Thermal Behaviour and Crystal Structure of Dichlorobis(methyl 2-methyldithiocarbazate-N^3S)cobalt(II)–Methyl 2-Methyldithiocarbazate (2/1), $[Co\{NH_2NMeC(=S)SMe\}_2Cl_2]\cdot0.5[NH_2NMeC(=S)SMe]$

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The crystal structure of $[Co^{II}(MeL)_{2.5}Cl_2]$ (MeL = methyl 2-methyldithiocarbazate) has been determined by *X*-ray diffraction methods in order to define the unusual stoicheiometry of the compound. Crystals are tetragonal, space group $I4_1/acd$, $Z = 16$, in a unit cell of dimensions $a = 12.23(1)$ and $c = 51.02(2)$ Å. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.068$ for 615 independent observed reflections. It consists of octahedral $[Co(MeL)_2Cl_2]$ units, having C_2 crystallographic symmetry, where the two MeL molecules act as chelating ligands, and of free, disordered MeL molecules. The complexes are joined in layers by N–H $\cdots$ Cl hydrogen bonds and the free MeL molecules occupy the interlayers empty space. The bond distances in the Co co-ordination polyhedron are: Co–S = 2.446(7), Co–N = 2.174(17), and Co–Cl = 2.417(6) Å. The thermal behaviour of $[Co(MeL)_{2.5}Cl_2]$ has been studied by thermal gravimetric analysis (t.g.a.) and differential scanning calorimetry (d.s.c.). Evidence for the reaction $2[Co(MeL)_2Cl_2]\cdot0.5MeL \longrightarrow [Co(MeL)_3][CoCl_4] + MeL$ has been obtained.

WE have recently investigated the complexes of cobalt with methyl dithiocarbazate (L) and methyl 2-methyldithiocarbazate (MeL);[1] one of these is a complex formulated as $[Co^{II}(MeL)_{2.5}Cl_2]$ which has unusual stoicheiometry for a cobalt(II) complex with ligands of this type. In order to clarify the role of the MeL molecules in this complex we have determined its *X*-ray crystal structure and have studied its thermal behaviour.

EXPERIMENTAL

Materials.—The ligand MeL was prepared as in ref. 2. 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.—The complex $[Co(MeL)_{2.5}Cl_2]$ was prepared as in ref. 1 from $CoCl_2\cdot6H_2O$ and MeL in either a 1 : 2 or 1 : 3 ratio. $[Co(MeL)_{1.5}Cl_2]$ was prepared by treating a boiling solution of $CoCl_2\cdot6H_2O$ (1.5 mmol in 10 cm^3 ethanol) with a boiling solution of MeL (3.0 mmol in 10 cm^3 ethanol). At room temperature the complex crystallizes (yield 70%) (Found: C, 16.3; H, 3.60; N, 12.7. Calc. for $C_{4.5}H_{12}Cl_2CoN_3S_3$: C, 16.15; H, 3.60; N, 12.6%).

The same compound is obtained by heating $[Co(MeL)_{2.5}Cl_2]$, in a thermobalance and a stream of N_2, and by stopping at the inflection point corresponding to the loss of 1 mol of ligand.

Physical Measurements.†—The visible reflectance spectra and i.r. spectra were recorded as in ref. 1.

Thermoanalytical Measurements.†—Thermogravimetric analyses (t.g.a.) were performed with a DuPont 950 Thermogravimetric Analyzer, and differential scanning calorimetry (d.s.c.) measurements with a DuPont 900 Thermal Analyzer fitted with a d.s.c. cell. Measurements were performed in a stream of N_2 (0.5 l min^{-1}) and *in vacuo* (10 mmHg); ‡ rate of heating: 1, 3, and 5 °C min^{-1}.

