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Supplementary Material Available: Listings of positional and thermal parameters of cations, thermal parameters of the anion, calculated H atom coordinates and temperature factors, and calculated and observed structure factors and a stereoview of the anion (36 pages). Ordering information is given on any current masthead page.

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Characterization of a Dimeric Iron(III) Complex of *N*,*N'*-Ethylenebis(salicylamine)

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In the literature there are a number of reports of iron(III) complexes of the ligand *N*,*N'*-ethylenebis(salicyclideneamine), salen, which include both five- and six-coordinate iron atoms as well as monomeric and dimeric species.[1-6] Some of the dimeric complexes contain oxo bridges while others contain an alkoxy bridge. The variations depend upon the method of preparation and the crystallization procedures used. Recently we have reported the preparation of a dihydroxy-bridged Fe(III) complex of the hydrogenated form of salen, namely, *N*,*N'*-ethylenebis(salicylamine), salen–H.[7] Here we report the preparation and characterization of a dialkoxy-bridged complex of this ligand. The ligand differs from salen in that it contains saturated nitrogen atoms; therefore, greater flexibility of the ligand is expected and the planarity of the ligand in bonding may be disturbed.

Experimental Section

(1) Preparation of [Fe(salen–H)Cl]$_2$·2H$_2$O. The procedures followed were those of Gerloch et al.[4] The ligand (1.4 g) was dissolved in 30 mL of ethanol (or methanol). Anhydrous $FeCl_3$ (1.0 g) was dissolved in 10 mL of ethanol. The iron solution was added to the ligand solution, and immediately a dark purple solution formed. This solution was stirred for 30 min and then filtered. A purple-black precipitate was collected and washed with water and then with ethanol; mp 250 °C dec. Anal. Calcd for $[Fe(C_{16}H_{18}N_2O_2)Cl]_2 \cdot 2H_2O$: C, 50.82; H, 5.31; N, 7.38; Fe, 14.71; Cl, 9.34. Found: C, 50.76; H, 5.06; N, 7.22; Fe, 15.49; Cl, 9.52. No molecular weight was obtained for this complex due to the low solubility in common organic solvents. All attempted procedures for crystallization failed. Similar procedures using $FeBr_3$ instead of the chloride gave no precipitate but only a deep purple solution; therefore characterization of a corresponding complex could not be done.

(2) Instrumentation. Thermal analysis was done on a Du Pont 751 thermogravimetric analyzer and a 990 thermal analyzer in an argon atmosphere with a flow rate of 50 cm^3/min and a heating rate of 100 °C/10 min.

Elemental analyses were done by Galbraith Laboratories, Knoxville, TN.

The mass spectrum was obtained on a Hewlett-Packard 5985B GC/MS system by direct probe. The temperature was varied from 30 to 300 °C over approximately a 15-min period of time.

The electric conductivity of methanol and acetone solutions was measured by mean of a Lazar Cond-156 conductivity probe.

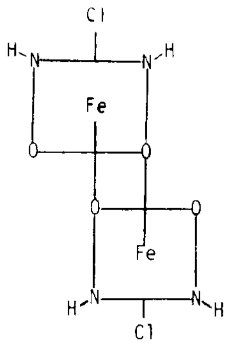

Figure 1. Proposed structure for $[Fe(salen\text{–}H)Cl]_2 \cdot 2H_2O$.

The UV–visible spectra were obtained on a Cary 14 spectrophotometer. Samples were run on 10^{-4} M solutions in methanol, water, and pyridine. The infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer. The samples were run as KBr pellets from 4000 to 200 cm^{-1} and on a polyethylene disk from 400 to 200 cm^{-1}.

The EPR spectra were taken on a Varian E-4 EPR spectrometer. A powder spectrum was obtained at room temperature, and a pyridine solution spectrum was obtained both at room temperature and at −180 °C in a quartz low-temperature cell. Variable-temperature magnetic susceptibility data were obtained on ~10-mg samples by using the Faraday method. Liquid nitrogen was used as the cryogenic material to obtain the low-temperature readings. The standard used was $Hg[Co(SCN)_4]$. Details of the Mössbauer spectrometer have been reported previously.[8]

Results and Discussion

The structure of $[Fe(salen\text{–}H)Cl]_2 \cdot 2H_2O$ is assumed to be that similar to the salen complex having the same formulation as shown in Figure 1. The only difference is that the compound presented here has waters of crystallization attached. The evidence in support of this structure is given in the following paragraphs as the experimental data are presented and discussed.

