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# Metal(III) Compounds of Potentially Septadentate [$N_4O_3$] Ligands. Part II.[a] Crystal and Molecular Structures of [$M(C_{27}H_{24}Cl_3N_4O_3)$]·$3H_2O$ (M = Cr, Mn)

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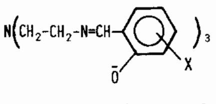
*The three-dimensional X-ray structural analyses are reported of the chromium(III) and manganese(III) compounds of the trianionic Schiff base ligand derived from tris(2-aminoethyl)amine and three mol of 5-chlorosalicylaldehyde. Both are isomorphous with the previously reported* $Fe^{III}$ *compound: space group* Ia*3 (No. 206) a = 22.521(2) Å [Cr], and 22.490 Å [Mn]. Data were collected by diffractometer {958 independent reflections for Cr (Cu-Kα radiation), and 852 for Mn (Mo-Kα radiation)}, and the structures were refined by block-diagonal least-squares to final Rs of 0.072 [Cr] and 0.050 [Mn]. Both are essentially octahedral [*$M(N_3O_3)$*] species, lying on three-fold crystallographic axes, and the Mn compound provides an unusual example of an undistorted octahedral* $d^4$ *system. Bond-lengths in the co-ordination polyhedra are: Cr–O 1.979(6), Cr–N 2.137(7), Mn–O 1.965(3), and Mn–N 2.137(4) Å. Non-bonded metal to apical (tertiary) nitrogen distances are hardly different from that found in the isomorphous* $Fe^{III}$ *compound: M–N = [Cr] 3.229(8), [Mn] 3.229(4), and [Fe] 3.260(4) Å.*

## Introduction

We have previously described [1, 2] the preparations and properties of a number of metal(III) compounds of the potentially septadentate ligands (I).



I

An X-ray analysis of the structure of the iron(III) compounds of I with X = 5-Cl was also reported.

The structures of the isomorphous manganese(III) and chromium(III) compounds have now been studied to ascertain if any changes occurred in the M–N (apical) distances, which could perhaps be correlated with bonding/antibonding interactions between these atoms. Additionally, the study provides comparative structural data for compounds of these metals.

## Experimental

### *Mn*

Dark green crystals were obtained from DMF. The crystal used had dimensions 0.18 × 0.30 × 0.35 mm.

#### *Crystal data*

$C_{27}H_{30}N_4O_6Cl_3Mn$, $M$ = 667.9, Cubic, $a$ = 22.490(2) Å at 18C, $U$ = 11375 Å$^3$, $Z$ = 16, $F(000)$ = 5504. Space group $Ia3$ (No. 206). Mo-Kα radiation, $\lambda$ = 0.7107 Å, $\mu$(Mo-Kα) = 8.61 cm$^{-1}$.

Data were collected on a Syntex $P2_1$ diffractometer, with graphite-monochromatised Mo-Kα radiation, to $2\theta_{max}$ of 60° at scan rates between 1° and 29.3° min$^{-1}$, depending on the intensity of a 2 s prescan, and with a scan width of ±0.4° ($2\theta$ around $\alpha_1$–$\alpha_2$). A set of 3227 reflections was collected ($+h \leqslant +k \leqslant +l$) and averaged to give 852 observed reflections ($I/\sigma I > 3.0$). They were corrected for Lorentz, polarisation and absorption effects.

The fractional co-ordinates found for the isomorphous iron compound [1] were used to start the refinement. Block-diagonal least-squares refinement reduced R to 0.110 with isotropic thermal parameters and 0.066 with anisotropic parameters. Hydrogen atoms were then inserted in calculated fixed positions, 0.98 Å from the appropriate carbons, and given fixed isotropic thermal parameters of 5.0 Å$^2$. This reduced R to 0.050.

For the final stages of refinement, anomalous dispersion corrections (both Δf′ and Δf″) were applied,

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[a] Part I – ref. 1.

TABLE I. Atomic Positions. Estimated standard deviations are in parentheses.

