Metal(III) Compounds of Potentially Septadentate[N_4O_3] Ligands Derived from Tris(2-aminoethyl)amine and Substituted Salicylaldehydes. Part I. Preparation of Gallium, Chromium, Manganese, Iron, and Cobalt Compounds, and the Crystal and Molecular Structure of the Iron Compound of Tris[2-(5-chloro-2-hydroxybenzylidene)ethyl]amine, [$Fe(C_{27}H_{24}Cl_3N_4O_3)$]·$3H_2O$

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The potentially septadentate and trianionic Schiff base ligands, prepared from tris(2-aminoethyl)amine and three moles of salicylaldehyde, react with Ga^{III}, Cr^{III}, Mn^{III}, Fe^{III}, and Co^{III} species to form 1 : 1 neutral compounds. This paper reports a range of such compounds, prepared from substituted aldehydes (3-OMe, 3-NO_2, 5-Cl, 5-Br, 5-OMe, and 5-NO_2) as well as the parent salicylaldehyde; details are given of their electronic spectra; some polymorphs and isomorphous series are classified from the *X*-ray powder diffraction patterns; and a full *X*-ray structural analysis of the iron(III) compound of the 5-chloro-substituted ligand is reported. Crystals of the latter were cubic with a = 22.497(1) Å, space group $Ia3$ (T_h^7, No. 206). Data were collected by diffractometer, and the structure solved from 1 081 independent reflections by conventional Patterson and Fourier techniques; it was refined by block-diagonal least-squares to a final R of 0.060. The molecule is essentially an [$Fe(O_3N_3)$] octahedral species [Fe–O 1.953(6), Fe–N 2.185(7) Å], lying on a three-fold crystallographic axis. The latter passes through the iron and the other (apical) nitrogen N(1), which appears to be antibonding with respect to the metal. This nitrogen is 3.26(2) Å from the metal atom, and almost co-planar with its three carbon-atom substituents. C–N(1)–C angles are 117.8 (15)°; and N(1) is only 0.2 Å below the C_3 plane. The water molecules, in the crystal, form a flattened octahedral set about the crystallographic C_3 axis, hydrogen-bonded to themselves and to the phenolic oxygens of the ligand.

As part of a general study of ligand steric effects and metal atom stereochemistry, we have been looking at the metal(III) compounds of the potentially septadentate [N_4O_3] trianionic ligands (I) (abbreviated in the following as X-strn).

They are structurally related to the metal compounds [1] of the neutral (potentially N_7) ligand (II) which have been the subject of *X*-ray structural analyses by Lingafelter and his co-workers.[2,3] In the series of cationic metal(II) compounds of this ligand (II; M = Mn, Fe,

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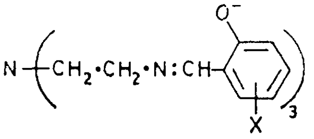
[1] L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, 1968, **90**, 6041.

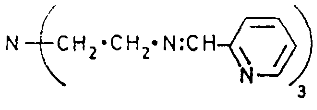
[2] C. Mealli and E. C. Lingafelter, *Chem. Comm.*, 1970, 885.

[3] E. C. Lingafelter, quoted in J. E. Huheey, 'Inorganic Chemistry: Principles of Structure and Reactivity,' Harper and Row, 1972, pp. 314 and 401.

Co, Ni, Cu, and Zn) there is an interesting variation of metal to apical (central) nitrogen atom distance, ranging



(I)



(II)

from 2.8 Å in the high-spin manganese(II) compound to 3.44 Å in the low-spin iron(II) compound. Such distances have been correlated with the electron population of non-bonding metal *d*-orbitals.[3]

The metal(III) compounds of the ligands (I) would appear to offer an extension of this work, giving a structurally related series for electron configurations $d^0 \rightarrow d^6$ (using, *e.g.* Ga^{III} and the transition-metals Ti→Co). Also, there are overlaps between the two series at d^5 (Mn^{II} and Fe^{III}) and d^6 (Fe^{II} and Co^{III}).

We had previously found, in parallel with the work reported by Broomhead and Robinson,[4] that [Fe(strn)] did not give crystals suitable for *X*-ray work (except an unstable $CHCl_3$ solvate). So, in this further study, we have used a variety of substituted salicylaldehydes to extend the range and to give a better chance of obtaining suitable crystals for *X*-ray studies.

The present report gives details of the preparations, mainly of the Cr^{III}, Mn^{III}, and Fe^{III} compounds, and an *X*-ray structural analysis of one of the Fe^{III} compounds.

EXPERIMENTAL

Preparation of Compounds.—Yellow or orange crystals of the Schiff base ligands were obtained by mixing the appropriate reagents in ethanol for X = H, 3-NO_2, 5-Cl, 5-Br, 5-Me, 5-OMe, and 5-NO_2. The ligand 3-OMe-strn did not crystallise, so the solution was evaporated to dryness, and the resulting gum was used to prepare the metal compound.

