sh) <sup>b</sup> 20 600 (sh) (850) <sup>c</sup>
(3)	9 300, 15 050, 19 600, 25 000 <sup>b</sup> 9 550 (630), 14 500 (1 220), 19 200 (8 570), 24 700 (12 400) <sup>c</sup>
(4)	22 200 <sup>b</sup> 22 200 (10 250) <sup>c</sup>
(5)	9 550, 13 300, 16 650, 21 050 <sup>b</sup> 9 250 (380), 14 000 (370), 17 550 (1 940), 20 850 (1 550) <sup>c</sup>
(6)	9 750, 13 500, 23 250 <sup>b</sup> 9 650 (390), 13 700 (330), 21 050 (sh), 23 250 (1 940) <sup>c</sup>

<sup>a</sup> Molar absorption coefficients ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) are given in parentheses. <sup>b</sup> Solid at room temperature. <sup>c</sup> Dichloroethane solution.

*Data Collection.*—A prismatic green crystal with dimensions  $0.075 \times 0.14 \times 0.45$  mm was used throughout the determination of lattice constants and data collection. All measurements were made with Mo-K $\alpha$  radiation monochromatized with a flat graphite crystal on a Philips PW 1100 automated diffractometer. The centred positions of 18 reflections in the range  $16 \leq 2\theta \leq 20^\circ$  and the setting angles thus obtained were used in the least-squares refinement of the cell parameters. The  $\theta$ – $2\theta$  scan procedure was employed with a scan range  $0.94^\circ$  in  $\theta$  at a scan rate of  $0.05^\circ \text{ s}^{-1}$ . The background measurement time was 5 s at

TABLE 3  
Atomic positional parameters ( $\times 10^4$ ) for  
[Co(tppmc)(S<sub>2</sub>CSCH<sub>3</sub>)] [BPh<sub>4</sub>]·1.5thf

(a) Anisotropically refined atoms

Atom	$x$	$y$	$z$
Co(1)	3 265(1)	1 798(2)	1 882(1)
P(1)	3 872(1)	2 329(3)	2 186(1)
P(2)	3 279(1)	2 690(3)	2 474(1)
P(3)	3 077(1)	3 640(3)	1 495(1)
S(1)	2 705(1)	817(3)	1 321(1)
S(2)	3 375(1)	–360(3)	2 053(1)
S(3)	2 767(1)	–2 124(3)	1 370(1)

(b) Isotropically refined atoms

B(1)	4 090(4)	7 120(15)	391(5)
C(61)	3 994(3)	3 932(11)	2 469(4)
C(62)	3 450(4)	4 397(12)	2 575(4)
C(63)	3 378(3)	5 042(11)	1 831(4)
C(64)	3 658(3)	4 842(12)	2 350(4)
C(65)	3 842(4)	6 226(12)	2 565(4)
C(66)	2 932(3)	–590(12)	1 560(4)
C(67)	2 329(4)	–1 987(17)	827(5)
C(1)	4 284(2)	1 366(8)	2 627(3)
C(2)	4 259(2)	490(8)	2 910(3)
C(3)	4 592(2)	–80(8)	3 285(3)
C(4)	4 950(2)	228(8)	3 375(3)
C(5)	4 975(2)	1 105(8)	3 092(3)
C(6)	4 642(2)	1 674(8)	2 717(3)
C(7)	3 965(2)	2 387(6)	1 745(3)
C(8)	4 044(2)	3 529(6)	1 598(3)
C(9)	4 094(2)	3 476(6)	1 241(3)
C(10)	4 064(2)	2 283(6)	1 033(3)
C(11)	3 985(2)	1 142(6)	1 180(3)
C(12)	3 936(2)	1 194(6)	1 536(3)
C(13)	3 586(2)	1 891(9)	3 033(3)
C(14)	3 456(2)	702(9)	3 090(3)
C(15)	3 680(2)	19(9)	3 504(3)
C(16)	4 033(2)	524(9)	3 861(3)
C(17)	4 164(2)	1 713(9)	3 805(3)
C(18)	3 940(2)	2 396(9)	3 391(3)
C(19)	2 837(2)	2 802(8)	2 452(3)
C(20)	2 842(2)	3 485(8)	2 796(3)
C(21)	2 513(2)	3 520(8)	2 797(3)
C(22)	2 180(2)	2 872(8)	2 453(3)
C(23)	2 175(2)	2 190(8)	2 109(3)
C(24)	2 504(2)	2 155(8)	2 109(3)
C(25)	2 583(2)	4 118(8)	1 271(2)
C(26)	2 496(2)	4 892(8)	1 524(2)
C(27)	2 115(2)	5 220(8)	1 342(2)
C(28)	1 821(2)	4 774(8)	906(2)
C(29)	1 907(2)	4 000(8)	652(2)