Crystal Data.—$C_{7.5}H_{20}Cl_2CoN_5S_5$, $M = 470.71$, Tetragonal, $a = 12.23(1)$, $c = 51.02(2)$ Å, $U = 7\,631(9)$ Å^3, $D_m = 1.63$ g cm^{-3}, $Z = 16$, $D_c = 1.64$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 17.05 cm^{-1}, space group $I4_1/acd$ from systematic absences.

Preliminary unit-cell parameters were determined from rotation and Weissenberg photographs, and refined by a least-squares procedure applied to the θ values of 11 reflections carefully measured on a Siemens AED single-crystal diffractometer.

Intensity Data.—Intensity data were collected on the same diffractometer, by use of niobium-filtered Mo-K_α radiation and the θ—2θ scan technique. A blue-violet platelet of dimensions *ca.* 0.40 × 0.35 × 0.02 mm was aligned with its *a* axis along the ϕ axis of the diffractometer and all the reflections with θ in the range 2.5—24° were measured. Of a total of 1 446 independent reflections, 615 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was made. The first absolute scaling and the overall isotropic temperature factor were obtained by Wilson's method.

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods and refined by least-squares full-matrix cycles using the SHELX system of computer programs[3] with initially isotropic thermal parameters, then anisotropic thermal parameters for the non-hydrogen atoms of the cobalt complex. No difficulty was experienced in localizing on the Fourier maps the atoms of the complex which evidently contained two co-ordinated MeL molecules; however, considerable effort was needed to localize the MeL molecule which was unco-ordinated and disordered. The difference electron-density (in the Figure deposited in SUP 22760 the difference electron-density map, projected on the plane (110), is represented at the crossing of three two-fold axes) agrees with a disordered distribution of the MeL unco-ordinated molecule in four equivalent positions. The difference synthesis was also valuable in locating the hydrogen atoms of the complexed MeL molecules.

The co-ordinates of these hydrogen atoms and those of the non-hydrogen atoms of the disordered MeL group were introduced with isotropic thermal parameters in the last

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† Performed by Mr. G. Chiozzini.

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

TABLE 1

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

Atom	x/a	y/b	z/c
Co	2 500	2 232(3)	0
Cl	3 773(5)	3 602(4)	−153(1)
S(1)	3 353(5)	1 945(5)	428(1)
S(2)	2 531(8)	575(7)	873(1)
N(1)	1 610(14)	655(13)	420(4)
N(2)	1 422(13)	978(14)	156(3)
C(1)	2 448(20)	1 082(16)	548(4)
C(2)	833(23)	−222(22)	518(7)
C(3)	3 599(33)	1 408(33)	1 025(7)
S(3)	−900	1 600	1 350
C(4)	0	2 500	1 200
C(6)	−650	1 780	1 700
N(3)	0	2 500	900

structure factors calculations, but not refined. Unit weights were chosen at every stage of the refinement by analysing the variation of $|\Delta F|$ with $|F_o|$. The final R was 0.068 (observed reflections only). The atomic scattering factors used (corrected for the anomalous dispersion of Co, S, and Cl) were taken from the International Tables.[4] Final atomic co-ordinates are given in Tables 1 and 2 (for non-hydrogen and hydrogen atoms respectively). Thermal parameters and observed and calculated structure factors are contained in Supplementary Publication No. SUP 22760 (9 pp.).*

TABLE 2

Fractional co-ordinates ($\times 10^3$) for the hydrogen atoms

Atom	x/a	y/b	z/c
H(1)	140	43	11
H(2)	78	141	18
H(21)	55	2	72
H(22)	120	−65	57
H(23)	6	−37	43
H(31)	371	120	123
H(32)	342	215	101
H(33)	436	130	92