The red or purple *iron*(III) *compounds* were usually prepared from dimethylformamide (DMF). A hot solution (20 ml) of $[Fe_3(OAc)_6O(H_2O)_3]Cl \cdot 3H_2O$ [5] (1 g) was added to a solution of the ligand (stoicheiometric amount) in hot DMF (50 ml), and the mixture was allowed to cool. The 3-OMe, α-5-Cl, α-5-Br, and α-5-Me compounds separated from the cooled solutions; the α-3-NO_2 and 5-NO_2 compounds were precipitated with ether whereas the β-5-Me compound separated out after the filtrate was set aside to evaporate at room temperature.

Alternatively, ethanol was used as solvent for the α-5-OMe and the unsubstituted species. The latter was isomorphous with that prepared by the method of Broomhead and Robinson.[4]

Recrystallisation from DMF gave the β-forms of the 3-NO_2, 5-Cl, and 5-OMe species; from methanol, the β-5-Br species; and from $CHCl_3$, an unstable solvate of the unsubstituted compound.

The orange-brown *chromium*(III) *compounds* were prepared by three different methods.

(i) $[Cr(H_2O)_6](NO_3)_3 \cdot 3H_2O$ (2.0 g) and the ligand (stoicheiometric amount) were heated together in ethanol (40 ml) until a brown solution was obtained. Brown crystals of the desired product (for X = H, 5-Cl, and 5-OMe) crystallised out when the solution was set aside to cool.

(ii) When $Cr(OAc)_3 \cdot H_2O$ was used instead of the nitrate, crystals of the compounds for X = H, 3-OMe, 5-Cl, 5-Br, α-5-Me, and 5-OMe were obtained.

(iii) The same compounds also were obtained for the 5-Cl and 5-Br derivatives when $[Cr(CO)_6]$ (1.1 g) was refluxed with stoicheiometric amounts of the ligands in dry toluene (100 ml) under N_2, until all reagents had dissolved. Water (5 ml) was then added to the cooled solution, and crystals separated when it was set aside overnight.

Recrystallisations were from DMF (X = H, 5-Cl, 5-Br, or 5-OMe), chloroform, or methanol (X = 3-OMe, β-5-Me, or 5-OMe).

The dark green *manganese*(III) *compounds* were prepared from either manganese(II) or manganese(III) reagents.

For the former, a solution of $Mn(OAc)_2 \cdot 4H_2O$ (2.50 g) or $MnSO_4 \cdot 4H_2O$ (2.23 g) in water (50 ml) was added to the ligand (stoicheiometric amount) in a minimum volume of hot ethanol. A yellow manganese(II) compound usually separated almost immediately. However, when the mixture was set aside at room temperature in the air, a dark green solution formed, and green crystals of the manganese(III) compound separated out. Times for this reaction varied between 1 h (for the 5-Me ligand) and 8—10 days (5-Cl and 5-Br). The solid product was separated from any remaining yellow manganese(II) compound by washing with chloroform, in which the latter was soluble. After further washing with ethanol, the manganese(III) compound was recrystallised from DMF. The method was successful for X = H, 3-OMe, 5-Cl, 5-Br, α-5-Me, and 5-OMe.

The initial yellow manganese(II) products could be recrystallised from $CHCl_3$, and their i.r. spectra showed that no sulphate or acetate were present. However, satisfactory mass spectra were not obtained, nor were crystals suitable for *X*-ray work, so we have not attempted further to characterise them.

Alternatively, the compounds were obtained by heating manganese(III) acetate [6] and the ligand in ethanol. Crystals of the compound soon formed for X = H, 5-Cl, and 5-Br, but a green solution of the compound was obtained for X = 3-OMe, 5-Me, and 5-OMe. The latter solutions were evaporated to small volume; the compounds were precipitated in crude form as a gum with Et_2O and triturated with acetone.

Attempts to prepare the chromium(III) and manganese(III) compounds of the ligands for which X = 3-NO_2 and 5-NO_2 were generally unsuccessful because of low ligand solubility, but a fairly pure sample of [Mn(5-NO_2-strn)] was obtained by extracting the ligand from a Soxhlet apparatus into a solution of manganese(III) acetate.

[Co(5-Cl-strn)]$\cdot 3H_2O$. $Co(OAc)_2 \cdot 4H_2O$ (2.48 g) and the ligand (5.61 g) were dissolved in a mixture of ethanol (200 ml) and DMF (50 ml), and air was drawn through the solution (24 h). Small purple crystals of the compound slowly separated out during this time. The product was recrystallised by dissolution in warm DMF (*ca.* 35 °C), filtration of the solution, and addition of water. It decomposed in hot DMF.

[Ga(5-Cl-strn)]$\cdot 3H_2O$. The following solutions were mixed in the order given: 4.9 ml of 20% (w/v) tren in

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[4] J. A. Broomhead and D. J. Robinson, *Austral. J. Chem.*, 1968, **21**, 1365.

[5] G. B. Robertson and B. N. Figgis, 1965, **205**, 694.

[6] L. W. Hassel and C. Romers, *Rec. Trav. chim.*, 1969, **88**, 545.

ethanol; 5-chlorosalicylaldehyde (3.25 g) in ethanol (*ca.* 120 ml); KOH (1.15 g) in water (5 ml); and $Ga(NO_3)_3 \cdot 9H_2O$ (2.5 g) in water (10 ml). The mixture was cooled in ice, stirred for 1 h, filtered, and then set aside at room temperature. Pale yellow cubes of the compound were deposited together with the ligand and gallium nitrate. A sample for analysis was obtained by recrystallisation from benzene.