TABLE 3 (continued)

Atom	$x$	$y$	$z$
C(30)	2 288(2)	3 671(8)	835(2)
C(31)	3 062(2)	3 686(7)	973(3)
C(32)	3 027(2)	4 894(7)	769(3)
C(33)	2 994(2)	4 953(7)	355(3)
C(34)	2 996(2)	3 803(7)	144(3)
C(35)	3 031(2)	2 595(7)	348(3)
C(36)	3 064(2)	2 536(7)	762(3)
C(37)	4 293(2)	8 478(9)	351(3)
C(38)	4 132(2)	9 720(9)	277(3)
C(39)	4 306(2)	10 795(9)	224(3)
C(40)	4 641(2)	10 627(9)	244(3)
C(41)	4 803(2)	9 385(9)	318(3)
C(42)	4 629(2)	8 311(9)	372(3)
C(43)	3 807(2)	7 509(9)	567(3)
C(44)	3 907(2)	7 285(9)	1 011(3)
C(45)	3 666(2)	7 712(9)	1 136(3)
C(46)	3 325(2)	8 363(9)	816(3)
C(47)	3 224(2)	8 587(9)	371(3)
C(48)	3 465(2)	8 160(9)	247(3)
C(49)	3 800(3)	6 449(8)	— 135(3)
C(50)	3 607(3)	5 295(8)	— 176(3)
C(51)	3 372(3)	4 689(8)	— 604(3)
C(52)	3 330(3)	5 237(8)	— 990(3)
C(53)	3 523(3)	6 391(8)	— 949(3)
C(54)	3 758(3)	6 997(8)	— 522(3)
C(55)	4 439(3)	6 075(7)	743(3)
C(56)	4 721(3)	6 501(7)	1 187(3)
C(57)	5 024(3)	5 673(7)	1 493(3)
C(58)	5 044(3)	4 418(7)	1 354(3)
C(59)	4 763(3)	3 991(7)	910(3)
C(60)	4 460(3)	4 819(7)	604(3)
*O(1) <sup>a</sup>	5 000	5 729(36)	2 500
*C(68)	5 390(7)	6 469(24)	2 688(8)
*C(69)	5 234(8)	7 828(32)	2 622(11)
*C(70) <sup>b</sup>	999(7)	1 537(27)	3 748(9)
*C(71)	801(14)	1 803(43)	706(17)
*C(72)	442(9)	1 014(33)	395(11)
*C(73)	834(10)	803(36)	1 233(12)
*C(74)	467(11)	202(38)	709(15)

<sup>a</sup> Atoms labelled (\*) belong to solvent molecules. <sup>b</sup> Atoms C(70)—C(74), although defining a thf molecule, are all labelled as carbon atoms (see text).

crystal had faces of the form {1,0,0}, {1,1,1}, {0,0,1} and the transmission factors had values in the range 0.92–0.97.

**Structure Determination and Refinement.**—Computation was carried out on SEL 32/70 computer using both the SHELX 76 and the X-RAY 76 <sup>11</sup> systems of programs. Scattering factors were taken from ref. 12. The structure was solved by direct methods. Full-matrix least-squares refinement was initiated after a number of  $F_o$  and  $\Delta F$  maps had enabled us to determine the positions of all the non-hydrogen atoms except for the solvent atoms. After two cycles using the isotropic thermal model for all the atoms located, the  $R$  factor ( $= \Sigma |\Delta F| / \Sigma |F_o|$ ) dropped to 0.12. A  $\Delta F$  map showed peaks not well resolved which were attributed to two thf solvent molecules. One of the molecules has crystallographic  $C_2$  symmetry. The atom lying on the two-fold axis was considered an oxygen atom, but all the five atoms of the other solvent molecule were refined as carbon atoms. In fact, due to disorder, it was not possible to define which one is the oxygen atom. All the phenyl rings were treated as rigid bodies with  $D_{6h}$  symmetry. The hydrogen atoms were introduced in the latest stages of refinement at calculated positions ( $C-H = 0.95$  Å). The final values of  $R$  and  $R'$   $\{= [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ ;  $w = 1/\sigma^2(F_o)\}$ , as obtained from two least-squares cycles where the cobalt, phosphorus, and sulphur atoms were allotted anisotropic temperature factors, are 0.069 and 0.073 respectively. The statistical validity of the least-squares refinement was checked by a weighting analysis to

