Crystal and Molecular Structures of Dichloromethane-solvated Tris-(morpholinocarbodithioato)-complexes of Chromium(III), Manganese(III), and Rhodium(III). Comparison of Co-ordination Spheres

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The title complexes [(I)—(III)] are nearly isomorphous with the known cobalt(III) analogue (IV). The principal differences between (I)—(III) arise from the nature of the central metal atoms, packing and other effects being essentially the same. They may be considered as trigonally distorted octahedra, with an approximate three-fold rotation axis. The manganese complex (II) deviated most significantly from this model, with elongated bonds in the *z* and slightly elongated bonds along the *x* direction, which can only be attributed to Jahn–Teller effects. The MS_6 co-ordination sphere is highly symmetrical in the chromium complex(I), as expected for the ^4A ground-state, even more so than in (IV). The mean increase in metal–ligand bond distance from Co^{III} to Rh^{III}, with identical d_6 ($^1A_1$) configurations, is very close to 0.1 Å. The ' bite ' angle of the bidentate ligand appears to be determined largely by M–L distance.

Crystal data: (I), space group $P\bar{1}$, $Z = 2$, $a = 13.255(9)$, $b = 10.642(5)$, $c = 11.395(1)$Å, $\alpha = 115.16(4)$, $\beta = 104.4(1)$, $\gamma = 100.19(6)°$, $R = 4.3\%$, 2 218 reflections; (II), space group $P\bar{1}$, $a = 13.067(3)$, $b = 10.824(6)$, $c = 11.475(5)$Å, $\alpha = 116.23(5)$, $\beta = 104.06(3)$, $\gamma = 100.19(4)°$, R 4.0%, 2 062 reflections; (III), space group, $P\bar{1}$ $Z = 2$, $a = 13.343(4)$, $b = 10.596(1)$, $c = 11.191(1)$Å, $\alpha = 114.20(1)$, $\beta = 103.18(2)$, $\gamma = 101.29(2)°$, R 4.3% 3 529 reflections.

DIFFICULTIES encountered in structural studies of metal(III) dithiocarbamates [1-3] have been frequently shown to arise from the fact that the unsolvated complexes fail to form good crystals while solvated crystals lose solvent molecules, sometimes without change in molar volume.[3] This problem was overcome in the case of tris(morpholinocarbodithioato)iron(III)–dichloromethane, $Fe(mc)_3 \cdot CH_2Cl_2$ (V), and its cobalt(III) analogue (IV), which are crystallographically isomorphous, and possess similar molecular structures and crystal packing. Thus comparison of the two structures enables a direct study of the effect of altering the *d* electron configuration from d^5 to d^6.

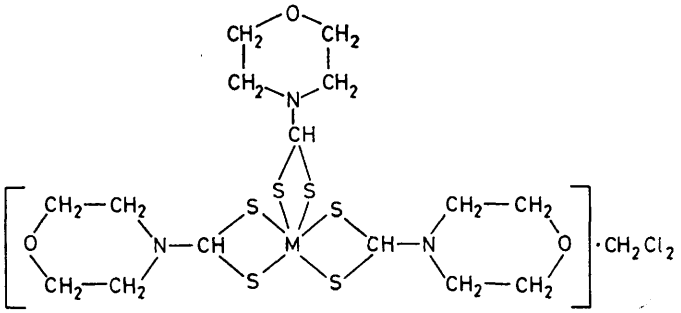
We report here the structures of (I) the chromium(III), (II) manganese(III), and (III) rhodium(III) analogues of (V) and compare the pseudo-octahedral complexes with $3d^3$, $3d^4$, $3d^5$, $3d^6$, and $4d^6$ configurations.

EXPERIMENTAL

Preparation of Complexes.—The potassium salt was prepared by slow addition of carbon disulphide to an ethanol solution of potassium hydroxide and morpholine, and recrystallised from ethanol. Complex (III) was formed by reaction of solid rhodium(III) chloride with a stirred solution of K(mc) in ethanol–water (1 : 1). (I) was prepared similarly, from chromium(II) acetate monohydrate, the oxidation being performed by a slow stream of air bubbled into the solution. (II) was prepared by the same method as for (I) except that manganese sulphate was used, with water as the solvent. In each case the precipitated complex was extracted with chloroform, recrystallised from chloroform–ethanol, and crystals were grown by slow evaporation of dichloromethane from a dichloromethane–ethanol solution. Crystals of (I) and (II) rapidly lost dichloromethane in air, and were sealed in glass capillaries for data collection.

Densities were determined by flotation in aqueous potassium iodide.

Crystal Data.—(*a*) (I). $C_{16}H_{29}Cl_2CrN_3O_3$, $M = 622$, $a = 13.255(9)$, $b = 10.642(5)$, $c = 11.395(1)$Å, $\alpha = 115.16(4)$, $\beta = 104.4(1)$, $\gamma = 100.19(6)°$, $U = 1\,334$ Å^3, $D_c = 1.57$, $Z = 2$, $D_m = 1.54$ g cm^{-3}. μ(Mo-K_α) = 11.3 cm^{-1}. Space group $P\bar{1}$.



M
(I) Cr
(II) Mn
(III) Rh
(IV) Co
(V) Fe

(*b*) (II). $C_{16}H_{29}Cl_2MnN_3O_3$, $M = 625$, $a = 13.067(3)$, $b = 10.824(6)$, $c = 11.457(5)$Å, $\alpha = 116.23(5)$, $\beta = 104.06(3)$, $\gamma = 100.19(4)°$, $U = 1\,333$ Å^3, $D_c = 1.56$, $Z = 2$, $D_m = 1.55$ g cm^{-3}. μ(Mo-K_α) = 11.9 cm^{-1}. Space group $P\bar{1}$.

(*c*) (III). $C_{16}H_{29}Cl_2N_3O_3Rh$, $M = 675$, $a = 13.343(4)$, $b = 10.596(1)$, $c = 11.191(1)$Å, $\alpha = 114.20(1)$, $\beta = 103.18(2)$, $\gamma = 101.29(2)°$, $U = 1\,329$ Å^3, $D_c = 1.68$, $Z = 2$, $D_m = 1.66$ g cm^{-3}. μ(Mo-K_α) = 12.9 cm^{-1}. Space group $P\bar{1}$.