Physical Measurements.—For details, see ref. 7. Magnetic moments in solution were determined by the Evans' method, using the shift of the solvent peaks, and in the solid by the Gouy method.

Preliminary *X*-ray photographic investigations on some of the compounds gave the following data.

[Cr(5-OMe-strn)]·MeOH: monoclinic, probably $P2_1/a$, $a = 13.0$, $b = 14.3$, $c \sin \beta = 16.1$ Å [β not measured, rotation (*a*), 0*kl* and 1*kl* films only]; [Mn(5-Me-strn)]: monoclinic [rotation (*b*) and *h*0*l* films only], $b = 14.26$ Å, $\beta = 98°$, other axes 12.18 and 15.80 Å; [Fe(5-OMe-strn)]: triclinic; [Fe(5-NO_2-strn)], monoclinic [rotation (*b*) and *h*0*l* films only], $b = 11.5$ Å, $\beta = 95°$, other axes 10.7 and 13.2 Å (or doubled).

X-*Ray Structural Analysis.*—The compound crystallised as dark purple rectangular bricks from DMF. The crystal used for data collection had dimensions *ca.* 0.28 × 0.28 × 0.24 mm.

Crystal Data.—$C_{27}H_{30}N_4O_6Cl_3Fe$, $M = 668.77$, Cubic, $a = 22.497(1)$, $U = 11\,386$ Å^3, $D_m = 1.55$ g cm^{-3} (by flotation), $Z = 16$, $D_c = 1.56$ g cm^{-3}, $F(000) = 5\,520$. Space group $Ia3$ (T_h^7, No. 206) from systematic absences and symmetry. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 8.76 cm^{-1}.

X-Ray data were collected on a Stöe Stadi-2 two-circle diffractometer, by use of graphite-monochromated Mo-K_α radiation ($2\theta_{\max.}$ 60°). Reflections with $I < 3\sigma$ were ignored, as generally were those with background difference $>4\sigma$. Corrections were applied, initially, for Lorentz and polarisation factors, and at a later stage for absorption and anomalous dispersion of the iron and the chlorine atoms. 1 121 Independent reflections were obtained by averaging observed intensities of each of the three reflections related by the C_3 rotation axis. Forty of these reflections were subsequently removed, six because of low-angle extinction, and the remainder because of bad agreement between the C_3 related intensities.

As each molecule has constrained C_3 symmetry, the structure is defined by one third of the molecule.

The structure was solved by conventional Patterson and Fourier techniques. Block-diagonal least-squares refinement of positional and isotropic thermal parameters reduced *R* to 0.101. The population of the solvent molecule was initially set as 0.50, but it refined to 1.00. The introduction of anisotropic thermal parameters reduced *R* to 0.072. A difference-Fourier then showed peaks in most of the positions where hydrogen atoms were expected. Thus the positions for the latter (except those of the water molecules) were calculated, assuming C–H 0.98 Å, and included (together with isotropic thermal parameters of 5.0 Å^2) but not varied in the final refinement to *R* 0.060.

Atomic scattering factors for neutral atoms were taken from ref. 8. Observed structure amplitudes and the calculated structure factors are deposited as Supplementary Publication No. SUP 21633 (12 pp., 1 microfiche).*

Programmes used are part of the Sheffield *X*-ray system. Calculations were performed on the Sheffield University ICL 1907 computer. Final atomic positional and vibrational parameters, with estimated standard deviations, are listed in Table 1.

TABLE 1

Atomic positions and thermal vibrational parameters, with estimated standard deviations in parentheses

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

Atom	*x/a*	*y/b*	*z/c*
Fe	1 384(1)	1 384(1)	1 384(1)
Cl	1 883(1)	4 002(1)	−542(1)
N(1)	547(9)	547(9)	547(9)
N(2)	1 510(3)	1 377(3)	421(3)
O(1)	1 426(2)	2 249(2)	1 316(2)
O(2)	2 451(3)	1 517(3)	2 871(3)
C(1)	906(4)	555(4)	15(4)
C(2)	1 542(4)	783(4)	133(3)
C(3)	1 647(3)	1 828(4)	101(3)
C(4)	1 627(3)	2 445(4)	290(3)
C(5)	1 520(3)	2 620(3)	879(3)
C(6)	1 513(4)	3 234(4)	1 006(4)
C(7)	1 615(3)	3 649(4)	574(4)
C(8)	1 730(3)	3 458(4)	4(4)
C(9)	1 740(4)	2 870(4)	−153(4)

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

H(1)	93	15	−14
H(1′)	72	82	−28
H(2)	175	50	40
H(2′)	176	81	−24
H(3)	178	175	−31
H(6)	143	336	14
H(7)	161	408	67
H(9)	182	274	−57

