Structure and Magnetism of Electronically Distorted Iron(III) Schiff-base Complexes†

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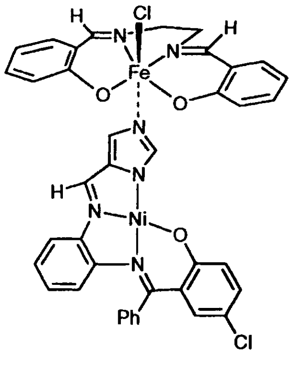
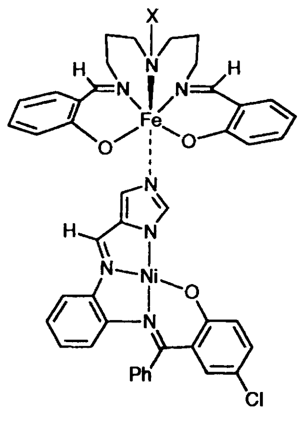
The reaction of [Fe(salen)Cl] [H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine] with an excess of L [imidazole (Him), 1-, 2- or 4-methylimidazole (1-, 2- or 4-mim)] in acetone resulted in the isolation of heterobisadducts, [Fe(salen)L(Cl)] (L = Him, 1- or 2-mim) and a homobisadduct, [Fe(salen)L_2]Cl (L = 4-mim). The structures of [Fe(salen)(1-mim)Cl] and [Fe(salen)(4-mim)$_2$]Cl were determined by single-crystal X-ray diffraction: [Fe(salen)(1-mim)Cl], monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.8510(10)$, $b = 15.9830(10)$, $c = 12.8350(10)$ Å, $\beta = 107.610(10)°$; [Fe(salen)(4-mim)$_2$]Cl, orthorhombic, space group $Fdd2$, $Z = 8$, $a = 21.7650(10)$, $b = 12.5040(10)$, $c = 18.508(2)$ Å. The structures were refined by full-matrix least-squares methods on F^2 to $R = 0.0537$ and 0.0338 for 2609 and 1207 reflections, respectively. A significant difference between the two structures is that the dihedral angle between the two phenyl rings of the salen ligand is 17.5° for [Fe(salen)(1-mim)Cl] and 4.4° for [Fe(salen)(4-mim)$_2$]Cl. All of the complexes were characterized by variable-temperature magnetic susceptibility and Mössbauer spectroscopy. The heterobisadducts, which have a N_3O_2Cl donor set, exhibit an admixed electronic ground state whereas the homobisadduct is high spin. Another N_3O_2Cl donor set molecule has been found to exhibit a temperature-dependent spin equilibrium, $^2T \rightleftharpoons {}^6A$, as evidenced by variable-temperature magnetic susceptibility, ESR and Mössbauer spectroscopies.

We recently reported the first heterodinuclear spin-crossover complexes which were prepared by the reaction of tetra- or penta-dentate Schiff-base complex of Fe^{III} with a nickel imidazolate chelate to give, in the case of the tetradentate ligand *N,N'*-bis(salicylidene)ethane-1,2-diamine (H_2salen), a N_3O_2Cl donor set **A** and, in the case of the pentadentate ligands a N_4O_2 donor set **B**.[1] It has been reported previously that the N_4O_2 donor set produces an overall ligand field close to the crossover point for Fe^{III} in salen Schiff-base complexes.[2] Whether or not a complex with this donor set exhibits the crossover phenomenon was found to depend on the counter ion, substituents on the salen ligand, structural features of the axial ligand, and intermolecular effects in the solid state. Therefore, the observation of spin crossover in the solid state in complexes derived from pentadentate Schiff-base ligands was not unexpected. However, the observation of spin crossover in the complex derived from [Fe(salen)Cl] and the nickel imidazolate chelate is the first example reported for Fe^{III} in a N_3O_2Cl donor set.



A



B X = H or Me

The objective of the present work was the synthesis of other examples of iron(III) complexes containing the N_3O_2Cl donor set which might show unusual electronic and structural properties. The compounds prepared were derived from [Fe(salen)Cl] or [Fe(5MeO-salen)Cl] and an imidazole donor to give an unsymmetrical heterobisadduct of the iron(III) Schiff base in which the imidazole donor occupies one axial site and chloride ion occupies the other. These complexes are also of interest in bioinorganic chemistry due to the importance of the structurally similar iron(III) porphyrin complexes with unsymmetrical axial ligation.[3] Previous synthetic efforts in iron(III) porphyrin chemistry have been hindered by the inability to produce monoimidazole adducts as are reported here.[4] The complexes [Fe(5MeO-salen)(NiL^1)Cl], [Fe(salen)(1-mim)Cl], [Fe(salen)(Him)Cl] and [Fe(salen)(2-mim)Cl] exhibit unsymmetrical axial ligation (H_2L^1 = 5-{*o*-[(5-chloro-2-hydroxyphenyl)phenylmethyleneamino]phenyliminomethyl}-imidazole; 1- and 2-mim = 1- and 2-methylimidazole, Him = imidazole). Of these complexes containing the N_3O_2Cl donor set, only the first exhibited spin crossover as determined by magnetic susceptibility measurements and Mössbauer and ESR spectroscopies. The others exhibited depressed magnetic moments and are best characterized as admixed-spin species. The high-spin homobisadduct [Fe(salen)(4-mim)$_2$Cl] was also prepared. All compounds were characterized by elemental analysis, Mössbauer spectroscopy, and magnetic susceptibility measurements, [Fe(salen)(1-mim)Cl] and the spin-crossover complex [Fe(5-MeO-salen)(NiL^1)Cl] were also characterized

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

by ESR spectroscopy and crystal structures were determined for [Fe(salen)(1-mim)Cl] and [Fe(salen)(4-mim)$_2$]Cl.