Cell dimensions were obtained and refined, and intensity data collected as described elsewhere,[4] by use of an Enraf-Nonius four-circle CAD 4 diffractometer controlled by a PDP8/M computer. The θ—2θ scan technique was used to record the intensities of all reflections having $0° < 2\theta < 48°$ for (I), $0° < 2\theta < 49°$ for (II), and $0° < 2\theta < 50°$ for (III). The symmetric scans were centred on the calculated peak positions [λ(Mo-K_α) 0.7107 Å]. Reflection data were considered unobserved if intensities registered less than 10 counts above background on a rapid prescan, and were rejected automatically by the computer.

For each crystal, the intensities of four standard reflections, monitored at 100 reflection intervals, were relatively constant throughout the data collection. The

[1] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, 1964, *A*280, 235.
[2] J. S. Ricci, jun., C. A. Eggars, and I. Bernal, *Inorg. Chim. Acta*, 1972, **6**, 97.
[3] P. C. Healy and E. Sinn, *Inorg. Chem.*, 1975, **14**, 109.
[4] E. Sinn, *J.C.S. Dalton*, in the press.

TABLE 1

Positional and thermal * parameters and their estimated standard deviations

(*a*) For (I)

Atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.2484(1)	0.2212(1)	0.4805(1)	0.0069(1)	0.0078(1)	0.0099(2)	0.0031(2)	0.0026(2)	0.0071(2)
Cl(1)	0.8347(3)	0.8314(4)	0.1200(4)	0.0187(5)	0.0357(6)	0.0601(8)	0.0037(8)	−0.009(1)	0.0599(9)
Cl(2)	0.9526(3)	0.6408(4)	0.1374(4)	0.0285(5)	0.0293(5)	0.0298(7)	0.0300(8)	0.006(1)	0.0174(9)
S(11)	0.1846(2)	−0.0084(2)	0.4793(3)	0.0103(2)	0.0096(3)	0.0149(3)	0.0034(4)	0.0105(4)	0.0111(4)
S(12)	0.3589(2)	0.0887(2)	0.3971(2)	0.0074(2)	0.0106(3)	0.0134(3)	0.0055(4)	0.0056(4)	0.0117(4)
S(21)	0.3459(2)	0.3552(2)	0.7266(2)	0.0079(2)	0.0091(2)	0.0097(3)	0.0017(4)	0.0023(4)	0.0105(4)
S(22)	0.3547(2)	0.4518(2)	0.5263(2)	0.0092(2)	0.0095(3)	0.0086(3)	0.0036(4)	0.0036(4)	0.0092(4)
S(31)	0.0747(2)	0.2837(2)	0.4900(2)	0.0093(2)	0.0145(3)	0.0084(3)	0.0095(4)	0.0049(4)	0.0072(5)
S(32)	0.1314(2)	0.1483(2)	0.2471(2)	0.0081(2)	0.0119(3)	0.0089(3)	0.0086(4)	0.0047(4)	0.0069(4)
O(1)	0.2995(5)	−0.4711(6)	0.2208(7)	0.0159(7)	0.0170(8)	0.0222(10)	0.019(1)	0.013(1)	0.018(1)
O(2)	0.5987(5)	0.9068(5)	1.0112(6)	0.0122(6)	0.0094(7)	0.0110(7)	0.003(1)	0.009(1)	0.006(1)
O(3)	−0.2351(5)	0.2507(6)	0.0737(6)	0.0110(6)	0.0210(8)	0.0180(9)	0.020(1)	0.003(1)	0.015(1)
N(1)	0.2994(6)	−0.1805(6)	0.3677(7)	0.0099(7)	0.0103(8)	0.0131(10)	0.007(1)	0.006(1)	0.009(1)
N(2)	0.4853(5)	0.6123(6)	0.7959(6)	0.0078(6)	0.0105(8)	0.0071(7)	0.007(1)	0.007(1)	0.010(1)
N(3)	−0.0518(6)	0.2223(7)	0.2375(7)	0.0101(6)	0.0221(10)	0.0087(9)	0.020(1)	0.008(1)	0.010(1)
C(11)	0.2815(7)	−0.0493(8)	0,4102(8)	0.0078(8)	0.0090(10)	0.0057(9)	0.003(1)	−0.000(1)	0.004(1)
C(12)	0.2457(9)	−0.2931(8)	0.3944(9)	0.0158(11)	0.0146(11)	0.0188(12)	0.012(2)	0.012(2)	0.025(2)
C(13)	0.2117(9)	−0.4456(8)	0.2662(10)	0.0145(11)	0.0072(10)	0.0187(14)	0.003(2)	0.003(2)	0.013(2)
C(14)	0.3821(8)	−0.2147(8)	0.3048(10)	0.0091(9)	0.0114(11)	0.0228(15)	0.010(2)	0.007(2)	0.016(2)
C(15)	0.3382(8)	−0.3685(9)	0.1839(10)	0.0148(10)	0.0182(13)	0.0197(15)	0.021(2)	0.015(2)	0.017(2)
C(21)	0.4058(6)	0.4892(7)	0.6931(7)	0.0060(7)	0.0080(9)	0.0092(9)	0.005(1)	0.006(1)	0.008(1)
C(22)	0.5265(8)	0.6492(8)	0.9407(8)	0.0115(9)	0.0083(10)	0.0099(11)	0.006(2)	0.002(2)	0.007(1)
C(23)	0.5343(7)	0.8043(8)	1.0350(8)	0.0101(9)	0.0105(10)	0.0100(10)	0.006(2)	0.005(2)	0.010(1)
C(24)	0.5486(7)	0.7207(8)	0.7684(8)	0.0093(9)	0.0108(11)	0.0092(10)	0.002(2)	0.006(2)	0.009(2)
C(25)	0.5513(8)	0.8707(8)	0.8704(9)	0.0157(10)	0.0107(11)	0.0164(12)	0.011(2)	0.016(2)	0.015(2)
C(31)	0.0408(7)	0.2171(8)	0.3157(8)	0.0062(7)	0.0078(10)	0.0126(11)	0.003(1)	0.002(2)	0.007(2)
C(32)	−0.1335(9)	0.2764(12)	0.2905(11)	0.0222(10)	0.0561(19)	0.0204(16)	0.059(2)	0.025(2)	0.039(3)
C(33)	−0.2023(9)	0.3098(13)	0.2168(11)	0.0166(10)	0.0560(24)	0.0140(16)	0.045(2)	0.012(2)	0.015(3)
C(34)	−0.0855(9)	0.1611(11)	0.0852(10)	0.0209(11)	0.0506(18)	0.0128(14)	0.052(2)	0.013(2)	0.029(2)
C(35)	−0.1581(9)	0.1991(12)	0.0263(11)	0.0176(11)	0.0487(21)	0.0144(16)	0.042(2)	0.005(2)	0.021(3)
C	0.9157(11)	0.7911(13)	0.2112(13)	0.0159(15)	0.0398(21)	0.0340(20)	−0.000(3)	−0.002(3)	0.074(3)

