Spectroscopic and Structural Studies on Cobalt Complexes of the Methyl Esters of Dithiocarbazic and 2-Methyldithiocarbazic Acids. Crystal Structure of $[Co\{NH_2NHC(=S)SMe\}\{NH_2N=C(S)SMe\}_2]Cl\cdot H_2O$ †

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The ligand behaviour of methyl esters of dithiocarbazic acid $NH_2NHC(=S)SMe$ (HL) and of 2-methyldithiocarbazic acid $NH_2NMeC(=S)SMe$ (MeL) in cobalt complexes has been investigated. Complexes of Co^{II} and Co^{III} have been prepared under different conditions and characterized by their electronic and i.r. spectra. HL can act as a ligand when neutral or when deprotonated (L^-); MeL can be deprotonated at the terminal N only after co-ordination. The crystal structure of $[Co(HL)L_2]Cl\cdot H_2O$ has been determined by *X*-ray diffraction methods: crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 12.085(9)$, $b = 8.903(8)$, $c = 17.287(16)$ Å, and $\beta = 104.2(1)°$. The structure has been solved by Patterson and Fourier methods and refined by block-diagonal least squares to $R = 0.042$ for 1 993 reflections. It consists of *cis*-octahedral $[Co(HL)L_2]^+$ cations, in which one neutral and two deprotonated molecules of methyl dithiocarbazate act as chelating ligands, chloride anions, and water molecules, held together by a network of hydrogen bonds. The bond distances in the co-ordination polyhedron are: Co–S 2.203(4), Co–N 1.993(6) Å for the neutral ligand; Co–S 2.212(5) and 2.218(3), Co–N 1.977(6) and 1.980(6) Å for the deprotonated ligands. The conformation of the three ligands is *cis,cis*, *i.e.* with both $NHNH_2$ and SMe groups bent towards the C=S bond.

THE ligating properties of N- and S-substituted derivatives of dithiocarbazic acid $NH_2NHC(=S)SH$ have been studied in recent years by us [1] and other workers.[2] Some of their co-ordination compounds have shown biological activity as pesticides [3] and, more recently, as carcinostatic agents.[4] The *S*-methyl dithiocarbazates show different ligating behaviour with the same metal (*e.g.* Ni) depending on the type of N-substitution and on the reaction conditions.[5] It was of interest to study the complexes of *S*-methyl dithiocarbazates with cobalt, which can also present different oxidation states depending on the reaction conditions and the co-ordination environment.

We started with $NH_2NHC(=S)SMe$ (HL) and $NH_2NMeC(=S)SMe$ (MeL); HL can act as a ligand when neutral or when deprotonated (L^-). The anion L^-, which is present also in the potassium salt, is characterized by the disappearance of the bands of ν(N–H) at 1 170 cm^{-1} and ν(C=S) at 1 010 cm^{-1} in the i.r. spectrum. Among the complexes obtained, $[Co(HL)L_2]Cl\cdot H_2O$ was chosen for the *X*-ray structure determination because both neutral and anionic forms of the ligand are present thus providing an opportunity to study whether structural modifications are induced by deprotonation of the ligand. The structure of the unco-ordinated ligand has already been described.[6]

EXPERIMENTAL

Materials.—The ligands HL and MeL were prepared as in refs. 2 and 7 respectively. All other chemicals were commercial analytical grade reagents and were used without further purification. Nitrogen gas was an ultra high-purity commercial product.

Preparations of the Complexes.—Previous studies [8] on the behaviour of HL in solvents with increasing polarity (anhydrous ethanol, ethanol, and water) showed that it is not deprotonated in anhydrous ethanol. By taking this into account, several complexes of Co^{III} and Co^{II} containing HL and/or L were prepared. Thus, $[Co(HL)_3]X_2$ (X = Cl or Br) was prepared from CoX_2 (1 mmol in 10 cm^3 anhydrous ethanol) and HL (3 mmol in 10 cm^3 of anhydrous ethanol) in a N_2 atmosphere. The precipitated compound was filtered off and dried under N_2 (yield 65%). The same compound can be obtained by working in ethanol acidified with 3.7% HCl (1 cm^3), thus preventing deprotonation of HL; yield 49%. The solid compound is stable under a N_2 atmosphere.

$[Co(HL)_2L]X_2$ (X = Cl *or* Br). These complexes were obtained by exposing to air finely powdered $[Co(HL)_3]X_2$; yield *ca.* 100%.

