Crystal Structure of Tris-(*NN*-diethyldithiocarbamato)manganese(III)

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The crystal and molecular structure of the title compound has been determined from single-crystal *X*-ray photographic data. The structure was solved by conventional Patterson and Fourier heavy-atom methods, and refined by block-diagonal least-squares techniques to R 0·11 for 1059 independent observed reflections. Crystals are monoclinic, space group $P2_1/a$, $a = 18{\cdot}04 \pm 0{\cdot}02$, $b = 8{\cdot}34 \pm 0{\cdot}02$, $c = 15{\cdot}88 \pm 0{\cdot}03$ Å, $\beta = 96{\cdot}7 \pm 0{\cdot}1°$, $Z = 4$. The molecule consists of three diethyldithiocarbamate ligands surrounding a central manganese atom, chelating through the sulphur atoms and being substantially planar. The outer geometry of the ligands compares well with that determined in similar structures. The inner geometry of the $Mn(CS_2)_3$ molecular core does not conform to the usual D_3 point-symmetry of transition-metal complexes of this type but shows heavy distortion, the manganese environment consisting of three approximately opposing and equivalent pairs of manganese–sulphur bonds ofl ength 2·38(1), 2·43(1), and 2·55(1) Å. The remainder of the inner geometry is similarly irregular, with C–S 1·65—1·77 Å and C–S–Mn 82—90°. This large distortion is attributed to the ^5E_g (O_h approximation) electronic ground state of the molecule which is expected to be susceptible to heavy Jahn–Teller distortion. Additional evidence is provided by band deformation in the i.r. spectrum.

THE d^4 configuration in transition-metal ions is of interest as the ' high spin ' electronic ground state, ^5E_g in octahedral and ^5E in trigonal complexes, is subject to strong Jahn–Teller effects.[1] However, as the configuration occurs only in the relatively unstable chromium(II) and manganese(III) compounds, studies in this area have been limited. Examination of the near-i.r. electronic spectra of several manganese(III) compounds [2,3] has revealed an intense band at *ca.* 7000 cm^{-1}. This has been assigned to a transition $^5A \rightarrow {}^5B$ within the components of a distorted ^5E state.

In tris(acetylacetonato)manganese(III), $[Mn(C_3H_7O_2)_3]$, the i.r. spectrum [4,5] displays a broadening of the (essentially) Mn–O stretching frequency which has been considered as evidence for tetragonal distortion. A subsequent structure determination, however, revealed no departure from the D_3 symmetry typical of complexes of the type.[6] This apparent lack of distortion has been explained by the assumption of a dynamic Jahn–Teller distortion rather than a static effect, *i.e.* the energy barrier between various static conformations is comparatively small at room temperature and the molecule undergoes a form of ' pseudorotation ' about the trigonal axis (*e.g.* ref. 3). Evidence of static distortion in reported *X*-ray structures of these complexes has been confined to various halide compounds [7,8] in which strong intermolecular interactions exist, and which foreshadow the distorting effects of the Jahn–Teller theorem.

Recently we have been investigating the structural and electronic properties of the tris[*NN*-(disubstituted)-dithiocarbamate]-transition-metal complexes, $M(S_2CNR_2)_3$ ($M = Cr^{III}$, Mn^{III}, Fe^{III}, and Co^{III}). The structures of the cobalt [9,10] and iron [11] complexes show the inner metal co-ordination sphere to be MS_6, the stereochemistry approximating to D_3. The greater twist angle found in these complexes compared to acetylacetonate systems is a consequence of the restraints imposed by the four-membered ring system.

^1H n.m.r.[10] and magnetic susceptibility [12,13] measurements on several manganese(III) dithiocarbamate complexes have established the ground state as ^5E_g (in O_h) for chloroform solution (210—330 K) and in the solid state (85—400 K) for a range of alkyl substituents, R. Dingle[2] has examined the electronic absorption spectrum of the diethyl derivative which bears a close resemblance to that of the acetylacetonate.

Amongst the manganese(III) systems studied, these complexes represent the sole example of sulphur coordination. It has been generally shown that thio-substituted ligands often induce remarkable changes, both electronically and structurally. We have therefore determined the *X*-ray structure of tris-(*NN*-diethyldithiocarbamato)manganese(III) in order to further define the stereochemistry in complexes of this type and to investigate the possibility of the occurrence of static or dynamic Jahn–Teller distortions.