*Mn*

*Atomic positions ($\times 10^4$) of the non-hydrogen atoms*

| *Atom* | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Mn | 1375.4(5) | 1375.4(5) | 1375.4(5) |
| Cl | 1878(1) | 4004(1) | −529(1) |
| N(1) | 546(3) | 546(3) | 546(3) |
| N(2) | 1517(3) | 1366(3) | 436(3) |
| O(1) | 1421(2) | 2247(2) | 1336(2) |
| O(2) | 2461(3) | 1505(2) | 2865(2) |
| C(1) | 908(4) | 557(4) | 16(4) |
| C(2) | 1539(4) | 777(3) | 142(3) |
| C(3) | 1640(3) | 1827(3) | 118(3) |
| C(4) | 1626(3) | 2440(3) | 298(3) |
| C(5) | 1514(3) | 2619(3) | 896(3) |
| C(6) | 1513(3) | 3236(3) | 1019(3) |
| C(7) | 1616(3) | 3648(4) | 584(3) |
| C(8) | 1726(3) | 3462(3) | 12(4) |
| C(9) | 1732(3) | 2873(3) | −138(3) |

*Hydrogen atom positions ($\times 10^3$)*[a]

| | | | |
|---|---|---|---|
| H(1) | 93 | 15 | −14 |
| H(1′) | 72 | 82 | −28 |
| H(2) | 175 | 49 | 40 |
| H(2′) | 177 | 81 | −23 |
| H(3) | 176 | 175 | −30 |
| H(6) | 144 | 337 | 144 |
| H(7) | 161 | 408 | 69 |
| H(9) | 181 | 274 | −56 |

*Cr*

*Atomic positions ($\times 10^4$) of the non-hydrogen atoms*

| *Atom* | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Cr | 1375.0(6) | 1375.0(6) | 1375.0(6) |
| Cl | 1880(1) | 4004(1) | −530(1) |
| N(1) | 547(3) | 547(3) | 547(3) |
| N(2) | 1514(3) | 1367(3) | 436(3) |
| O(1) | 1423(3) | 2251(3) | 1334(3) |
| O(2) | 2462(3) | 1508(3) | 2864(3) |
| C(1) | 909(5) | 558(4) | 19(5) |
| C(2) | 1543(5) | 785(4) | 149(4) |
| C(3) | 1639(4) | 1827(4) | 126(4) |
| C(4) | 1622(4) | 2446(4) | 308(4) |
| C(5) | 1514(3) | 2616(4) | 896(4) |
| C(6) | 1516(4) | 3230(4) | 1017(4) |
| C(7) | 1618(4) | 3641(4) | 590(4) |
| C(8) | 1726(4) | 3456(4) | 12(4) |
| C(9) | 1733(4) | 2870(4) | −137(4) |

*Hydrogen atom positions ($\times 10^3$)*[a]

| | | | |
|---|---|---|---|
| H(1) | 97(5) | 17(5) | −13(5) |
| H(1′) | 78(5) | 78(5) | −22(5) |
| H(2) | 177(5) | 55(5) | 42(5) |
| H(2′) | 175(5) | 79(5) | −22(5) |
| H(3) | 176(5) | 180(5) | −25(5) |
| H(6) | 147(5) | 331(5) | 140(5) |
| H(7) | 162(5) | 402(5) | 65(5) |
| H(9) | 181(5) | 272(5) | −50(5) |

[a] Hydrogen atom numbers are those of the carbons to which they are attached, with primes used to distinguish the pairs on the same carbon.

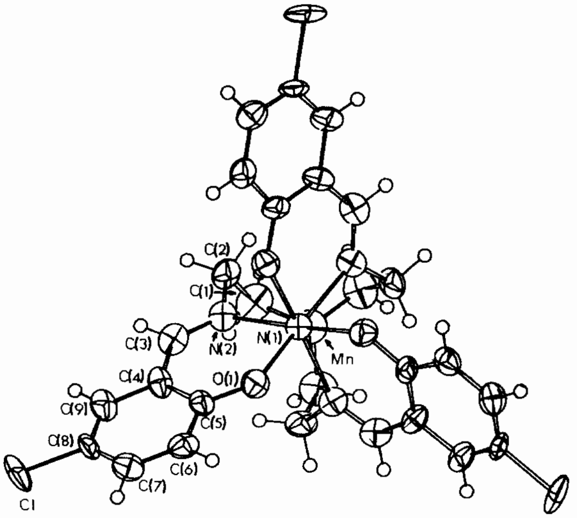


Fig. 1. Molecular geometry and the atom-labelling scheme.

and a non-unit weighting scheme was used. The latter was of the form:

$w = 1/\{1 + [(|F_o| - 30)/30]^2\}$, to give maximum weight to intermediate reflections

*Cr*

Brown crystals were obtained from DMF. The crystal used had dimensions 0.20 × 0.12 × 0.04 mm.