ensure that the average value of  $w\Delta F^2$  was the same for various ranges of  $|F_o|$  and of  $(\sin\theta)/\lambda$ . No obvious trends were found. Final parameters are given in Table 3. Calculated and observed structure factors, thermal parameters, and some bond lengths and angles are listed in Supplementary Publication No. 23231 (25 pp.).\*

TABLE 4

Selected bond distances (Å) and angles (°) for [Co(tppe)-(S<sub>2</sub>CSCH<sub>3</sub>)] [BPh<sub>4</sub>].1.5thf (5), with estimated standard deviations in parentheses

## (a) Distances

Co—P(1)	2.214(4)	C(66)—S(1)	1.667(12)
Co—P(2)	2.258(5)	C(66)—S(2)	1.695(10)
Co—P(3)	2.193(4)	C(66)—S(3)	1.693(12)
Co—S(1)	2.279(3)	S(3)—C(67)	1.756(12)
Co—S(2)	2.265(4)		

## (b) Angles

P(1)—Co—P(2)	92.5(1)	P(3)—Co—S(1)	90.0(1)
P(1)—Co—P(3)	90.0(1)	P(3)—Co—S(2)	161.7(2)
P(2)—Co—P(3)	92.4(2)	S(1)—Co—S(2)	75.9(1)
P(1)—Co—S(1)	150.9(2)	S(1)—C(66)—S(2)	112.4(7)
P(1)—Co—S(2)	96.1(1)	S(1)—C(66)—S(3)	127.5(6)
P(2)—Co—S(1)	116.6(2)	S(2)—C(66)—S(3)	120.0(7)
P(2)—Co—S(2)	104.5(2)	C(66)—S(3)—C(67)	107.4(7)

## RESULTS AND DISCUSSION

The reaction pathways involving both the formation and the further reactivity of compounds (1) and (2) are conveniently summarized in the Scheme.

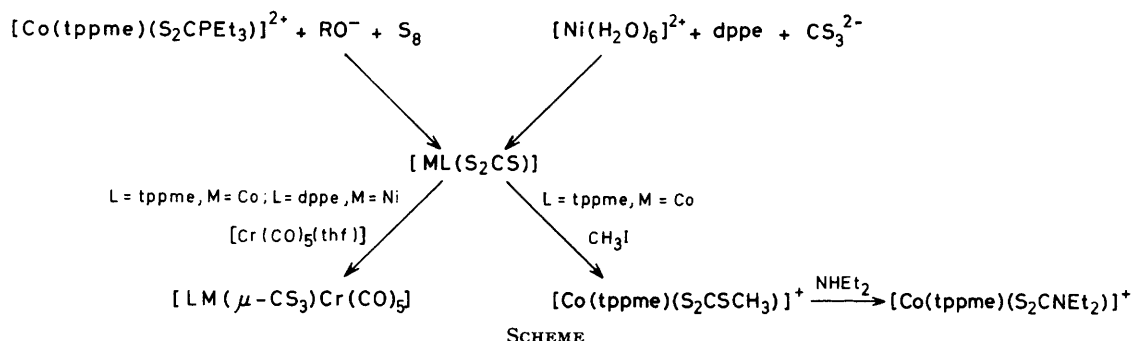
By reaction of sodium trithiocarbonate with nickel(II) aqua-cations and dppe, orange crystals of empirical formula [Ni(dppe)(S<sub>2</sub>CS)] (2) are obtained. Compound (2) is diamagnetic and air-stable both in the solid state and in solution. It is sparingly soluble in common organic solvents and the solutions do not conduct electricity. The electronic spectrum, with no absorption below 20 000 cm<sup>-1</sup>, is typical of square-planar nickel(II) complexes.<sup>13</sup> The i.r. spectrum shows three bands at 1 055, 1 045, and 870 cm<sup>-1</sup>. The bands at higher frequency are assigned to the  $\nu(C=S)$  stretching vibration while the lower frequency band is assigned to the  $\nu_{sym}$ , (C—S) stretching vibration. These data are consistent with those reported for some dihapto-co-ordinated CS<sub>3</sub> complexes.<sup>1</sup> All the information gathered from the spectroscopic, magnetic, and conductivity measurements is suggestive of square-planar co-ordination around the nickel atom as in (II), the two phosphorus atoms of the dppe ligand and two sulphur atoms of the trithiocarbonate ligand serving as donor atoms.