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) In the co-ordination polyhedron			
Co–Cl	2.417(6)	Co–N	2.174(17)
Co–S	2.446(7)		
Cl–Co–S(1)	96.5(2)	S(1)–Co–N(2)	80.2(5)
Cl–Co–N(2)	176.6(5)	S(1)–Co–N(2^{I})	88.1(4)
Cl–Co–Cl^{I}	92.2(2)	S(1)–Co–S(1^{I})	163.5(3)
Cl–Co–N(2^{I})	88.9(5)	N(2)–Co–N(2^{I})	90.2(6)
Cl–Co–S(1^{I})	94.9(3)		
(*b*) In the molecules of 2-methyldithiocarbazic acid methyl ester			
S(1)–C(1)	1.65(2)	C(1)–N(1)	1.32(3)
S(2)–C(1)	1.77(2)	N(1)–N(2)	1.42(3)
S(2)–C(3)	1.83(4)	N(1)–C(2)	1.52(3)
S(3)–C(4)	1.73	N(3)–C(4)	1.53
S(3)–C(6)	1.83	N(3)–C(6^{II})	1.29
S(1)–C(1)–S(2)	122(1)	C(2)–N(1)–N(2)	114(2)
S(1)–C(1)–N(1)	126(2)	C(6)–S(3)–C(4)	104
S(2)–C(1)–N(1)	112(2)	S(3)–C(4)–N(3)	116
C(3)–S(2)–C(1)	104(1)	S(3)–C(4)–S(3^{III})	128
C(1)–N(1)–N(2)	119(2)	C(4)–N(3)–C(6^{II})	113
C(1)–N(1)–C(2)	127(2)	C(6^{II})–N(3)–C(6^{IV})	133
(*c*) Hydrogen bonds			
N(2) · · · Cl^{V}	3.31(2)	H(1)–N(2)–Cl^{V}	9
H(1) · · · Cl^{V}	2.62		
N(2) · · · Cl^{VI}	3.28(2)	H(2)–N(2)–Cl^{VI}	26
H(2) · · · Cl^{VI}	2.46		

Roman numeral superscripts refer to the following co-ordinate transformations:

I $\frac{1}{2} - x, y, -z$
II $-y, \frac{1}{4} - x, \frac{1}{4} - z$
III $-x, \frac{1}{2} - y, z$
IV $-\frac{1}{4} + y, \frac{1}{4} + x, \frac{1}{4} - z$
V $\frac{1}{2} - x, y - \frac{1}{2}, z$
VI $x - \frac{1}{2}, \frac{1}{2} - y, -z$
VII $-\frac{1}{4} - y, -\frac{1}{4} + x, \frac{1}{4} - z$
VIII $\frac{1}{4} - y, -\frac{1}{4} + x, \frac{1}{4} + z$

All the calculations were performed on a CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with financial support from the University of Parma.

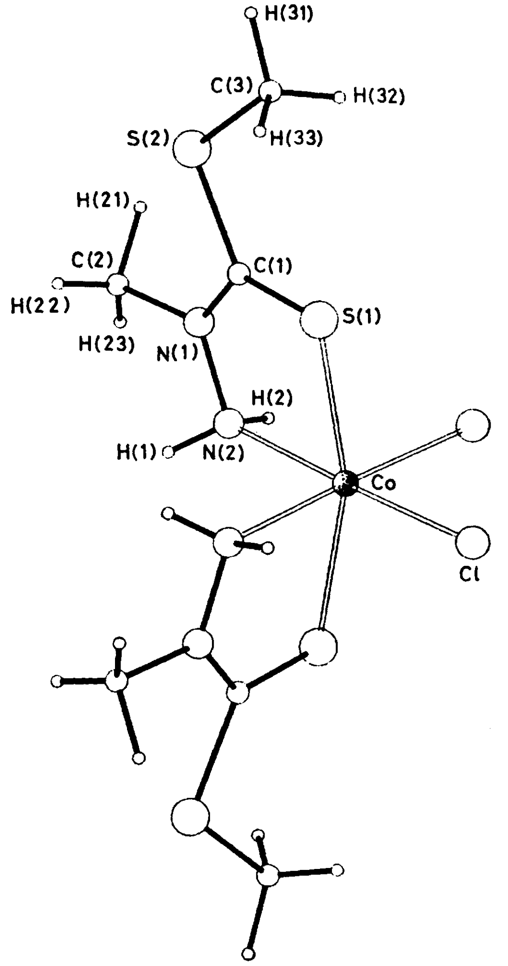

FIGURE 1 View of the complex $[Co(MeL)_2Cl_2]$ showing the molecular shape and the atomic numbering scheme