EXPERIMENTAL AND RESULTS

The compound was prepared as described previously.[12]

The i.r. spectrum was recorded, by use of a Perkin-Elmer 521 spectrophotometer, for both Nujol mull and KBr disc, there being no appreciable difference between the recorded spectra. The spectrum is shown, together with that of the cobalt(III) analogue (whose crystal structure is well established) for comparison in Figure 1 (KBr discs, 1600—300 cm^{-1}; above 1600 cm^{-1} the only features present in the spectrum are the C–H frequencies at *ca.* 3000 cm^{-1}). We have not tabulated the frequencies observed *in extenso* as the majority are associated with the Et_2N part of the molecule and are of little interest.

Crystal Structure Determination.—Crystals suitable for

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[2] R. Dingle, *Acta Chem. Scand.*, 1966, **20**, 33.

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[5] K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 1066.

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[7] M. Hepworth, K. H. Jack, and R. S. Nyholm, *Acta Cryst.*, 1957, **10**, 345.

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[11] P. C. Healy and A. H. White, *J.C.S. Dalton*, 1972, 1163.

[12] R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, W. C. Tennant, and A. H. White, *J. Chem. Phys.*, 1970, **52**, 3105.

[13] R. M. Golding, P. C. Healy, and A. H. White, *Trans. Faraday Soc.*, 1971, **67**, 1672.

X-ray work were obtained by the slow addition of cyclohexane to a solution of the substance in chloroform, care being taken to prevent hydrolysis. A crystal suitable for data collection (0·08 × 0·15 × 0·07 mm) was obtained as a section of a larger crystal, the form being typically a thick plate elongated along *b*. Intensities were collected by the multiple-film equi-inclination Weissenberg method on a non-integrating Nonius Weissenberg camera, the same crystal section being mounted about the *b* and *a* axes respectively, calibration being effected on zero-layer single-film Weissenberg photographs about those axes with aluminium powder (a_{298K} 4·0494 Å).[14] As crystals of the complex are subject to decomposition in the atmosphere data were collected as rapidly as possible on an unprotected crystal in dry weather using unfiltered copper radiation [$\lambda(K_{\alpha1}) = 1\cdot5406$; $\lambda(K_{\alpha2}) = 1\cdot5444$; $(K_{\beta}) = 1\cdot3922$ Å].[15] The data and the physical appearance of the crystal after the completion of data collection (3 days) showed no decline in quality; and this was confirmed later by agreement analysis on the various layers employed.

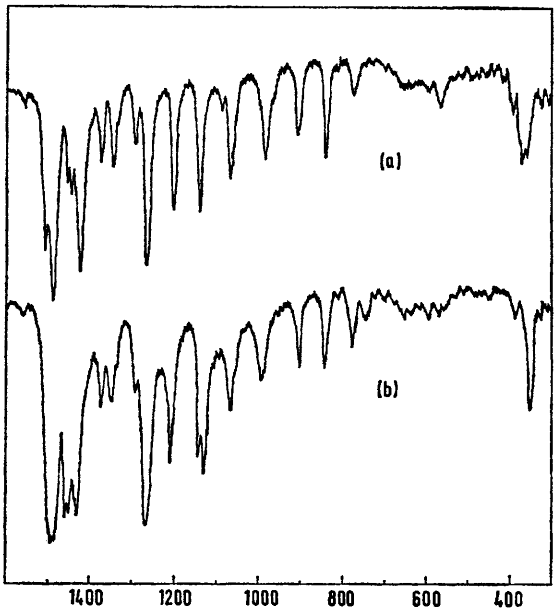

FIGURE 1 I.r. spectra (KBr discs) in the range 300—2000 cm^{-1} for (a) [Mn(CS$_2$·NEt$_2$)$_3$] and (b) [Co(CS$_2$·NEt$_2$)$_3$]

Crystal Data.—$C_{15}H_{30}N_3MnS_6$, $M = 499$, Monoclinic, $a = 18\cdot04 \pm 0\cdot02$, $b = 8\cdot34 \pm 0\cdot02$, $c = 15\cdot88 \pm 0\cdot03$ Å, $\beta = 96\cdot7 \pm 0\cdot1°$, $U = 1992$ Å^3, D_m (by flotation) $= 1\cdot37 \pm 0\cdot05$, $Z = 4$, $D_c = 1\cdot40$. Space group $P2_1/a$ (C^5_{2h}, No. 14, ref. 16) from systematic absences $\{h0l\}$, $h = 2n + 1$, $\{0k0\}$, $k = 2n + 1$.