	x	*y*	*z*	*B*/Å²		*x*	*y*	*z*	*B*/Å²
H(121)	0.1777(8)	−0.2779(8)	0.4133(9)	5.0000(11)	H(242)	0.5110(7)	0.6983(8)	0.6697(8)	5.0000(8)
H(122)	0.2973(8)	−0.2924(8)	0.4765(9)	5.0000(11)	H(251)	0.4732(8)	0.8716(8)	0.8518(9)	5.0000(10)
H(131)	0.1536(8)	−0.4520(8)	0.1859(9)	5.0000(11)	H(252)	0.5936(8)	0.9452(8)	0.8550(9)	5.0000(10)
H(132)	0.1844(8)	−0.5247(8)	0.2851(9)	5.0000(11)	H(321)	−0.0887(8)	0.3710(11)	0.3820(13)	5.0000(7)
H(141)	0.4484(7)	−0.2047(8)	0.3795(10)	5.0000(8)	H(322)	−0.1707(8)	0.2032(11)	0.3102(13)	5.0000(7)
H(142)	0.4044(7)	−0.1417(8)	0.2755(10)	5.0000(8)	H(331)	−0.1796(8)	0.4154(13)	0.2583(13)	5.0000(7)
H(151)	0.4003(8)	−0.3880(9)	0.1512(10)	5.0000(9)	H(332)	−0.2742(8)	0.2750(13)	0.2323(13)	5.0000(7)
H(152)	0.2782(8)	−0.3713(9)	0.1093(10)	5.0000(9)	H(341)	−0.0165(9)	0.1986(12)	0.0677(11)	5.0000(9)
H(221)	0.6020(7)	0.6392(7)	0.9644(8)	5.0000(9)	H(342)	−0.1077(9)	0.0541(12)	0.0402(11)	5.0000(9)
H(222)	0.4763(7)	0.5800(7)	0.9550(8)	5.0000(9)	H(351)	−0.2034(8)	0.1058(12)	−0.0657(12)	5.0000(8)
H(231)	0.5676(7)	0.8282(8)	1.1336(8)	5.0000(8)	H(352)	−0.1208(8)	0.2736(12)	0.0080(12)	5.0000(8)
H(232)	0.4579(7)	0.8110(8)	1.0161(8)	5.0000(8)	H(1)	0.8779(13)	0.7790(15)	0.2757(14)	5.0000(18)
H(241)	0.6252(7)	0.7164(8)	0.7808(8)	5.0000(8)	H2	0.9825(13)	0.8792(15)	0.2689(14)	5.0000(18)

(*b*) For (II)

Atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	0.2451(1)	0.2269(1)	0.4870(1)	0.0072(1)	0.0104(1)	0.0084(1)	0.0035(2)	0.0033(2)	0.0080(2)
Cl(1)	0.8418(3)	0.8376(3)	0.1273(4)	0.0156(4)	0.0319(5)	0.0503(6)	0.0013(7)	−0.0111(8)	0.0492(7)
Cl(2)	0.9562(3)	0.6432(3)	0.1421(3)	0.0258(4)	0.0312(5)	0.0297(5)	0.0277(7)	0.0089(8)	0.0216(8)
S(11)	0.2020(2)	−0.0008(2)	0.4967(2)	0.0108(2)	0.0133(3)	0.0149(3)	0.0057(4)	0.0124(4)	0.0116(4)
S(12)	0.3630(2)	0.0795(2)	0.3843(2)	0.0085(2)	0.0126(3)	0.0131(3)	0.0039(4)	0.0057(4)	0.0144(4)
S(21)	0.3517(2)	0.3647(2)	0.7315(2)	0.0077(2)	0.0111(2)	0.0094(2)	0.0017(4)	0.0029(3)	0.0117(3)
S(22)	0.3631(2)	0.4584(2)	0.5339(2)	0.0091(2)	0.0120(3)	0.0084(2)	0.0043(4)	0.0044(4)	0.0104(3)
S(31)	0.0657(2)	0.2837(2)	0.4927(2)	0.0091(2)	0.0183(3)	0.0074(2)	0.0093(4)	0.0047(4)	0.0095(4)
S(32)	0.1332(2)	0.1530(2)	0.2544(2)	0.0083(2)	0.0171(3)	0.0083(2)	0.0106(4)	0.0052(4)	0.0094(4)
O(1)	0.2990(5)	−0.4711(5)	0.2233(6)	0.0166(7)	0.0165(7)	0.0226(8)	0.017(1)	0.0097(13)	0.0194(12)
O(2)	0.6072(4)	0.9120(5)	1.0243(5)	0.0113(5)	0.0111(7)	0.0106(6)	0.003(1)	0.0084(9)	0.0078(9)
O(3)	−0.2354(4)	0.2488(5)	0.0661(5)	0.0129(6)	0.0224(7)	0.0142(7)	0.022(1)	0.0054(11)	0.0147(11)
N(1)	0.3063(5)	−0.1754(6)	0.3709(6)	0.0088(6)	0.0154(8)	0.0149(8)	0.010(1)	0.010(1)	0.018(1)
N(2)	0.4943(5)	0.6211(6)	0.8061(5)	0.0074(5)	0.0096(7)	0.0083(6)	0.003(1)	0.007(1)	0.007(1)
N(3)	−0.0568(5)	0.2153(6)	0.2340(6)	0.0092(5)	0.0269(10)	0.0109(7)	0.023(1)	0.009(1)	0.018(1)
C(11)	0.2913(6)	−0.0467(7)	0.4125(7)	0.0074(7)	0.0095(9)	0.0104(9)	0.008(1)	0.003(1)	0.007(1)
C(12)	0.2614(8)	−0.2816(8)	0.4079(8)	0.0164(10)	0.0174(11)	0.0178(10)	0.011(2)	0.014(2)	0.023(2)
C(13)	0.2179(8)	−0.4358(8)	0.2837(8)	0.0158(11)	0.0136(10)	0.0214(11)	0.007(2)	0.007(2)	0.024(1)
C(14)	0.3818(7)	−0.2204(8)	0.2987(9)	0.0089(8)	0.0162(11)	0.0225(12)	0.009(2)	0.006(2)	0.022(2)
C(15)	0.3307(8)	−0.3763(9)	0.1775(9)	0.0124(9)	0.0198(12)	0.0209(14)	0.017(2)	0.010(2)	0.016(2)
C(21)	0.4155(6)	0.4997(6)	0.7057(6)	0.0059(6)	0.0057(7)	0.0085(8)	0.003(1)	0.004(1)	0.007(1)
C(22)	0.5357(7)	0.6575(7)	0.9520(7)	0.0111(9)	0.0107(9)	0.0077(8)	0.006(1)	0.001(1)	0.009(1)
C(23)	0.5390(7)	0.8081(8)	1.0435(7)	0.0131(9)	0.0140(10)	0.0079(8)	0.009(2)	0.010(1)	0.009(1)
C(24)	0.5578(6)	0.7280(8)	0.7810(7)	0.0081(7)	0.0137(10)	0.0099(9)	0.002(2)	0.007(1)	0.010(1)
C(25)	0.5615(7)	0.8783(7)	0.8851(7)	0.0135(9)	0.0107(9)	0.0108(9)	0.007(2)	0.010(1)	0.011(1)
C(31)	0.0372(6)	0.2189(7)	0.3185(7)	0.0074(7)	0.0087(9)	0.0099(9)	0.006(1)	0.005(1)	0.005(1)