RESULTS AND DISCUSSION

X-Ray Structure of $[Co(MeL)_2Cl_2]\cdot 0.5MeL$.—The structure consists of neutral octahedral $[Co(MeL)_2Cl_2]$ units, with an imposed crystallographic two-fold axis, linked in layers by N–H · · · Cl hydrogen bonds, and of disordered free MeL molecules in a ratio of 2 : 1. Bond distances and angles are given in Table 3. Two S and two N atoms from the MeL molecules, acting as chelating ligands, and two Cl atoms co-ordinate to Co^{II} in a *cis*(N), *trans*(S), *cis*(Cl) octahedral arrangement (Figure 1). The Co–Cl and Co–N bond distances [2.417(6) and 2.174(17) Å respectively] are in good agreement with

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

those generally found in octahedral cobalt(II) complexes.[5-7] On the contrary, the Co–S bond distance [2.446(7) Å] is shorter than those reported in the octahedral cobalt(II) complexes with sulphur-donor ligands (2.502—2.584 Å) [8,9] which are fairly common, but much longer than those reported for the tetrahedral cobalt(II) complexes (2.30—2.33 Å),[10-12] which are more common.

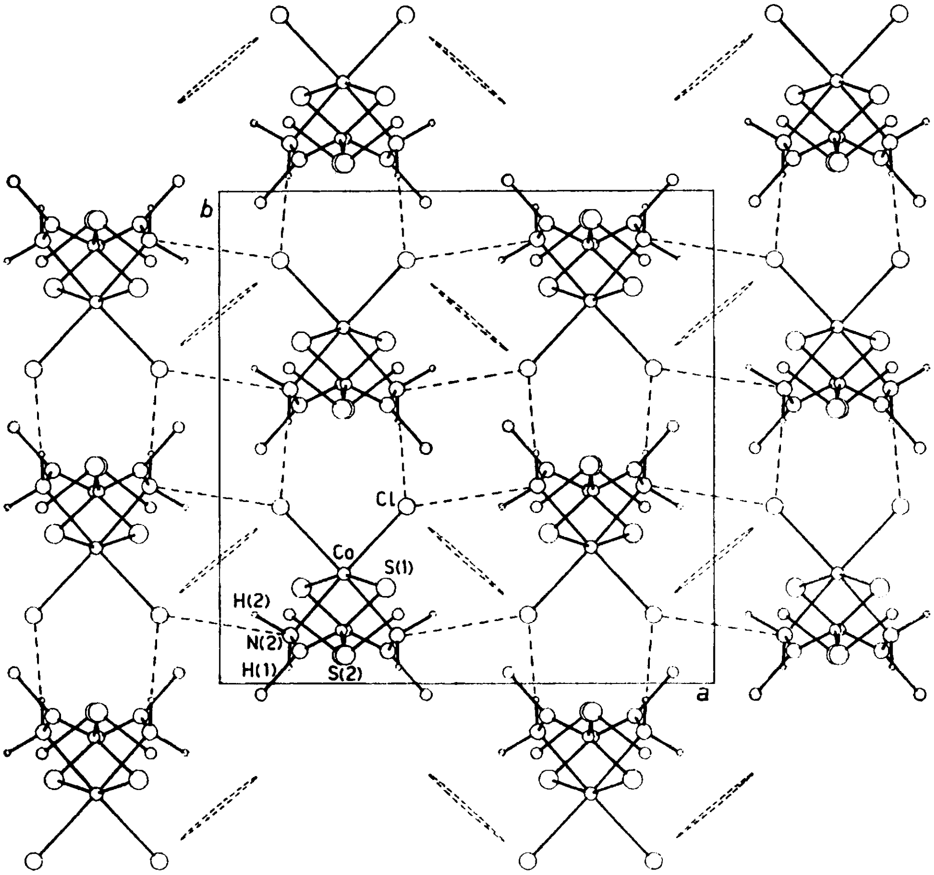

FIGURE 2 Projection of the structure along *c*, showing a layer of complexes with Co atoms at $z = 0$. The dashed lines indicate the hydrogen bonds in the layer, the dashed closed curves indicate the positions of the nearly planar disordered MeL molecules at the crossing of the two-fold axes at $z = \pm\frac{1}{8}$

The conformation of the chelating MeL ligand is *cis,cis*, *i.e.* with both $-NH_2$ and –Me(S) groups *cis* to the C=S bond, and differs from the *trans,cis* conformation of the uncomplexed molecule.[13]

