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The Crystal Structure of Bis[N-(2-aminoethyl)salicylaldiminato] iron(III) Chloride Monohydrate, a Low Spin Iron(III) Complex Stabilized by Lattice Water [1]

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The crystal structure and molecular configuration of bis[N-(2-aminoethyl)salicylaldiminato] iron(III) chloride monohydrate, $Fe(III)(Saen)_2Cl\cdot H_2O$, has been determined by X-ray diffraction techniques. The crystals are orthorhombic with space group Pbca and cell dimensions a = *32.694(22),* b = *10.083(7) and* c = *12.274(8)Å. The structure was solved by the heavy atom technique and refined by the full-matrix least-squares method with 1587 reflections to an* R *factor of 0.114 (on* F*).*

The iron atom is octahedrally coordinated by the two tridentate ligands in the meridional configuration. Strong hydrogen bonding occurs between the ammine hydrogens, water molecule and chloride ion, accounting for the stabilization of the low spin state in the hydrated solid over the high spin state found when dehydrated.

Introduction

A series of compounds of general formula M(III)-$(Saen)_2X\cdot nH_2O$ has been prepared for M = Cr, Fe and Co. The value of n can be 1 or 0 depending on the anion X. The chlorides of all three metals are monohydrates, and powder diffraction data indicated that all three compounds are isostructural. These complexes, as well as other hydrates in the series, show unusual features arising from the presence of the water molecule.

A brief summary follows:

(1) The water molecule gives rise to two intense bands in the O–H stretch region of the i.r. spectrum. The first band occurs at 3620 cm^{-1} and is extremely narrow with a peak width at half-height ($\nu_{1/2}$) of 20 cm^{-1}. The second is slightly broader ($\nu_{1/2}$ = 50 cm^{-1}) and occurs between 3,350 and 3,450 cm^{-1}. The position of this latter band is different for each metal and also varies with the nature of X.

(2) Experiments conducted on the isostructural chloride salts showed that the iron and chromium compounds can be dehydrated by heating at 100 °C in a vacuum for several hours. It is not possible to dehydrate the cobalt complex.

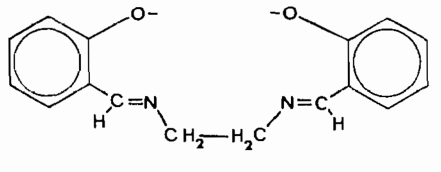
(3) Evidence from n.m.r. and conductance studies suggests the water remains bound in solution.

(4) The iron complex is low spin ($\mu_{eff.}$ = 2.11 B.M.) but high spin when dehydrated and in solution ($\mu_{eff.}$) = 5.96 B.M.). Iron complexes with n = 0 are high spin (*e.g.* $Fe(Saen)_2I$, $\mu_{eff.}$ = 6.06 B.M. [2]).

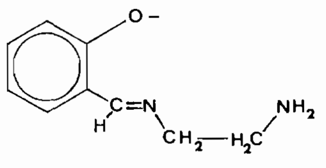
This structure determination was undertaken in order to ascertain the mode of bonding of the water molecule, which stabilizes the low spin state of iron-(III).

Details of the preparation, spectra and chemical properties of the series of compounds will be the subject of a later publication.

Salen



Saen



Experimental

Crystals suitable for structure determination were prepared by reaction of Iron(III)Salen Chloride and 1,2 diaminoethane in ethanol. Subsequent recrystallization from ethanol–diisopropyl ether gave deep blue plates.