The thermogravimetric analysis (TGA) curve shows a decrease in weight of approximately 4% at 250 °C. This corresponds to the loss of two waters of crystallization (4.6% calcd) and is similar to other reports of the loss of water from iron complexes.[9,10] Loss of HCl corresponding to a hydrochloride salt would require the loss of 9.5% by weight. Gradual decomposition of the complex occurs in the range 280–650 °C, and then the TGA curve levels off. No organic material was found in the final residue and is therefore assumed to be Fe_2O_3.[10]

Since no molecular weight could be obtained in solution, the mass spectrum of the solid was taken to see if any information could be obtained. The spectrum did not reveal a parent peak expected at *m/e* 759 for the proposed dimer, at *m/e* 722 with the loss of the two waters of crystallization, or at *m/e* 686 for $[Fe(salen\text{–}H)OH]_2$ with the loss of HCl from a hydrochloride salt. Instead, peaks were observed at *m/e* 361 and 359. The peak at *m/e* 361 can easily be explained by the

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Table I. Some IR Bands and Their Assignments for $[Fe(salen\text{-}H)Cl]_2 \cdot 2H_2O$

freq, cm^{-1}	intens	assignt
3400	broad, medium	water of crystn
3230	weak	NH str
3070-3030	weak	arom C-H str
2930-2870	weak	aliph C-H str
1599	strong	phenyl ring
1570	weak	N-H bend
1290	strong	C-C str
1270	strong	phenolic C-O str
1240, 1230, 1190	medium	C-H in-plane bend
960, 948, 940	medium	arom in-plane bend
870	medium	Fe-O-Fe moiety
370, 348	medium	Fe-N str
275	medium	Fe-Cl str

cleavage of the dimer to produce the ion $[Fe(salen\text{-}H)Cl]^+$. It is reasonable to assume that the waters of crystallization should be removed at a low temperature under a vacuum and that the alkoxy bridge would break under the conditions present in the mass spectrometer.

The dimeric complex is very insoluble in most organic solvents and in water; however, the molar conductivity, Λ_M, was determined for 10^{-4} M solutions. Values of 19.7 and 13.6 Ω^{-1} cm^2 mol^{-1} were obtained for a 10^{-4} M methanol solution and a 0.6×10^{-4} M acetone solution, respectively. Values reported in acetone of some iron(III) complexes that are 2:1 electrolytes are in the range 206–288 Ω^{-1} cm^2 mol^{-1} for 10^{-4} M solutions.[11] The low values determined here indicate that the complex is not strongly conducting at this molarity; therefore, the chloro groups probably are coordinated to the iron atoms.

A 10^{-4} M methanol solution of the complex appears purple to the eye and has a rather intense absorption at 525 nm ($\epsilon \simeq 4000$). This can be assigned to a charge-transfer band, a transition from $p\pi$ orbitals on the phenolate oxygen atom to the half-filled $d\pi^*$ orbitals of the Fe(III).[12] Examples of other iron(III) complexes in the literature that are purple and give charge-transfer bands include $Na[Fe(EDBHA)] \cdot 4H_2O$, where EDBHA is ethylenediaminebis[(*o*-hydroxyphenyl)acetate] and the iron is surrounded by two phenolic oxygens, two amine nitrogens, and two carboxylate oxygens. In this case, the charge-transfer band appears at 475 nm (ϵ 4000). In $Fe[H_3EDBHA)Cl_2] \cdot 2H_2O$ the iron is assumed to be surrounded by two chloro groups, two amines, one phenolic oxygen, and possibly a water molecule to give a monomer or possibly a dimer bonding through the phenolic oxygen or chloro group.[13] In this case, the charge-transfer band assignment is made for the peak that appears at 510 nm (ϵ 3140). It has been observed that complexation with an increasing number of phenolic oxygens produces a blue shift in the visible spectrum.[14] The interaction of more phenolic oxygen $p\pi$ electrons is expected to raise the energy of the antibonding $d\pi$ orbitals of iron. This is observed in this case since the EDBHA complex with two phenolic oxygens has a charge-transfer band at 475 nm and the complex with one phenolic oxygen has a strong band at 510 nm. The salen-H complex contains two phenolic oxygens as well as one in the bridging position. The fact that this charge-transfer band lies lower in energy than those of the EDBHA complexes is not understood; however, one explanation might be to consider the extended conjugation involved once dimerization occurs. A shift to lower energy of the charge-transfer band in going from the monomeric to dimeric form of a complex has been observed by others.[15,16]