The structural parameters of the MeL ligand are also in good agreement with those of the uncomplexed molecule;[13] the more significant differences concern the S(1)–C(1)–N(1), C(1)–N(1)–C(2), and N(2)–N(1)–C(2) angles probably as a consequence of chelation to the metal which promotes the change from *trans,cis* to *cis,cis* conformation. The hydrogen atoms of the SMe group are *gauche* with respect to the S(2)–C(1) bond and the hydrogen atoms of the NMe group are *gauche* and *eclipsed* with respect to the N(1)–C(1) and N(1)–N(2) bonds respectively. The N(1)C(1)S(1)S(2) moiety is planar with small insignificant displacements of the atoms. Analysis of the planarity shows that the mean plane through this NCSS moiety leaves the co-ordinated N(2) atom and the C(3) atom of the SMe group on the same side and the C(2) atom of the NMe group on the opposite side. (Tables of the internal rotation angles of the SMe and NMe groups and equations of the best least-squares planes are deposited in SUP 22760.)

The five-membered chelate ring is nearly planar, the maximum deviation from the mean plane being 0.081 Å for C(1). The dihedral angle between the two symmetry related chelate rings is 93.9°.

The octahedral complexes are linked by N–H ··· Cl hydrogen bonds, involving the co-ordinated N atoms and Cl atoms of adjacent complexes, in layers parallel to (001) with the Co atoms at $z = 0, \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$ (Figure 2).

Disordered MeL molecules occupy the empty space between these layers lying at the crossing of the three two-fold axes at $z = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$, and $\frac{7}{8}$, in such a way that the ratio of free MeL to complexed MeL is 1 : 2. Normal van der Waals contacts determine the packing of the free MeL molecules and the complex units, the shortest contacts being S(3) ··· S(2$^{\mathrm{VII}}$) (3.57 Å) and C(5) ··· Cl$^{\mathrm{VIII}}$ (3.40 Å). This is an unusual example of a cobalt compound containing free molecules of the ligand; two other examples involve pyridine or piperidine molecules, but in these cases the compounds were separated from pyridine or piperidine as solvent.[14,15]