Experimental

The complexes [Fe(salen)Cl], [Fe(5MeO-salen)Cl][5] and [NiL^1][6] were prepared as described previously. Imidazole, 1-, 2- and 4-methylimidazole were obtained from Aldrich and used without further purification. Solvents were of reagent grade and used without further purification. Analytical data, given in Table 1, were determined by MHW Laboratories for all new compounds.

Syntheses of Adducts of [Fe(salen)Cl].—The mononuclear imidazole adducts of [Fe(salen)Cl] with imidazole and its methyl derivatives were obtained from the reaction of [Fe(salen)Cl] with a three- to four-fold excess of the base in acetone as described below for [Fe(salen)(1-mim)Cl]. The product was the heterobisadduct [Fe(salen)L(Cl)], for all cases except 4-methylimidazole, which gave exclusively the homobisadduct under identical conditions. The reaction of [Fe(salen)Cl] with 2-methylimidazole was performed in a Vacuum Atmospheres Dri-Lab under helium to prevent hydrolysis of [Fe(salen)Cl] to the μ-oxo dimer under the reaction conditions. The solid product is stable in air.

1-Methylimidazole (0.0715 g, 0.871 mmol) in acetone (5 cm^3) was added to a freshly prepared and hot filtered solution of [Fe(salen)Cl] (0.1001 g, 0.280 mmol) in acetone (40 cm^3). The reaction mixture was heated gently for 5–10 min and set aside to cool. After several hours the reaction mixture was filtered to give 0.1045 g black crystals (85% yield). Crystals of [Fe(salen)(1-mim)Cl] and [Fe(salen)(4-mim)$_2$]Cl suitable for X-ray analysis were obtained by substituting heptan-2-one for acetone as the solvent in the above reaction.

Synthesis of [Fe(5MeO-salen)(NiL^1)Cl].—The complex [NiL^1] (0.0182 g, 0.0397 mmol) was dissolved in CHCl$_3$ (7 cm^3), and the resulting solution was added to a solution (7–10 cm^3) of [Fe(5MeO-salen)Cl] (0.0162 g, 0.0388 mmol) in 95% ethanol. The reaction mixture was set aside to concentrate. After 2 d a brown powder (12.1 mg, 0.0138 mmol, 36% yield) was filtered off. Further concentration of the filtrate resulted in the precipitation of the μ-oxo dimer of [Fe(5MeO-salen)Cl]. The reaction was easily scaled up to produce 122 mg product at 61% yield. Attempts to produce diffraction-quality crystals failed.

Spectra.—The ESR spectra were obtained on either a solution or polycrystalline samples at 80 K on a Varian model E3 spectrometer. Mössbauer spectra were obtained on a Ranger Scientific model MS-900 spectrometer in the acceleration mode with moving-source geometry at 80 K or room temperature. They were analysed by a constrained least-squares fit to Lorentzian-shaped lines. The samples were mounted in polyethylene cells. The velocity range was calibrated with Na$_2$[Fe(CN)$_5$(NO)], and the isomer shift values converted into the iron standard by subtracting 0.257 mm s^{-1}.

Magnetism.—The magnetic susceptibilities were measured between 80 and 300 K on a computer-controlled Faraday system consisting of a Cahn 2000 microbalance, Applied Magnetics electromagnet, Lake Shore Cryotronics temperature controller, platinum-resistance thermometer, and Abbess instrument cryostat. A Data Translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with Hg[Co(NCS)$_4$].[7] The raw data were corrected for the susceptibility of the holder and the diamagnetism of the ligand atoms by Pascal's constant,[8] and converted into molar susceptibilities from which the magnetic moments were calculated as $\mu = 2.828(\chi_M T)^{\frac{1}{2}}$.

Table 1 Elemental analysis data for compounds prepared in this work

Complex	Analysis (%)* C	H	N
[Fe(5MeO-salen)(NiL^1)Cl]	56.15 (56.25)	4.00 (3.80)	9.45 (9.60)
[Fe(salen)(1-mim)Cl]	54.80 (54.65)	4.80 (4.60)	12.75 (12.75)
[Fe(salen)(Him)Cl]·0.5H$_2$O	52.25 (52.50)	4.45 (4.40)	12.45 (12.90)
[Fe(salen)(2-mim)Cl]	54.45 (54.65)	4.65 (4.60)	12.55 (12.75)
[Fe(salen)(4-mim)$_2$]Cl	55.55 (55.25)	5.75 (5.00)	15.80 (16.10)

* Calculated values in parentheses.

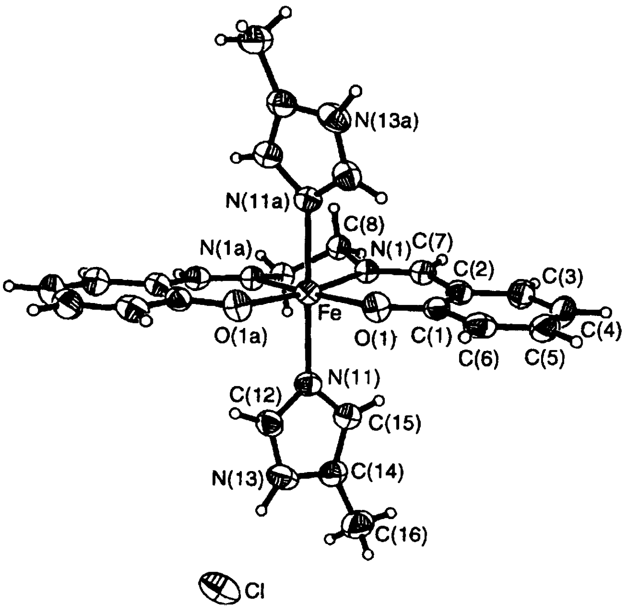

Fig. 1 Crystal structure diagram for [Fe(salen)(4-mim)$_2$]Cl showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity

