Complexes with Sulphur and Selenium Donor Ligands. Part 8.[1] Some 4-Phenylthiosemicarbazone Complexes of Cobalt(II) and the Crystal Structure of Bis(acetone 4-phenylthiosemicarbazone)cobalt(II) Bromide (Green Form)

By **Giulia Dessy, Vincenzo Fares, Lucio Scaramuzza,** and **Anthony A. G. Tomlinson,*** Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del C.N.R., Via Montorio Romano 36, 00131 Roma, Italy
Giovanni De Munno, Istituto di Chimica Generale ed Inorganica dell'Università di Roma, 00185, Roma Italy

Some thiosemicarbazone complexes of Co^{II} of general formula CoL_2X_2 and $Co(L - H)_2$ ($L = NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CR^1R^2$; X = Cl, Br, or I) have been prepared and characterised by spectroscopic methods in the solid state and in some non-aqueous solutions. When R^1 and/or R^2 is an aryl group the ligand is unidentate and tetrahedral complexes are obtained. When R^1 and R^2 are alkyl groups the ligand is bidentate and trigonal-bipyramidal complexes $[CoL_2X]X$ are obtained. Phenyl substitution at position 4 of the thiosemicarbazone thus seems to exert little effect on the stereochemistry adopted, and the complexes are similar to those of the unsubstituted ligand analogues. The crystal structure of the green form of $[Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)Br]Br$ has been determined. Crystals are orthorhombic, space group *Fddd*, with unit-cell dimensions $a = 17.039(3)$, $b = 24.184(8)$, $c = 24.852(7)$ Å, and $Z = 16$. The structure has been solved by Patterson and Fourier methods from automatic diffractometer data and refined by least-squares techniques to R 0.077 from 612 independent non-zero reflections. The ligands are bidentate, the co-ordination about Co^{II} being trigonal bipyramidal of chromophore $[CoS_2N_2Br]$, with two sulphur atoms and the bromine atom lying in the trigonal plane. Possible structures for these complexes in solution and for some corresponding thiocyanates containing unsubstituted thiosemicarbazones are briefly discussed.

COMPLEXES formed by thiosemicarbazones with transition-metal ions are of interest because of the light they may throw on the biological activity of many such compounds.[2] We recently showed that, contrary to previous opinion,[3] potentially bidentate thiosemicarbazones (general formula $NH_2{\cdot}CS{\cdot}NH{\cdot}N{:}CR^1R^2$) may also act as unidentate ligands when R^1 and/or R^2 is an aryl group.[4] We have now studied some cobalt(II) complexes with 4-phenyl-substituted thiosemicarbazones to see whether this substitution affects co-ordination by the sulphur atom and to test the generality of the behaviour found previously. A further point of interest is the characterisation of spectral differences between low-symmetry tetrahedral and five-co-ordinate cobalt(II) complexes, which might aid in the assignment of the stereochemistry of Co^{II}-substituted metalloproteins.[5]

EXPERIMENTAL

Thiosemicarbazide (Merck), 4-phenylthiosemicarbazide (Fluka), and the ketones and aldehydes were best-purity products and were used as received. The ligands were prepared by the usual methods,[6] recrystallised from ethanol–water mixtures, and checked for purity by elemental analysis and m.p. determination. Complexes were

TABLE 1

Elemental analyses (%)

	Complex	Colour	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
(1)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2Cl_2{\cdot}Me_2CO$	Blue	45.6	5.40	13.7	45.9	5.35	14.0
(2a)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2Br_2$	Green	37.6	4.25	13.95	37.95	4.15	13.3
(2b)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2Br_2{\cdot}CHCl_3$	Blue	33.3	3.70	11.15	33.5	3.60	11.2
(2c)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2Br_2$	Blue		4.35	13.3	37.95	4.15	13.25
(3a)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2I_2{\cdot}H_2O$	Green	32.1	3.45	11.0	33.2	3.80	11.25
(3b)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2I_2{\cdot}2H_2O$	Beige	31.1	3.80	10.7	31.5	3.95	11.0
(4)	$Co(NH_2{\cdot}CS{\cdot}NH{\cdot}N{:}CC_6H_{10})_2(CNS)_2$	Violet	37.35	5.05	21.75	37.15	5.05	21.65
(5)	$Co(NH_2{\cdot}CS{\cdot}NH{\cdot}N{:}CHPh)_2(CNS)_2$	Orange	40.4	3.45	21.0	40.5	3.40	21.0
(6)	$Co(NH_2{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2(ClO_4)_2{\cdot}2H_2O$	Pale violet	17.85	3.70	15.05	17.85	3.75	15.6
(7)	$Co(NH_2{\cdot}CS{:}N{\cdot}N{:}CMe_2)_2{\cdot}0.25Me_2CO$	Violet-green	31.05	5.45		31.2	5.25	26.3
(8)	$Co(NHPh{\cdot}CS{:}N{\cdot}N{:}CMe_2)_2$	Green	51.15	5.40	17.6	50.95	5.15	17.8
(9)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CHPh)_2Cl_2{\cdot}Me_2CO$	Green		4.65	11.5	51.9	4.75	11.7
(10)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CHPh)_2Br_2$	Green	44.45	3.70	11.25	45.0	3.75	11.25
(11)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CHPh)_2I_2$	Yellow-green	40.55	3.10	9.85	40.85	3.15	10.2
(12)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMePh)_2Cl_2$	Green	52.8	4.55	12.4	53.9	4.50	12.55
(13)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMePh)_2Br_2$	Green	48.15	4.25	11.35	47.5	4.00	11.1
(14)	$Co(NHPh{\cdot}CS{\cdot}NH{\cdot}N{:}CMePh)_2I_2$	Yellow-green	42.15	3.50	9.60	42.3	3.55	9.85