(*c*) Anisotropic thermal parameters [b] ($\times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Fe	133(4)	133(4)	133(4)	−13(12)	−13(12)	−13(12)
N(1)	206(38)	206(38)	206(38)	−29(86)	−29(86)	−29(86)
N(2)	143(13)	179(14)	156(13)	−92(24)	−13(22)	0(24)
O(1)	222(12)	120(9)	132(11)	2(17)	19(21)	1(20)
Cl(1)	272(6)	231(6)	207(5)	173(9)	−94(9)	−30(10)
C(1)	238(21)	207(20)	187(18)	−96(37)	−45(37)	−48(35)
C(2)	266(23)	167(18)	141(18)	−60(29)	6(32)	28(33)
C(3)	158(17)	199(19)	141(17)	2(30)	−30(27)	−28(30)
C(4)	155(16)	159(17)	132(15)	0(27)	−3(26)	−21)28)
C(5)	112(15)	164(18)	157(16)	9(27)	−65(25)	48(25)
C(6)	149(18)	183(18)	178(18)	32(30)	5(28)	39(29)
C(7)	188(18)	171(18)	166(17)	−36(30)	−75(29)	46(31)
C(8)	157(16)	207(19)	161(16)	139(32)	−99(31)	18(30)
C(9)	174(18)	212(20)	131(18)	11(29)	−41(28)	−6(32)
O(2)	277(17)	296(17)	290(17)	48(30)	−39(30)	17(31)

[a] Hydrogen atoms are numbered according to the carbon to which they are attached, with primes used to distinguish the pairs on the same carbon. [b] The expression used for the temperature factor is $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

RESULTS AND DISCUSSION

The compounds prepared in this study are listed in Table 2, together with the analytical data, and some of the *X*-ray powder diffraction data.† In many cases, different crystalline forms were characterised by the latter, and isomorphous series were observed as follows: (i) 5-Cl-strn (Ga, Cr, Mn, α-Fe, and Co), 5-Br-strn (Cr only), and 5-Me-strn (β-Mn only)—all isomorphous with the iron compound described herein; (ii) strn (Fe

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

† Full details of the *X*-ray data are available from the authors.

[7] B. M. Higson and E. D. McKenzie, *J.C.S. Dalton*, 1972, 269.

[8] 'International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

and Mn); (iii) 5-Me-strn (α-Fe and α-Mn); and (iv) 5-NO_2-strn (Fe and Mn).

The compounds were further characterised by their mass and i.r. spectra. The former had well-defined parent peaks, except for the nitro-substituted species, and characteristically showed strong fragment ions corresponding to the loss of $\{CH_2{\cdot}CH_2{\cdot}N{:}CH{\cdot}C_6H_4(X,O)\}$. The i.r. spectra were unexceptionable for Schiff base compounds of this type, being mainly used to check the presence of solvent of crystallisation in the solids.

TABLE 2

The compounds prepared, the analytical data, and some of the *X*-ray powder diffraction data

	Analyses (%)								
	Found				Calculated				
Compound [a]	C	H	N	Halogen	C	H	N	Halogen	*X*-Ray powder data (*d*-spacings)
Ga^{III}									
5-Cl ($3H_2O$)	48.3	4.7	7.9	Cl, 14.9	47.5	4.4	8.2	Cl, 15.6	*e*
Cr^{III}									
H	63.5	5.6	11.3		63.9	5.4	11.0		
3-OMe	60.0	5.2	9.4		60.3	5.6	9.4		
5-Cl ($3H_2O$)	48.5	4.4	8.5	Cl, 15.8	48.8	4.6	8.4	Cl, 16.0	*e*
5-Br ($3H_2O$)	40.8	3.6	7.0	Br, 29.0	40.6	3.8	7.0	Br, 30.0	*e*
α-5-Me (H_2O)	63.2	6.2	10.2		63.5	6.1	9.9		15.8m, 11.7br, w, 10.1m, 9.25m, 7.96w, 7.30ms, 6.56br, m
β-5-Me ($1.5H_2O$)	62.3	6.2	9.6		62.5	6.1	9.7		16.8m, 14.9s, 13.2w, 9.20w, 8.70s, 8.29m
5-OMe (MeOH)	59.0	6.1	8.8		59.1	5.9	8.9		
Mn^{III}									
H	63.6	5.4	11.3		63.5	5.3	11.0		
3-OMe ($1.5H_2O$)	58.0	5.5	8.2		57.4	5.8	8.9		
5-Cl ($3H_2O$)	48.5	4.6	8.9	Cl, 15.8	48.6	4.5	8.4	Cl, 15.9	*e*
5-Br (H_2O)	42.8	4.0	7.0	Br, 30.2	42.4	3.4	7.3	Br, 31.3	
α-5-Me	64.9	5.9	10.2		65.2	6.0	10.1		*f*
β-5-Me [d]	60.5	6.2	8.8						
5-OMe ($1.5H_2O$)	58.0	5.5	8.7		57.4	5.8	8.9		
5-NO_2 [c]	51.2	3.9	15.7		50.2	3.8	15.3		
Fe^{III}									
H	62.8	5.8	10.7		63.4	5.3	11.0		
3-OMe	61.9	6.2	9.3		59.9	5.8	9.3		
α-3-NO_2	49.0	4.8	15.4		50.2	3.7	15.2		9.85s, 5.66m, 5.01m, 4.70m, 4.37m
β-3-NO_2	49.6	4.9	15.3		50.2	3.7	15.2		13.3ms, 10.7s, 9.4s, 6.81m
α-5-Cl ($3H_2O$)	50.2	4.4	8.0	Cl, 16.2	48.5	4.5	8.4	Cl, 15.9	9.25ms, 6.00s, 3.56ms, 3.06ms
β-5-Cl ($3H_2O$)	49.3	4.6	8.8	Cl, 15.6	48.5	4.5	8.4	Cl, 15.9	10.5br, s, 7.01ms, 5.97br, ms, 5.08ms
α-5-Br (DMF)	43.7	3.9	8.4	Br, 28.8	43.9	3.8	8.5	Br, 29.2	16.0m, 10.7m, 9.6s, 5.57br, s, 4.18ms
β-5-Br	43.2	3.6	7.2	Br, 32.2	43.4	3.2	7.5	Br, 32.0	7.29m, 6.14ms, 5.26s, 3.71s
α-5-Me	64.9	6.2	10.3		65.1	6.0	10.1		13.2br, ms, 12.4m, 11.2w, 7.90s
β-5-Me	65.2	6.3	10.0		65.1	6.0	10.1		12.2s, 7.04ms, 6.60ms, 6.11ms, 5.26s
α-5-OMe	60.0	6.2	9.0		59.9	5.8	9.3		13.9ms, 10.6s, 6.57ms, 5.99s
β-5-OMe	59.3	5.8	9.3		59.9	5.8	9.3		10.5s, 7.09m, 5.37ms, 4.88ms, 3.13ms
5-NO_2	49.9	3.7	15.2		50.2	3.7	15.2		
Co^{III}									
5-Cl ($3H_2O$)	48.4	4.6	8.3	Cl, 16.0	48.3	4.5	8.3	Cl, 15.8	