*Crystal data*

$C_{27}H_{30}N_4O_6Cl_3Cr$, $M$ = 664.9, Cubic, $a$ = 22.521(2) Å, $U$ = 11423 Å$^3$, $Z$ = 16, $F(000)$ = 5488. Space group $Ia3$ (No. 206). Cu-Kα radiation, λ = 1.5418 Å, μ(Cu-Kα) = 64.12 cm$^{-1}$.

Data were collected under conditions similar to those used for the Mn compound, except that $2\theta_{max}$ = 150° and a scan range of ±0.7° around $\alpha_1$–$\alpha_2$ were used. 2086 reflections were collected and averaged to give 958 observed reflections ($I/\sigma I > 3.0$). The same corrections were applied.

Block-diagonal least-squares refinement, using anisotropic thermal parameters for the non-hydrogen atoms, and fixed isotropic thermal parameters of 5.0 Å$^2$ for the hydrogens, reduced R to a final value of 0.072. Unit weights were used throughout. We attribute the higher R value here to the substantially greater absorption correction needed with Cu rather than Mo radiation.

TABLE II. Anisotropic Thermal Parameters ($\times 10^5$). Estimated standard deviations are in parentheses. The expression used for the temperature factor is $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12}]$.

| *Atom* | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{23}$ | $b_{13}$ | $b_{12}$ |
|---|---|---|---|---|---|---|
| *Mn* | | | | | | |
| Mn | 134(1) | 134(1) | 134(1) | −18(4) | −18(4) | −18(4) |
| Cl | 281(6) | 230(6) | 199(6) | 148(9) | −83(9) | −35(10) |
| N(1) | 216(12) | 216(12) | 216(12) | −32(28) | −32(28) | −32(28) |
| N(2) | 156(13) | 181(14) | 154(13) | −7(24) | −21(22) | −25(24) |
| O(1) | 212(12) | 172(11) | 133(10) | −11(19) | 5(21) | 14(21) |
| O(2) | 187(12) | 217(13) | 203(12) | −18(22) | −11(22) | 55(22) |
| C(1) | 248(21) | 243(21) | 186(18) | −105(37) | −40(37) | −52(38) |
| C(2) | 237(21) | 164(17) | 138(17) | −53(27) | 43(30) | 2(31) |
| C(3) | 161(16) | 201(18) | 128(15) | −50(29) | −35(26) | −37(30) |
| C(4) | 151(16) | 178(17) | 113(14) | 27(27) | −41(25) | −42(28) |
| C(5) | 93(14) | 174(17) | 160(15) | 59(27) | −32(24) | 1(25) |
| C(6) | 134(16) | 217(19) | 147(16) | −14(30) | −32(27) | 37(29) |
| C(7) | 186(17) | 187(18) | 181(17) | 0(32) | −42(29) | 15(32) |
| C(8) | 139(15) | 179(17) | 161(15) | 111(30) | −16(29) | 14(28) |
| C(9) | 169(17) | 222(19) | 115(15) | 41(28) | −58(27) | −14(31) |
| *Cr* | | | | | | |
| Cr | 128(2) | 128(2) | 128(2) | −20(5) | −20(5) | −20(5) |
| Cl | 275(7) | 222(6) | 189(6) | 148(10) | −86(11) | −33(11) |
| N(1) | 194(14) | 194(14) | 194(14) | −19(32) | −19(32) | −19(32) |
| N(2) | 171(17) | 177(16) | 151(16) | −28(29) | −7(27) | −42(30) |
| O(1) | 230(15) | 160(13) | 131(12) | −19(22) | 18(25) | −9(25) |
| O(2) | 188(15) | 228(17) | 220(17) | −2(28) | −5(27) | 33(28) |
| C(1) | 254(26) | 213(24) | 201(23) | −143(44) | −83(44) | −38(45) |
| C(2) | 251(26) | 195(23) | 145(21) | −42(36) | 42(38) | −1(41) |
| C(3) | 143(19) | 246(24) | 127(20) | 9(37) | −19(31) | −17(37) |
| C(4) | 129(18) | 174(20) | 158(19) | 10(34) | −14(32) | −10(33) |
| C(5) | 114(18) | 176(21) | 152(18) | 41(33) | −57(31) | −27(31) |
| C(6) | 186(22) | 220(24) | 134(19) | 8(35) | −17(34) | 26(38) |
| C(7) | 191(22) | 175(21) | 208(23) | 15(40) | −46(37) | 31(38) |
| C(8) | 158(20) | 221(23) | 168(20) | 129(39) | −73(37) | 19(37) |
| C(9) | 187(22) | 189(22) | 139(21) | −6(35) | −38(34) | 8(36) |