$[Co(HL)L_2]Cl\cdot H_2O$. Treatment of $CoCl_2\cdot 6H_2O$ (3.4 mmol in 15 cm^3 ethanol) with HL (10.2 mmol in 15 cm^3 ethanol) gave a mixture of $[Co(HL)_2L]Cl_2$ and $[Co(HL)L_2]Cl\cdot H_2O$. After crystallization from boiling ethanol, crystals of the less-soluble $[Co(HL)L_2]Cl\cdot H_2O$ were obtained, yield 20%.

$[CoL_3]$. This complex was obtained from $CoCl_2\cdot 6H_2O$ (1 mmol in 10 cm^3 water) and HL (3 mmol in 100 cm^3 water) (yield 95%), or from water and any compound containing HL and/or L reported in this work.

$[Co(HL)_3]Cl_3\cdot H_2O$. This was prepared from $CoCl_2\cdot 6H_2O$ (2 mmol in 30 cm^3 ethanol) and HL (6 mmol in 30 cm^3 ethanol with 4 cm^3 of 37% HCl), by bubbling O_2 to increase the reaction velocity, yield 55%.

$[Co^{III}(HL)_3]_2[Co^{II}X_4]_3$ (X = Cl *or* Br). These complexes were prepared from the cobalt halide (1.5 mmol in anhydrous ethanol) and HL (1.8 mmol in 20 cm^3 anhydrous ethanol). The compounds, precipitated after evaporation of part of the solvent *in vacuo* (15 mmHg),‡ are hygroscopic and can be dried at 100 °C *in vacuo* (1 mmHg), yield 37% for X = Cl, 54% for X = Br.

$[Co^{II}(MeL)_{2.5}Cl_2]$ § was prepared from $CoCl_2\cdot 6H_2O$ (1.5 mmol in 10 cm^3 ethanol) and MeL (3 mmol in 40 cm^3

† (Methyl dithiocarbazate-N^3S)bis[methyl dithiocarbazato-(1–)-N^3S]cobalt(III) chloride monohydrate.

‡ Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

§ *Note added at proof:* preliminary results of the *X*-ray crystal analysis of this compound have shown that it must be formulated as $[Co^{II}(MeL)_2Cl_2]\cdot 0.5MeL$.

TABLE 1

Analytical data

Compound	Colour	Analysis (%) * C	H	N	Cl
$[Co(HL)_3]Cl_3\cdot H_2O$	Red-brown	12.85 (13.1)	3.85 (3.65)	15.3 (15.3)	19.15 (19.35)
$[Co(HL)_2L]Cl_2$	Brown	14.65 (14.55)	3.80 (3.45)	16.9 (16.95)	14.25 (14.3)
$[Co(HL)_2L]Br_2$	Brown	12.15 (12.35)	3.05 (2.95)	14.3 (14.4)	
$[Co(HL)L_2]Cl\cdot H_2O$	Brown	15.25 (15.1)	3.90 (3.80)	17.8 (17.6)	7.30 (7.45)
$[CoL_3]$	Brown	17.1 (17.05)	3.65 (3.60)	19.7 (19.9)	
$[Co(HL)_3]_2[CoCl_4]_3$	Dark brown	10.2 (9.90)	2.85 (2.50)	11.45 (11.55)	29.15 (29.3)
$[Co(HL)_3]_2[CoBr_4]_3$	Dark brown	7.25 (7.25)	1.80 (1.85)	8.45 (8.45)	
$[Co(MeL)_3]Cl_3\cdot 3H_2O$	Red-brown	17.5 (17.2)	4.85 (4.80)	13.35 (13.4)	16.85 (16.95)
$[Co(MeL)_2(MeL - H)]Br_2$	Brown	17.15 (17.25)	3.80 (3.70)	13.35 (13.4)	
$[Co(MeL)_2(SO_4)]$	Pink	16.9 (16.85)	3.75 (3.75)	12.95 (13.1)	
$[Co(MeL)_{2.5}Cl_2]$	Blue	19.15 (19.15)	4.40 (4.30)	15.0 (14.9)	15.3 (15.05)
$[Co(MeL)_3]_2[CoCl_4]_3$	Dark brown	14.55 (14.05)	3.30 (3.15)	10.8 (10.95)	27.5 (27.7)
$[Co(MeL)_3]_2[CoBr_4]_3$	Dark brown	10.4 (10.45)	2.40 (2.35)	8.00 (8.10)	

* Calculated values are given in parentheses.

ethanol) in a N_2 atmosphere. The compound precipitated after evaporation of part of the solvent in a stream of N_2, yield 82%. The same compound was obtained by working with different mol ratios of the reagents (*e.g.* 1 : 3).