TABLE 1 (*Continued*)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(32)	−0.1470(8)	0.2582(10)	0.2784(9)	0.0191(10)	0.0463(17)	0.0160(11)	0.042(2)	0.020(2)	0.034(2)
C(33)	−0.2026(8)	0.3206(11)	0.2127(9)	0.0131(9)	0.0400(19)	0.0179(14)	0.028(2)	0.010(2)	0.019(3)
C(34)	−0.0886(8)	0.1476(9)	0.0817(8)	0.0186(9)	0.0430(15)	0.0094(9)	0.040(2)	0.012(2)	0.028(2)
C(35)	−0.1487(8)	0.2106(9)	0.0264(8)	0.0152(10)	0.0304(15)	0.0139(12)	0.023(2)	0.002(2)	0.018(2)
C	0.9278(10)	0.7992(11)	0.2214(10)	0.0193(14)	0.0389(19)	0.0211(13)	0.012(3)	0.011(2)	0.034(2)

	x	y	z	B/Å^2		x	y	z	B/Å^2
H(121)	0.1992(9)	0.7418(9)	0.4376(9)	5.0000(11)	H(242)	0.6370(7)	0.7295(8)	0.8027(8)	5.0000(8)
H(122)	0.3221(9)	0.7252(9)	0.4841(9)	5.0000(11)	H(251)	0.4823(8)	0.8852(9)	0.8532(8)	5.0000(10)
H(131)	0.1511(9)	0.5530(8)	0.2114(9)	5.0000(12)	H(252)	0.6085(8)	0.9522(9)	0.8637(8)	5.0000(10)
H(132)	0.1970(9)	0.4951(8)	0.3169(9)	5.0000(12)	H(321)	−0.1114(9)	0.3368(12)	0.3830(10)	5.0000(11)
H(141)	0.4512(8)	0.7889(9)	0.3676(10)	5.0000(9)	H(322)	−0.2003(9)	0.1743(12)	0.2676(10)	5.0000(11)
H(142)	0.4010(8)	0.8459(9)	0.2629(10)	5.0000(9)	H(331)	−0.1582(9)	0.4228(12)	0.2557(10)	5.0000(10)
H(151)	0.3874(8)	0.5966(10)	0.1348(10)	5.0000(10)	H(332)	−0.2750(9)	0.3170(12)	0.2352(10)	5.0000(10)
H(152)	0.2640(8)	0.6153(10)	0.1071(10)	5.0000(10)	H(341)	−0.1205(8)	0.0461(10)	0.0366(8)	5.0000(10)
H(221)	0.6117(8)	0.6388(8)	0.9693(8)	5.0000(11)	H(342)	−0.0118(8)	0.1734(10)	0.0678(8)	5.0000(10)
H(222)	0.4840(8)	0.5777(8)	0.9580(8)	5.0000(11)	H(351)	−0.1874(9)	0.1341(11)	−0.0755(9)	5.0000(11)
H(231)	0.5783(8)	0.8420(8)	1.1517(9)	5.0000(10)	H(352)	−0.1005(9)	0.2961(11)	0.0363(9)	5.0000(11)
H(232)	0.4651(8)	0.8222(8)	1.0364(9)	5.0000(10)	H(1)	0.9030(10)	0.8035(11)	0.3035(10)	5.0000(12)
H(241)	0.5241(7)	0.7046(8)	0.6836(8)	5.0000(8)	H2	1.0049(10)	0.8883(11)	0.2792(10)	5.0000(12)