Both compounds (1) and (2) can be conveniently employed to investigate the nucleophilic character of the unco-ordinated sulphur atom of  $\eta^2$ -bonded CS<sub>3</sub> groups. We have been able to prove experimentally that compounds (1) and (2) displace the weakly bound thf ligand from [Cr(CO)<sub>5</sub>(thf)] to give the dinuclear complexes [(tppe)Co( $\mu$ -CS<sub>3</sub>)Cr(CO)<sub>5</sub>] (3), and [(dppe)Ni( $\mu$ -CS<sub>3</sub>)Cr(CO)<sub>5</sub>] (4) respectively. These complexes are red-brown and orange in colour respectively, quite air-

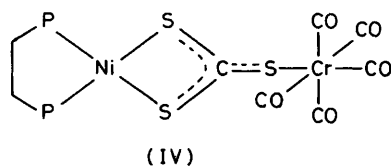
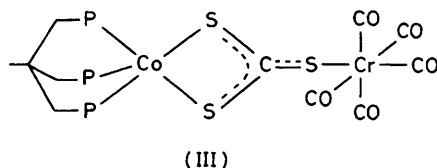
\* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

stable and soluble in common organic solvents where they behave as non-electrolytes. Compound (4) is diamagnetic, whereas (3) is paramagnetic with a magnetic moment corresponding to a doublet ground state. The electronic spectrum of (3) is practically unchanged both in the solid state and in solution and has four bands at

borate, to be used as a counter ion, is mandatory or the reaction does not occur. All the attempts to isolate a product with different counter ions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , or  $\text{I}_3^-$ , failed. Compound (5) is air-stable in the solid state and in solution. It is soluble in common organic solvents, in which it behaves as a 1 : 1 electrolyte. The



9 300, 15 050, 19 600, and 25 000  $\text{cm}^{-1}$ , whereas that of (4) has only one band at 22 200  $\text{cm}^{-1}$ . The i.r. spectra show a band at 1 015 and 1 025  $\text{cm}^{-1}$  for (3) and (4) respectively, attributable to the C=S stretch. This band has been found in complexes containing a  $\text{CS}_3$  group bridging between two metal atoms.<sup>14</sup> The absorption bands in the  $\nu(\text{CO})$  stretching region at 2 058, 1 983, 1 935, and 1 870  $\text{cm}^{-1}$  and at 2 058, 1 985, 1 920, and 1 890  $\text{cm}^{-1}$  for (3) and (4) respectively, compare well with those found for the  $\text{CS}_2$ -bridged dinuclear complex  $[(\text{tpppe})\text{Co}(\mu\text{-CS}_2)\text{Cr(CO)}_5]$ , whose structure has been established by X-ray analysis.<sup>2</sup> On the basis of all of these data it is therefore reasonable to assign the structures (III) and (IV) to the complexes (3) and (4) respectively.