$[Co(MeL)_2(SO_4)]$. This was obtained from $Co[SO_4]\cdot 7H_2O$ (1.1 mmol in 10 cm^3 methanol) and MeL (3.3 mmol in 20 cm^3 methanol) in a N_2 atmosphere. The solution was evaporated to dryness by N_2 bubbling. The excess of MeL was sublimed off at 85 °C *in vacuo* (1 mmHg), yield 90%.

$[Co(MeL)_3]Br_2$. This complex was prepared from $CoBr_2$ (1 mmol in 20 cm^3 ethanol) and MeL (3 mmol in 40 cm^3 of ethanol) in a N_2 atmosphere. The compound precipitated after evaporation of the solvent by N_2 bubbling. It was filtered off and dried in a stream of N_2, yield 76%. The solid is stable under N_2.

$[Co(MeL)_2(MeL - H)]Br_2$. This was obtained in *ca.* 100% yield by exposing finely powdered $[Co(MeL)_3]Br_2$ to air. The deprotonated ligand [MeL–H = NHNMeC(=S)SMe] necessarily involves the loss of one hydrogen from the co-ordinated terminal N. We have already observed the same behaviour for MeL in the corresponding nickel complexes.[1c]

$[Co(MeL)_3]Cl_3\cdot 3H_2O$. This complex was prepared from $CoCl_2\cdot 6H_2O$ (0.7 mmol in 20 cm^3 ethanol with 1 cm^3 of 37% HCl) and MeL (2.1 mmol in 20 cm^3 ethanol with 1 cm^3 of 37% HCl). Crystals of the compound separated after some days, yield 49%.

$[Co^{III}(MeL)_3]_2[Co^{II}X_4]_3$ (X = Cl *or* Br). These complexes were obtained from the cobalt halide (2.3 mmol in 15 cm^3 water) and MeL (2.7 mmol in 60 cm^3 water). The compounds precipitated after evaporation of part of the solvent *in vacuo* (1 mmHg), yield 32% for X = Cl, 47% for X = Br.

In general, all the compounds described in this work dissolve only in polar solvents, and undergo modifications. Analytical data are given in Table 1.

Physical Measurements.—The visible reflectance spectra of the finely powdered solids were recorded on a Beckman DK2 spectrophotometer fitted with a standard reflectance attachment and MgO in the reference beam. Solution spectra were obtained for ethanol solutions at room temperature on a Beckmann DK2 spectrophotometer (concentration range 10^{-5}—10^{-3} mol dm^{-3}). Infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer as Nujol or poly(chlorotrifluoroethylene) mulls. Magnetic measurements were performed on solid samples with a Gouy balance calibrated with $Hg[Co(SCN)_4]$.

Crystal Data.—$C_6H_{18}ClCoN_6OS_6$, $M = 476.93$, Monoclinic, $a = 12.085(9)$, $b = 8.903(8)$, $c = 17.287(16)$ Å, $\beta = 104.2(1)°$, $U = 1\,803(3)$ Å^3, $Z = 4$, $D_c = 1.76$ g cm^{-3}, $F(000) = 976$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 17.73 cm^{-1}, space group $P2_1/c$ from systematic absences.

Preliminary unit-cell parameters were determined from rotation and Weissenberg photographs, and refined by a least-squares procedure applied to the diffractometer measurements of θ for 15 reflections.

Intensity Data.—Intensity data were collected on a Siemens AED single-crystal diffractometer, by use of zirconium-filtered Mo-K_α radiation and the ω—2θ scan technique. A prismatic crystal of dimensions *ca.* 0.15 × 0.25 × 0.35 mm was aligned with its *b* axis along the ϕ axis of the diffractometer and all the reflections with $2\theta < 50°$ were measured. Of 3 179 independent reflections, 1 993 having $I > 2\sigma(I)$ were considered observed and used in the analysis. Intensity data were corrected for Lorentz and polarization factors, but not for absorption effects. The absolute scale and the overall temperature factor were determined by Wilson's method.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by block-diagonal least squares, first with isotropic, then with anisotropic, thermal parameters. Hydrogen atoms were located directly from a ΔF map. Further least-squares cycles were computed, including isotropic thermal parameters for the hydrogen atoms. Unit weights were chosen at every stage of the refinement by analyzing the variation of $|\Delta F|$ with $|F_o|$. The final R was 0.042 (observed reflections only). Atomic scattering factors for non-hydrogen atoms were taken from ref. 9 and for hydrogen atoms from ref. 10. Final atomic co-ordinates are given in Table 2. Thermal parameters, observed and calculated structure factors, hydrogen-atom parameters, details of hydrogen bonding, rotation angles of SMe groups, and electronic and magnetic data are in Supplementary Publication No. SUP 22523 (21 pp.).*

All the calculations were performed on a CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna).