(*c*) For (III)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.234 76(4)	0.225 48(5)	0.478 93(5)	0.006 73(3)	0.007 96(5)	0.008 23(5)	0.003 87(6)	0.003 92(6)	0.003 95(7)
Cl(1)	0.8240(3)	0.8225(3)	0.1054(4)	0.0194(4)	0.0409(5)	0.0546(6)	0.0016(7)	−0.0066(8)	0.0634(7)
Cl(2)	0.9412(3)	0.6350(3)	0.1338(3)	0.0313(4)	0.0342(5)	0.0248(5)	0.0334(7)	0.0148(7)	0.0145(8)
S(11)	0.1659(1)	−0.0055(2)	0.4682(2)	0.0087(1)	0.0098(2)	0.0133(2)	0.0032(3)	0.0085(3)	0.0068(3)
S(12)	0.3534(1)	0.0949(2)	0.4117(2)	0.0071(1)	0.0103(2)	0.0143(2)	0.0048(2)	0.0067(3)	0.0091(3)
S(21)	0.3407(1)	0.3525(2)	0.7204(2)	0.0079(1)	0.0092(2)	0.0094(2)	0.0022(2)	0.0033(2)	0.0078(2)
S(22)	0.3475(1)	0.4537(2)	0.5224(2)	0.0091(1)	0.0097(2)	0.0087(2)	0.0047(2)	0.0055(2)	0.0070(3)
S(31)	0.0785(1)	0.3004(2)	0.4891(2)	0.0090(1)	0.0129(2)	0.0075(2)	0.0091(3)	0.0055(2)	0.0040(3)
S(32)	0.1288(1)	0.1493(2)	0.2473(2)	0.0080(1)	0.0118(2)	0.0082(2)	0.0081(2)	0.0053(2)	0.0030(3)
O(1)	0.2928(5)	−0.4659(5)	0.2415(6)	0.0165(5)	0.0129(5)	0.0245(8)	0.0159(8)	0.0116(11)	0.0146(10)
O(2)	0.5952(4)	0.9014(4)	1.0053(4)	0.0123(4)	0.0089(5)	0.0124(5)	0.0024(8)	0.0080(8)	0.0031(8)
O(3)	−0.2342(4)	0.2475(5)	0.0639(5)	0.0109(4)	0.0220(7)	0.0139(6)	0.0182(8)	0.0037(9)	0.0093(10)
H(1)	0.2843(4)	−0.1790(5)	0.3736(6)	0.0098(5)	0.0110(6)	0.0170(7)	0.0086(8)	0.0082(9)	0.0127(10)
N(2)	0,4814(4)	0.6121(5)	0.7914(5)	0.0080(4)	0.0100(6)	0.0098(5)	0.0041(8)	0.0048(8)	0.0080(8)
N(3)	−0.0520(4)	0.2264(5)	0.2316(5)	0.0101(4)	0.0160(5)	0.0092(6)	0.0161(8)	0.0064(8)	0.0063(10)
C(11)	0.2703(5)	−0.0488(6)	0.4135(6)	0.0073(5)	0.0088(7)	0.0109(7)	0.0037(9)	0.0015(10)	0.005(1)
C(12)	0.2218(7)	−0.2955(7)	0.3916(8)	0.0149(8)	0.0145(8)	0.0173(9)	0.0124(13)	0.0111(14)	0.015(1)
C(13)	0.1983(7)	−0.4421(7)	0.2687(9)	0.0168(9)	0.0096(8)	0.0215(12)	0.0052(14)	0.0098(17)	0.011(2)
C(14)	0.3763(6)	−0.2074(8)	0.3309(9)	0.0095(6)	0.0144(9)	0.0267(13)	0.0101(12)	0.0079(15)	0.014(2)
C(15)	0.3423(6)	−0.3584(8)	0.2109(9)	0.0119(6)	0.0171(10)	0.0289(14)	0.0167(12)	0.0168(15)	0.016(2)
C(21)	0.4016(5)	0.4901(6)	0.6925(6)	0.0064(4)	0.0075(6)	0.0098(6)	0.0053(8)	0.0049(9)	0.005(1)
C(22)	0.5217(6)	0.6439(6)	0.9371(6)	0.0105(6)	0.0104(7)	0.0097(7)	0.0040(11)	0.0030(11)	0.007(1)
C(23)	0.5310(6)	0.7984(7)	1.0314(7)	0.0116(6)	0.0114(8)	0.0113(7)	0.0066(12)	0.0077(11)	0.008(1)
C(24)	0.5424(6)	0.7220(7)	0.7618(6)	0.0105(6)	0.0104(7)	0.0125(7)	0.0030(11)	0.0100(10)	0.009(1)
C(25)	0.5477(6)	0.8714(7)	0.8660(7)	0.0128(6)	0.0092(7)	0.0172(9)	0.0060(11)	0.0135(12)	0.012(1)
C(31)	0.0369(5)	0.2253(6)	0.3107(6)	0.0072(4)	0.0088(7)	0.0095(7)	0.0066(9)	0.0041(9)	0.003(1)
C(32)	−0.1324(7)	0.2860(10)	0.2857(8)	0.0226(7)	0.0504(14)	0.0150(9)	0.0557(13)	0.0219(13)	0.027(2)
C(33)	−0.2027(7)	0.3077(11)	0.2071(9)	0.0157(6)	0.0578(18)	0.0144(11)	0.0481(14)	0.0104(14)	0.014(2)
C(34)	−0.0838(7)	0.1604(9)	0.0805(7)	0.0193(7)	0.0379(13)	0.0081(8)	0.0378(14)	0.0101(13)	0.015(2)
C(35)	−0.1606(7)	0.1895(11)	0.0142(9)	0.0186(7)	0.0596(19)	0.0108(10)	0.0495(16)	0.0098(14)	0.016(2)
C	0.9056(8)	0.7909(12)	0.2054(10)	0.0114(9)	0.0521(22)	0.0242(13)	0.0043(24)	0.0036(18)	0.042(2)

	x	y	z	B/Å^2		x	y	z	B/Å^2
H(121)	0.1515(6)	−0.2799(7)	0.3991(7)	5.0000(7)	H(242)	0.6177(5)	0.7171(6)	0.7711(6)	5.0000(5)
H(122)	0.2648(6)	−0.2929(7)	0.4788(7)	5.0000(7)	H(251)	0.4724(6)	0.8770(6)	0.8508(7)	5.0000(6)
H(131)	0.1475(7)	−0.4490(7)	0.1840(8)	5.0000(8)	H(252)	0.5926(6)	0.9469(6)	0.8500(7)	5.0000(6)
H(132)	0.1631(7)	−0.5209(7)	0.2883(8)	5.0000(8)	H(321)	−0.0871(6)	0.3883(10)	0.3678(8)	5.0000(6)
H(141)	0.4347(6)	−0.1966(7)	0.4110(9)	5.0000(6)	H(322)	−0.1663(6)	0.2249(10)	0.3198(8)	5.0000(6)
H(142)	0.4045(6)	−0.1343(7)	0.3007(9)	5.0000(6)	H(331)	−0.1851(6)	0.4138(10)	0.2442(9)	5.0000(6)
H(151)	0.4079(6)	−0.3777(8)	0.1892(9)	5.0000(6)	H(332)	−0.2721(6)	0.2682(10)	0.2236(9)	5.0000(6)
H(152)	0.2890(6)	−0.3650(8)	0.1280(9)	5.0000(6)	H(341)	−0.1043(7)	0.0534(9)	0.0423(7)	5.0000(7)
H(221)	0.5950(6)	0.6314(6)	0.9592(6)	5.0000(6)	H(342)	−0.0160(7)	0.1967(9)	0.0608(7)	5.0000(7)
H(222)	0.4699(6)	0.5751(6)	0.9529(6)	5.0000(6)	H(351)	−0.2016(6)	0.1029(13)	−0.0866(14)	5.0000(4)
H(231)	0.5646(6)	0.8219(7)	1.1303(6)	5.0000(6)	H(352)	−0.1239(7)	0.2590(11)	−0.0148(8)	5.0000(7)
H(232)	0.4561(6)	0.8070(7)	1.0155(6)	5.0000(6)	H(1)	0.8721(8)	0.7836(12)	0.2748(9)	5.0000(8)
H(241)	0.5042(5)	0.7024(6)	0.6649(6)	5.0000(5)	H2	0.9740(8)	0.8764(12)	0.2545(9)	5.0000(8)