Crystal Structure Determination.—Crystals of [Fe(salen)(4-mim)$_2$]Cl and [Fe(salen)(1-mim)Cl] were obtained as described above. Crystallographic data and other parameters are given in Table 2. The data were collected on a Siemens P4/RA diffractometer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results

Crystal Structures.—The structures of [Fe(salen)(4-mim)$_2$]Cl and [Fe(salen)(1-mim)Cl] were solved by direct and Fourier-difference methods using SHELXS 86[9] and refined on F^2. Table 3 contains final atomic coordinates for [Fe(salen)(4-mim)$_2$]Cl and [Fe(salen)(1-mim)Cl]. Bond distances and angles are given in Table 4. Crystal structure diagrams showing labelling schemes are displayed in Figs. 1 and 2.

Mössbauer Spectroscopy.—Mössbauer spectral data for all of the complexes were obtained at liquid-nitrogen and room temperatures and are given in Table 5. The spectra of all the mononuclear compounds are rather similar to one another regardless of whether the complex is a heterobisadduct, [Fe(salen)L(Cl)], or the homobisadduct, [Fe(salen)L$_2$]Cl. The isomer shifts vary between 0.34 and 0.54 mm s^{-1} and the

Table 2 Crystal data for [Fe(salen)(1-mim)Cl] and [Fe(salen)(4-mim)$_2$]Cl

	[Fe(salen)(1-mim)Cl]	[Fe(salen)(4-mim)$_2$]Cl
Empirical formula	$C_{20}H_{20}ClFeN_4O_2$	$C_{24}H_{24}ClFeN_6O_2$
M	439.70	519.79
T/K	293(2) K	293(2)
λ/Å	1.541 84	0.710 73
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Fdd2$
a/Å	9.8510(10)	21.7650(10)
b/Å	15.9830(10)	12.5040(10)
c/Å	12.8350(10)	18.508(2)
β/°	107.610(10)	
U/Å^3	1926.2(3)	5036.9(7)
Z	4	8
D_c/Mg m^{-3}	1.516	1.371
μ/mm^{-1}	7.757	0.737
F(000)	908	2152
Crystal size/mm	0.5 × 0.06 × 0.06	0.3 × 0.2 × 0.2
2θ/° range for data collection	4.55–57.74	3.43–24.98
hkl ranges	−1 to 10, −1 to 17, −14 to 13	−1 to 25, −1 to 14, −1 to 22
Reflections collected	3411	1404
Independent reflections (R_{int})	2609 (0.0393)	1207 (0.0212)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data, restraints, parameters	2600, 0, 253	1207, 1, 156
Goodness-of-fit on F^2	1.064	0.795
Final R* indices [$I > 2\sigma(I)$]	$R = 0.0465$, $R' = 0.1339$	$R = 0.0309$, $R' = 0.0898$
(all data)	$R = 0.0537$, $R' = 0.1411$	$R = 0.0338$, $R' = 0.0943$
Largest difference peak and hole/e Å^{-3}	0.581, −0.484	0.196, −0.191
Absolute structure parameter		−0.01(2)

* Weighting scheme $w = 1/[\sigma^2(F^2) + (c_1P)^2 + c_2P]$ where $c_1 = 0.10$, $c_2 = 0$ and $P = [(\max F_o^2, 0) + 2F_c^2]/3$.

Table 3 Atomic coordinates (× 10^4) for [Fe(salen)(4-mim)$_2$]Cl and [Fe(salen)(1-mim)Cl]

Atom	x	y	z	Atom	x	y	z
(*a*) [Fe(salen)(4-mim)$_2$]Cl							
Fe	2 500	−2 500	10 035(1)	N(1)	1 929(1)	−2 113(2)	10 918(2)
Cl	2 500	−7 500	8 524(1)	C(1)	1 255(2)	−1 901(3)	9 523(2)
N(11)	2 204(1)	−4 148(2)	10 041(2)	C(2)	1 005(2)	−1 747(3)	10 224(2)
C(12)	2 482(2)	−4 880(3)	9 646(3)	C(3)	379(2)	−1 463(3)	10 298(3)
N(13)	2 180(2)	−5 800(3)	9 637(2)	C(4)	11(2)	−1 349(4)	9 696(3)
C(14)	1 656(2)	−5 675(3)	10 051(3)	C(5)	245(2)	−1 488(3)	9 016(3)
C(15)	1 683(2)	−4 650(3)	10 303(2)	C(6)	865(2)	−1 755(3)	8 928(2)
C(16)	1 215(2)	−6 577(4)	10 168(4)	C(7)	1 363(2)	−1 812(3)	10 886(2)
O(1)	1 837(1)	−2 146(2)	9 403(1)	C(8)	2 254(2)	−2 063(3)	11 613(2)
(*b*) [Fe(salen)(1-mim)Cl]							
Fe	814(1)	7 805(1)	1 043(1)	O(2)	2 274(3)	7 051(2)	1 835(2)
Cl	1 962(1)	9 012(1)	2 022(1)	C(11)	3 637(4)	6 819(2)	587(3)
O(1)	−650(3)	7 789(2)	1 753(2)	C(12)	3 293(4)	6 660(2)	1 564(3)
N(1)	−559(4)	8 573(2)	−194(3)	C(13)	4 109(4)	6 050(3)	2 280(3)
C(1)	−2 481(4)	8 662(2)	600(3)	C(14)	5 175(4)	5 608(3)	2 038(4)
C(2)	−1 925(4)	8 136(2)	1 518(3)	C(15)	5 494(5)	5 755(3)	1 076(4)
C(3)	−4 615(3)	8 878(2)	1 139(3)	C(16)	4 734(5)	6 355(3)	371(4)
C(4)	−2 752(3)	7 993(2)	2 208(3)	C(17)	2 986(4)	7 474(3)	−167(3)
C(5)	−4 076(4)	8 352(3)	2 022(4)	N(31)	−295(3)	6 733(2)	54(2)
C(6)	−3 844(4)	9 021(3)	437(3)	C(32)	9(4)	6 293(2)	−726(3)
C(7)	−1 771(4)	8 836(3)	−199(3)	N(33)	−885(3)	5 655(2)	−1 062(2)
C(8)	−62(5)	8 728(3)	−1 158(4)	C(34)	−1 840(5)	5 679(3)	−482(3)
C(9)	1 491(5)	8 649(3)	−850(4)	C(35)	−1 477(4)	6 344(3)	197(3)
N(2)	1 960(4)	7 942(2)	−104(3)	C(36)	−890(5)	5 073(3)	−1 937(3)