[a] All compounds were of the same general type [M(X-strn)]. They are defined here, in groups of the same metal, by listing the substituent X of the salicyl moiety. Solvent of crystallisation is given in parentheses. [b] We list several of the prominent characteristic low-angle diffraction lines (*d*-spacings) only where this is necessary to distinguish our labelling of the different crystalline forms of some of the compounds. [c] We did not obtain a bulk sample of this compound free from traces of the ligand. [d] Poor analyses, therefore not fully characterised. [e] Isomorphous with α-[Fe(5-Cl-strn)]·$3H_2O$. [f] Isomorphous with α-[Fe(5-Me-strn)].

The Electronic Spectra and Magnetism.—Representative examples of the electronic absorption spectra of the compounds of the different metals (Table 3) are given in Figure 1. In describing these, it is convenient to distinguish three different regions.

In the low-energy region, near 9 000—10 000 cm^{-1}, absorption is observed usually only for the manganese compounds. The extinction coefficients for such bands in the solution spectra are rather higher than is usual ($\varepsilon_{max.} \geqslant 100$ l mol^{-1} cm^{-1}). However, bands in this region appear [9] to be quite common for Mn^{III}.

At higher energy, but still within the visible region, absorptions are observed for all the transition-metal compounds. Those of the chromium, manganese, and cobalt compounds appear to be of normal octahedral type,[9] with bands at 16 000—18 000 cm^{-1}, but much of the detail is obscured by overlap with higher energy transitions. Intensities are within the expected range for what can be classified as *d–d* transitions. By contrast, the iron compounds are characterised by a relatively strong absorption in this region ($\varepsilon_{max.}$ = 4 000—8 000 l mol^{-1} cm^{-1}). It is almost certainly of charge-transfer origin (phenol→Fe^{III}). Such bands are a characteristic of iron(III) compounds of the phenols, and have been used as a test for phenols.

In the near-u.v. region, which certainly contains

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[9] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, London, 1968.

allowed ligand transitions ' perturbed ' by the metal, there probably are ' phenol→metal ' charge-transfer bands for the other metals. Certainly, there are significant differences of spectra here, which especially distinguish the manganese and iron spectra from the other two. However, there is no point in attempting to assign individual transitions.

The cobalt(III) compound is diamagnetic, but all the other transition-metal compounds prepared appear to be high-spin. Since the electronic spectra were all of the same class, magnetic measurements at *ca.* 300 K were made on only the 5-chloro-species. These gave: [Fe(5-Cl-strn)]$\cdot$3H_2O, 6.03 B.M. (solid) and 6.00 B.M. (DMF solution); [Mn(5-Cl-strn)], 5.05 B.M. (DMF solution); and [Cr(5-Cl-strn)], 4.10 B.M. (DMF solution).

There is nothing in this data which might be used *a priori* to distinguish six- from seven-co-ordination at the metal—that is whether the apical nitrogen of the potentially septadentate ligand is bonded to the metal. For this we need to turn to *X*-ray methods.