Atomic scattering factors for neutral atoms and correction parameters were taken from 'International Tables for X-ray Crystallography', Vol. IV. Observed structure amplitudes and the calculated structure factors are available from the Editor.

Principal programmes used for the refinement were part of the Sheffield X-ray system. Calculations were performed on the Sheffield University ICL1907 computer.

Final atomic positional and vibrational parameters are listed in Tables I and II, and the atom-labelling scheme is given in Fig. 1.

## Results and Discussion

The high-spin [1] chromium(III), manganese(III), and iron(III) compounds all have essentially the same molecular geometry, a view of which is shown in Fig. 1. The metal and N(1) atoms are on crystallographic $C_3$ axes, the asymmetric unit being one-third of the molecule. Details of the molecular geometries are in Tables III and IV.

The co-ordination polyhedra of the metal atoms are essentiallly [$MN_3O_3$] octahedra, with the fourth (apical) nitrogen atom being non-bonded. Observed interatomic distances for the latter are Cr–N(1) = 3.229(8), Mn–N(1) = 3.229(6), and Fe–N(1) = 3.260(4) Å.

The geometries of the [$MN_3O_3$] octahedra are close to the ideal for such a chelated system. The $N_3$ and $O_3$ equilateral triangles are mutually staggered by 62.2° (Cr), 62.5° (Mn) and 60.2° (Fe). Bond angles within the salicylaldiminate chelate rings {N(2)–M–O(1)} are 87.4° (Cr), 87.6° (Mn) and 85.6° (Fe). These latter, together with the non-chelate ring angles {N(2)–M–O($1^{I}$)} of near 85°, define a flattening of the octahedra along the $C_3$ axes. Perhaps the most significant distortions are in the {N(2)–M–N($2^{I}$)} non-chelate angles which are close to 98°.

TABLE III. Interatomic Distances (A) and Angles (°). Estimated standard deviations are in parentheses. The Roman numeral superscripts refer to atom positions as follows: I = *y, z, x*; II = *z, x, y*; III = ½ – *y*, ½ – *z*, ½ – *x*; IV = ½ – *z*, ½ – *x*, ½ – *y*.