TABLE I. Positional and Thermal Parameters ($\times 10^4$). The form of the anisotropic thermal ellipsoid is Exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	1522 (1)	357 (3)	251 (3)	4.6 (0.3)	55.9 (2.7)	27.9 (3.9)	−0.6 (0.8)	0.5 (0.8)	3.4 (2.6)
Cl	2204 (2)	871 (6)	4890 (7)	7.7 (0.6)	86.5 (6.1)	80.6 (9.8)	3.8 (1.5)	−6.2 (1.7)	−9.6 (6.1)
O(1)	1026 (4)	−428 (14)	−173 (13)	6 (1)	90 (16)	26 (19)	2 (4)	−2 (4)	−11 (14)
O(2)	1264 (4)	1721 (13)	1056 (14)	5 (1)	86 (17)	29 (19)	7 (4)	2 (3)	−11 (13)
O(3)	3473 (6)	1328 (16)	162 (19)	15 (2)	78 (18)	137 (28)	10 (6)	1 (7)	7 (18)
N(1)	1553 (5)	−636 (16)	1592 (16)	4 (2)	68 (19)	38 (24)	2 (5)	0 (5)	0 (15)
N(2)	1518 (5)	1347 (14)	−1119 (16)	7 (2)	45 (17)	29 (23)	−10 (5)	5 (5)	−30 (14)
N(3)	2072 (5)	1064 (18)	713 (20)	5 (2)	67 (19)	55 (26)	−1 (5)	−4 (5)	15 (16)
N(4)	1796(5)	−1058 (17)	−681 (20)	7 (2)	35 (16)	68 (27)	−1 (5)	−4 (5)	16 (16)
C(1)	757 (6)	−972 (20)	518 (22)	7 (3)	67 (24)	36 (35)	11 (6)	6 (6)	16 (21)
C(2)	367 (7)	−1223 (23)	100 (26)	7 (2)	98 (27)	57 (37)	7 (6)	4 (7)	−4 (24)
C(3)	87 (7)	−1852 (30)	822 (30)	7 (3)	167 (40)	51 (43)	−4 (8)	5 (8)	−21 (30)
C(4)	179 (8)	−2265 (28)	1872 (32)	7 (3)	142 (37)	80 (47)	−12 (8)	13 (8)	−12 (29)
C(5)	559 (9)	−2044 (26)	2266 (29)	13 (3)	80 (26)	92 (42)	−6 (7)	2 (9)	−1 (26)
C(6)	866 (6)	−1402 (17)	1582 (22)	8 (2)	29 (19)	43 (33)	−4 (5)	1 (6)	−7 (18)
C(7)	1265 (7)	−1220 (21)	2149 (25)	9 (2)	63 (21)	49 (35)	9 (6)	−3 (7)	13 (20)
C(8)	1959 (8)	−568 (23)	2163 (31)	9 (2)	67 (25)	77 (38)	4 (6)	−1 (7)	2 (23)
C(9)	2134 (7)	793 (25)	1923 (26)	8 (2)	95 (26)	43 (35)	−8 (7)	−9 (7)	−2 (22)
C(10)	1044 (6)	2690 (19)	633 (23)	[a] 2.35 (0.43)					
C(11)	768 (8)	3435 (26)	1313 (24)	11 (3)	99 (26)	24 (33)	8 (7)	3 (7)	3 (23)
C(12)	548 (7)	4459 (21)	911 (26)	11 (3)	57 (23)	40 (34)	13 (7)	9 (7)	−20 (20)
C(13)	580 (7)	4827 (24)	−202 (29)	7 (2)	92 (28)	71 (37)	9 (7)	−13 (7)	−19 (25)
C(14)	816 (7)	4103 (21)	−888 (26)	9 (2)	37 (20)	88 (37)	2 (6)	1 (7)	9 (20)
C(15)	1060 (6)	3056 (20)	−484 (23)	[a] 2.40 (0.42)					
C(16)	1316 (6)	2446 (23)	−1332 (26)	7 (2)	72 (22)	55 (36)	−3 (6)	−2 (7)	5 (20)
C(17)	1768 (8)	757 (24)	−1988 (26)	[a] 3.52 (0.51)					
C(18)	1717 (6)	−734 (23)	−1882 (27)	4 (2)	88 (26)	101 (38)	4 (6)	2 (7)	28 (23)

[a] Isotropic thermal parameter refinement only for C(10), C(15), and C(17).

TABLE II. Hydrogen Atoms. Positional ($\times 10^4$) and Isotropic Thermal Parameters.[a]

	x/a	y/b	z/c	B (Å^2)
C(2) H	295	–994	–600	3.50
C(3) H	175	–1997	574	3.50
C(4) H	15	–2683	2293	3.50
C(5) H	624	–2297	2966	3.50
C(7) H	1306	–1504	2853	3.50
C(8) H(1)	2194	–1288	1876	4.50
C(8) H(2)	1920	–688	2982	4.50
C(9)H(1)	2438	810	2106	4.50
C(9) H(2)	1986	1493	2373	4.50
C(11) H	741	3208	2036	3.50
C(12) H	375	4923	1364	3.50
C(13) H	441	5556	–457	3.50
C(14) H	817	4295	–1621	3.50
C(16) H	1335	2832	–2009	3.50
C(17) H(1)	1669	1070	–2732	4.50
C(17) H(2)	2068	1013	–1891	4.50
C(18) H(1)	1922	–1215	–2366	4.50
C(18) H(2)	1427	–1006	–2095	4.50
N(3) H(1)	2273	654	324	3.50
N(3) H(2)	2083	1953	590	3.50
N(4) H(1)	2070	–1062	–550	3.50
N(4) H(2)	1690	–1868	–518	3.50
O(3) H(1)	3468	145	216	3.50
O(3) H(2)	3318	332	78	3.50

[a] All parameters calculated except the positional parameters for O(3) H(1) and O(3) H(2).