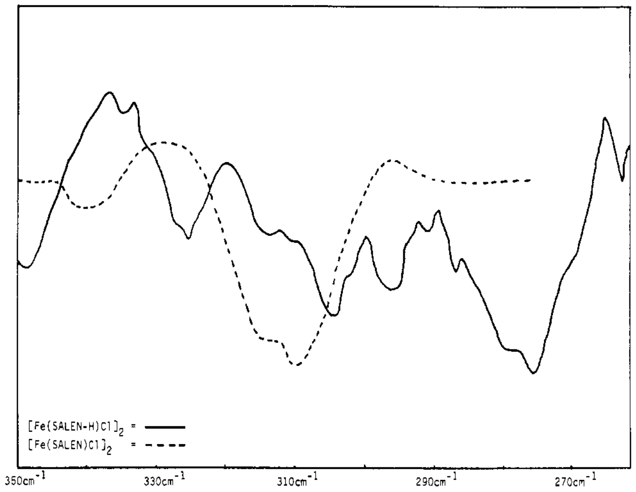

Figure 2. IR spectra of $[Fe(salen\text{–}H)Cl]_2$ and $[Fe(salen)Cl]_2$ from 350 to 260 cm^{-1}.

Table II. Magnetic Data of $[Fe(salen\text{-}H)Cl]_2 \cdot 2H_2O$

T, K	$10^2\chi_{cor}$,[a] cgsu	μ_{eff},[b] μ_B	*T*, K	$10^2\chi_{cor}$,[a] cgsu	μ_{eff},[b] μ_B
80	3.53	4.78	273	1.55	5.79
128	2.57	5.15	296	1.40	5.79
153	2.25	5.28	323	1.34	5.92
198	1.88	5.47	343	1.15	5.64
233	1.66	5.58	373	1.09	5.74

[a] $\chi_d = -1.49 \times 10^{-4}$ cgsu/Fe(III) based on Pascal's constants.
[b] $\mu_{eff} = 2.84(\chi_{cor}T)^{1/2}$.

In Table I some of the IR bands are listed along with their assignments. The broad peak at 3400 cm^{-1} confirms the presence of water in the compound. The peak at 3230 cm^{-1} has been shifted approximately 60 cm^{-1} from that assigned to the NH stretch in the ligand. This may be the result of complexation with iron or of hydrogen bonding, as discussed later. The 870-cm^{-1} peak assigned to the Fe–O–Fe moiety corresponds to the peak at 865 cm^{-1} assigned to this unit in the corresponding salen complex. The peaks at 370 and 348 cm^{-1} correspond to 388 and 357 cm^{-1} in $[Fe(salen)Cl]_2$ and to 374 and 340 cm^{-1} in $[Fe(salen\text{–}H)OH]_2$. These can be assigned to the Fe–N stretch, similar to the values reported by Saito et al. for Fe(III)–N stretches of bipyridyl and phenanthroline complexes.[17] A terminal Fe–Cl stretching band should be observed in the 400–200-cm^{-1} region of the IR spectrum.[18] A comparison of the spectra of $[Fe(salen)Cl]_2$, $[Fe(salen\text{–}H)Cl]_2$, and $[Fe(salen\text{–}H)OH]_2$ leads to the assignment of the strong peak at 275 cm^{-1} to the Fe–Cl band in the $[Fe(salen\text{–}H)Cl]_2$ complex. Such a peak is absent in the hydroxy complex of salen–H and appears similar in shape and intensity to the peak at 309 cm^{-1} in the salen compound[19] (see Figure 2). A similar assignment has been made for the Fe–Cl stretching band at 310 cm^{-1} for $Fe(S_2CNEt_2)Cl$.[20] This shift to lower energy in the salen–H complex is probably the result of hydrogen bonding involving the chloro group and the hydrogens that appear on the nitrogen atoms of this ligand which are not on the salen ligand. A similar shift to lower

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Table III. Mössbauer Spectroscopy Data[a] for $[Fe(salen-H)Cl]_2 \cdot 2H_2O$

T, K	δ	ΔE	Γ_1	Γ_2	Γ_1/Γ_2	A_1/A_2
300	0.401	0.837	0.397	0.404	0.98	0.99
77	0.468	0.888	0.397	0.370	1.07	1.01

[a] In mm/s relative to 6.4 μm thick natural iron foil.

energy is also observed for the Fe–N bond, presumably due to the same effect.

The powder EPR spectrum of $[Fe(salen-H)Cl]_2$ at room temperature gives a very broad signal at $g = 2.19$ and is similar in nature to that observed for other iron(III) dimers.[7] In pyridine solution no signal was observed at room temperature; however, at −180 °C, a broad signal was observed at $g = 4.23$. Many monomeric iron(III) complexes show a signal of this nature.[21,22] The dimer apparently dissociates into monomeric units in the solvent pyridine.