| | *Cr* | *Mn* | *Fe* |
|---|---|---|---|
| *Co-ordination polyhedron* | | | |
| (i) *Bond lengths* | | | |
| M–N(1) | 3.229(8) | 3.229(4) | 3.260(4) |
| M–N(2) | 2.137(7) | 2.137(4) | 2.185(4) |
| M–O(1) | 1.979(6) | 1.965(3) | 1.953(3) |
| Cl(1)–C(8) | 1.771(10) | 1.756(8) | 1.768(8) |
| O(1)–C(5) | 1.30(1) | 1.31(1) | 1.31(1) |
| N(1)–C(1) | 1.44(1) | 1.44(1) | 1.44(1) |
| N(2)–C(2) | 1.46(1) | 1.48(1) | 1.49(1) |
| N(2)–C(3) | 1.28(1) | 1.29(1) | 1.28(1) |
| C(1)–C(2) | 1.54(1) | 1.53(1) | 1.54(1) |
| C(3)–C(4) | 1.45(1) | 1.44(1) | 1.45(1) |
| C(4)–C(5) | 1.40(1) | 1.42(1) | 1.40(1) |
| C(5)–C(6) | 1.42(1) | 1.41(1) | 1.41(1) |
| C(6)–C(7) | 1.35(1) | 1.37(1) | 1.37(1) |
| C(7)–C(8) | 1.39(1) | 1.38(1) | 1.37(1) |
| C(8)–C(9) | 1.36(1) | 1.37(1) | 1.37(1) |
| (ii) *Bond Angles* | | | |
| N(2)–M–N(2$^{\mathrm{I}}$) | 97.9(3) | 98.0(1) | 97.1(1) |
| N(2)–M–O(1) | 87.4(3) | 87.6(1) | 85.6(1) |
| N(2)–M–O(1$^{\mathrm{II}}$) | 173.7(2) | 173.6(1) | 176.2(1) |
| N(2)–M–O(1$^{\mathrm{I}}$) | 84.7(3) | 84.5(1) | 85.3(1) |
| O(1)–M–O(1$^{\mathrm{I}}$) | 89.7(2) | 89.7(1) | 92.0(1) |
| N(1)–M–N(2) | 60.6(3) | 60.6(1) | 59.9(1) |
| N(1)–M–O(1) | 125.5(3) | 125.5(1) | 123.9(1) |
| C(1)–N(1)–C(1$^{\mathrm{I}}$) | 118.1(7) | 118.0(4) | 117.8(4) |
| M–N(2)–C(2) | 116.8(5) | 117.1(2) | 116.4(3) |
| M–N(2)–C(3) | 124.4(4) | 124.9(3) | 125.7(3) |
| C(2)–N(2)–C(3) | 118.3(6) | 117.6(6) | 117.0(6) |
| M–O(1)–C(5) | 132.0(4) | 132.6(3) | 134.7(3) |
| N(1)–C(1)–C(2) | 111.7(7) | 112.0(5) | 112.2(5) |
| N(2)–C(2)–C(1) | 109.8(6) | 109.9(6) | 109.4(6) |
| N(2)–C(3)–C(4) | 128.1(6) | 127.5(7) | 125.6(7) |
| C(3)–C(4)–C(5) | 121.8(6) | 122.8(6) | 123.5(7) |
| C(3)–C(4)–C(9) | 116.5(7) | 117.7(6) | 115.9(7) |
| C(5)–C(4)–C(9) | 121.7(6) | 119.6(6) | 120.6(7) |
| C(4)–C(5)–C(6) | 116.4(6) | 117.6(6) | 117.9(7) |
| C(4)–C(5)–O(1) | 125.7(6) | 124.0(6) | 124.0(6) |
| C(6)–C(5)–O(1) | 117.9(6) | 118.4(6) | 118.1(6) |
| C(5)–C(6)–C(7) | 122.3(7) | 121.6(7) | 121.4(7) |
| C(6)–C(7)–C(8) | 119.3(7) | 119.5(7) | 118.8(7) |
| C(7)–C(8)–C(9) | 121.7(7) | 121.9(7) | 123.0(7) |
| C(7)–C(8)–Cl(1) | 118.1(6) | 118.2(6) | 117.9(6) |
| C(9)–C(8)–Cl(1) | 120.2(6) | 119.9(6) | 119.1(6) |
| C(8)–C(9)–C(4) | 118.7(7) | 119.8(7) | 118.3(7) |
| *The H-bonded system* | | | |
| (i) *Bond lengths* | | | |
| O(1)–O(2$^{\mathrm{I}}$) | 2.896(8) | 2.891(7) | 2.919(8) |
| O(1)–O(2$^{\mathrm{II}}$) | 3.303(8) | 3.305(7) | 3.313(8) |
| O(2)–O(2$^{\mathrm{III}}$) | 2.816(9) | 2.821(7) | 2.795(10) |
| O(2)–O(2$^{\mathrm{IV}}$) | 2.816(9) | 2.821(7) | 2.795(10) |