* The form of the anisotropic thermal parameter is: $\exp[-(B_{11}{}^*h^{*2}h + B_{22}{}^*k^{*2}k + B_{33}{}^*l^{*2}l + B_{12}{}^*h^*k + B_{13}{}^*h^*l + B_{23}{}^*k^*l)]$.

raw intensity data were corrected for Lorentz and polarisation effects, but not for absorption. Of 3 040 and 4 061 (II) independent intensities 2 218 and 2 062 had $F_o^2 > 2\sigma(F_o^2)$, while for (III) 3 529 of the 4 791 independent intensities had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics as detailed in ref. 5. These data were used in the final refinement of the structure parameters.

Refinement of the Structures.—Full-matrix least-squares

[5] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

refinement was based on F, and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where weights w were taken as $[2F_o/\sigma(F_o^2)]^2$. Atomic scattering factors for non-hydrogen were taken from ref. 6 and for hydrogen from ref. 7. The effects of anomalous dispersion were included in F_c ($\Delta f'$, $\Delta f''$).[8] The weighted agreement factor is defined as $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

To minimise computer time, the initial calculations were carried out on the first 1 000 reflections collected on each compound. For (I) and (II), the metal and sulphur atoms were inserted and refined at the calculated positions of the corresponding atoms in the known structure (IV) with which these complexes are approximately isomorphous.[3] For (III), the metal atom alone was initially inserted at the calculated position. Remaining non-hydrogen atoms were added subsequently, with further refinement. Remaining diffraction data were added to the calculations, anisotropic temperature factors were introduced, and hydrogen atoms inserted as fixed atoms at the tetrahedral positions in the methylene carbons, with isotropic temperature factors of 5.0, assuming C–H 1.00 Å. After convergence, hydrogen atoms were inserted at their new calculated positions. The model converged with R 4.3, R' 4.8% for (I), R 4.0, R' 3.6% for (II), and R 4.3, R' 4.8% for (III). The error in an observation of unit weight is 1.35 (I), 0.892 (II), and 1.78 (III). A structure-factor calculation with all observed and unobserved reflections included (no refinement) gave R 7.1 (I), 6.2 (II), and 4.8% (III); on this basis, it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

TABLE 2

Bond distances (Å)

	(I)	(II)	(III)
M–S(11)	2.417(3)	2.486(3)	2.382(2)
M–S(12)	2.397(3)	2.529(3)	2.352(2)
M–S(21)	2.407(3)	2.385(3)	2.375(1)
M–S(22)	2.407(3)	2.447(3)	2.371(1)
M–S(31)	2.419(3)	2.534(3)	2.382(2)
M–S(32)	2.386(3)	2.385(3)	2.353(1)
S(11)–C(11)	1.694(10)	1.693(11)	1.713(6)
S(12)–C(11)	1.720(9)	1.713(11)	1.710(5)
S(21)–C(21)	1.739(8)	1.729(9)	1.705(5)
S(22)–C(21)	1.688(8)	1.733(9)	1.719(5)
S(31)–C(31)	1.701(9)	1.709(10)	1.717(5)
S(32)–C(31)	1.697(9)	1.709(10)	1.723(5)
C(11)–N(1)	1.357(9)	1.327(10)	1.331(6)
N(1)–C(12)	1.467(11)	1.469(13)	1.462(7)
N(1)–C(14)	1.468(12)	1.451(14)	1.456(8)
C(12)–C(13)	1.538(13)	1.518(15)	1.505(8)
C(13)–O(1)	1.410(13)	1.419(15)	1.407(8)
C(14)–C(15)	1.504(13)	1.517(15)	1.498(9)
C(15)–O(1)	1.390(12)	1.390(15)	1.408(8)
C(21)–N(2)	1.338(9)	1.311(10)	1.334(6)
N(2)–C(22)	1.449(10)	1.464(10)	1.463(6)
N(2)–C(24)	1.493(10)	1.477(11)	1.482(6)
C(22)–C(23)	1.505(10)	1.484(12)	1.501(7)
C(23)–O(2)	1.425(10)	1.438(12)	1.421(7)
C(24)–C(25)	1.510(11)	1.516(12)	1.509(7)
C(25)–O(2)	1.415(10)	1.407(10)	1.413(7)
C(31)–N(3)	1.350(9)	1.350(10)	1.314(6)
N(3)–C(32)	1.457(13)	1.463(15)	1.471(8)
N(3)–C(34)	1.478(12)	1.470(12)	1.455(7)
C(32)–C(33)	1.285(14)	1.381(15)	1.258(9)
C(33)–O(3)	1.387(13)	1.410(14)	1.380(3)
C(34)–C(35)	1.259(12)	1.347(14)	1.289(9)
C(35)–O(3)	1.361(13)	1.382(14)	1.363(7)
C–Cl(1)	1.550(13)	1.603(14)	1.563(9)
C–Cl(2)	1.686(17)	1.687(16)	1.730(12)

A final Fourier-difference map was featureless. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21497 (35 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Final positional and thermal parameters for the atoms are given in Table 1, and bond lengths and angles in Tables 2 and 3. The estimated standard deviations were derived from the inverse matrix in the course of least-squares refinement calculations. The labelling system of the atoms is as indicated for one of the ligands in Figure 1.