RESULTS AND DISCUSSION

X-*Ray Structure of* $[Co(HL)L_2]Cl\cdot H_2O$.—The structure is shown in Figure 1; bond distances and angles are

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

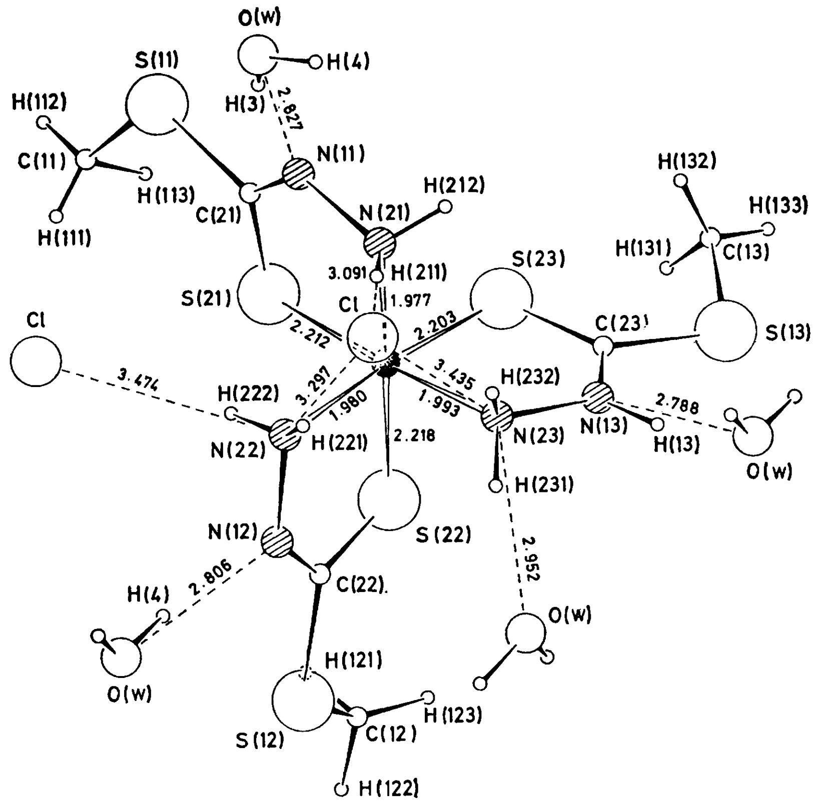

FIGURE 1 Structure of $[Co(HL)L_2]Cl\cdot H_2O$ with the atom-labelling system

given in Table 3. The structure consists of octahedral $[Co(HL)L_2]^+$ cations linked to the chloride anions and to the water molecules by a network of hydrogen bonds. One neutral and two deprotonated methyl dithiocarbazate molecules, acting as chelating ligands through sulphur and nitrogen, co-ordinate to Co^{III} in a *cis*-octahedral arrangement. The S and N atoms of the Co^{III} S_3N_3 chromophore are at the corners of two nearly equilateral triangles [N(21)–N(22) 2.858(6), N(22)–N(23) 2.825(7), N(21)–N(23) 2.811(6), S(21)–S(22) 3.197(4), S(22)–S(23) 3.108(3), S(21)–S(23) 3.105(4) Å], which are almost parallel, the dihedral angle they form being 179°. The distortion of the co-ordination octahedron is mainly due to the different size of the ligand atoms; nevertheless this distortion does not influence the dihedral angles between the main planes of the octahedron which are near to 90°. The conformation of the three independent ligands is *cis,cis*, *i.e.* both the NH_2 and methyl groups are *cis* with respect to the C=S bond. This conformation is different from the *cis,trans* one found for the uncomplexed molecule.[6] There are no regular differences between corresponding bond distances and angles in the neutral and deprotonated ligands, even if some of these differences are significant. In all the three complexed molecules the N–N distances and the N–N–C, S–C–S, and N–C–SMe angles are significantly different with respect to those found for the uncomplexed ester: the lengthening of the N–N distances and the narrowing of the N–N–C angles in the chelating esters are probably related to the chelation to the metal, while the variations of the S–C–S and N–C–SMe angles are probably related to steric effects due to the transition from the *cis,trans* to *cis,cis* conformation. In all the ligands the hydrogen atoms of the SMe groups are *gauche* with respect to the $S-CH_3$ bond.