TABLE III. *(Continued)*

| | | | |
|---|---|---|---|
| (ii) *Bond angles* | | | |
| O(2$^{\mathrm{I}}$)–O(1)–M | 116.0(2) | 116.3(2) | 114.3(2) |
| O(2$^{\mathrm{I}}$)–O(1)–C(5) | 111.1(5) | 110.1(4) | 109.9(4) |
| O(1$^{\mathrm{I}}$)–O(2)–O(2$^{\mathrm{III}}$) | 85.5(3) | 85.6(2) | 85.8(2) |
| O(1$^{\mathrm{I}}$)–O(2)–O(2$^{\mathrm{IV}}$) | 123.6(2) | 123.4(2) | 124.1(2) |

TABLE IV. Equations to Some Least-Squares Planes. These are given in the form $lX + mY + nZ = d$ (where $X$, $Y$, and $Z$ are coordinates in A referred to the axes *a*, *b*, and *c*). Deviations (A) of the various atoms from these planes are given in square brackets. Primed atoms are at *y, z, x* and doubly primed atoms at *z, x, y*.

| | *l* | *m* | *n* | *d* |
|---|---|---|---|---|
| Plane (1): N(2), O(1), C(3)–C(9) | | | | |
| *Mn* | 0.9803 | –0.0486 | 0.1914 | 3.4341 |
| [Mn 0.040, Cl 0.041, C(2) –0.07, N(2) –0.05, O(1) 0.03, C(3) 0.03] | | | | |
| *Cr* | 0.9804 | –0.0507 | 0.1906 | 3.4270 |
| [Cr 0.042, Cl 0.039, C(2) –0.05, N(2) –0.05, O(1) 0.03, C(3) 0.04] | | | | |
| Plane (2): M, N(1), N(2) | | | | |
| *Mn* | 0.6487 | –0.7538 | 0.1051 | 0 |
| [C(1) 0.38, C(2) 0.96] | | | | |
| *Cr* | 0.6502 | –0.7528 | 0.1025 | 0 |
| [C(1) 0.39, C(2) 0.96] | | | | |
| Plane (3): M, N(2), O(1) | | | | |
| *Mn* | –0.9878 | 0.0455 | –0.1489 | –3.3755 |
| [C(3) –0.12, C(4) –0.09, C(5) –0.02] | | | | |
| *Cr* | –0.9881 | 0.0469 | –0.1465 | –3.3682 |
| [C(3) –0.13, C(4) –0.09, C(5) –0.02] | | | | |
| Plane (4): M, N(1), O(1) | | | | |
| *Mn* | 0.7391 | –0.0691 | –0.6700 | 0 |
| *Cr* | 0.7400 | –0.0712 | –0.6688 | 0 |
| Plane (5): C(1), C(1′), C(1″) | | | | |
| *Mn* | 0.5774 | 0.5774 | 0.5744 | 1.9225 |
| [N(1) 0.21] | | | | |
| *Cr* | 0.5774 | 0.5774 | 0.5744 | 1.9319 |
| [N(1) 0.20] | | | | |

*Angles (°) between planes:*

| | *Cr* | *Mn* |
|---|---|---|
| (1)–(2) | 46.0 | 46.2 |
| (2)–(4) | 62.2 | 62.5 |
| (1)–(3) | 177.4 | 177.5 |

TABLE V. Selected Non-Bonded Distances (Å).

| *Atoms* | *Cr* | *Mn* | *Fe* |
|---|---|---|---|
| O(1)–O(1$^I$) | 2.791 | 2.771 | 2.810 |
| N(2)–N(2$^I$) | 3.224 | 3.225 | 3.274 |
| O(1)–N(2) | 2.846 | 2.842 | 2.818 |
| O(2)–O(2$^I$) | 3.844 | 3.847 | 3.819 |

I Atoms at *y, z, x*.

whilst the {O(1)–M–O(1$^I$)} angles remain close to 90°.

These distortions seem to be largely caused by the constraints of the ligand geometry, especially those imposed by the 'capping' ($N(C_2H_4N:)_3$ or 'tren' moiety, within the constraints also of metal → donor-atom distances. The 'tren' moiety causes a spreading of the three N(2) {N(2)···N(2$^I$) ≈ 3.22 Å} and a 'compression' of the O(1) donors (Table V). The latter is shown by the short non-bonded O(1)–O(1$^I$) distances of 2.79 Å (Cr), and 2.77 Å (Mn).