It has been previously shown that the unco-ordinated sulphur atom of trithiocarbonate complexes can participate in nucleophilic substitutions of alkyl halides.<sup>14b</sup> Again we have checked if our compounds undergo a similar reaction. We have thus observed that a suspension of (1) in thf reacts with an excess of methyl iodide and  $\text{NaBPh}_4$  to give the green (trithiocarbonato)-cobalt(II) complex  $[(\text{tpppe})(\text{S}_2\text{CSCH}_3)]^+[\text{BPh}_4]^- \cdot 1.5\text{thf}$  (5). However, the presence of sodium tetraphenyl-

borate, to be used as a counter ion, is mandatory or the reaction does not occur. All the attempts to isolate a product with different counter ions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , or  $\text{I}_3^-$ , failed. Compound (5) is air-stable in the solid state and in solution. It is soluble in common organic solvents, in which it behaves as a 1 : 1 electrolyte. The room-temperature value  $\mu_{\text{eff}}$  is 2.09 B.M.,\* as expected for a low-spin  $d^7$  configuration. The i.r. spectrum shows a band at 970  $\text{cm}^{-1}$  attributable to the C-S stretching mode of the chelated trithiocarbonate ligand.<sup>15,16</sup> Figure 1 presents the molecular structure of the  $[(\text{Co}(\text{tpppe})(\text{S}_2\text{CSCH}_3))^+]$  cation. Tetraphenylborate anions and discrete thf solvent molecules are also interspersed in the unit cell. No unusually short intermolecular contacts are observed. Bond distances and angles of interest are reported in Table 4. Other bond distances and angles are reported in Table 5 which is in SUP 23231. The cobalt atom is five-co-ordinated by three phosphorus atoms of the tpppe ligand and by two sulphur atoms of the trithiocarbonate anion, the third sulphur atom being linked to a terminal methyl group. The  $\text{Co}(\text{tpppe})$  fragment has the classical 'emioctahedral' geometry, with the P-Co-P angles close to 90° and the P-Co distances in the range 2.193(4)–2.258(5) Å. The metal is also inserted in a strained four-membered ring formed together with the  $\text{CS}_2$  group. The structure is analogous to that of the compound  $[(\text{Co}(\text{tpppe})(\text{O}_2\text{COCH}_3))][\text{BPh}_4]$ ,<sup>9</sup> although the S(1)-Co-S(2) angle, 75.9(1)°, is much less strained than the corresponding O-Co-O angle, 65.5(7)°, in the acetate structure. An  $\eta^3$  co-ordination, rather than the more classical dihapto-co-ordination of the  $\text{CS}_3$  grouping, was found in the trithiocarbonate complex  $[\text{MoO}(\text{S}_2\text{CSR})_2]$  ( $\text{R} = i\text{-C}_3\text{H}_7$ ).<sup>16</sup> In the present case, however, a dihedral angle of only 6.8° between the Co, S(1), S(2) and S(1), C(66), S(2) planes rules out the former mode of co-ordination. Other points of interest with regard to the trithiocarbonate geometry are the near coplanarity of the methyl carbon atom with the  $\text{CS}_3$  group [the torsion angle at the C(66)-S(3) bond is small, at 7.5°] and the non-equivalence of the S-C-S angles. The largest angle, 127.5° for S(1)-C(66)-S(3), is found on the same side as the methyl group, and the most strained, 112.4(7)°, is relative to the chelating side of the ligand.

\* Throughout this paper: 1 B.M. =  $0.927 \times 10^{-23}$  A m<sup>2</sup>.



This result is common for other co-ordinated trithiocarbonate molecules.<sup>16</sup>

Noteworthy is the orientation of the trithiocarbonate plane with respect to the Co(tppmc) fragment. The plane defined by Co,S(1),S(2) is almost bisected by the plane defined by the P(2) atom and the ideal three-fold axis\* of the CoP<sub>3</sub> skeleton (dihedral angle *ca.* 80°).