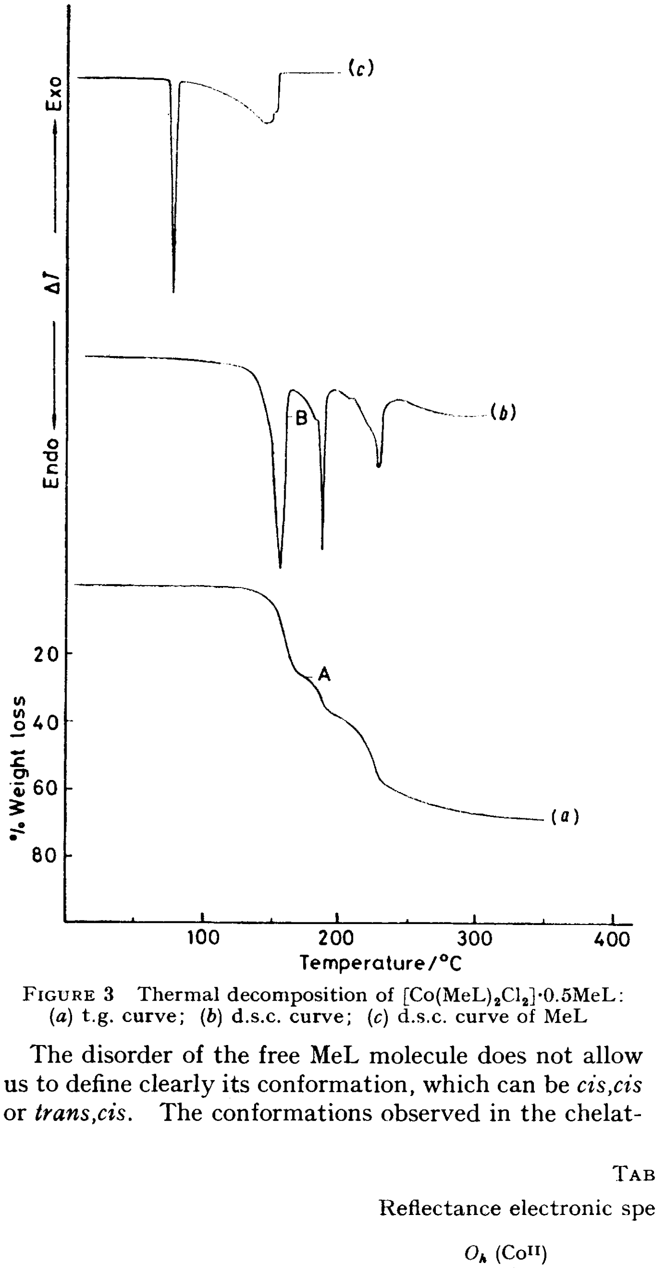

FIGURE 3 Thermal decomposition of $[Co(MeL)_2Cl_2]\cdot 0.5MeL$: (*a*) t.g. curve; (*b*) d.s.c. curve; (*c*) d.s.c. curve of MeL

The disorder of the free MeL molecule does not allow us to define clearly its conformation, which can be *cis,cis* or *trans,cis*. The conformations observed in the chelating and free molecule confirm, as already pointed out by theoretical studies [16] supported by n.m.r. spectra,[17,18] that the *cis,trans* and *trans,trans* conformations are not stable.

TABLE 4

Reflectance electronic spectra [a] of $[Co(MeL)_3][CoCl_4]$

	O_h (Co^{II})			T_d (Co^{II})	
Compound	$\nu_1(^4T_{2g}\leftarrow{}^4T_{1g})$	$\nu_2(^4A_{2g}\leftarrow{}^4T_{1g})$	ν_3 [b]	$\nu_2[^4T_{1g}(F)\leftarrow{}^4A_2]$	$\nu_3[^4T_1(P)\leftarrow{}^4A_2]$
$[Co(MeL)_3][CoCl_4]$	10.4	19.1	26.3	4.8, 5.5, 6.2	14.4, (14.7), 16.3
$[Co(MeL)_3]Br_2$ [c]	10.7, (16.1)	(19.0), 19.8	(25.6)		
$[NBu_4]_2[CoCl_4]$ [d]				4.8, 5.1, 5.4, 5.9	14.3, 14.9, 15.8, 16.2

[a] Band maxima ν in 10^3 cm^{-1}; shoulders in brackets. [b] ν_3 Probably corresponds to a charge-transfer band. [c] Ref. 1. [d] Ref. 19.