Intensity data were obtained from the layers 0—2*kl*, *h*0—3*l*, and were estimated visually by use of an intensity strip calibrated on a Joyce–Loebl Mark IIIB microdensitometer yielding 1059 independent observed reflections, which were used in the subsequent structure determination.

All intensities were corrected for absorption using the algorithm of ABSCOR.[17] ($\mu = 95$ cm^{-1}; transmission coefficient range = 0·33—0·76). After correction for Lorentz and polarization factors using a local program (SCAL1), the data were internally correlated and scaled by the method of Hamilton *et al.*[18] all reflections being assigned unit weights.

Structure Determination.—An unmodified three-dimensional Patterson synthesis computed on all observed data, showed that the manganese was located on or close to (0·375, 0·250, 0·250) with the manganese–sulphur vectors lying parallel to the axes, leading to a large degree of ambiguity in possible solutions. Correct phasing of the subsequent electron-density distributions was only obtained by considering all possible independent solutions and geometrically postulating carbon and nitrogen positions for the ligands so that the three S_2CNC_2 groups were tentatively defined. These were cautiously refined by block diagonal (3 × 3, 6 × 6) least-squares procedures; of the four possible postulated solutions, only one refined in a satisfactory manner, *R* falling to 0·42 for this solution and remaining at *ca.* 0·55 for the remaining three. A three-dimensional Fourier synthesis was computed at this stage, and enabled the postulated atomic positions to be readjusted and others located. The structure then readily refined to *R* 0·26 when a further Fourier synthesis enabled the remaining atoms to be located. With independent isotropic thermal parameters allowed to vary for all atoms, the system refined further to *R* 0·13. At this stage a weighting scheme of form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced,[19] *a* and *b* being progressively adjusted to minimize $\Sigma w(|F_o| - |F_c|)^2$; anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)]$ were introduced for the manganese and sulphur atoms also. Refinement ceased at *R* 0·110, the weighted factor *R'* 0·140 [$R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. (A statistical test indicated that the introduction of anisotropic thermal parameters was significant.[20]). Final values for *a* and *b* were 32·0 and 0·019. During the final round of least-squares refinement all parameter shifts were $< 0\cdot2\sigma$, the shifts for the heavy atoms being appreciably less. A difference-Fourier synthesis computed at this stage showed no significant peaks ($< 0\cdot4$ carbon atoms). (In view of the proximity of the sulphur atoms to the planes $y = 0$, 0·25, and 0·50, and $z = 0\cdot25$, the possibility was considered that the sulphur atoms had refined to false positions on the wrong side of these planes. The validity of this hypothesis was tested by reflecting these atoms through these planes where appropriate and refining the resulting positions. The initial *R* was 0·37 which was reduced rapidly to 0·11 as all atoms returned to the positions of the original solution.) There was no evidence for disorder in the structure. Scattering factors were taken from ref. 21 for neutral manganese, sulphur, carbon, and nitrogen atoms, that for manganese being corrected for anomalous dispersion according to the values of ref. 22. Refinement programs were local [SFLS1, 2 (A. I. M. Rae) and FCURV, (B. J. Ong)]. The final set of observed and calculated structure factors are listed in

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[15] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 59.

[16] Ref. 15, vol. I, p. 99.

[17] ABSCOR program, N. W. Alcock, in ' Crystallographic Computing,' Munksgaard, Copenhagen, 1971, p. 271.

[18] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

[19] D. W. Cruickshank, in ' Computing Methods in Crystallography,' Pergamon Press, Oxford, 1965, p. 114.

[20] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[21] Ref. 15, p. 210.

[22] Ref. 15, p. 213.