---

[1] Part 7, A. C. Villa, C. Guastini, P. Porta, and A. A. G. Tomlinson, *J.C.S. Dalton*, 1978, 956.

[2] See, for example, M. J. M. Campbell, *Co-ordination Chem. Rev.*, 1976, **15**, 279; F. A. French, E. J. Blanz, jun., S. C. Shaddix, and W. Brockman, *J. Medicin. Chem.*, 1974, **17**, 172.

[3] I. M. Issa, R. M. Issa, and M. K. Hassan, *Egypt. J. Chem.*, 1973, **16**, 19.

[4] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *Crystal Struct. Comm.*, 1975, **4**, 629; C. Bellitto, A. A. G. Tomlinson, C. Furlani, and G. De Munno, *Inorg. Chim. Acta*, 1978, **27**, 269.

[5] S. Lindskog, *Structure and Bonding*, 1970, **8**, 153.

[6] P. T. T. Sah and T. C. Daniels, *Rec. Trav. chim.*, 1970, **63**, 1545.

obtained by simply treating the hydrated metal compound (1 mmol) with ligand (2 mmol) in ethanol or acetone and recrystallising from the same solvent. Preparations giving isomers are described.

TABLE 2

Electronic spectra (10^3 cm^{-1}) (ε/dm^3 mol^{-1} cm^{-1} in parentheses, assuming the same species as in the solid); r = reflectance, a = in acetone