Thermal Behaviour.—The d.s.c. curve (Figure 3) shows a two-stage endothermic reaction at 155 °C which is impossible to resolve even by working under various experimental conditions. In the same temperature range (135—160 °C) the t.g. curve (Figure 3) shows a one-step weight loss, corresponding to 1 mol MeL. The compound isolated after this loss at a temperature corresponding to A in the t.g. curve and to B in the d.s.c. curve (Figure 3), has the formula $[Co(MeL)_3][CoCl_4]$, as clearly suggested by its electronic spectrum showing features characteristic of both octahedral and tetrahedral Co^{II} co-ordination (Figure 4, Table 4). In addition its i.r. spectrum shows bands at 302 and 312 cm^{-1} attributable to ν(Co–Cl) of the $[CoCl_4]^{2-}$ anion.[20]

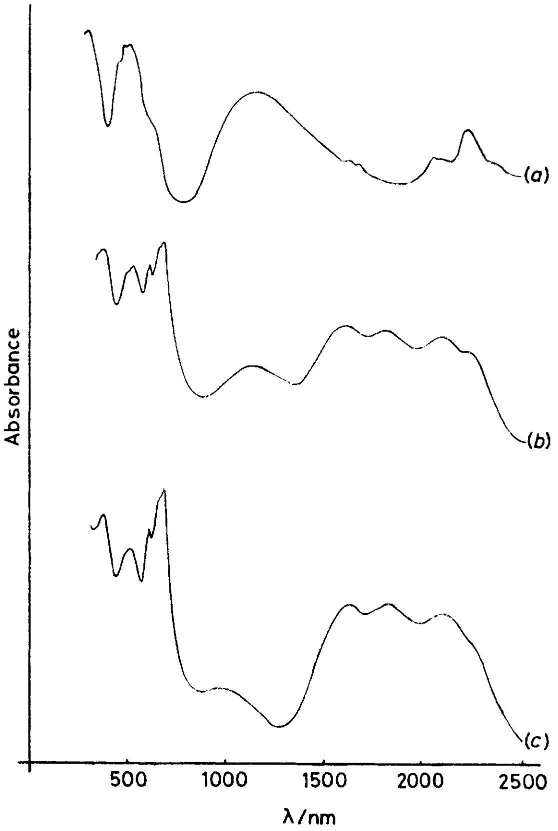

FIGURE 4 Reflectance spectra of (*a*) $[Co(MeL)_2Cl_2]\cdot 0.5MeL$, (*b*) residue corresponding to a weight loss of 0.5 mol MeL, and (*c*) $[Co(MeL)_3][CoCl_4]$

In order to ascertain the role of the MeL molecules, both trapped and co-ordinated, in the decomposition of $[Co(MeL)_{2.5}Cl_2]$ intermediate decomposition products have been isolated by t.g.a. at temperatures corresponding to weight losses of 0.20, 0.50, and 0.75 mol MeL.

At a weight loss of 0.2 mol MeL, i.r. and electronic spectra already show the bands characteristic of $[Co(MeL)_3][CoCl_4]$ and the electronic spectra of the subsequent residues clearly develop to that of this compound (Figure 4).

This suggests that the loss of MeL molecules and the stereochemical rearrangements of the complex are simultaneous and correspond to the first endothermic peak in the d.s.c. curve, but does not allow us to distinguish between the behaviour of the different MeL molecules.

Since the thermal decomposition of the complex $[Co(MeL)_{2.5}Cl_2]$ starts at a temperature higher than that of melting and evaporation of crystals of MeL under the same experimental conditions (Figure 3) the 'free' ligand, trapped in crystals, should have a reticular energy greater than that of crystalline MeL. At higher temperatures, the consecutive loss of ligand results only in the production of mixtures. The final stage at 600 °C represents the conversion to Co_9S_8 identified by *X*-ray powder diagrams and by comparison with A.S.T.M. tables.[21]

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