The magnetic susceptibility data of the iron dimer are presented in Table II. By use of the spin–spin coupling model for an $S_1 = S_2 = {}^5/_2$ system, with $\Theta = 0$ K and $N\alpha = 0$ assumed, an exchange constant of -8.3 cm^{-1} is calculated. This agrees very well with the case of other complexes that have a Fe–O–Fe angle of ~90° and is consistent with an antiferromagnetic exchange between the iron atoms via the oxygen bridges.

The Mössbauer spectrum at 300 K is shown in Figure 3. $[Fe(salen-H)Cl] \cdot 2H_2O$ exhibits an essentially symmetric quadrupole doublet at 300 and 77 K (Table III). The symmetry and magnitude of the doublet strongly favor our formulation of this material as the dimer $[Fe(salen-H)Cl]_2$, analogous to the well-known $[Fe(salen)Cl]_2$.[6] If the compound were monomeric, the low symmetry suggested by the ligand environment (a pseudo-square-pyrimidal FeN_2O_2Cl chromophore) should lead to zero-field splitting of the single-ion spin-sextet ground state. This in turn should result in slow paramagnetic relaxation broadening of the Mössbauer spectra, at high temperatures for $D > 0$ and low temperatures for $D < 0$, where D is the axial zero-field-splitting parameter. There is no indication of this, certainly not to the extent as observed with documented square-pyramidal, high-spin ferric systems, e.g. ferric hemin chloride[23] ($D < 0$) or $[Fe(acac)_2Cl]$.[24]

For an antiferromagnetically coupled dimer, the ground state is the diamagnetic $S_{\text{total}} = 0$ spin level, which cannot contribute to Mössbauer spectra line broadening. The broadening that results from the higher energy $S_T = 1$–5 levels depends on (1) the extent of population of these states, (2) the magnitudes of their zero-field splittings, and (3) the *interdimer* metal–metal separation, if it is assumed that the broadening mechanism is slow interdimer spin–spin relaxation.

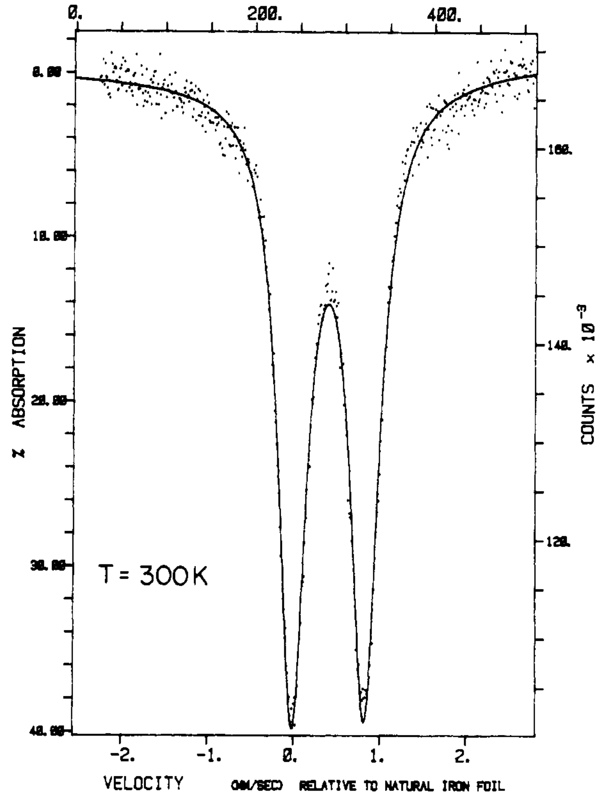

Figure 3. Mössbauer spectrum of $[Fe(salen-H)Cl]_2$ at 300 K.

It seems reasonable that the smallest interdimer Fe–Fe separation for the proposed dimeric $[Fe(salen-H)Cl]_2 \cdot 2H_2O$ is similar to that (~7 Å) in $[Fe(salen)Cl]_2$, a system that clearly exhibits slow interdimer relaxation broadening with increasing temperature.[25,26] The S_T state population for these dimers should be comparable at similar temperatures since their exchange parameters (J) are comparable at ~10 cm^{-1} (vide supra). Thus, the absence of significant relaxation broadening for $[Fe(salen-H)Cl]_2 \cdot 2H_2O$ leads one to the conclusion that its spin states are less zero-field split. This is consistent with a less distorted metal ion environment for $[Fe(salen-H)Cl]_2$ vs. $[Fe(salen)Cl]_2$, at least when viewed in terms of their quadrupole splittings 0.84 mm/s vs. 1.40 mm/s at 300 K.[27]

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Registry No. $[Fe(salen-H)Cl]_2 \cdot 2H_2O$, 87039-40-5.

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