TABLE 3

The electronic spectra

Compound [a]			Absorption bands (kK) [b]			
X	M	Phase				
H	Cr	solid	(26.1) 24.8	18.6		
		DMF	26.0 [10 700]	18.1 [135]		
H	Mn	solid	25.2		16.7	8.3
		DMF	28.7 [11 500]	(26.5) [10 300]	(17.8 [620]	9.0 [110]
H	Fe	solid	27.6	22.7	18.5	9.3
		DMF		22.9 [4 000]	19.4 [5 600]	
		$CHCl_3$	(27.0) [10 100]	22.9 [3 500]	19.2 [5 100]	
		py	(27.2) [11 200]	22.7 [2 900]	19.2 [4 700]	
3-OMe	Fe	solid	26.5	21.9	18.0	
		DMF		(22.2) [4 200]	18.4 [6 300]	
		$CHCl_3$	(27.5) [13 100]	(22.2) [3 800]	18.2 [6 100]	
		py	(27.0) [13 700]	(22.1) [3 800]	18.4 [6 200]	
3-NO_2	Fe	solid	24.7		18.4	
		DMF	25.6 [15 100]		19.0 [4 100]	
		$CHCl_3$	27.0 [14 400]	(22.6) [5 000]	19.2 [4 000]	
		py	25.6 [16 200]		18.8 [4 600]	
5-Cl	Cr	solid	24.5 23.0	(18.0)		
		DMF	24.5 [8 600]	(17.3) [200]		
5-Cl	Mn	solid		24.8	(16.9)	9.1
		DMF	28.1 [13 500]	(25.9) [12 100]	(17.9) [820]	8.9 [140]
5-Cl	Fe	solid	26.6	22.2	17.6	
		DMF	(27.8) [14 200]	22.2 [4 800]	18.8 [7 000]	
		$CHCl_3$	(27.3) [13 800]	22.0 [4 200]	18.3 [6 600]	
		py	(27.1) [11 300]	22.2 [3 800]	18.4 [5 600]	
5-Cl	Co	solid	23.9	(19.8)	(18.0)	
		DMF	24.4 [13 000]		(18.0) [580]	
5-Br	Cr	solid	24.8 23.5	(18.0)		
		DMF	25.8 [11 100]	(18.1) [150]		
5-Br	Fe	solid	26.1	(22.1)	17.2	(9.3)
		DMF	(27.4) [8 900]	22.7 [3 400]	18.9 [4 900]	
		$CHCl_3$	(27.4) [12 700]	22.2 [4 300]	18.8 [6 900]	
		py	(27.2) [11 700]	22.2 [3 900]	18.6 [6 200]	
5-Me	Cr	solid	24.6	23.2	(17.7)	
		DMF	25.6 [10 200]	(23.3) [7 600]	(17.5) [140]	
5-Me	Mn	solid	26.8	24.8	16.8	9.3
		DMF	28.0 [11 600]	(25.5) [10 200]	(16.3) [700]	8.9 [130]
5-Me	Fe	solid	26.3	22.2	18.2	
		DMF	(27.4) [9 700]	(22.2) [4 300]	18.7 [6 300]	
		$CHCl_3$	(27.0) [12 700]	22.0 [4 000]	18.3 [6 000]	
		py	(27.3) [14 700]	22.2 [4 500]	18.4 [6 800]	
5-OMe	Fe	DMF	29.7 [11 200]	(22.8) [3 600]	18.1 [4 200]	
		$CHCl_3$	29.3 [9 400]	(22.8) [2 900]	17.8 [3 800]	
		py	29.6 [11 000]	(22.7) [3 300]	18.0 [4 200]	
5-NO_2	Fe	solid	26.0	(22.9)	18.6	
		DMF	27.1 [47 300]	(23.4) [15 500)	19.0 [8 900]	
		$CHCl_3$	27.8 [42 400]	(23.6) [10 100]	18.7 [8 800]	
		py	27.4 [43 800]	(23.8) [15 600]	19.0 [8 800]	

[a] X defines the substituents on the salicyl moieties of the ligands (I), and M is the central metal atom. [b] Shoulders are given in parentheses, and extinction coefficients (l mol^{-1} cm^{-1}) in square brackets. There were no significant differences observed in the spectra of the different crystalline forms or solvates of the same compound.

The X-*Ray Structure Analysis*.—The molecular structure of [Fe(5-Cl-strn)] is shown in Figure 2, together with the atom labelling scheme. Details of the various bond lengths and angles are given in Table 4, and equations of relevant least-squares planes in Table 5.

The Fe and the apical nitrogen [N(1)] lie on a crystallographic three-fold axis, so that the rest of the molecule is defined by the positions of only one-third of the other atoms.

The iron co-ordination polyhedron is essentially octahedral, with the apical nitrogen non-bonded (see later). The N_3 and O_3 equilateral triangles are mutually staggered by 60.2°, almost exactly the correct angle. However, there is a distinct flattening of the octahedron along the C_3 axis. {Angles at the iron between pairs of nitrogens [N(2) and N(2)′], *etc.*, are 97°, those between pairs of oxygens 92°, whereas the N(2)–Fe–O(1) angles are near 85°.} Most of these angular distortions are clearly a result of ligand steric constraints: the large chelate rings spanning the nitrogen donors appear to be responsible for opening-up the N–Fe–N angles, whereas