The ligand seems to fit Fe$^{III}$ best. The preferred, longer M–N(2) bonds fit with the tendency of the ligand to spread the N(2) donors, and the iron structure does show the least distortion: the staggering of the $N_3$and $O_3$ equilateral triangles is nearly ideal, and the O(1)–O(1$^I$) non-bonded distances are, at 2.81 Å, the longest of the three (Table V).

Generally bond-lengths in the first co-ordination spheres (Table III) are within the ranges defined by previous determinations [3]:

*Fe.* Details were discussed in ref. 1.

*Mn.* This is a unique example so far of a manganese(III) compound with $C_3$ symmetry. All other previously determined octahedral Mn$^{III}$ structures [3–5] have shown distorted 4 + 2 or 2 + 4 geometries, of the type conventionally ascribed, without good reason, to the operation of the 'Jahn–Teller effect'. Earlier descriptions of the trisacetylacetonatomanganese(III) structure, with equal Mn–O bond-lengths are now known [4] to refer instead to a determination of the cobalt compound. Hence, comparisons with known structures of Mn$^{III}$ compounds with ligands similar to the present type [6–9] are complicated by the inequalities of Mn–N and Mn–O distances inherent in the tetragonal distortions. However, our observed bond-lengths {Mn–N(2) = 2.137(4), and Mn–O(1) = 1.965(3) Å} are in very good agreement with appropriately weighted averages (2.13 and 1.97) of those in the two known compounds [8, 9] which are closest in type to the present molecule.

There are no anomalies in the anisotropic thermal parameters suggestive of a 'dynamic distortion' of the Mn$^{III}$ polyhedron.

*Cr.* Although a reasonable number of chromium(III) structures are known [3, 10–12] very few of the molecules contain ligands of the present type, and only one [12] is a neutral [$CrN_3O_3$] molecule – tris-(8-hydroxyquinolinato)chromium(III). However, these few [10–12], together with the full range of other determinations, are sufficient to show that there are unusually long Cr–O and Cr–N bonds in the present molecule. [*cf.* Cr–O = 1.979(6) and Cr–N = 2.137(7) Å, against values of 1.949(7) and 2.063(8) Å for the 8-hydroxoquinoline [12] compound]. Where directly comparable data (isomorphous series) are available [13, 14], Cr–O bond-lengths are ~0.04 Å shorter than Fe–O bond-lengths, yet here Cr–O > Fe–O. Thus, for the present ligand, there seems to be a relatively fixed minimum-sized 'hole' into which the metals fit.

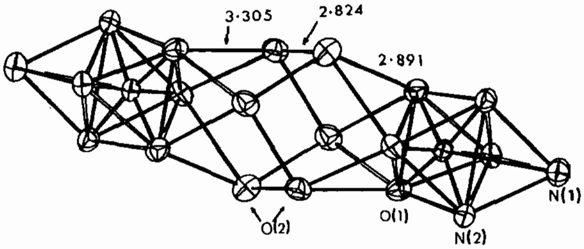
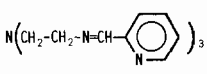
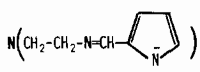


Fig. 2. The co-ordination polyhedra of two metal atoms, with the linking network of hydrogen-bonded water molecules. The distances given are those for the Mn compound.

This 'hole' in the ligand is apparently too large for seven-co-ordination, in contrast to the [$N_7$] ligands [15, 16] such as II and III.



II



III

One well-defined trend in the present series is a decrease in the bond-length differences (M–N) – (M–O) in the order Fe > Mn > Cr.

Bond-lengths and angles within the ligands are generally unexceptionable. The only distortions that seem significant here are in the 'tren' moiety, where the apical nitrogen {N(1)} is only 0.2 Å out of the plane of the three symmetry-related C(1) atoms (in all three species).

The water molecules link the phenolic ends of adjacent complex molecules along the 3-fold axis by a hydrogen-bond network (Fig. 2, Table III b). The oxygen atom of each water molecule is strongly H-bonded to one phenolic oxygen (2.89 Å), and more weakly to another (3.30 Å). On the other side, it is linked to two other water molecules (related by symmetry, 2.82 Å), and these are in turn attached to the phenolic oxygen atoms of another molecule. The water molecules themselves form a flattened octahedron centred on the 3-fold axis.

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