quadrupole splittings between 1.13 and 1.60 mm s^{-1}. Each complex exhibits a nearly temperature-independent spectrum with regard to its isomer shift, quadrupole splitting, intensity and shape. The lines in the spectrum of [Fe(salen)(1-mim)Cl] are extremely sharp and symmetrical, while those of the others are asymmetric. The spectra of [Fe(salen)(Him)Cl] and [Fe(salen)(2-mim)Cl] show a prominent low-velocity line with a less-intense and poorly resolved high-velocity line, that of [Fe(salen)(4-mim)$_2$]Cl exhibits well resolved lines with a more intense higher-velocity component and the dinuclear complex [Fe(5MeO-salen)(NiL^1)Cl] exhibits two sets of quadrupole splittings at room temperature and a single set at liquid-nitrogen temperature.

Magnetism.—Magnetic susceptibilities for all new compounds were measured by the Faraday technique between liquid-nitrogen and room temperatures. There were no abrupt changes in susceptibility for any of the complexes. The magnetic

Table 4 Bond lengths (Å) and angles (°)

(*a*) [Fe(salen)(4-mim)$_2$]Cl

Fe–O(1)	1.909(3)	C(12)–N(13)	1.326(5)	N(1)–C(7)	1.289(5)	C(2)–C(7)	1.453(5)
Fe–N(1)	2.111(3)	N(13)–C(14)	1.382(6)	N(1)–C(8)	1.468(4)	C(3)–C(4)	1.378(6)
Fe–N(11)	2.159(3)	C(14)–C(15)	1.366(6)	C(1)–C(6)	1.402(5)	C(4)–C(5)	1.367(7)
N(11)–C(12)	1.317(5)	C(14)–C(16)	1.497(6)	C(1)–C(2)	1.421(5)	C(5)–C(6)	1.401(6)
N(11)–C(15)	1.385(5)	O(1)–C(1)	1.322(5)	C(2)–C(3)	1.416(5)	C(8)–C(8$^{\text{I}}$)	1.530(7)

O(1)–Fe–O(1$^{\text{I}}$)	104.5(2)	C(12)–N(11)–C(15)	104.9(3)	C(1)–O(1)–Fe	132.5(3)	C(3)–C(2)–C(7)	116.7(4)
O(1)–Fe–N(1)	88.61(11)	C(12)–N(11)–Fe	121.5(3)	C(7)–N(1)–C(8)	119.3(3)	C(1)–C(2)–C(7)	123.9(3)
O(1$^{\text{I}}$)–Fe–N(1)	166.6(1)	C(15)–N(11)–Fe	132.7(2)	C(7)–N(1)–Fe	126.4(2)	C(4)–C(3)–C(2)	120.5(4)
N(1)–Fe–N(1$^{\text{I}}$)	78.4(2)	N(11)–C(12)–N(13)	112.4(4)	C(8)–N(1)–Fe	113.8(2)	C(5)–C(4)–C(3)	121.0(4)
O(1)–Fe–N(11)	89.95(12)	C(12)–N(13)–C(14)	107.7(3)	O(1)–C(1)–C(6)	118.6(4)	C(4)–C(5)–C(6)	119.8(4)
O(1$^{\text{I}}$)–Fe–N(11)	90.43(12)	C(15)–C(14)–N(13)	105.1(3)	O(1)–C(1)–C(2)	123.4(3)	C(5)–C(6)–C(1)	121.5(4)
N(1)–Fe–N(11)	92.25(12)	C(15)–C(14)–C(16)	133.2(4)	C(6)–C(1)–C(2)	118.0(3)	N(1)–C(7)–C(2)	124.5(3)
N(1$^{\text{I}}$)–Fe–N(11)	87.27(12)	N(13)–C(14)–C(16)	121.6(4)	C(3)–C(2)–C(1)	119.3(4)	N(1)–C(8)–C(8$^{\text{I}}$)	107.9(2)
N(11)–Fe–N(11$^{\text{I}}$)	179.4(2)	C(14)–C(15)–N(11)	109.9(4)				

(*b*) [Fe(salen)(1-mim)Cl]