TABLE 2

Fractional atomic co-ordinates for non-hydrogen atoms ($\times$ 10^4) with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
Co	2 909(1)	2 172(1)	1 303(1)
Cl	6 150(1)	2 326(2)	2 489(1)
S(11)	1 826(2)	229(2)	3 530(1)
S(21)	1 697(1)	792(2)	1 772(1)
S(12)	3 208(1)	−695(2)	−903(1)
S(22)	2 144(1)	1 458(2)	57(1)
S(13)	1 960(1)	7 042(2)	401(1)
S(23)	1 693(1)	4 057(2)	1 140(1)
N(11)	3 205(4)	1 932(6)	3 045(3)
N(21)	3 590(4)	2 750(5)	2 423(2)
N(12)	4 024(4)	−182(5)	595(2)
N(22)	3 987(4)	479(5)	1 354(2)
N(13)	3 527(4)	5 025(5)	692(2)
N(23)	3 979(3)	3 549(5)	939(2)
C(11)	902(6)	−1 128(9)	3 013(4)
C(21)	2 349(5)	1 103(7)	2 772(3)
C(12)	1 872(5)	−110(8)	−1 553(3)
C(22)	3 188(4)	200(6)	1(3)
C(13)	688(5)	7 207(8)	758(4)
C(23)	2 499(4)	5 302(6)	767(3)
O(W)	4 848(3)	2 104(4)	4 521(2)

The NCSS group is strictly planar in the deprotonated anions (Table 4), with small but significant displacement from planarity in the neutral molecule indicating that there is more conjugation through the NCSS group in the anions. The analysis of the planarity shows that

TABLE 3

Bond distances (Å) and angles (°)

(*a*) In the co-ordination polyhedron

Co–N(21)	1.977(4)	Co–S(21)	2.212(5)
Co–N(22)	1.980(6)	Co–S(22)	2.218(3)
Co–N(23)	1.993(6)	Co–S(23)	2.203(4)
N(21)–Co–N(22)	92.5(2)	S(21)–Co–S(23)	89.4(1)
N(21)–Co–N(23)	90.2(2)	N(22)–Co–S(23)	175.3(1)
N(21)–Co–S(21)	86.5(2)	N(23)–Co–S(21)	175.3(1)
N(21)–Co–S(23)	91.8(2)	S(22)–Co–N(22)	86.5(1)
N(21)–Co–S(22)	178.4(2)	S(22)–Co–N(23)	91.0(1)
N(22)–Co–N(23)	90.7(2)	S(22)–Co–S(21)	92.4(1)
N(22)–Co–S(21)	92.8(1)	S(22)–Co–S(23)	89.3(1)
N(23)–Co–S(23)	87.4(1)		