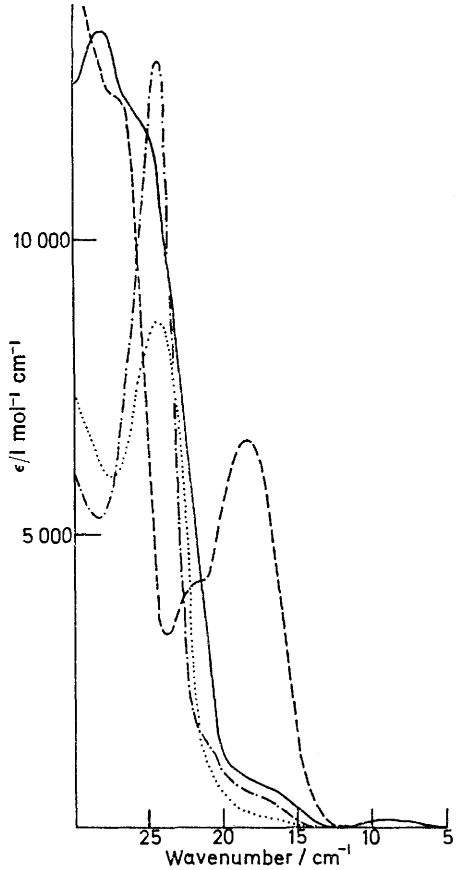


FIGURE 1 The electronic absorption spectra in DMF of the compounds [M(5-Cl-strn)]: (· · · ·) M = Cr; (——) M = Mn; (— — —) M = Fe; and (— · — · —) M = Co

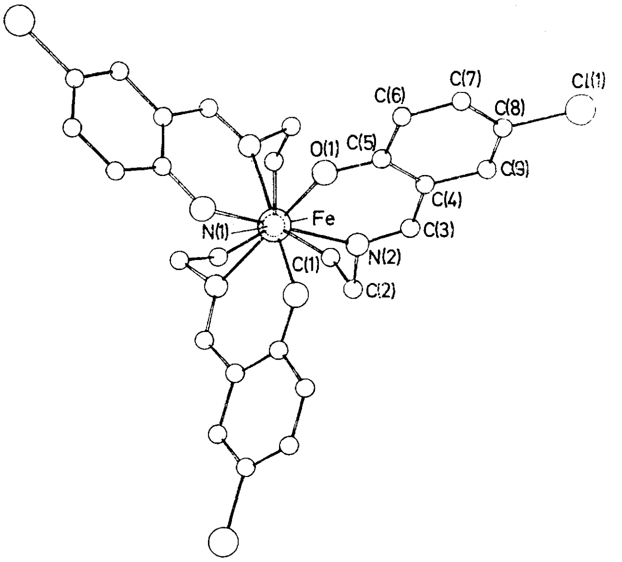


FIGURE 2 Molecular geometry and the atom-labelling scheme. N(1) lies behind the Fe in this view [O(2) belongs to the water molecule]

TABLE 4

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

(*a*) Co-ordination sphere of metal			
(i) Bond lengths			
Fe–N(1)	3.26(2)	Fe–O(1)	1.953(6)
Fe–N(2)	2.185(7)		
(ii) Bond angles			
N(2)–Fe–N(2′)	97.1(2)	O(1)–Fe–O(1′)	92.0(2)
N(2)–Fe–O(1)	85.6(2)	N(1)–Fe–N(2)	59.9(4)
N(2)–Fe–O(1′)	176.2(3)	N(1)–Fe–O(1)	123.9(4)
N(2)–Fe–O(1″)	85.3(2)		
(*b*) The 5-Cl-strn ligand			
(i) Bond lengths			
Cl(1)–C(8)	1.768(8)	C(3)–C(4)	1.453(11)
O(1)–C(5)	1.308(8)	C(4)–C(5)	1.401(10)
N(1)–C(1)	1.444(22)	C(5)–C(6)	1.411(11)
N(2)–C(2)	1.486(10)	C(6)–C(7)	1.369(11)
N(2)–C(3)	1.282(10)	C(7)–C(8)	1.374(11)
C(1)–C(2)	1.544(12)	C(8)–C(9)	1.370(11)
(ii) Bond angles			
C(1)–N(1)–C(1′)	117.8(15)	N(2)–C(3)–H(3)	117.2(7)
Fe–N(2)–C(2)	116.4(5)	C(3)–C(4)–C(5)	123.5(7)
Fe–N(2)–C(3)	125.7(5)	C(3)–C(4)–C(9)	115.9(7)
C(2)–N(2)–C(3)	117.0(6)	C(5)–C(4)–C(9)	120.6(7)
Fe–O(1)–C(5)	134.7(5)	C(4)–C(5)–C(6)	117.9(7)
N(1)–C(1)–C(2)	112.2(10)	C(4)–C(5)–O(1)	124.0(6)
N(1)–C(1)–H(1)	108.8(11)	C(6)–C(5)–O(1)	118.1(6)
C(2)–C(1)–H(1)	108.8(7)	C(5)–C(6)–C(7)	121.4(7)
H(1)–C(1)–H(1′)	109.5(8)	C(6)–C(7)–C(8)	118.8(7)
N(2)–C(2)–C(1)	109.4(6)	C(7)–C(8)–C(9)	123.0(7)
N(2)–C(2)–H(2)	109.5(7)	C(7)–C(8)–Cl(1)	117.9(6)
C(1)–C(2)–H(2)	109.5(7)	C(9)–C(8)–Cl(1)	119.1(6)
H(2)–C(2)–H(2′)	109.5(7)	C(8)–C(9)–C(4)	118.3(7)
N(2)–C(3)–C(4)	125.6(7)		