Fe–O(2)	1.916(3)	C(1)–C(2)	1.416(5)	C(9)–N(2)	1.462(5)	C(14)–C(15)	1.383(6)
Fe–O(1)	1.924(3)	C(1)–C(6)	1.416(6)	N(2)–C(17)	1.279(5)	C(15)–C(16)	1.375(6)
Fe–N(2)	2.121(3)	C(1)–C(7)	1.432(6)	O(2)–C(12)	1.314(4)	N(31)–C(32)	1.331(5)
Fe–N(1)	2.135(3)	C(2)–C(3)	1.392(5)	C(11)–C(16)	1.405(6)	N(31)–C(35)	1.380(5)
Fe–N(31)	2.214(3)	C(3)–C(6)	1.362(5)	C(11)–C(12)	1.418(5)	C(32)–N(33)	1.331(5)
Fe–Cl	2.391(1)	C(3)–C(4)	1.381(6)	C(11)–C(17)	1.438(6)	N(33)–C(34)	1.365(5)
O(1)–C(2)	1.321(4)	C(8)–C(9)	1.465(7)	C(12)–C(13)	1.412(5)	N(33)–C(36)	1.457(5)
N(1)–C(7)	1.264(5)			C(13)–C(14)	1.376(6)	C(34)–C(35)	1.353(6)
N(1)–C(8)	1.483(6)						

O(2)–Fe–O(1)	106.9(1)	N(31)–Fe–Cl	176.8(1)	C(3)–C(6)–C(1)	121.8(4)	C(14)–C(13)–C(12)	122.1(4)
O(2)–Fe–N(2)	87.78(12)	C(2)–O(1)–Fe	133.1(2)	N(1)–C(7)–C(1)	126.7(4)	C(13)–C(14)–C(15)	120.6(4)
O(1)–Fe–N(2)	164.3(1)	C(7)–N(1)–C(8)	119.3(3)	C(9)–C(8)–N(1)	110.0(3)	C(16)–C(15)–C(14)	118.7(4)
O(2)–Fe–N(1)	164.0(1)	C(7)–N(1)–Fe	125.4(3)	N(2)–C(9)–C(8)	110.0(4)	C(15)–C(16)–C(11)	122.4(4)
O(1)–Fe–N(1)	87.86(12)	C(8)–N(1)–Fe	115.0(3)	C(17)–N(2)–C(9)	120.7(3)	N(2)–C(17)–C(11)	125.7(4)
N(2)–Fe–N(1)	76.99(13)	C(2)–C(1)–C(6)	118.4(4)	C(17)–N(2)–Fe	125.5(3)	C(32)–N(31)–C(35)	104.7(3)
O(2)–Fe–N(31)	88.72(12)	C(2)–C(1)–C(7)	124.1(3)	C(9)–N(2)–Fe	113.8(3)	C(32)–N(31)–Fe	131.0(3)
O(1)–Fe–N(31)	87.15(12)	C(6)–C(1)–C(7)	117.5(4)	C(12)–O(2)–Fe	132.0(2)	C(35)–N(31)–Fe	124.2(3)
N(2)–Fe–N(31)	87.46(12)	O(1)–C(2)–C(3)	119.0(3)	C(16)–C(11)–C(12)	119.0(4)	N(31)–C(32)–N(33)	111.8(3)
N(1)–Fe–N(31)	85.77(12)	O(1)–C(2)–C(1)	122.8(3)	C(16)–C(11)–C(17)	117.7(4)	C(32)–N(33)–C(34)	107.4(3)
O(2)–Fe–Cl	93.99(9)	C(3)–C(2)–C(1)	118.2(3)	C(12)–C(11)–C(17)	123.2(4)	C(32)–N(33)–C(36)	125.9(3)
O(1)–Fe–Cl	93.75(8)	C(6)–C(3)–C(4)	119.5(3)	O(2)–C(12)–C(13)	119.1(3)	C(34)–N(33)–C(36)	126.6(3)
N(2)–Fe–Cl	90.87(9)	C(4)–C(3)–C(2)	121.8(3)	O(2)–C(12)–C(11)	123.7(3)	C(35)–C(34)–N(33)	106.4(4)
N(1)–Fe–Cl	91.14(9)	C(3)–C(4)–C(3)	120.3(4)	C(13)–C(12)–C(11)	117.2(3)	C(34)–C(35)–N(31)	109.7(4)

Symmetry transformation used to generate equivalent atoms: I $-x + \frac{1}{2}, -y - \frac{1}{2}, z$.

Table 5 Mössbauer spectral data * and magnetic moments

Complex	T/K	Isomer shift/ mm s^{-1}	Quadruple splitting/ mm s^{-1}	$\mu_{\text{eff}}/\mu_{\text{B}}$
[Fe(5MeO-salen)(NiL^1)Cl]	295	0.22, 0.25	1.13, 0.19	5.67
	80	0.44	1.15	5.23
[Fe(salen)(1-mim)Cl]	295	0.40	1.53	5.55
	80	0.52	1.53	5.38
[Fe(salen)(Him)Cl]	295	0.45	1.60	5.62
	80	0.54	1.54	5.70
[Fe(salen)(2-mim)Cl]	295	0.34	1.29	4.82
	80	0.41	1.13	4.74
[Fe(salen)(4-mim)$_2$]Cl	295	0.45	1.43	5.58
	80	0.48	1.42	5.58

* Mössbauer spectral parameters ± 0.02 mm s^{-1} and are relative to iron metal.

moment ranges are given in Table 5. All complexes exhibit moments below 5.92 μ_B; however, they differ in the amount of this deviation and the temperature dependence of the data. The only homobisadduct, [Fe(salen)(4-mim)$_2$]Cl, shows the smallest depression and exhibits a temperature-independent magnetic moment. The heterobisadducts, [Fe(salen)L(Cl)] show a greater deviation of the magnetic moment from 5.92 μ_B and exhibit temperature dependence.