TABLE 1

(*a*) Final atomic cell fractional co-ordinates and isotropic temperature factors

	x	y	z	B/Å^2
Mn	0·3801(2)	0·2395(5)	0·2483(2)	[4·4(1)] *
S(a1)	0·2496(3)	0·1915(9)	0·1989(3)	[4·0(2)] *
S(a2)	0·3594(3)	0·3106(9)	0·0916(4)	[4·9(3)] *
S(b1)	0·4109(3)	0·9655(9)	0·2335(4)	[4·6(3)] *
S(b2)	0·5151(3)	0·2276(9)	0·2648(4)	[4·5(3)] *
S(c1)	0·3681(4)	0·2493(9)	0·4072(4)	[5·2(3)] *
S(c2)	0·3742(4)	0·5134(9)	0·2890(4)	[4·5(2)] *
C(a1)	0·268(1)	0·257(3)	0·103(1)	4·9(5)
C(b1)	0·505(1)	0·032(3)	0·252(1)	4·3(5)
C(c1)	0·373(1)	0·456(3)	0·390(1)	3·6(5)
N(a1)	0·215(1)	0·283(2)	0·038(1)	3·5(4)
N(b1)	0·558(1)	0·911(2)	0·255(1)	4·1(4)
N(c1)	0·376(1)	0·556(3)	0·456(1)	4·9(4)
C(a2)	0·134(1)	0·225(4)	0·041(1)	5·7(6)
C(a3)	0·229(1)	0·359(3)	0·954(1)	4·7(6)
C(a4)	0·083(1)	0·382(4)	0·046(2)	6·8(7)
C(a5)	0·244(1)	0·216(4)	0·892(2)	6·5(7)
C(b2)	0·544(1)	0·736(3)	0·246(1)	4·8(5)
C(b3)	0·639(1)	0·974(3)	0·271(1)	4·1(4)
C(b4)	0·543(2)	0·686(4)	0·152(2)	7·1(8)
C(b5)	0·664(1)	0·964(4)	0·370(2)	6·8(7)
C(c2)	0·384(1)	0·507(4)	0·546(1)	6·0(6)
C(c3)	0·372(1)	0·740(3)	0·436(1)	5·4(5)
C(c4)	0·308(2)	0·520(4)	0·582(2)	8·8(9)
C(c5)	0·446(2)	0·820(4)	0·455(2)	7·2(7)

* Temperature factors with all atoms isotropic, *R* 0·13.

(*b*) Anisotropic temperature factors ($\times 10^4$) for manganese and sulphur atoms

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Mn	32(1)	9(7)	−1(2)	151(8)	−11(6)	41(1)
S(a1)	34(2)	17(11)	10(4)	20(17)	−11(10)	32(2)
S(a2)	31(2)	0(11)	6(4)	191(16)	5(11)	44(3)
S(b1)	24(2)	15(11)	−10(4)	162(14)	2(12)	55(3)
S(b2)	33(2)	−18(12)	2(4)	181(15)	−15(12)	53(3)
S(c1)	42(2)	−7(13)	8(4)	157(14)	−2(11)	43(3)
S(c2)	43(2)	5(13)	11(4)	160(15)	0(12)	40(3)

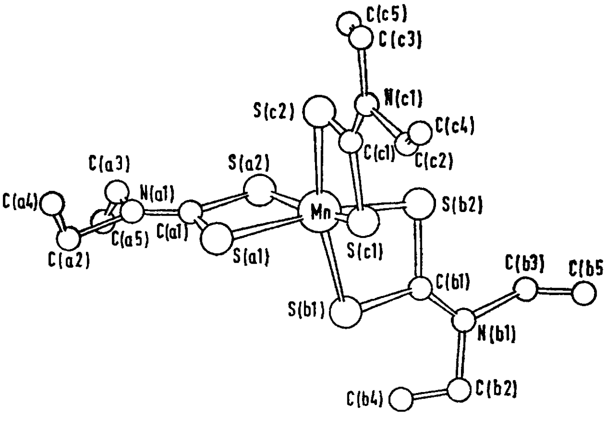

FIGURE 2 Diagram showing the relative disposition of the atoms in the molecule together with the atomic numbering system used

Supplementary Publication No. SUP 20433 (4 pp., 1 microfiche).†

Final atomic positional and thermal parameters are given in Table 1, together with estimated standard deviations derived by block-diagonal least-squares procedure and therefore likely to be underestimates.