Complex											
(9)	r		19.5w	17.5 (sh)	16.1	15	14	7.7	6.7	5.4	4.6 (sh)
	a	21 (45)			16.9 (sh) (225)	15.4 (320)	14.5 (340)	7.4 (47)	6 (58)	5.3 (68)	
(10)	r	21 (sh)w	19.1 (w)	17.1 (sh)	15.5	14.7	13.6	7.3	6.6	5.3	4.6 (sh)
	a	20.8 (47)		16.7 (sh) (180)	16 (sh) (242)	15 (385)	14.4 (395)	7.2 (48)	5.9 (64)	5.3 (68)	
(11)	r	19.6 (sh)w	18.7 17.8 (sh)w		14.4		13.3	7.8	6	4.8	
	a			15.7 (sh) (270)	14.8 (sh) (390)	14.1 (565)	13.4 (590)	6.8 (69)	5.9 (70)		
(12)	r		19.3 18.5 (sh)w		15.9	15.2	14.1	7.4	6.2	5.4	4.7 (sh)
	a			17.9 (sh) (145)	15.6 (370)	14.5 (362)	13.9 (362)	7.6 (55)		5.4 (87)	
(13)	r	20 (sh)w	18.1 17.4 (sh)w		15.3	14.3	13.3	8	6.2	4.9	
	a			16.6 (sh) (185)	14.9 (425)	14.1 (535)		7.4 (63)	5.9 (67)	5.2 (78)	
(14)	r		18.5 17.6 (sh)w		14.6		13.4	7.7	6.1	4.8	
	a			15.8 (250)	14.1 (sh) (600)	13.5 (785)	12.6 (sh) (250)	7.1 (92)	5.9 (70)		
(1)	r		19.3 (sh)	18.1 (sh)	16.7	14.2	12.3	80w	5.8	4.8	
	a		18 (220)	17.5 (sh) (125)	15.5 (192)	14.2 (380)		7.8 (52)	5.8 (32)		
(2b)	r	20.7w	18.5	16.8			12.4		5.8	4.7	
	a		As for (2a)								
(2a)	r		18.5 (sh)	17.2		14.4	12.6	7.8w	5.8	4.8	
	a		17.5 (212) 17.2 (223)	16.7 (130)	15.1 (257)	14.2 (504)		6.5 (6.5)	5.7 (34)		
(3a)	r	20.5 (sh)	18 (sh)	16.4	14	12.6 (sh)	11 (sh)	7.2	5.5	4.5	
	a		As for (3b)								
(3b)	r			18.3		14.4			5.9	4.1	
	a			16 (275)	14.4 (sh) (395)	13.6 (680)		7.1 (67)	5.8 (30)		
(6)	r		19.8	18		14.6			5.7	5.1	
	a	26.2 (96)		19.1 (sh) (51)	17.8 (66)		13.9 (31)	5.9 (26)	5.4 (26)	4.8 (26)	
(5) orange	r			18.6	14.4		9	6.6			
	a			16.8 (sh) (305)	15.6 (474)	14.9 (425)	14.2 (335)	8 (98)	7.3 (100)	6.85 (88)	
(4) violet	r		19.6 (sh)	17.6		13.6			5.8	4.2	
	a		18.4 (65)	16.8 (295)	15.8 (475)	14.7 (sh) (271)		8.1 (79)	7.5 (80)	6.6 (71)	
(7)	r	23.6 (sh)	21.6 (sh)	18.6 (sh)	17.4 (sy)	16.3		10.1 (sh)	8.5	6.5 (sh)	
	a	24 (sh) (312)		18 (sh) (167)	16.7 (312)	15.9 (540)		9.8 (68)	8.2 (69)	6.6 (42)	
(8)	r		21.8 (sh)	18.6 (sh)	17.2 (sh)	16.3		10.2	8.4	6.7	
	a			18.85 (sh) (170)	16.8 (385)	16 (630)		9.8 (68)	8.2 (82)	6.4 (38)	
(5) green	r			17.2 (sh)	16.1 (sh)	15.3	14.6		7.6	6.6	
(4) blue	r		18.6 (sh)	17.2	16.1	14.5 (sh)		9	7.8	6.6	
In ethanol											
(1)		25.6 (160)	18 (sh) (60)	16.9 (71)	16.1 (sh) (66)	14.4 (44.6)	12.3 (25)	7.5 (sh)	5.5 (50)		
(2a)		25.6 (210)	17.8 (sh) (60)	16.8 (73)	15.8 (sh) (62)	14.1 (44)	12.3 (26)	7.3 (sh) (12)	5.5 (28)		
(2b)			As for (2a)								
(3a)		23 (169)	17.4 (87)	16.1 (78)		14.4 (57)	13.6 (61)	12.1 (28)	6.8 (sh) (11)	5.5 (19)	
(3b)			As for (3a)								

Blue and Green Forms of Bis(acetone 4-phenylthiosemicarbazone)bromocobalt(II) *Bromide*, (2).—An acetone solution of $CoBr_2 \cdot 3H_2O$ and ligand (1 : 2 mol ratio) was left to evaporate slowly and the major component (2a) (green crystals) separated mechanically from the minor one (2c) (blue crystals) and dried *in vacuo*; (2a) is stable in air. A solution of $CoBr_2 \cdot 3H_2O$ (1 mmol) in acetone (10 cm^3) was added to a chloroform solution of the ligand (2 mmol in 50 cm^3). Diffusion of light petroleum into the mixture gave blue well developed prismatic crystals of (2b). These contain chloroform (see Table 1) and slowly revert (*ca.* 1 month) to the green form (2a).

Bis(acetone 4-phenylthiosemicarbazone)iodocobalt(II) *Iodide*, (3).—Light petroleum (b.p. 40—60 °C) was added to an acetone solution (40 cm^3) of CoI_2 (1 mmol) and ligand (2 mmol) and the walls of the vessel were scratched. The green powder (3a) which precipitated was filtered off and dried *in vacuo*. A suspension of (3a) in 95% ethanol immediately gave a beige powder (3b).

Bis(acetone 4-phenylthiosemicarbazonato)- and Bis(acetone thiosemicarbazonato)-cobalt(II), (8) *and* (7).—The presence of trace amounts of water in the reaction between $CoI_2\cdot 2H_2O$ and ligand (1 : 2 mol ratio) was sufficient to deprotonate the ligand. Microcrystalline products could be obtained from all the halides by adding a solution of K[OH] in ethanol to an acetone solution of the components.

Bis(benzaldehyde thiosemicarbazone)cobalt(II) *and Bis(cyclohexanone thiosemicarbazone)cobalt*(II) *Dithiocyanates*, (5) *and* (4).—These complexes were prepared from ethanol as orange and violet crystals, respectively. On grinding, the former gave a green powder and the latter a blue powder. Care was taken in obtaining spectra of the crystalline forms to avoid contamination by the isomers.