Discussion

Structures of [Fe(salen)(4-mim)$_2$]Cl *and* [Fe(salen)Cl(1-mim)].—The salient structural features of the [Fe(salen)-(Him)$_2$]Y (Y = ClO$_4$, BF$_4$, or PF$_6$) complexes reported by Murray and co-workers[10] are relevant to the discussion of the structures determined in this work. For the high-spin complex (Y = PF$_6$) it was found that the two phenyl rings of the Schiff base are approximately coplanar with a dihedral angle of 1.4°.

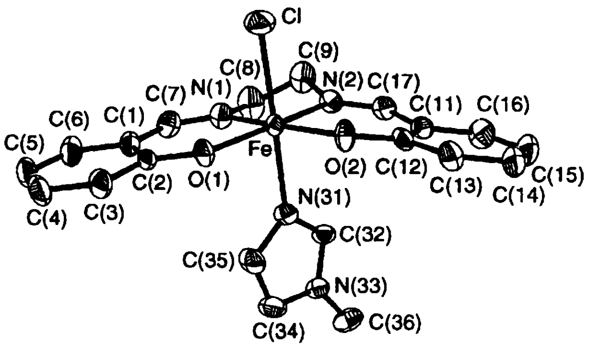

Fig. 2 Crystal structure diagram for [Fe(salen)(1-mim)Cl] showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity

The five-membered ring comprising the iron atom, the two Schiff-base nitrogens, and the intervening carbon atoms of the ethylenediamine fragment assume a *meso* configuration in which the two C atoms are displaced in opposite directions from their adjacent phenyl rings. Iron atom deviations from these planes are approximately equal and in opposite directions. In contrast, the structures of the crossover complexes (Y = ClO_4 or BF_4) revealed a substantial angle of 21–22° between the two phenyl rings of the Schiff-base ligand. In these cases one of the two carbon atoms of the five-membered FeN_2C_2 ring deviates substantially more than the other from its adjacent phenyl ring plane, and the central iron atom deviates significantly from one phenyl ring plane relative to the other. The resulting conformation of the FeN_2C_2 ring is described as an envelope with one of the carbon atoms distorted from coplanarity with the other four atoms. It is suggested that a planar ligand, as observed in the (high-spin) PF_6^- derivative, imposes a constraint on the complex which results in an inability to adapt to a spin-state change; thus the complex is locked in the high-spin form. The authors also observed that in the high-spin complex the planes of both imidazole ligands lie parallel to the two O–Fe–N axes of the Schiff-base plane (an eclipsed conformation), while in the crossover complexes one of the imidazole ligands is similarly disposed but the other is parallel to the long axis of the Schiff-base chelate (a staggered conformation). For both high-spin and crossover complexes, close contacts are detected between the imidazole C(2)–H and the Schiff-base oxygen atom for the imidazole ligands which are disposed coplanar with an O–Fe–N system of the Schiff base. Consistent with this observation a pronounced asymmetry between the Fe–N_{im}–C(2) and the Fe–N_{im}–C(5) angles of imidazole was observed for the imidazole ligands aligned with an O–Fe–N axis but not for the imidazole ligands which are not aligned with an O–Fe–N axis.

The complex [Fe(salen)(4-mim)$_2$]Cl is six-co-ordinate with the 4-mim ligands occupying axial positions. The iron atom is in the N_2O_2 co-ordination plane of salen. Iron to imine nitrogen bond distances are in the range for a high-spin assignment of the iron(III). The two phenyl rings are approximately coplanar with a dihedral angle of 4.4°. The iron atom deviations from these planes are equal (±0.114 Å). The five-membered ring composed of Fe, N(1), C(8), C(8a) and N(1a) adopts a *meso* conformation with symmetric deviations of the bridging carbon atoms, C(8) and C(8a), from their adjacent phenyl rings of ±0.343 Å. The planes of the imidazole ligands are aligned with an O–Fe–N axis of the Schiff-based ligand. The Fe–N(11,11a)–C(12,12a) angle (121.5°) is substantially smaller than the Fe–N(11,11a)–C(15,15a) angle (132.7°), resulting in a significant 'tilt' of the 4-methylimidazole rings toward the oxygen atom of the Schiff-base ligand. Overall the structure of [Fe(salen)(4-mim)$_2$]Cl is consistent with high-spin iron(III) based on the findings of Murray and co-workers.[10]

The complex [Fe(salen)(1-mim)Cl] is six-co-ordinate with 1-methylimidazole and chloride occupying axial positions. The iron atom lies within 0.073 Å of the central co-ordination plane comprising Fe, N(1), N(2), O(1) and O(2) compared to a zero deviation for the homobisadduct. Iron to imine nitrogen bond distances of 2.12 and 2.13 Å are in the range for a high-spin assignment for iron(III). However, the other structural features and magnetic data do not support this assignment. The structure exhibits several of the same features found in those of the spin-crossover examples reported by Murray and co-workers.[10] They are a substantial angle of 17.5° between the two phenyl rings of the Schiff base, asymmetric deviations of C(9) (0.353 Å) and C(8) (−0.178 Å) from the central co-ordination plane defined by Fe, N(1), N(2), O(1) and O(2), asymmetric deviations from their adjacent phenyl rings of 0.376 Å for C(9) and −0.278 Å for C(8), asymmetric deviations of the iron atom from the two phenyl ring planes [0.047 Å from the plane comprising C(1)–C(6) and −0.254 Å from that comprising C(11)–C(16)]. The plane of the 1-methylimidazole ligand is aligned with an O–Fe–N axis of the Schiff-based ligand (dihedral angle 5.8°). The complex also shows a tilt of the imidazole ring toward the Schiff base O(1) with Fe–N(31)–C(35) and Fe–N(31)–C(32) angles of 124.2 and 131.0°, respectively. The non-planar salen ligand observed here and previously by Murray and co-workers[10] is also observed in the tetradentate Schiff-base ligand formed by the condensation of 2-aminobenzaldehyde and ethylenediamine and may be implicated in the spin-crossover behaviour for its iron(III) complexes.[11] In contrast, another heterobisadduct, [Fe(3MeO-salen)(5-pim)(H_2O)]BPh_4 (5-pim = 5-phenylimidazole), which is characterized as high spin, was found to contain a planar Schiff-base ligand.[12]