The atomic numbering system used is defined in Figure 2 which shows the molecular configuration. Interatomic distances and angles, together with their estimated standard

TABLE 2

Molecular geometry

(*a*) Intramolecular bond lengths (Å)

Mn–S(a1)	2·431(7)	C(b1)–N(b1)	1·40(3)
Mn–S(a2)	2·541(7)	N(b1)–C(b2)	1·48(3)
S(a1)–S(a2)	2·94(1)	N(b1)–C(b3)	1·54(3)
S(a1)–C(a1)	1·69(2)	C(b2)–C(b4)	1·56(4)
S(a2)–C(a1)	1·74(2)	C(b3)–C(b5)	1·58(3)
C(a1)–N(a1)	1·34(3)		
N(a1)–C(a2)	1·54(3)	Mn–S(c1)	2·557(7)
N(a1)–C(a3)	1·52(3)	Mn–S(c2)	2·383(8)
C(a2)–C(a4)	1·61(4)	S(c1)–S(c2)	2·91(1)
C(a3)–C(a5)	1·60(4)	S(c1)–C(c1)	1·75(3)
		S(c2)–C(c1)	1·67(2)
Mn–S(b1)	2·373(9)	C(c1)–N(c1)	1·33(3)
Mn–S(b2)	2·428(7)	N(c1)–C(c2)	1·49(3)
S(b1)–S(b2)	2·89(1)	N(c1)–C(c3)	1·57(4)
S(b1)–C(b1)	1·77(2)	C(c2)–C(c4)	1·55(4)
S(b2)–C(b1)	1·65(3)	C(c3)–C(c5)	1·50(4)

(*b*) Intramolecular angles (°)

S(a1)–Mn–S(a2)	72·4(2)	S(a2)–C(a1)–N(a1)	119(2)
S(a1)–Mn–S(b1)	92·3(3)	S(b1)–C(b1)–S(b2)	115(1)
S(a1)–Mn–S(b2)	162·6(3)	S(b1)–C(b1)–N(b1)	115(1)
S(a1)–Mn–S(c1)	97·6(3)	S(b2)–C(b1)–N(b1)	130(2)
S(a1)–Mn–S(c2)	100·0(3)	S(c1)–C(c1)–S(c2)	116(1)
S(a2)–Mn–S(b1)	97·9(3)	S(c1)–C(c1)–N(c1)	119(2)
S(a2)–Mn–S(b2)	98·4(3)	S(c2)–C(c1)–N(c1)	124(2)
S(a2)–Mn–S(c1)	159·6(3)	C(a1)–N(a1)–C(a2)	121(2)
S(a2)–Mn–S(c2)	92·0(2)	C(a1)–N(a1)–C(a3)	124(2)
S(b1)–Mn–S(b2)	74·1(2)	C(a2)–N(a1)–C(a3)	114(2)
S(b1)–Mn–S(c1)	100·1(3)	N(a1)–C(a2)–C(a4)	107(2)
S(b1)–Mn–S(c2)	166·1(3)	N(a1)–C(a3)–C(a5)	107(2)
S(b2)–Mn–S(c1)	95·5(3)	C(b1)–N(b1)–C(b2)	127(2)
S(b2)–Mn–S(c2)	94·9(3)	C(b1)–N(b1)–C(b3)	113(2)
S(c1)–Mn–S(c2)	71·9(2)	C(b2)–N(b1)–C(b3)	120(2)
Mn–S(a1)–C(a1)	87·2(8)	N(b1)–C(b2)–C(b4)	110(2)
Mn–S(a2)–C(a1)	82·7(8)	N(b1)–C(b3)–C(b5)	108(2)
Mn–S(b1)–C(b1)	85·0(8)	C(c1)–N(c1)–C(c2)	125(2)
Mn–S(b2)–C(b1)	85·8(8)	C(c1)–N(c1)–C(c3)	117(2)
Mn–S(**c1**)–C(c1)	82·2(7)	C(c2)–N(c1)–C(c3)	117(2)
Mn–S(c2)–C(c1)	89·5(8)	N(c1)–C(c2)–C(c4)	111(2)
S(a1)–C(a1)–S(a2)	118(1)	N(c1)–C(c3)–C(c5)	112(2)
S(a1)–C(a1)–N(a1)	123(2)		

TABLE 3

Equations of best least-squares planes for the ligand atoms in the form $AX + BY + CZ = 0$; * deviations (Å) of atoms from the planes are given in square brackets; atoms used in plane calculation in italics

Ligand (a): $-0{\cdot}2251X + 0{\cdot}9171Y + 0{\cdot}3290Z = 7{\cdot}094$

[*Mn 0·19, S(a1) 0·08, S(a2) −0·06, C(a1) −0·04, N(a1) 0·02, C(a2) 0·80, C(a3) −0·08,* C(a4) −1·43, C(a5) 1·36]

Standard deviation of ligand atoms plane: 0·06 Å.