Physical Measurements.—Electronic and i.r. spectra and thermal analyses (where necessary) were obtained as described previously.[1,4]

Crystal Structure of Complex (2a).—*Crystal data*. $C_{20}H_{26}Br_2CoN_6S_2$, $M = 597.33$, Orthorhombic, $a = 17.039(3)$, $b = 24.184(8)$, $c = 24.852(7)$ Å, $U = 10\,240.8$ Å^3, $D_m = 1.53$ (by flotation), $Z = 16$, $D_c = 1.55$ g cm^{-3}, $F(000) = 4\,679.4$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, graphite monochromator, $\mu(\text{Mo-}K_\alpha) = 41.8$ cm^{-1}, space group *Fddd* (D_{2h}^{24}, no. 70) from systematic absences.

Structure determination and refinement. Unit-cell constants were determined by least-squares refinement of the setting angles of 15 reflections on a Syntex $P2_1$ automatic diffractometer. Intensities were collected on the same diffractometer by the ω-scan technique, within the limit $\theta \leqslant 35°$. 612 Independent reflections, $I \geqslant 3\sigma(I)$ were used for structure determination *via* Patterson and Fourier methods, and for the refinement. Only Lorentz and polarisation corrections were applied to the data.

The structure was refined by full-matrix least squares using anisotropic temperature factors for Co, Br, and S atoms. The weighting scheme was $w = (70.0 + |F_o| + 0.001|F_o|^2)^{-1}$. The final refinement gave R 0.077. No attempt was made to locate the hydrogen-atom positions. Atomic scattering factors were obtained from ref. 7 and the corrections for real dispersion (heavy atoms only) from ref. 8. Calculations were carried out on a Univac 1110 computer at Rome University using the system of programs of the Laboratorio di Strutturistica Chimica of the C.N.R.[9] Thermal parameters and structure factors are available as Supplementary Publication No. SUP 22317 (5 pp.).*

RESULTS AND DISCUSSION

Solid-state Structures.—*Halogeno-complexes and those with deprotonated Ligands.* The reflectance spectra of the aryl thiosemicarbazone complexes are typical of tetrahedral Co^{II}.[1,10] Those of the cobalt halides of $NHPh\cdot CS\cdot NH\cdot N{:}CR^1R^2$ ($R^1 = Ph$, $R^2 = H$ or Me) are very similar, with ν_2 and ν_3 in the order Cl > Br > I, as are also *Dq* and *B* (see Table 3).[1,11] In particular, the two iodides give *Dq* and *B* values very close to those for $[Co(NH_2\cdot CS\cdot NH\cdot N{:}CMePh)_2]I_2$,[4] having a distorted-tetrahedral structure of chromophore CoS_2I_2.[4] We conclude that these ligands are also unidentate, giving CoS_2X_2 chromophores.

In contrast, the electronic spectra of the two complexes of the deprotonated ligands, (7) and (8), show ν_2 and ν_3 at much higher energies and give *Dq* and *B* values very different from those of the complexes with the neutral ligands. (Small spectral differences between the unsubstituted and the 4-phenyl-substituted thiosemicarbazone complex are presumably due to differences in angular distortions and/or electronic effects. This can be resolved only by a crystal-structure analysis; suitable crystals have not yet been obtained.) An assignment of chromophore CoS_2N_2 to these deprotonated complexes is then reasonable, the spectra being different from those expected for other, non-mononuclear, formulations. This assignment is also supported by the appearance of charge-transfer (c.t.) bands in the 21 000—24 500 cm^{-1} region, *i.e.* at much lower energy than occurs in complexes with unidentate ligands. This is as expected for bonding by a more 'thiolic' sulphur atom, brought about by deprotonation at N(2).[12]

Turning to the alkyl 4-phenylthiosemicarbazones, the reflectance spectra of all the halides (Table 2) contain a band in the 11 000—14 000 cm^{-1} region, characteristic of a trigonal-bipyramidal structure.[1,14]

TABLE 3

Spectrochemical parameters found using the methods described in ref. 11 (10^3 cm^{-1})

Complex	ν_2	ν_3	10*Dq*	*B*
(9)	6.55	15.45	3.75	0.81
(10)	6.30	15.0	3.64	0.82
(11)	6.30	13.9	3.66	0.75
(12)	6.7	15.1	3.88	0.82
(13)	5.4	14.55	3.71	0.79
(14)	6.3	14.1	3.66	0.77
(7)	8.8	17.8	5.16	0.95
(8)	8.6	17.3	5.05	0.92
(4)	7.6	16.5	4.43	0.89
(5)	7.55	15.6	4.42	0.84

The reflectance spectrum of the beige form of the iodide (3b) has bands at energies very close to those in $[Co(NH_2\cdot CS\cdot NH\cdot N{:}CMe_2)_2(OH_2)]I_2\cdot H_2O$[4] and is thus assigned a chromophore CoS_2N_2O, whilst the green form (3a) has a CoS_2N_2I chromophore.