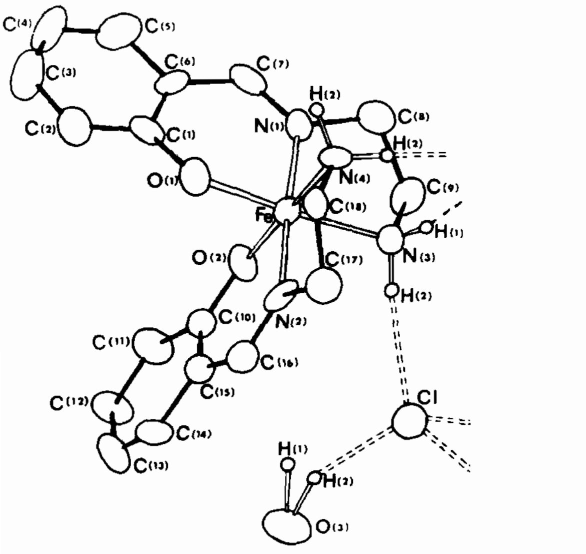


Figure 1. Perspective view showing the atom labelling scheme.

Preliminary Weissenberg photographs (CuKα radiation Ni filter) established the space group, and the cell parameters were estimated from the ω scans of h00, 0k0 and 00l reflections on a Stoe Weissenberg automatic diffractometer.

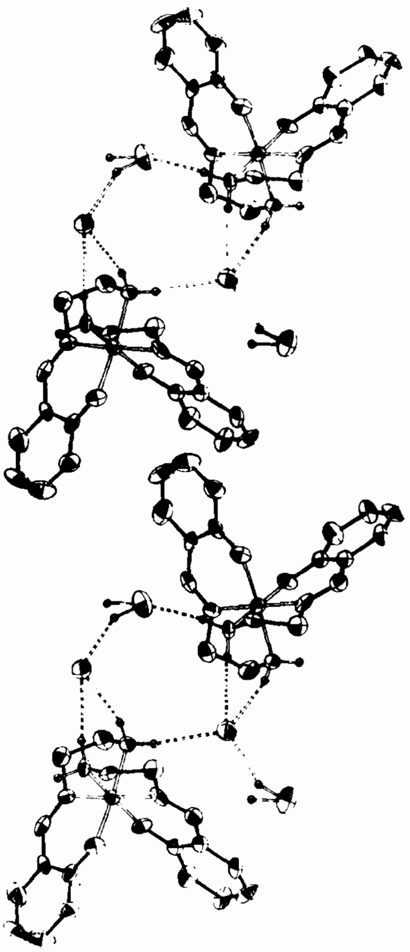


Figure 2. Stereoscopic view of the molecular structure with thermal ellipsoids drawn at 50% probability. (except for H atoms, where the scale is arbitrary).

The crystal data are:

Space Group, Pbca; M = 435.7; a = 32.694(22); b = 10.083(7); c = 12.274(8) Å; U = 4046.2 Å^3; D_c = 1.430; D_m = 1.43(1) gcm^{-3} (by flotation); Z = 8; μ(MoKα) = 8.4 cm^{-1}; λ(MoKα) = 0.7107 Å.

Intensities were measured on the diffractometer with MoKα radiation, utilizing the ω scan technique controlled by variable scan and scan time routines as previously described [3]. A single crystal, mounted along c, (0.15 × 1.0 × 1.5 mm^3) was used and data for hk0–7 collected, yielding a total of 2718 reflections, including 1587 non-zero reflections [$I \geqslant 3\sigma(I)$] used to solve the structure. Absorption, Lorentz and polarization corrections were applied.

Structure Determination

The three dimensional Patterson function enabled location of the iron position. The chloride ion, carbon, nitrogen and oxygen atom positions were

TABLE III. Interatomic Distances and Angles with Their Standard Deviations.