Ligand (b): $-0{\cdot}1438X - 0{\cdot}0896Y + 0{\cdot}9855Z = 1{\cdot}913$.

[*Mn 0·09, S(b1) −0·01, S(b2) 0·02, C(b1) −0·01, N(b1) −0·01, C(b2) 0·02, C(b3) −0·01,* C(b4) −1·43, C(b5) 1·49]

Standard deviation of ligand atoms from plane: 0·01 Å.

Ligand (c): $0{\cdot}9970X - 0{\cdot}0172Y + 0{\cdot}0758Z = 6{\cdot}392$

[*Mn 0·25, S(c1) −0·07, S(c2) 0·08, C(c1) 0·00, N(c1) 0·00, C(c2) 0·08, C(c3) −0·08,* C(c4) −1·31, C(c5) 1·22]

Standard deviation of atoms from plane: 0·06 Å.

* X, Y, and Z are orthogonal co-ordinates in (Å) defined by $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$.

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

deviations, are given in Table 2, computed by use of the BONDSCAN program.[23]

Planes of best fit were determined for the ligands, together with deviations of atoms from the planes and are listed in Table 3.

DISCUSSION

The crystals are composed of discrete molecules of $[Mn(CS_2{\cdot}N(Et_2)_3]$, all atoms occupying general positions in the unit cell. The unit cell contents are displayed in Figure 3.

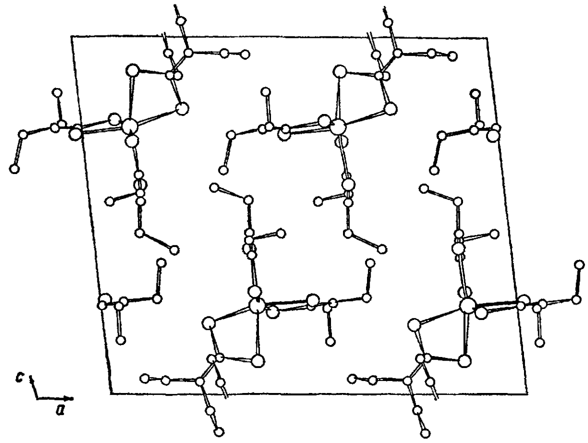

FIGURE 3 The unit cell contents viewed in projection down the *b* axis

As in the previously studied tris-(*NN*-dialkyldithiocarbamato)-iron(III) and -cobalt(III) derivatives, the metal is surrounded by three dithiochelate ligands conferring an approximate overall molecular point-symmetry of D_3. Whereas in the iron(III) and cobalt(III) derivatives this is more or less a tolerably exact representation of the metal environmental symmetry, in this complex the magnitude of the distortions observed show this observation to be superficial. The manganese atom is surrounded by three opposing pairs of sulphur atoms at distances of *ca.* 2·38 [Mn–S(b1), Mn–S(c2)], *ca.* 2·43 [Mn–S(a1), Mn–S(b2)], and 2·55 Å [Mn–S(a2), Mn–S(c1)]. To test the validity of the discrepancies observed here, *R* was recalculated, first, with the four shorter distances equalized and constrained to 2·41 Å [S(a1), (0·251, 0·192, 0·199); S(b1), (0·411, 0·963, 0·233); S(b2), (0·514, 0·228, 0·265); and S(c2), (0·374, 0·517, 0·289)]. Application of significance tests [20] on the resulting *R* 0·111 and *R'* 0·141 implied that the hypothesis that these bonds were equal could only be rejected at a low level of significance. However, equalization of the remaining two bonds at 2·41 Å [S(a2), (0·359, 0·311, 0·100); and S(c1), (0·368, 0·249, 0·397)], conforming the system to D_3 symmetry, gave *R* 0·16, and *R'* 0·21, indicating that these differences were highly significant.[20] The picture that emerges from these results is that the central MS_6 core approximates possibly to point-group C_1, or, at best, C_2. If we make the more drastic assumption that the system is a distortion of O_h symmetry, rather than D_3, then the overall symmetry is very crudely D_{4h} (or D_{2h}) corresponding basically to a tetragonal distortion, which is then superimposed on the overall D_3 molecular symmetry. Unlike the tris(acetylacetonato)manganese(III) system,[6] it appears that this molecule displays a very pronounced distortion of a type which conforms to the requirements of the Jahn–Teller theorem and which is quite unprecedented. This distortion is reflected in the MnS_6 angular geometry as well as the bond lengths. The intraligand S(*i*1)–Mn–S(*i*2) angles vary between 72 and 74°; interligand S(*in*)–Mn–S(*jn*) angles between 92 and 100° ($n = 1$ and $n = 2$ correspond to the upper and lower triangular systems of the D_3 approximation) and the opposing S–Mn–S systems (which, in O_h, would be 180°) between 160 and 166°. The intraligand S(*i*1)–S(*i*2) distances vary between 2·89 and 2·94 Å.