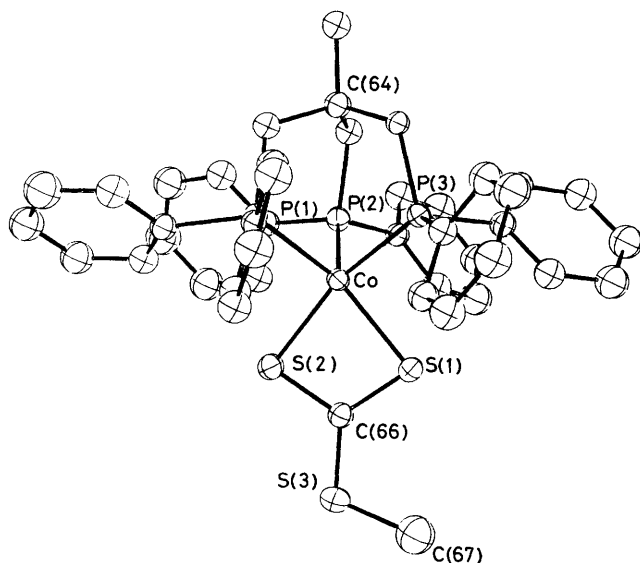


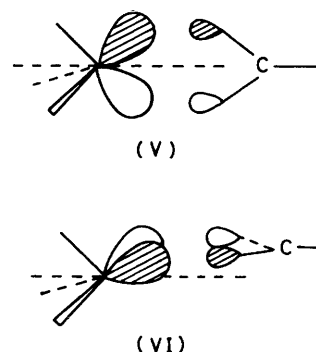
FIGURE ORTEP drawing of the cation [Co(tppmc)(S<sub>2</sub>CSCH<sub>3</sub>)]<sup>+</sup>

In this particular orientation the complex does not possess specular symmetry because of the presence of the terminal methyl group. Conversely, a 90° rotation of the trithiocarbonate molecule would have allowed C<sub>s</sub> symmetry for the complex. Qualitative reasoning in terms of molecular orbital (m.o.) theory allows the prediction that the barrier to rotation of the trithiocarbonate group must be low in the absence of major steric hindrance. The orbitals of octahedral isolobal fragments such as Co(CO)<sub>3</sub> or Co(PH<sub>3</sub>)<sub>3</sub> are known in detail.<sup>17</sup> There is one lower set of three non-bonding orbitals which derive directly from the *t*<sub>2g</sub> level in a pure octahedral complex, while at higher energy there is a degenerate *e* level made up of a mixture of metal *d* and *p* orbitals. Being partially *dp* hybridized, these orbitals are tilted and directed toward the 'missing' ligands. One of them can interact with an opportune combination of the two sulphur σ orbitals, to form either the (V) or (VI) bonding networks. Energy and overlap arguments do not privilege one interaction over the other. Thus the stabilization in the solid state of one of the two possible mutual dispositions of ML<sub>3</sub> and trithiocarbonate fragments may well depend on steric or packing effects.†

\* The direction of the three-fold axis has been calculated as the least-squares line through the atoms Co, C(64), C(65).

† Small geometrical distortion of the CoP<sub>3</sub> octahedron, due to the Jahn-Teller effect, may indeed break down the degeneration of the metal *e* set of orbitals and lead to the stabilization of one orientation over the other.

The crystal structure shows indeed that the preferred conformation is that corresponding to (VI). As a result the metal hybrid shown in (VI) is stabilized by bonding and is fully occupied. The antibonding combination corresponding to (VI), pushed up in energy, is very likely the lowest unoccupied molecular orbital of the molecule. The metal hybrid shown in (V), non-bonding toward the trithiocarbonate ligand (in the absence of any significant π interaction between the two sulphur atoms), keeps the unpaired electron of the *d*<sup>7</sup> configuration and represents the highest occupied molecular orbital of the molecule.



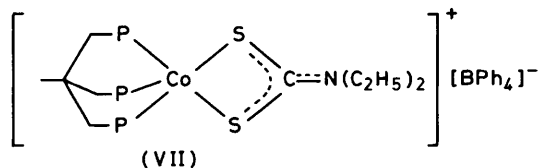
An indirect structural confirmation of the tilting of the metal hybrid in (VI) is the observed value of 7.5° of the angle between the Co,S(1),S(2) plane and the trace of the three-fold axis of CoP<sub>3</sub>.

As a final consideration, if (VI) is the main bonding interaction between the Co(tppmc) and the CS<sub>3</sub> fragments [this should hold also for the unmethylated trithiocarbonate complex (1)] there is an evident charge delocalization from CS<sub>3</sub> grouping toward the metal, not counterbalanced from π-type back-donation. Nevertheless, the unco-ordinated sulphur atom seems still to be sufficiently electron-rich to undergo nucleophilic attack, with the advantage of an improved overall stability of the trithiocarbonate molecule. We envisage a different situation for η<sup>2</sup>-CS<sub>2</sub> co-ordinated molecules.<sup>2</sup> The possibility of π back-donation from the metal together with a not very effective σ donation may be the origin of the nucleophilic activation at the unco-ordinated sulphur atom. Other factors such as the bending of CS<sub>2</sub> upon co-ordination play a role which is not easily interpretable and are worthy of investigation by quantitative m.o. calculations.