Distances

Fe–Cl	4.37 (.01) Å	C(3)–C(4)	1.39 (0.4) Å	C(11)–C(12)	1.35 (.04) Å
Fe–O (3)	4.06 (.02)	C(4)–C(5)	1.35	C(12)–C(13)	1.42
Fe–O (1)	1.88	C(5)–C(6)	1.46	C(13)–C(14)	1.36
Fe–O (2)	1.89	C(6)–C(1)	1.42	C(14)–C(15)	1.41
Fe–N(1)	1.93	C(6)–C(7)	1.49	C(15)–C(10)	1.42
Fe–N(2)	1.96	C(7)–N(1)	1.31 (.03)	C(15)–C(16)	1.47
Fe–N(3)	2.02	N(1)–C(8)	1.50	C(16)–N(2)	1.32 (.03)
Fe–N(4)	2.04	C(8)–C(9)	1.52 (.04)	N(2)–C(17)	1.47
O(1)–C(1)	1.34 (.03)	C(9)–N(3)	1.52 (.03)	C(17)–C(18)	1.52 (.04)
C(1)–C(2)	1.40 (.04)	O(2)–C(10)	1.32	C(18)–N(3)	1.53 (.03)
C(2)–C(3)	1.42	C(10)–C(11)	1.44 (.04)		

Angles

O(1)–Fe–O(2)	93.7 (2.0)°	C(5)–C(6)–C(1)	119.5 (2.5)°
O(1)–Fe–N(1)	93.6	C(1)–C(6)–C(7)	127.6
O(1)–Fe–N(2)	88.3	C(6)–C(7)–N(1)	116.3 (2.0)
O(1)–Fe–N(3)	175.8	C(7)–N(1)–C(8)	114.5
O(1)–Fe–N(4)	86.0	N(1)–C(8)–C(9)	106.5
O(2)–Fe–N(1)	87.4	C(8)–C(9)–N(3)	107.6
O(2)–Fe–N(2)	94.3	C(9)–N(3)–Fe	109.2
O(2)–Fe–N(3)	89.7	Fe–O(2)–C(10)	125.2
O(2)–Fe–N(4)	177.2	O(2)–C(10)–C(15)	123.5
N(1)–Fe–N(2)	177.3	C(15)–C(10)–C(11)	116.5 (2.5)
N(1)–Fe–N(3)	84.1	C(10)–C(11)–C(12)	121.3
N(1)–Fe–N(4)	95.3	C(11)–C(12)–C(13)	120.7
N(2)–Fe–N(3)	93.9	C(12)–C(13)–C(14)	120.0
N(2)–Fe–N(4)	83.0	C(13)–C(14)–C(15)	120.3
N(3)–Fe–N(4)	90.8	C(14)–C(15)–C(10)	120.9
Fe–O(1)–C(1)	124.3	C(10)–C(15)–C(16)	126.5
O(1)–C(1)–C(6)	123.0	C(15)–C(16)–N(2)	119.8 (2.0)
C(6)–C(1)–C(2)	120.7 (2.5)	C(16)–N(2)–C(17)	118.2
C(1)–C(2)–C(3)	116.0	N(2)–C(17)–C(18)	106.0
C(2)–C(3)–C(4)	124.9	C(17)–C(18)–N(4)	106.0
C(3)–C(4)–C(5)	118.9	C(18)–N(4)–Fe	108.4
C(4)–C(5)–C(6)	119.9	N_3–Cl–N_4	52.0

TABLE IV. Interatomic Distances and Angles for Potential Hydrogen Bonds, A–H······B.

A	H	B	A–B	A–H	H··B	Angles
O(3)	H(1)	Cl	3.15 Å	1.19 Å	2.49 Å	113°
O(3)	H(2)	Cl	3.15	1.12	2.10	153
N(3)	H(1)	Cl	3.23	0.91	2.36	160
N(3)	H(2)	Cl	3.28	0.91	2.39	166
N(4)	H(1)	Cl	3.35	0.91	2.44	175
N(4)	H(2)	O(3)	2.97	0.91	2.07	167

obtained from three dimensional difference syntheses. Full-matrix least-squares refinement employing anisotropic temperature factors for all atoms (except C(10), C(15) and C(17)) converged to a conventional *R* value of 0.12. A difference Fourier Synthesis showed no peaks of height greater than 1.03 e $Å^{-3}$. Two of the more intense peaks were in the region of atom O(3). At this stage, the positions of all ligand hydrogen atoms were calculated and included in further cycles of refinement. After convergence to a final *R* value of 0.114 [4], a further difference synthesis revealed the two peaks near atom O(3) were still present. These peaks were assigned to hydrogen atoms O(3) H(1) and O(3) H(2). Scattering factors were taken from ref. 5, those for iron and chlorine being corrected for the effects of anomalous scattering ($\Delta f'$, $\Delta f''$) [6]. All data processing was carried out on a CDC 6400 computer at Adelaide University with programs described previously [3].