TABLE 3

Bond angles (°)

	(I)	(II)	(II)
S(11)–M–S(12)	73.7(1)	71.1(1)	73.5(1)
S(21)–M–S(22)	73.9(1)	73.3(1)	73.5(1)
S(31)–M–S(32)	73.8(1)	72.3(1)	73.6(1)
S(11)–M–S(21)	93.2(1)	90.7(1)	96.3(1)
S(11)–M–S(31)	97.3(1)	99.5(1)	97.9(1)
S(21)–M–S(31)	97.8(1)	98.8(1)	99.5(1)
S(12)–M–S(22)	94.2(1)	95.4(1)	95.8(1)
S(12)–M–S(32)	90.0(1)	87.6(1)	93.4(1)
S(22)–M–S(32)	95.0(1)	94.9(1)	96.8(1)
S(11)–M–S(32)	99.9(1)	103.7(1)	94.7(1)
S(12)–M–S(21)	100.3(1)	103.8(1)	94.9(1)
S(22)–M–S(31)	98.7(1)	100.3(1)	95.0(1)
S(11)–M–S(22)	160.6(1)	156.2(1)	164.8(1)
S(21)–M–S(32)	165.2(1)	164.0(1)	167.8(1)
S(12)–M–S(31)	160.1(1)	155.4(1)	164.0(1)
M–S(11)–C(11)	85.3(3)	86.4(3)	86.9(3)
M–S(12)–C(11)	85.4(3)	84.6(3)	87.9(3)
M–S(21)–C(21)	84.9(3)	87.9(3)	87.3(3)
M–S(22)–C(21)	86.0(3)	85.9(3)	87.1(3)
M–S(31)–C(31)	84.4(3)	83.3(3)	87.3(3)
M–S(32)–C(31)	85.5(3)	88.1(3)	88.1(3)
S(11)–C(11)–S(12)	115.5(5)	117.7(6)	111.7(3)
S(11)–C(11)–N(1)	123.7(8)	121.4(9)	124.7(5)
S(12)–C(11)–N(1)	120.9(8)	120.9(9)	123.6(5)
C(11)–N(1)–C(12)	122.2(9)	124(1)	123.4(6)
C(11)–N(1)–C(14)	122.7(9)	124(1)	121.8(5)
C(12)–N(1)–C(14)	114.8(8)	112(1)	114.0(5)
N(1)–C(12)–C(13)	109.8(9)	111(1)	110.2(6)
C(12)–C(13)–O(1)	112.3(9)	112(1)	112.8(6)
N(1)–C(14)–C(15)	110.9(9)	112(1)	110.7(6)
C(14)–C(15)–O(1)	112(1)	111(1)	111.8(7)
C(13)–O(1)–C(15)	110.9(8)	110(1)	109.2(5)
S(21)–C(21)–S(22)	115.2(5)	112.9(6)	112.1(3)
S(21)–C(21)–N(2)	120.4(7)	123.4(8)	123.9(4)
S(22)–C(21)–N(2)	124.4(7)	123.7(8)	124.1(4)
C(21)–N(2)–C(22)	125.1(8)	123.5(9)	122.9(4)
C(21)–N(2)–C(24)	121.9(7)	123.2(9)	123.0(4)
C(22)–N(2)–C(24)	112.8(7)	113.1(8)	113.9(4)
N(2)–C(22)–C(23)	111.1(7)	109.3(8)	109.8(5)
C(22)–C(23)–O(2)	111.9(8)	111.7(9)	112.3(5)
N(2)–C(24)–C(25)	107.1(8)	108.0(9)	108.1(5)
C(24)–C(25)–O(2)	113.3(8)	112.6(8)	112.3(5)
C(23)–O(2)–C(25)	109.1(7)	108.9(8)	109.6(4)
S(31)–C(31)–S(32)	116.2(5)	116.3(6)	111.0(3)
S(31)–C(31)–N(3)	121.6(7)	122.7(8)	125.2(4)
S(32)–C(31)–N(3)	122.1(8)	121.1(8)	123.8(4)
C(31)–N(3)–C(32)	124.2(9)	124(1)	123.5(5)
C(31)–N(3)–C(34)	123.0(9)	124(1)	123.0(5)
C(32)–N(3)–C(34)	112.6(9)	111.3(9)	113.4(5)
N(3)–C(32)–C(33)	117(1)	115(1)	118.0(8)
C(32)–C(33)–O(3)	125(1)	117(1)	127.4(7)
N(3)–C(34)–C(35)	118(1)	114(1)	118.5(6)
C(34)–C(35)–O(3)	127(1)	121(1)	126.6(7)
C(33)–O(3)–C(35)	111.3(9)	110(1)	111.8(5)
Cl(1)–C–Cl(2)	120.6(9)	118.5(9)	118.3(6)

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Figures 1 and 2 are stereoscopic pairs for the molecular structure of (II) and for the molecular packing in the unit cell. The structures of the other two molecules conform closely to this except for specific differences now discussed. Although there is only one molecule of dichloromethane per molecule of metal complex, the approach of the solvent molecules to the complex is shown by inclusion of the three nearest solvent molecules in Figure 1. As is evident from the packing diagram (Figure 2) and from the nearest intermolecular contact distances (Table 4), the crystal structures consist of well separated molecules of the metal complex with solvent molecules fitting into 'crystallographic holes' in the lattice.