(*b*) In the organic ligands

N(21)–N(11)	1.466(7)	N(21)–H(211)	1.09(6)
N(11)–C(21)	1.264(8)	N(21)–H(212)	1.02(5)
C(21)–S(21)	1.737(6)	C(11)–H(111)	0.85(7)
C(21)–S(11)	1.769(6)	C(11)–H(112)	0.95(9)
S(11)–C(11)	1.737(8)	C(11)–H(113)	1.07(7)
N(22)–N(12)	1.449(5)	N(22)–H(221)	1.02(5)
N(12)–C(22)	1.297(7)	N(22)–H(222)	0.81(5)
C(22)–S(22)	1.708(7)	C(12)–H(121)	1.12(5)
C(22)–S(12)	1.760(6)	C(12)–H(122)	1.00(7)
S(12)–C(12)	1.803(7)	C(12)–H(123)	1.01(7)
N(23)–N(13)	1.447(6)	N(23)–H(231)	0.95(5)
N(13)–C(23)	1.304(9)	N(23)–H(232)	0.92(5)
C(23)–S(23)	1.703(6)	C(13)–H(131)	0.97(6)
C(23)–S(13)	1.738(6)	C(13)–H(132)	0.90(5)
S(13)–C(13)	1.798(9)	C(13)–H(133)	0.84(6)
N(13)–H(13)	1.08(6)		
N(21)–N(11)–C(21)	113.2(5)	H(211)–N(21)–H(212)	103(5)
N(11)–C(21)–S(21)	126.5(5)	S(11)–C(11)–H(111)	129(5)
N(11)–C(21)–S(11)	112.9(4)	S(11)–C(11)–H(112)	121(5)
S(11)–C(21)–S(21)	120.7(4)	S(11)–C(11)–H(113)	97(4)
C(21)–S(11)–C(11)	103.1(3)	H(111)–C(11)–H(112)	104(7)
N(11)–N(21)–H(211)	114(3)	H(111)–C(11)–H(113)	101(6)
N(11)–N(21)–H(212)	108(3)	H(112)–C(11)–H(113)	97(6)
N(22)–N(12)–C(22)	114.8(4)	H(221)–N(22)–H(222)	110(5)
N(12)–C(22)–S(12)	114.0(4)	S(12)–C(12)–H(121)	105(3)
N(12)–C(22)–S(22)	124.8(4)	S(12)–C(12)–H(122)	103(4)
S(12)–C(22)–S(22)	121.3(3)	S(12)–C(12)–H(123)	116(4)
C(22)–S(12)–C(12)	102.6(3)	H(121)–C(12)–H(122)	105(4)
N(12)–N(22)–H(221)	106(3)	H(121)–C(12)–H(123)	110(5)
N(12)–N(22)–H(222)	106(4)	H(122)–C(12)–H(123)	116(5)
N(23)–N(13)–C(23)	116.3(4)	N(23)–N(13)–H(13)	115(3)
N(13)–C(23)–S(23)	124.2(4)	C(23)–N(13)–H(13)	129(3)
N(13)–C(23)–S(13)	114.4(4)	S(13)–C(13)–H(131)	106(4)
S(23)–C(23)–S(13)	121.3(3)	S(13)–C(13)–H(132)	116(4)
C(23)–S(13)–C(13)	102.9(3)	S(13)–C(13)–H(133)	104(4)
N(13)–N(23)–H(231)	106(3)	H(131)–C(13)–H(132)	109(5)
N(13)–N(23)–H(232)	110(3)	H(131)–C(13)–H(133)	110(6)
H(231)–N(23)–H(232)	97(4)	H(132)–C(13)–H(133)	111(6)

(*c*) In the water molecule

O(W)–H(3)	0.79(5)	H(3)–O(W)–H(4)	111(6)
O(W)–H(4)	0.88(7)		

the plane running through the NCSS conjugated system leaves the N(22) and C(12) atoms on the same side and the terminal N atoms and the C atoms of the SMe groups of the other two ligands on opposite sides.

The three five-membered chelating rings are not perfectly planar (Table 4). They show slight but different puckering as indicated by the puckering parameters calculated following ref. 11:

Ring	q_2/Å	ψ_2/°
N(21)N(11)C(21)S(21)Co	0.158	341
N(22)N(12)C(22)S(22)Co	0.180	331
N(23)N(13)C(23)S(23)Co	0.054	138

The conformation of these groups is intermediate between the envelope and half-chair.

It is worthy of note that the neutral ligand forms the less puckered chelation ring, while it is the only ligand which is not perfectly planar.

The packing is determined by a network of intermolecular hydrogen bonds involving the chloride ions, the water molecules, and the N atoms of the ligands.

TABLE 4

Equations of the best least-squares planes in the form $mX + nY + pZ = d$ where X,Y,Z are co-ordinates (Å) referred to orthogonal axes $X \equiv x$, $Y \equiv y$, and Z perpendicular to X,Y. Deviations (Å) of relevant atoms from the planes are in square brackets

	m	*n*	*p*	*d*
Plane (I): C(21), S(11), S(21), N(11)	0.6273	−0.7788	−0.0070	0.2454
[C(21) 0.001(6), S(11) −0.001(2), S(21) −0.001(2), N(11) −0.001(5), N(21) −0.103(5), C(11) 0.384(8)]				
Plane (II): C(22), S(12), S(22), N(12)	0.6303	0.7437	−0.2229	2.5617
[C(22) −0.002(5), S(12) 0.001(2), S(22) 0.001(2), N(12) 0.001(5), N(22) −0.075(5), C(12) −0.214(7)]				
Plane (III): C(23), S(13), S(23), N(13)	−0.1394	−0.3907	−0.9099	−3.3702
[C(23) −0.019(5), S(13) 0.003(2), S(23) 0.003(2), N(13) 0.014(4), N(23) 0.089(4), C(13) −0.364(7), H(13) −0.10(5)]				
Plane (IV): S(21), C(21), N(11), N(21)	0.6635	−0.7474	−0.0333	0.2351
[S(21) 0.001(2), C(21) −0.020(6), N(11) 0.023(5), N(21) −0.003(5), Co 0.213(5)]				
Plane (V): S(22), C(22), N(12), N(22)	0.6298	0.7541	−0.1862	2.5765
[S(22) 0.001(2), C(22) −0.016(5), N(12) 0.020(5), N(22) −0.004(5), Co 0.341(1)]				
Plane (VI): S(23), C(23), N(13), N(23)	−0.1642	−0.3489	−0.9227	−3.2791
[S(23) −0.001(2), C(23) 0.004(5), N(13) −0.004(4), N(23) 0.001(4), Co 0.103(2)]				