TABLE 5

Equations to some least-squares planes given in the form $lX + mY + nZ = d$ (where X, Y, and Z are co-ordinates in Å referred to the axes a, b, and c). Deviations (Å) of the various atoms from these planes are given in square brackets

	l	m	n	d
Plane (1): N(2), O(1), C(3)—(9)				
	0.9796	−0.0502	0.1945	3.4270
[Fe 0.073, Cl 0.034, C(2) −0.06, N(2) −0.07, O(1) 0.04, C(3) 0.04]				
Plane (2): Fe, N(1), N(2)				
	0.6570	−0.7484	0.0914	0.0000
[C(1) 0.41, C(2) 0.99]				
Plane (3): Fe, N(2), O(1)				
	−0.9907	0.0374	−0.1305	−3.3748
[C(3) −0.17, C(4) −0.13, C(5) −0.05]				
Plane (4): Fe, N(1), O(1)				
	0.7470	−0.0880	−0.6590	0.0000
Plane (5): C(1), C(1′), C(1″)				
	0.5774	0.5774	0.5774	1.9160
[N(1) 0.22]				

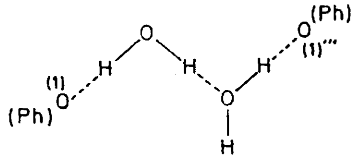
Angles (°) between planes: (1)–(2) 45.7, (2)–(4) 60.2, (1)–(3) 176.2.

the chelate angles of 85.6° for the salicylaldiminato-moieties are normal.[10]

The Fe–O and Fe–N(2) bond distances [1.953(6) and 2.185(7) Å] are quite different from one another, as is usual for iron(III) salicylaldiminates.[10] No rationalisation of these differences is yet available, although a sometimes convenient phenomenological description can be given [11] in terms of ' hard ' and ' soft ' atoms.

Bond lengths and angles within the ligand are generally as expected, except for the angles at N(1) (see later). The atoms of the salicylaldiminate moiety are essentially co-planar (Table 5). The atom C(2) is also in this plane, and the staggered conformation of the dimethylene moieties is shown by the deviations of C(1) and C(2) from the Fe, N(1), N(2) plane [0.4 and 1.0 Å].

The only other feature to notice, before returning to the apical nitrogen, is the hydrogen-bonded network of the water of crystallisation. The iron(III) molecules, along the same C_3 axis are lined up ' head-to-head ' and ' tail-to-tail,' and the phenolic oxygens of adjacent molecules (on the same C_3 axis) are linked by three pairs of hydrogen-bonded water molecules. (III) Shows one such pair. The three C_3 related pairs together give a flattened octahedron of six water molecules.



(III)

The Fe–N(1) *Distance.*—This distance of [3.26(2) Å] is unexpectedly long; the C–N–C angles at N(1) [117.8(15)°] are much larger than the expected tetrahedral value, and N(1) is only 0.2 Å out of the C_3 plane (*cf.* 0.5 Å for a regular tetrahedron).

By contrast, Mn–N(1) is *ca.* 2.8 Å in the isoelectronic (but cationic) compound [3] of the ligand (II) $[\mathrm{Mn(L_{II})}]$-$(\mathrm{ClO_4})_2$ and the other Mn–N distances at *ca.* 2.3 and 2.15 Å* are longer than those in the present iron compound.

These differences between the isoelectronic $\mathrm{Fe^{III}}$ and $\mathrm{Mn^{II}}$ structures do not appear to result simply from different steric effects in the two ligands. Certainly, the ligands (I), with six-membered chelate rings, are more bulky than the ligands (II) with their five-membered chelate rings, but this effect alone appears to account for only *ca.* 0.2 Å of the Fe–N(1) ' bond ' lengthening (from framework molecular models). Indeed there appears to be no obvious major obstacle to the nitrogen approaching to within *ca.* 2.8 Å of the metal, if there was a sufficient attractive force.

Perhaps some rationalisation of the repulsion of N(1) by the $\mathrm{Fe^{III}}$ atom, but not the $\mathrm{Mn^{II}}$ atom, can be given in terms of the nett charge on the metal. The non-bonding metal orbitals may be more compact for $\mathrm{Fe^{III}}$ and thus more effectively repel N(1).

Whatever the rationalisation, it is clear that N(1) is being excluded from the covalent co-ordination polyhedron of the $\mathrm{Fe^{III}}$ compound, but included in that of Lingafelter's $\mathrm{Mn^{II}}$ compound. The reasons may become clearer when further structural data for the series [M(5-Cl-strn)] are available.

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* These are estimates taken from the Table in Huheey (ref. 3).

[10] J. E. Davies and B. M. Gatehouse, *Acta Cryst.*, 1973, **B29**, 1934, and refs. therein.

[11] E. O. Schlemper, *Inorg. Chem.*, 1967, **6**, 2012.