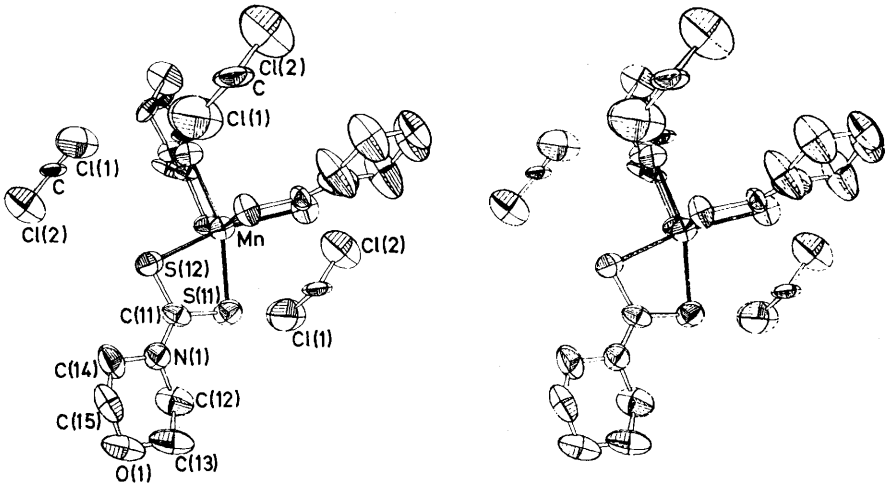

FIGURE 1

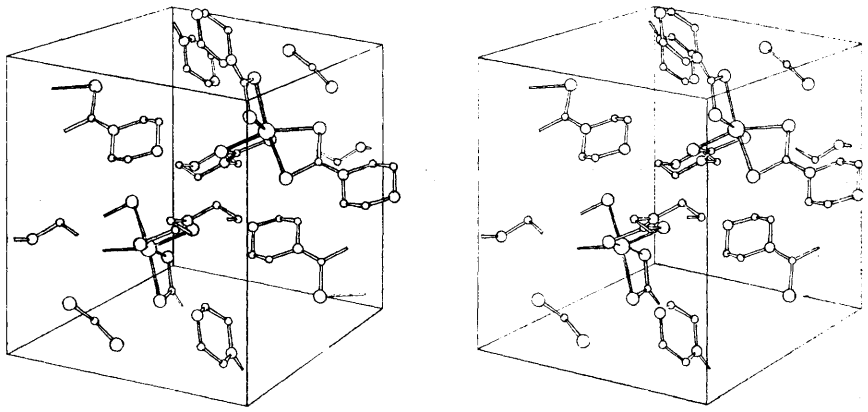

FIGURE 2

TABLE 4

Intermolecular distances (Å)

	(I)	(II)	(III)
S(11) · · · C	3.60(1)	3.63(2)	3.546(8)
S(12)–C(14)	3.72(1)	3.75(1)	3.673(7)
C(12)–C(24)	3.564(9)	3.56(1)	3.568(6)
S(12)–C(25)	3.69(1)	3.64(1)	3.758(7)
S(31)–C	3.79(2)	3.75(1)	3.889(9)
S(32)–C(34)	3.62(1)	3.60(1)	3.597(7)
Cl(1)–C(22)	3.78(1)	3.70(1)	3.745(6)
Cl(1)–O(2)	3.430(8)	3.375(8)	3.388(5)
Cl(1)–C(31)	3.807(9)	3.73(1)	3.975(6)
Cl(1)–N(3)	3.662(9)	3.58(1)	3.775(6)
Cl(1)–C(34)	3.70(2)	3.61(2)	3.70(1)
C(15)–C(22)	3.70(1)	3.70(2)	3.821(9)
C(15)–O(3)	3.71(1)	3.68(2)	3.809(9)
O(1)–C(21)	3.85(1)	3.72(1)	4.053(7)
O(1)–N(2)	3.46(1)	3.40(1)	3.672(7)
O(1)–C(22)	3.61(1)	3.58(2)	3.830(8)
O(1)–C(24)	3.63(1)	3.61(1)	3.807(7)
C(21)–C(33)	3.80(1)	3.74(2)	3.809(9)
C(23)–O(3)	3.71(1)	3.70(1)	3.735(8)
C(25)–O(3)	3.80(1)	3.69(1)	3.813(7)
O(2)–O(3)	3.59(1)	3.62(1)	3.625(6)

The metal–ligand co-ordination sphere MS_6, in each of the five morpholinodithiocarbamato-complexes of known structure approximates a trigonally distorted octahedron. Complex (II) deviates most significantly from this model with uneven Mn–S bond lengths. Since this tetragonal distortion is not observed in any of the complexes with spherically symmetrical ground states (Co, Rh, or Cr), it can only be attributed to Jahn–Teller distortion. Pure trigonal distortion cannot lift the degeneracy of the e_g orbitals, but this is evidently achieved by elongation of one pair of Mn–S bonds on opposite sides of the metal atom (conventionally the z axis). The mean bond length in the z direction is 2.532 Å, longer by 0.11 Å than that in the (approximate) xy plane. In addition to the tetragonal distortion,

there is a further, though smaller, axial distortion in the *xy* plane, with a difference of 0.08 Å in the mean bond lengths along the two axes. This will have the effect of removing the degeneracy of the d_{xz} and d_{yz} orbitals, which is not however required by the Jahn–Teller theorem. The t_{2g} degeneracy will already have been partially removed by the tetragonal distortion (as well as the trigonal) which lifts the d_{xy} orbital above the other two, so that even in the absence of any trigonal distortion, the axial bond-length distortions will ensure that no two of the *d* orbitals will have the same energies.

The mean metal–ligand (M–L) bond length increases vertically downwards in the Periodic Table as expected for the two metals with d^6 configurations: means, Co–S 2.275 and Rh–S 2.369 Å. Within the same transition series, the M–L distance increases with increasing unpaired-electron occupancy in the *d* shell: means, Cr–S (d^3) 2.406, Mn–S (d^4) 2.461, and Fe–S 2.430 Å. The apparently anomalous placement of the iron(III) is due to the spin-state crossover in this system which is therefore partially spin-paired at room temperature. The half-filled t_{2g}^3 subshell in the chromium complex dramatically lengthens (0.13 Å) the M–L distance over that observed for the filled t_{2g}^6 configuration in the Co complex (IV). The ' bite ' angle S–M–S of the ligand is approximately correlated with the M–L distance, and appears to be quite independent of other factors such as tetragonal or trigonal distortion or packing effects as far as can be determined from literature data.[3]

The mean interatomic angles in the MS_6 co-ordination sphere define the trigonality of the complexes and are given in Table 5, where $\delta = \langle S_{i1}\text{–}M\text{–}S_{i2}\rangle$, $\zeta = \langle S_{i1}\text{–}M\text{–}S_{j1}\rangle$ and $\langle S_{i2}\text{–}M\text{–}S_{j2}\rangle$, $\zeta' = \langle S_{i1}\text{–}M\text{–}S_{j2}\rangle$, and $\gamma = \langle S_{i1}\text{–}M\text{–}S_{j2}\rangle$; δ is the ligand ' bite,' ζ and ζ' are the angles between *cis*-pairs of metal–ligand bonds, and γ is the angle between *trans*-bonds. In an ideal octahedron, $\delta = \zeta = \zeta' = 90°$ and $\gamma = 180°$.

TABLE 5

Mean interatomic angles (°) within the MS_6 polyhedron

	δ	ζ	γ	ζ'
Cr	73.8	94.6	162.0	99.6
Mn	72.2	94.5	158.5	102.6
Fe	72.6	93.6	157.3	104.5
Co	76.1	94.2	165.4	97.1
Rh	73.5	96.6	165.5	94.8

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