Tables I to IV show the final parameters and molecular geometry, with estimated standard deviation in parentheses. The atom labelling scheme is shown in Figure 1. Final observed and calculated structure factor tables are available.*

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*Copies are available on application to the Editor-in-Chief.

Discussion

The cation clearly has a bis-tridentate ligand arrangement in common with the recently determined structures of Cr(III)(Saen)$_2$I [7] and Co(III)(Saen)$_2$I·H$_2$O [8], in the meridional configuration.

The possible hydrogen bonding interactions between the complex cation, water molecule and chloride ion are listed in Table IV. According to accepted criteria, regarding interatomic distances and angles for such interactions [9], all may be considered as hydrogen bonds, with the exception of the O(3)–H(1)·····Cl interaction where the angle of 113° is far too low. Figure 2 shows the hydrogen bonding interactions as broken lines. The water molecule has specific interactions with both the complex and the anion and lies in a well defined position in the lattice. One hydrogen atom of the water molecule interacts with the anion whereas the other may be considered as effectively 'free' of significant interactions.

In hydrates where both hydrogen atoms are known to be involved in hydrogen bonds, the O–H stretching band is observed as a single broad envelope with a band width typically of the order of 200 cm^{-1} [10].

However, it is well known that O–H stretching bands can be extremely sharp. In discussions of the O–H stretching region of the infra-red, many authors assign a very sharp band between 3650 and 3590 cm^{-1} to 'free' O–H [10, 11]. Examination of published i.r. spectra of alcohols reveals the band width is often as low as $\nu_{1/2}$ = 20 cm^{-1} [12]. The sharpness of the bands observed in this complex must be related to the mode of bonding of the water molecule, in particular the presence of only one hydrogen-bonded arm. A simple qualitative description of the observed spectrum is to assign the band at 3620 cm^{-1} as a free O–H stretch and the other as a hydrogen bonded O–H stretch.

The low spin state of this iron(III) complex, which is further supported by the large quadrupole splitting of 2.75 mm sec^{-1} obtained from the Mössbauer spectrum [13], is of interest because of its effect on the Fe to donor-atom distances. As recently discussed in a review article on the related Salen series, the metal to imine-nitrogen bond distance is sensitive to the nature of the metal [14]. It appears that such distances are dependent on the number of unpaired electrons on the metal. In the case of high-spin iron(III) Salen complexes, the metal to imine-nitrogen distances are in the range 2.06–2.10 Å, whereas in this study the range is 1.93–1.96 Å. This apparent contraction is not due to the difference in ligand as the corresponding distances for Co(III) and Cr(III) Saen complexes agree with those in the Salen series [7, 8]. It must then be considered as consistent with the presence of a low spin central metal ion.

Although the crystal structure does not clarify the role played by the water molecule in stabilization of the low spin state, it is known that small changes in the crystal field can bring about crossover [15]. As a possible explanation, it is suggested that the environment of the ammine hydrogens may be responsible for such a variation in crystal field.

The crystal structure of the non-hydrated species Cr(Saen)$_2$I shows that only two of the ammine hydrogens on the cation are able to form hydrogen bonds [7]. The high spin complex Fe(Saen)$_2$I has been assumed to have a similar molecular geometry on the basis of the similarity of the respective i.r. spectra [2]. Figure 2 clearly shows that in this study all four ammine hydrogens are involved in interactions, three with chloride ions, one with the water molecule. This would be expected to result in a slight increase in electron density on the ammine nitrogen, and enhance the crystal field experienced by the central metal ion.

Much interest has been shown of late in spin-crossover systems and consequently a number of review articles have appeared in the literature for both iron(II) and (III) complexes. In both cases, the data presented suggest that the spin state is extremely sensitive to apparently minor variations in the ligand [15]. In the complex described above then, it is perhaps not surprising that such a subtle interaction as that between a ligand and a lattice water molecule may be sufficient to 'tip the balance' in favour of the stabilization of the low spin state.

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