Electronic Spectra.—The cobalt(III) complexes exhibit electronic spectra which fit pseudo-octahedral patterns for a d^6 configuration of $\approx O_h$ geometry, according to their diamagnetism. The nearly coincident values for the electronic transitions of all the compounds indicate the same co-ordination environment in each case. The chromophore is, indeed, *cis*-$Co^{III}N_3S_3$, as indicated by the *X*-ray structure determination of $[Co(HL)L_2]Cl{\cdot}H_2O$. The close similarity of the electronic spectra of compounds containing neutral and/or anionic ligands is indicative of high charge delocalization in the N$\cdots$C($\cdots$S)SMe moiety as already suggested by photoelectron spectral measurements on nickel *S*-methyl dithiocarbazates [12] and clearly confirmed by *X*-ray structural data.

The spectroscopic parameters $\Delta = 10Dq = 19\,900$ cm^{-1}, $B = 389$ cm^{-1}, and $\beta = 0.355$ (calculated following ref. 13) for $[Co(MeL)_3]Cl_3{\cdot}3H_2O$ can be extended to all the cobalt(III) compounds. The low value of β agrees with the presence of S in the co-ordination sphere. The electronic spectra of $[Co^{III}(HL)_3]_2[Co^{II}X_4]_3$ and $[Co^{III}(MeL)_3]_2[Co^{II}X_4]_3$ (X = Cl or Br) exhibit features which are characteristic of both octahedral Co^{III} and tetrahedral Co^{II}.

The complexes $[Co(HL)_3]X_2$ (X = Cl or Br), $[Co(MeL)_3]Br_2$, $[Co^{II}(MeL)_{2.5}Cl_2]$, and $[Co(MeL)_2(SO_4)]$ exhibit electronic spectra which fit pseudo-octahedral models for a d^7 configuration, according to their magnetic moments. The coincident spectra of $[Co(HL)_3]Cl_2$ and $[Co(HL)_3]Br_2$ suggest that both compounds have the same chromophore. This can be reasonably considered to be $Co^{II}N_3S_3$, as suggested by their easy oxidation in the air in the solid state to $[Co(HL)_2L]X_2$, whose chromophore is $Co^{III}N_3S_3$. The reflectance spectra of $[Co(HL)_3]X_2$ and $[Co(HL)_2L]X_2$ are given in Figure 2. Δ = 9 100 cm^{-1} (ref. 14) for both $[Co(HL)_3]X_2$ and $[Co(MeL)_3]Br_2$ indicates the same ligand-field strength for both these ligands in cobalt(II) complexes, as already observed for the nickel(II) complexes.[5] The stoicheiometries of the compounds $[Co^{II}(MeL)_{2.5}Cl_2]$ and $[Co(MeL)_2(SO_4)]$ suggest co-ordination of the anions, as is also indicated by the electronic spectra. The broadening of the first spin-allowed band and the splitting of the second spin-allowed band indicate a significant lowering of O_h symmetry due to the presence of Cl and O in the co-ordination environment, respectively.

Infrared Spectra (*Tables* 5 *and* 6).—All the complexes show $\nu(NH_2)$ and $\delta(NH_2)$ frequencies and bands attributable to the NCSS group, in the 900—1 200 cm^{-1} region, split and lowered upon co-ordination, confirming the N,S co-ordination. The complexes $[Co^{III}(HL)_3]_2[Co^{II}Cl_4]_3$ and $[Co^{III}(MeL)_3]_2[Co^{II}Cl_4]_3$ show absorption frequencies comparable with those of $[Co(HL)_3]Cl_3{\cdot}H_2O$ and $[Co(MeL)_3]Cl_3{\cdot}3H_2O$, confirming that they possess the same co-ordination sphere, as already suggested by the electronic spectra.

The presence of the deprotonated ligand L [NH_2N=C-(S^-)SMe] in $[Co(HL)_2L]Cl_2$, $[Co(HL)L_2]Cl{\cdot}H_2O$, and $[CoL_3]$ is accompanied by the appearance of a band, in the 1 500—1 550 cm^{-1} region, which is essentially a CN vibration with enhanced double-bond character. Moreover, for $[CoL_3]$ ν(C=S) disappears and a new band, assignable to ν_{asym}[C(S^-)SMe] appears at 995 cm^{-1}. The same band is also present in the spectra of all compounds containing L.