The difference in colour between the two forms of the bromide (2), despite the similar reflectance spectra (both show a band diagnostic of a trigonal bipyramid at 12 600 cm^{-1}, see Table 2), prompted the crystal-structure analysis of the green form (2a) in the hope of finding an isomer in which the ligands are in a conformation different from those in $[Co(NH_2\cdot CS\cdot NH\cdot N{:}CMe_2)_2Cl]Cl\cdot H_2O$.

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] R. Spagna, unpublished work.

[10] C. Furlani, A. A. G. Tomlinson, C. Bellitto, and O. Piovesana, *J.C.S. Dalton*, 1972, 404 and refs. therein.

[11] E. König, *Structure and Bonding*, 1971, **9**, 175.

[12] C. K. Jørgensen, *Inorg. Chim. Acta*, 1968, **2**, 65.

The Molecular Structure of Complex (2a).—The atomic co-ordinates are listed in Table 4. The stereochemistry is shown in Figure 1 and bond distances and angles in Table 5.

TABLE 4

Atomic co-ordinates (× 10^4) for complex (2a) with standard deviations in parentheses

Atom	x/a	y/b	z/c
Co	1 250(0)	4 075(2)	1 250(0)
Br(1)	1 250(0)	5 077(2)	1 250(0)
Br(2)	6 849(3)	3 750(0)	3 750(0)
S	198(4)	3 553(3)	1 539(3)
N(1)	1 610(12)	4 000(9)	2 110(8)
N(2)	1 031(10)	3 739(9)	2 420(7)
N(4)	−72(14)	3 311(9)	2 579(9)
C(3)	373(12)	3 536(8)	2 198(7)
C(5)	−795(18)	3 056(11)	2 511(11)
C(6)	−1 237(23)	2 983(13)	2 993(13)
C(7)	−1 972(23)	2 708(15)	2 967(15)
C(8)	−2 266(20)	2 516(15)	2 497(15)
C(9)	−1 824(19)	2 527(13)	2 036(14)
C(10)	−1 124(20)	2 813(12)	2 039(12)
C(11)	2 279(15)	4 102(10)	2 342(10)
C(12)	2 466(18)	3 977(12)	2 935(12)
C(13)	2 877(17)	4 400(11)	2 011(12)

TABLE 5

Molecular geometry of (2a) within the chemical unit, with estimated standard deviations in parentheses

(*a*) Distances (Å)			
Co–Br(1)	2.422(7)	C(11)–C(12)	1.54(4)
Co–S	2.306(8)	C(11)–C(13)	1.49(4)
Co–N(1)	2.23(2)	C(5)–C(6)	1.43(4)
S–C(3)	1.67(2)	C(6)–C(7)	1.42(5)
C(3)–N(4)	1.33(3)	C(5)–C(10)	1.43(4)
C(3)–N(2)	1.34(3)	C(7)–C(8)	1.35(5)
N(4)–C(5)	1.39(4)	C(8)–C(9)	1.37(5)
N(1)–N(2)	1.40(3)	C(9)–C(10)	1.38(5)
N(1)–C(11)	1.30(3)		
(*b*) Angles (°)			
Br(1)–Co–S	123.2(2)	N(1)–C(11)–C(12)	125(2)
S–Co–S^I	113.7(3)	N(1)–C(11)–C(13)	116(2)
N(3)–Co–N(1^I)	170.6(8)	C(12)–C(11)–C(13)	119(2)
Br(1)–Co–N(1)	94.7(5)	C(3)–N(4)–C(5)	127(2)
S–Co–N(1)	82.6(6)	N(4)–C(5)–C(6)	115(3)
Co–S–C(3)	100.5(8)	N(4)–C(5)–C(10)	129(3)
Co–N(1)–N(2)	112(1)	C(5)–C(6)–C(7)	119(3)
Co–N(1)–C(11)	131(2)	C(5)–C(10)–C(9)	123(3)
S–C(3)–N(4)	128(2)	C(6)–C(5)–C(10)	116(3)
S–C(3)–N(2)	123(2)	C(6)–C(7)–C(8)	122(3)
N(4)–C(3)–N(2)	110(2)	C(7)–C(8)–C(9)	121(3)
C(3)–N(2)–N(1)	122(2)	C(8)–C(9)–C(10)	119(3)
N(2)–N(1)–C(11)	117(2)		

Roman numeral superscripts are defined in Figure 1.