Adducts of [Fe(salen)Cl].—Studies of the reaction of imidazole donors with iron(III) tetradentate Schiff bases and of iron(III) porphyrins have indicated a pronounced preference for the isolation of 1:2 compared to 1:1 adducts. For iron(III) porphyrins this is readily understood because the resultant low-spin FeN_6 bisadducts are thermodynamically more stable than the high-spin monoadduct.[13] The iron(III) tetradentate Schiff-base complexes also show preference for the formation of the homobisadduct despite the fact that the ligand-field strength due to the N_4O_2 donor set is considerably weaker than for the N_6 donor set in the prophyrin bisadducts. In fact many of the iron(III) Schiff-base N_4O_2 complexes have zero crystal-field stabilization and are high spin. Using reaction conditions very similar to that employed in the present study, Murray and co-workers[10,12] observed that [Fe(salen)]$^+$ yielded only homobisadducts for all bases and counter ions used. Attempts to force heterobisligation by using sterically hindered imidazole bases resulted in impure product mixtures. However, they were able to produce high-spin heterobisligated iron(III) complexes of 3R-salen (R = OMe or OEt) by means of sterically hindered 4(5)-phenylimidazole and rapid isolation techniques.

Quite the opposite result was found under the reaction conditions employed in the present work. The use of a three- to four-fold excess of base, slow isolation techniques, and sterically unhindered imidazoles should have favoured the formation of the homobisadduct. However, only 4-mim produced a homobisadduct with [Fe(salen)Cl] while Him, 1- and 2-mim yielded exclusively the heterobisadduct. Two of the imidazoles containing N–H bonds, Him and 2-mim, both form heterobisadducts while the third, 4-mim, which also contains an N–H bond, forms the homobisadduct. Hydrogen bonding to the imidazole N–H moiety does not appear to be relevant to the formation of heterobisadducts. The isolation of [Fe(salen)(1-mim)Cl] from the reaction mixture is in opposition to what was observed in solution. The ESR spectrum at 77 K of the [Fe(salen)Cl] and 1-methylimidazole reaction mixture revealed two sets of signals, one at $g = 4.0$, typical of high-spin Fe^{III} and one at $g_{av} = 2.0$ ($g_x \neq g_y \neq g_z$), typical of low-spin Fe^{III}. The three low-spin signals are presumably due to the formation of the thermodynamically favoured homobisadduct, [Fe(salen)-(1-mim)$_2$]Cl, in solution while the high-spin signal can be attributed to the heterobisadduct and/or starting complex. Further to complicate the picture, the reaction of [Fe(5MeO-salen)Cl] with an excess of 1-mim or of Him in acetone produced the high-spin homobisadducts exclusively whereas [Fe(salen)Cl] yielded only heterobisadducts under identical conditions. Isolation of hetero- *vs* homo-bisadducts is not easily predicted or explained in terms of the imidazole donor, iron ligand, counter ion, or reaction solvent. Obviously, in these cases where the ligand field does not greatly stabilize the low-spin product, very subtle factors, such as minor conformational changes and crystal-packing forces, are involved in determining the product of a particular reaction.

The spin states of the solid mononuclear adducts of [Fe(salen)Cl] were assigned on the basis of magnetic susceptibility, X-ray diffraction, and Mössbauer spectral results; ESR was not useful in this regard as the solid-state spectral lines were extremely broad, and solution spectra are inconclusive because the complexes undergo dissociation. As seen in Table 5, the heterobisadducts all exhibit magnetic moments between 4.8 and 5.6 μ_B at 295 K, which are depressed from the expected value of 5.9 μ_B and show some temperature variation. Depressed moments of [Fe(salen)Cl] complexes could be attributed to (*i*) weak antiferromagnetic coupling arising from a dimeric structure in which adjacent iron(III) centres interact *via* phenolic oxygens of the salen ligand, (*ii*) a spin-crossover behaviour, (*iii*) contamination of sample by the strongly antiferromagnetic μ-oxo dimer, or (*iv*) mixing, *via* spin–orbit coupling, of low-multiplicity ^{4}T or ^{2}T terms into the ^{6}A ground-state term. The structure of [Fe(salen)(1-mim)Cl], the temperature-independent Mössbauer spectra, and the analytical data rule out the first three of these possibilities. In addition, a structure determination of [Fe(salen)(1-mim)Cl] at 193 K revealed no significant differences in bond distances from those in the room-temperature structure, which also argues against a spin crossover. The conclusion for the heterobisadducts, [Fe-(salen)L(Cl)] (L = Him, 1-mim or 2-mim), is that they have lower-multiplicty state(s) mixed into the ground-state term and are thus best described as admixed-spin systems. Earlier investigators characterized [Fe(salen)]$^+$ complexes with slightly depressed moments as arising from mixing of the ^{4}T term into the ground state.[5,14] Recently Morgenstern-Badarau and co-workers[15] have proposed an admixture of the $S = \frac{5}{2}$, $\frac{3}{2}$ and $\frac{1}{2}$ states to explain the similar behaviour (magnetic moments between 5.65 and 5.75 μ_B) of complexes prepared from reaction of [Fe(salen)Cl] or [Fe(nta)] (H_3nta = nitrilotriacetic acid) and oxalate (ox) to give [Fe(salen)(ox)]$^-$ and [Fe(nta)-(ox)]$^{2-}$.[15] There is no significant difference in these two admixed approaches as the extent of low-spin contribution in the latter complexes was calculated to be 1%.