In the spectrum of $[Co(MeL)_2(SO_4)]$, bands indicating

TABLE 5

Infrared spectra (cm^{-1}) of the cobalt(III) complexes

HL *	MeL	$[Co(HL)_3]$-$Cl_3{\cdot}H_2O$	$[Co(MeL)_3]$-$Cl_3{\cdot}3H_2O$	$[Co(HL)_3]_2$-$[CoCl_4]_3$	$[Co(MeL)_3]_2$-$[CoCl_4]_3$	$[Co(HL)_2L]Cl_2$	$[Co(HL)L_2]$-$Cl{\cdot}H_2O$	$[CoL_3]$	Tentative assignments
			3 380br	3 400	3 400				ν(O–H)
3 280	3 290s	3 060	3 040	3 060		3 070	3 160 (sh)	3 200	ν(N–H)
3 210	3 235m						3 040w		
3 170	3 190w								
		2 620br	2 590br						ν(N–H · · · Cl)
1 600	1 608	1 620 (sh)	1 645	1 600br	1 600br	1 610	1 610	1 580	$\delta(NH_2)$
1 580		1 600	1 600			1 590	1 585		
		1 570	1 590 (sh)						
1 520						1 510w	1 510w	1 520s	ν(C⋯N) + δ(NH)
						1 070 (sh)	1 070 (sh)		
1 155s	1 100	1 070s	1 095m	1 070s	1 090s	1 060s	1 060s	1 235m	ν(NCSS) + ν(C=S)
		1 035m	1 015m	1 035m	1 015	1 010 (sh)			
1 010	1 030 (sh)	970vs	975s	985vs	975vs	980s	960s		ν(C⋯S)
	1 050s								
						995 (sh)	990	995s	ν_{asym}[C(S^-)-SMe]
975 (sh)	965 (sh)	955s	955w	960s	960 (sh)	950	950 (sh)	960s	ν(N–N)
945s	945s								ν(C–S)
						915 (sh)	915 (sh)	915m	ν_{sym}[C(S^-)-SMe]

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TABLE 6

Infrared (cm^{-1}) spectra of the cobalt(II) complexes

$[Co(HL)_3]Cl_2$	$[Co(MeL)_{2.5}Cl_2]$	$[Co(MeL)_2(SO_4)]$ *	$[Co(MeL)_3]Br_2$	Tentative assignments
3 100	3 085	3 208	3 145	ν(N–H)
	3 040	3 156	3 100	
		3 116	3 048	
1 615	1 616	1 605	1 617	$\delta(NH_2)$
			1 600	
1 080s	1 096s	1 096vs	1 100m	ν(NCSS) + ν(C=S)
	1 084 (s)			
970	996s	992vs	1 000vs	ν(C⋯S)
	964s	964vs	980s	
960vs	960s	960vs	960s	ν(N–N)
	896m		905m	

* SO stretching frequencies ν_1 at 1 015vs, ν_3 at 1 036s, 1 100vs, 1 104vs, and 1 145s, and ν_4 at 598vs, 628m, and 652 cm^{-1}.

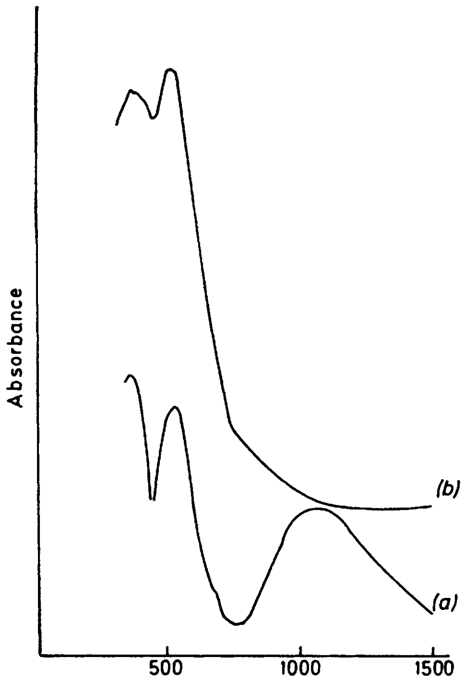

FIGURE 2 Reflectance spectra of (*a*) $[Co(HL)_3]X_2$ and (*b*) $[Co(HL)_2L]X_2$ (X = Cl or Br)

co-ordination of the SO_4 group are also present. The splitting of ν_3 and ν_4 suggests a bridging co-ordination.[15]

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