The distortion which is present in the MnS_6 core appears to impose itself on the remainder of the ligand system. Thus, within the MnS_2C four-membered rings, the Mn–S–C angles vary between 83 and 90° and the S–C–S angles between 115 and 118°. S–C distances vary between 1·65 and 1·77 Å, although the standard deviations on these distances are rather large (0·02 Å). Within the remainder of the ligand system distances and angles are normal compared with those found in related systems (Table 4).

TABLE 4

Molecular dimensions in first-row transition-metal tris(dithiocarbamate) derivatives

		Distances/Å				Angles/°	
Compound	Ground state (O_h)	⟨M–S⟩	⟨C–S⟩	⟨C–N⟩	⟨N–C⟩	⟨S–M–S⟩	⟨S–C–S⟩
$[Mn(CS_2{\cdot}NEt_2)_3]$ [a]	^5E_g	2·37—2·56(1)	1·65—1·77(2)	1·35(3)	1·52(4)	71·9—74·1(2)	116(1)
$[Fe(CS_2{\cdot}NBu^n{}_2)_3]$ [b]	*ca.* $^6A_{1g}$	2·42(1)	1·70(1)	1·41(3)		72·8(2)	115(1)
$[Fe(CS_2{\cdot}N(CH_2)_4)_3]$ [c]	$^6A_{1g}$	2·38—2·44(1)	1·70(3)	1·31(2)	1·50(8)	74·5(3)	117(2)
$[Fe(CS_2{\cdot}NMePh)_3]$ [c]	*ca.* $^2T_{2g}$	2·28—2·33(1)	1·68(3)	1·37(2)	1·50(8)	75·1(3)	113(2)
$[Co(CS_2{\cdot}NEt_2)_3]$ [d]	$^1A_{1g}$	2·26(1)	1·71(1)	1·31(1)	1·50(1)	76·1(1)	110(1)

[a] This work (a range of values is quoted where the spread exceeds 3σ). [b] B. F. Hoskins and B. P. Kelly, *Chem. Comm.*, 1968, 1517. [c] Ref. 11. [d] Refs. 9 and 10.

The i.r. spectrum is of interest when compared with that of the cobalt(III) analogue. In the latter compound, the equivalence of the three S_2CNC_2 systems is clearly established as is the symmetry of the CoS_6 core, which is a very good approximation to D_3, the six metal–sulphur distances ranging from 2·26 to 2·27 Å.[9,10] Thus, for the latter complex we might expect a series of sharp, well-defined i.r. frequencies, whereas for the manganese

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[23] BONDSCAN program, M. E. Pippy and F. R. Ahmed, Divn. Pure Appl. Physics, NRC, Ottawa, Canada, Program NRC-12.

derivative they should be broadened or split. There is little conclusive evidence in the carbon–sulphur stretching region at *ca.* 1000 cm^{-1} to suggest that this is so; however, the manganese–sulphur band at *ca.* 370 cm^{-1} is extremely broad whereas that in the cobalt derivative (*ca.* 350 cm^{-1}) is comparatively narrow (Figure 1). In the manganese derivative, the frequency at *ca.* 1500 cm^{-1} typical of the conjugated carbon–nitrogen stretching vibration is split into two components (1490 and 1510 cm^{-1}), one of approximately twice the intensity of the other, whereas in the cobalt derivative one broad band only is observed (1490 cm^{-1}). There are other small differences in the carbon–carbon and carbon–hydrogen regions of the spectrum, probably due to the differing proton environments in the two complexes.

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