The structure consists of discrete mononuclear units and may be formulated as $[CoL_2Br]Br$. The Co and Br(1) atoms lie on the *f* two-fold axis (origin at $\bar{1}$) and Br(1) on *e*, so that there is only one independent ligand molecule. The geometry about the Co^{2+} ion is better described as a distorted trigonal bipyramid than as a distorted square-based pyramid. This is seen by noting that the two-fold crystallographic axis bisecting the S–Co–S angle gives equal S–Co–Br angles [123.2(2)°] and equal Co–S and Co–N bond lengths. The major distortion from a regular trigonal-bipyramidal geometry lies in the angle [113.7(3)°] for S–Co–S, which is much smaller than that of S–Co–Br. This distortion appears to be much smaller than would have been expected had there been significant steric hindrance between the phenyl groups on N(4).

From previous crystallographic work on trigonal-bipyramidal high-spin cobalt(II) complexes, a lengthening of the axial bonds may be assigned to ligand–ligand repulsion, whereas the *d* electrons have little stereochemical effect since they are uniformly distributed in the σ-antibonding orbitals $d_{x^2-y^2}$, d_{xy}, and d_{z^2}. The Co–N lengths are, indeed, longer (see Table 6) than Co–$N_{eq.}$ bonds for all three trigonal-bipyramidal comcomplexes. Comparisons are less ready for the Co–Br lengths, Co–$Br_{eq.}$ in (2a) being shorter than Co–$Br_{ax.}$ in $[Co\{N(CH_2CH_2CH_2NH_2)_3\}Br]^+$ but of similar length to Co–$Br_{ax.}$ in $[Co\{N(CH_2CH_2NMe_2)_3\}Br]^+$. The Co–S distances for both (2a) and $[Co(NH_2{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2)_2Cl]^+$ are similar to those in tetrahedral cobalt(II) complexes with thiourea-like ligands, which is surprising. The Co–S distance (less than the corresponding Pauling distance of 2.36 Å) presumably indicates some π bonding. This is also evident in Co–S_{eq} in $[Co(NH_2{\cdot}CS{\cdot}NH{:}CMe_2)_2Cl]^+$.

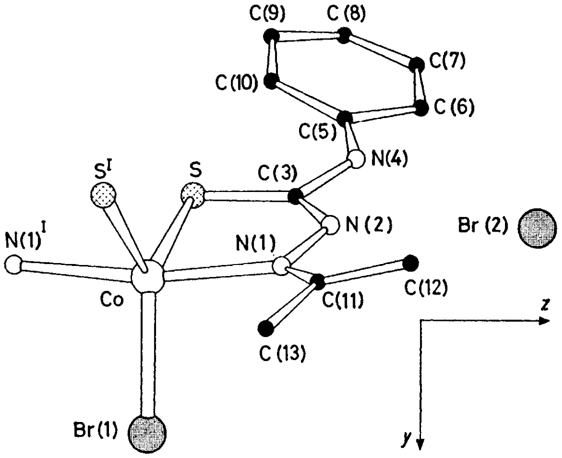
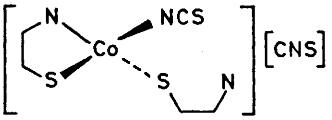


FIGURE 1 [100] Projection of the asymmetric unit of complex (2a) with the two crystallographically equivalent atoms bonded to the metal. The Roman numeral superscript refers to the equivalent position $\frac{1}{4} - x, y, \frac{1}{4} - z$

Bond lengths in the ligand are in agreement with those for thiosemicarbazone structures reported previously. The 4-phenyl group makes a dihedral angle of 19° with the aliphatic chain (excluding the two methyl groups).

The crystal structure has confirmed that alkyl substituents at N(4) lead to trigonal-bipyramidal complexes, while aryl substituents give tetrahedral complexes where the thiosemicarbazone bonds only *via* the S atom. It also supports the diagnostic use of electronic spectra to distinguish between gross stereochemistries even of low symmetry.

Thiocyanates.—Complex (4) exists in two forms. The violet form, exhibiting a reflectance spectrum typical of trigonal-bipyramidal stereochemistry, and a blue form. Since the i.r. spectrum of the former gives ν(CN) bands at 2 090 (*N*CS) and 2 030 cm^{-1} (free $[CNS]^-$) we assign a formulation $[CoL_2(NCS)][CNS]$. The blue form of (4), obtained by simply grinding the violet form or by evaporation of an acetone solution of the components, has a tetrahedral-type spectrum (no band characteristic of trigonal-bipyramidal structures in the 11 000—14 000 cm^{-1} region) with ν_2 and ν_3 close to those for the deprotonated complex (7) (see Table 2). A reasonable structure is:



The i.r. spectrum is the same as that of the violet isomer.