It is well known that metal trithiocarbonates undergo ligand nucleophilic substitution with amines to form dithiocarbamates.<sup>18</sup> Since mercaptide groups are good leaving groups for nucleophilic substitution, the same kind of reaction can be carried out on metal trithiocarbonates. Indeed compound (5) reacts with diethylamine in methylene chloride solution to form yellow-green crystals of the composition [Co(tppmc)(S<sub>2</sub>CNET<sub>2</sub>)]·[BPh<sub>4</sub>]<sup>+</sup>·0.5CH<sub>2</sub>Cl<sub>2</sub> (6).

This compound is stable in air and soluble in common organic solvents, in which it behaves as a 1 : 1 electrolyte.

It is paramagnetic with  $\mu_{\text{eff}}$  close to that expected for an unpaired spin. The i.r. spectrum shows a band at  $1\,510\text{ cm}^{-1}$  attributable to the C $\equiv$ N stretch, which agrees very well with that found for other dithiocarbamate



complexes.<sup>18,19</sup> The u.v. spectrum is fully comparable with that of compound (5). On the basis of these results a structure (VII) can be assigned to (6) where the cobalt atom is five-co-ordinated by the three phosphorus atoms of the tppme ligand and by the two sulphur atoms of the dithiocarbamate ligand.

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#### REFERENCES

- <sup>1</sup> D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 443.
- <sup>2</sup> C. Bianchini, C. Mealli, A. Meli, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, 1980, **19**, 2968 and refs. therein.
- <sup>3</sup> G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1979, 1612.
- <sup>4</sup> C. Bianchini, A. Meli, and A. Orlandini, *Angew. Chem. Int. Ed. Engl.*, in the press.
- <sup>5</sup> W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1962, 1490.
- <sup>6</sup> E. W. Yeoman, *J. Chem. Soc.*, 1921, **119**, 38.
- <sup>7</sup> L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, 1968, **7**, 1417.
- <sup>8</sup> E. O. Fischer and M. Herberhold, *Experientia, Suppl. IX*, 1964, 259.
- <sup>9</sup> C. Mealli, S. Midollini, and L. Sacconi, *Inorg. Chem.*, 1975, **14**, 2513.
- <sup>10</sup> G. M. Sheldrick, 'SHELX 76' system of programs, University of Cambridge, 1976.
- <sup>11</sup> J. M. Stewart, 'X RAY 76' Computer Science Technical Report, University of Maryland, 1976.
- <sup>12</sup> 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- <sup>13</sup> A. B. P. Lever, 'Inorganic Electron Spectroscopy,' Elsevier, Amsterdam, 1968, and refs. therein.
- <sup>14</sup> (a) W. P. Fehlhammer, A. Mayr, and H. Stolzenberg, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 626; (b) I. B. Benson, J. Hunt, S. A. R. Knox, and V. Oliphant, *J. Chem. Soc., Dalton Trans.*, 1978, 1240.
- <sup>15</sup> R. Bruce and G. R. Knox, *J. Organomet. Chem.*, 1966, **6**, 67.
- <sup>16</sup> J. Hyde, K. Venkatasubramanian, and J. Zubietta, *Inorg. Chem.*, 1978, **17**, 414.
- <sup>17</sup> (a) M. Elia, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, *Inorg. Chem.*, 1976, **15**, 1148; (b) T. A. Albright, P. Hoffmann, and R. Hoffmann, *J. Am. Chem. Soc.*, 1977, **99**, 7546; (c) R. H. Summerville and R. Hoffmann, *ibid.*, 1979, **101**, 3821.
- <sup>18</sup> J. P. Fackler, jun., and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.
- <sup>19</sup> I. J. B. Lin, H. W. Chen, and J. P. Fackler, jun., *Inorg. Chem.*, 1978, **17**, 394.