The Mössbauer spectra for both the mononuclear homobisadduct and heterobisadducts of [Fe(salen)Cl] are not useful in spin-state determination as the admixed heterobisadduct and high-spin homobisadduct have rather similar quadrupole splittings. Values in the range reported here have been observed by earlier workers[16] for other admixed and pure high-spin complexes of [Fe(salen)]$^+$.

[Fe(5MeO-salen)(NiL^1)Cl].—Under identical reaction conditions previously reported for the preparation of [Fe(salen)-(NiL^1)Cl], the analogous complex [Fe(5MeO-salen)(NiL^1)Cl] was produced in 61% yield as a fine brown powder. Elemental analysis, magnetic susceptibility, Mössbauer and ESR spectral data are consistent with its formulation as a dinuclear complex. In particular, the ESR and Mössbauer spectral data confirm the spin-crossover phenomenon. The room-temperature Mössbauer spectrum shows two quadrupole doublets corresponding to the high- and low-spin forms. At liquid-nitrogen temperature only the outer doublet (low-spin form) is observed. This behaviour is consistent with spin-crossover behaviour. It contrasts with that of [Fe(salen)(NiL^1)Cl] and [Fe(L^2)(NiL^1)]BPh$_4$ [H_2L^2 = N′-methyl-*N*,*N*″-bis(salicylidene)-4-azaheptane-1,7-diamine], both of which showed a single quadrupole splitting at 295 and 80 K which was highly temperature dependent, but is similar to that of [FeL^3(NiL^1)]BPh$_4$ [H_2L^3 = *N*,*N*″-bis(salicylidene)-4-azaheptane-1,7-diamine], which exhibited two sets of quadrupole splittings at both temperatures.[1] The different behaviours of all of these spin-crossover heterodinuclear complexes are attributed to differences in relaxation rates and to the relative position of the equilibrium at the observation temperature. Observation of two doublets indicates that the spin crossover is slow on the Mössbauer time-scale, whereas observation of a single doublet indicates that it is fast or that only a single spin state is present at the observation temperature.[17] The complex [Fe(5MeO-salen)(NiL^1)Cl] relaxes slowly on the Mössbauer time-scale as evidenced by the observation of both spin states at room temperature. The ESR spectrum of the solid complex at liquid-nitrogen temperature, shown in Fig. 3, clearly indicates the presence of both the high (g = 4.0) and low (g = 2.0) spin states in the sample. The magnetic susceptibility data alone provide no direct proof of a spin crossover for this complex as there are no abrupt changes with temperature, nor does the moment at 80 K provide evidence for a significant population of the low-spin state. However, when the magnetic data are examined along with the ESR and Mössbauer spectral data, there is compelling evidence that this compound exhibits a spin crossover of the continuous type.

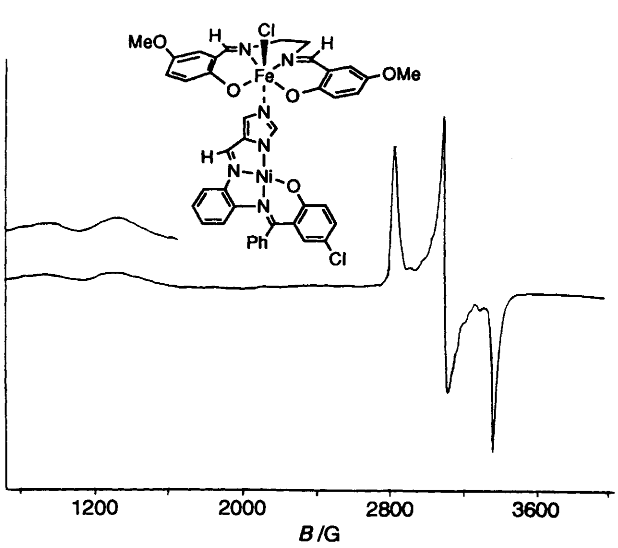

Fig. 3 The ESR spectrum of solid [Fe(5MeO-salen)(NiL^1)Cl] at 77 K

Conclusion

Four new N_3O_2Cl complexes of iron(III) were prepared by the reaction of a chloroiron(III) tetradentate Schiff base with various imidazole donors. The mononuclear imidazole complexes, [Fe(salen)L(Cl)] (L = Him, 1-mim or 2-mim), are admixed spin as evidenced by magnetic susceptibility and X-ray crystallography. The magnetism shows depressed magnetic moments, and the structure reveals a significantly distorted salen conformation with a 17.5° dihedral angle between the phenyl rings, which is much larger than the coplanar arrangement found for pure high-spin complexes but slightly smaller than found in spin-crossover complexes. The dinuclear complex [Fe(5MeO-salen)(NiL^1)Cl], which exhibits a spin crossover between the ^{2}T and ^{6}A states as determined by ESR, Mössbauer spectra, and magnetic susceptibility, is similar to the previously reported [Fe(salen)(NiL^1)Cl]. The observation of spin-crossover behaviour in the two dinuclear complexes rather than admixed behaviour, which is observed in the three mononuclear complexes, may be due to differences in the conformation of the salen ligand, which in turn may be attributed to the greater donor strength of the imidazole ligand.

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