Complex (5) also exists as two isomers, the green form apparently having been overlooked previously.[13] The electronic spectrum of the orange form supports the previous assignment of an octahedral stereochemistry.[13] The green isomer has a reflectance spectrum characteristic of tetrahedral stereochemistry (see Figure 2). The spectrochemical parameters are very similar to those for $[Co\{SC(NH_2)_2\}_4][NO_3]_2$[14] having a tetrahedral CoS_4 stereochemistry. However, the i.r. spectrum shows only a single sharp ν(CN) band at the same wavenumber as that of the orange isomer (2 050 cm^{-1}), a value taken as diagnostic of *N*-bonded or ionic thiocyanate.[15] The only formulation then seems to be $[CoL_2][CNS]_2$, in agreement with the fact that Co^{II}–SCN complexes are rare. The difference between the spectrochemical parameters for this complex and the two deprotonated ones [*i.e.* (7) and (8)] presumably indicates that the deprotonated alkyl thiosemicarbazones are stronger ligands than the non-deprotonated aryl thiosemicarbazones, in line with the tendency of the latter to be unidentate. Unfortunately, it was not possible to prepare crystals of the green form of (5) to confirm this by *X*-ray methods.

TABLE 6

A comparison of some Co–L bond lengths

Complex	Co–S	Co–N	Co–Br
(2a)	2.306(8)	2.19	2.422
$[Co(NH_2\cdot CS\cdot NH\cdot N{:}CMe_2)_2Cl]Cl\cdot H_2O$ [a]	2.300(1)	2.222(4) 2.249(4)	
	2.303(1)		
$Co\{SC(NHEt\}_2Cl_2$ [b]	2.310(5) 2.336(7)		
$Co(NH_2\cdot CS\cdot NH\cdot N{:}CMePh)_2I_2$ [c]	2.30		
$[Co\{N(CH_2CH_2CH_2NH_2)_3\}Br]Br\cdot 0.5EtOH$ [d]		ax. 2.19(1) eq. 2.06(1)	ax. 2.658(3)
$[Co\{N(CH_2CH_2NMe_2)_3\}Br]$ [e]		ax. 2.15(2) eq. 2.08(2)	ax. 2.431(4)

[a] G. Dessy, V. Fares, and L. Scaramuzza, *Crystal Struct. Comm.*, 1976, **5**, 605. [b] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1973, 876. [c] Ref. 4. [d] J. L. Shafer and K. N. Raymond, *Inorg. Chem.*, 1971, **10**, 1799. [e] M. di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **6**, 955.

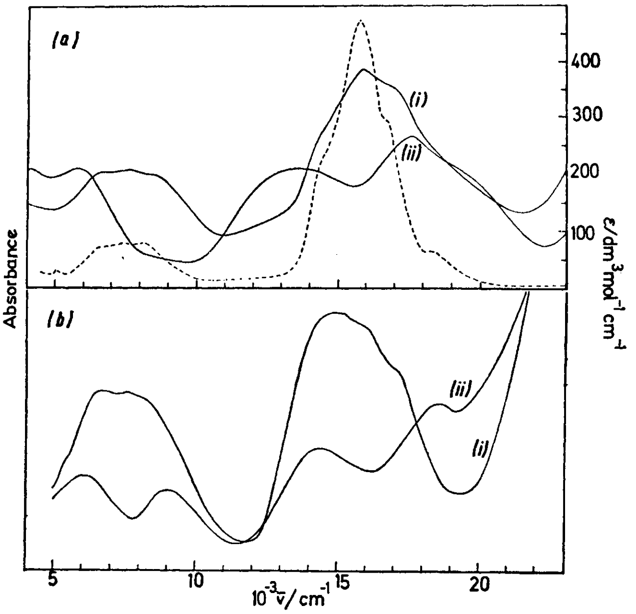


FIGURE 2 (*a*) Electronic (— — —) and reflectance spectra (——) of complex (4) in acetone: (*i*) violet isomer, (*ii*) blue isomer. (*b*) Reflectance spectra of complex (5): (*i*) green isomer, (*ii*) orange isomer

Stereochemistries in Solution.—In acetone, the complexes of $NHPh\cdot CS\cdot NH\cdot N{:}CR^1R^2$ (R^1 = Ph, R^2 = Me; X = Cl, Br, or I) have the same stereochemistry as in the solid state, *i.e. ca.* C_{2v} CoS_2X_2, as shown by the ν_2 and ν_3 values. Conductivity measurements confirm that both halide ligands bond to the Co^{II}, although some residual conductivity indicates partial solvation by acetone (see Table 2). Solvation is greater for the benzaldehyde complexes than for those with acetophenone. The same comments apply to the complexes of the deprotonated thiosemicarbazones.

In acetone, the $NHPh\cdot CS\cdot NH\cdot N{:}CMe_2$ complexes (X = Cl, Br, or I) have spectra which are different from those in the solid state. The conductivities are very low and the absorption spectra very similar to those of the unsubstituted analogues in acetone. We again suggest a stereochemistry as for the latter: tetrahedral $CoNSX_2$.[4] In anhydrous ethanol these complexes have conductivities in the range for 1 : 1 electrolytes.[16] Variable-temperature solution spectra for the chloride and bromide clearly show that an equilibrium between a five-co-ordinate (presumably trigonal-bipyramidal) struc-

---

[13] M. A. Malik and D. J. Phillips, *Austral. J. Chem.*, 1975, **28**, 305.

[14] F. A. Cotton, C. D. Faut, and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 17.

[15] A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1976, **17**, 231.

[16] S. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

ture and a tetrahedral structure is set up. This equilibrium is more evident in chloroform, the spectra in Figure 3 showing that a distinction between tetrahedral and trigonal-bipyramidal geometries is relatively straightforward for these ligands. The iodide (3) behaves differently in chloroform, the absence of isosbestic points at different concentrations and temperatures suggesting the presence of more than two species. Two geometries are apparent: one five-co-ordinate (having bands at the same energies as those in the reflectance spectrum of the green isomer) and the other tetrahedral (with bands as for the deprotonated ligand species).

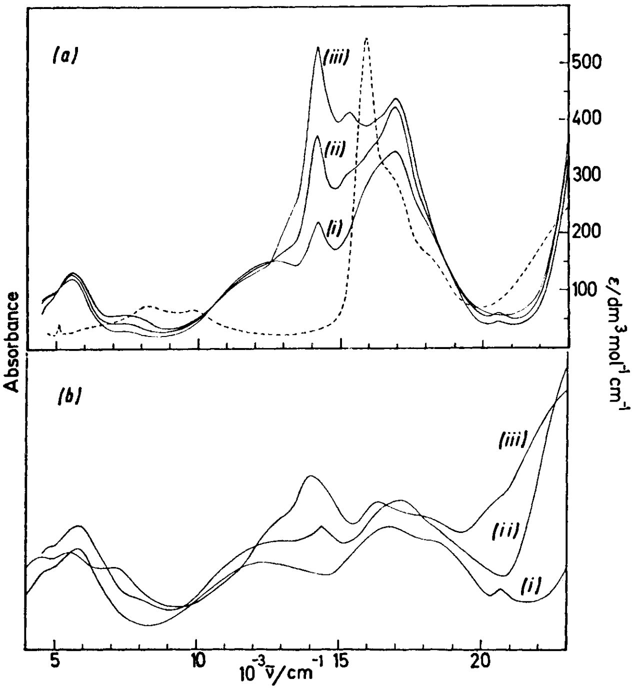


FIGURE 3 (*a*) Solution spectra of complex (7) in acetone (— — —), and of (2b) in $CHCl_3$ (——) at a concentration of (*i*) 3.3×10^{-2}, (*ii*) 6.4×10^{-2}, and (*iii*) 3.0×10^{-3} mol dm^{-3}. (*b*) Reflectance spectra of (*i*) complex (2c) (blue), (*ii*) (2a) (green), and (*iii*) (3a) (green)

Complex (4) in acetone solution gives an electronic spectrum similar to that of the tetrahedral species, and a conductivity higher than those of the halide complexes. Both complexes (5) exhibit spectra in acetone in which ν_2 lies in almost the same position as for the violet isomer of (4), ν_3 is a slightly lower energy, and their conductivities are comparable.

The electronic spectra of Co^{II} ions are commonly used as a structure reporter in metalloenzymes.[5] The spectra reported here and in ref. 1 show that, despite the low symmetry of both five-co-ordinate and tetrahedral complexes, the presence of the band between 13 500 and 14 500 cm^{-1} is still diagnostic of trigonal-bipyramidal stereochemistry. Unfortunately, most electronic spectra of Co^{II}-substituted proteins have not included the i.r. region.[5] However, very recently, Solomon *et al.*[17] recorded the m.c.d. and c.d. spectra of Co^{II}-substituted blue-type proteins concluding that the environment of Co^{II} is tetrahedral. The form of the spectra is similar to those for complexes (7) and (8), confirming a probable tetrahedral structure, although fine details *i.e.* splittings within the $^4A_2 \rightarrow {}^4T_1, {}^4P$ manifold are different, reflecting differences in the nature of the ligand.

[7/1007 *Received*, 13*th June*, 1977]

---

[17] E. I. Solomon, J. Rawlings, D. R. McMillin, P. J. Stephens, and H. B. Gray, *J. Amer. Chem. Soc.*, 1976, **98**, 7046.