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Isolation and Detailed Characterization of the *trans*-$[(H_2O)_2FeCl_4]^-$ Anion: Stabilization of Novel Iron(III) Species by Large Organic Cations

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1,2-Diaminoethane (en) and $FeCl_3$ give (enH_2) $[FeCl_5(H_2O)]$ (**1**) in concentrated HCl, extending the aquapentachloroferrate(III) series. For **1**: $C_2H_{12}N_2Cl_5OFe$, orthorhombic, $P2_12_12_1$, $a = 14.531(6)$ Å, $b = 10.772(4)$ Å, $c = 6.888(2)$ Å, $Z = 4$. Diazabicyclo[2.2.2]octane dihydrochloride (DABCO·2HCl) and $FeCl_3$ in concentrated HCl form a tetrachloroferrate(III) derivative whose subsequent ethanol treatment (restricted water access) results in the formation of a compound of composition $(DABCOH_2)_2$ $[FeCl_4(H_2O)_2]Cl_3$ (**2**). This contains the *trans*-$[FeCl_4(H_2O)_2]^-$ anion, in which the *trans*-Fe−O distances are 2.049(4) Å. For **2**: $C_{12}H_{32}N_4Cl_7O_2Fe$, orthorhombic, *Pnma*, $a = 16.378(3)$ Å, $b = 7.3323(6)$ Å, $c = 19.431(3)$ Å, $Z = 4$. A combination of ^{57}Fe Mössbauer spectroscopy and ac susceptibility data confirm uncanted 3D antiferromagnetic ground states with $T_{\text{Néel}}$ ~3.4 K for $(enH_2)[FeCl_5(H_2O)]$ and ~2.0 K for $[DABCOH_2]_2[FeCl_4(H_2O)_2]Cl_3$.

Introduction

The interesting series of low-temperature antiferromagnetic materials containing the $[FeCl_5(H_2O)]^{2-}$ anion arising from reactions in which iron(III) chloride and alkali metal or ammonium chlorides interact in hydrochloric acid solutions has been well-documented.[1] On the other hand, rather less systematization has proved to be forthcoming concerning the properties of salts of "large" organic cations formed with chloroferrate(III) systems, despite excellent individual studies on such systems. For example, in addition to expected complexes such as the tetrachloroferrates(III), the extensive studies on substituted pyridinium salts have revealed complexes having formulas $(pyH)_3[Fe_2Cl_9]$ (pyH = pyridinium or substituted pyridinium ion), but which effectively aggregate as $[(pyH)_3Cl]^{2+}$ and two $[FeCl_4]^-$ in the solid state, even though the crystals were also obtained from hydrochloric acid media.[2] Additional effects have also been observed at the iron(III) center when organic cations have been employed. A chloroferrate containing a coordinated methanol molecule, analogous to the very stable aquapentachloroferrate(III) ion, was stabilized when the dimethyl quaternized dication from the base diazabicyclo[2.2.2]octane was introduced.[3] Further, the *unsolvated* $[FeCl_5]^{2-}$ anion was characterized crystallographically for the first time when it crystallized directly from analogous reactions employing the tetramethylpiperazinium and imidazolium cations.[4] An unusual type of chloroferrate double salt also has been identified which involves the presence of both the $[FeCl_6]^{3-}$ and $[FeCl_4]^-$ anions in the same lattice in the 1,6-hexanediammonium derivative which crystallized from concentrated hydrochloric acid solution.[5] Even more complex materials containing the $[Fe^{II}Cl_4]^{2-}$, $[Fe^{III}Cl_4]^-$, $[Fe^{II}Cl_5]^{3-}$ and $[Fe^{III}Cl_6]^{3-}$ anions in the same salt have been reported recently.[6] It is evident that organic cations are able to affect chloroferrate(III) systems and their various complexation/lattice energy balances and interplays in a number of ways via their charge, steric, or shape characteristics and by introducing new hydrogen-bonding possibilities into the ionic interactions in the solids.

In this paper, the low-temperature Mössbauer and magnetic susceptibility results for two derivatives from simple diamines (1,2-diaminoethane, having a short, flexible carbon chain; diazabicyclo[2.2.2]octane (DABCO), otherwise "triethylenediamine", having a short chain, but rigid system) are reported. Using the cation of the latter organic base, an octahedral chloroferrate(III) anion having trans water ligands has been observed and structurally characterized, while the former leads to a salt containing the familiar $[FeCl_5(H_2O)]^{2-}$ species. A preliminary report of the crystallographic and susceptibility results of this work was given earlier.[7] Subsequent to this, the

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isolation and structure of another complex salt containing the chloroferrate anion of **2** has been reported.[8]

Experimental Section

Syntheses. All reagents were obtained from commercial sources and were used without further purification. The dihydrochloride salts of triethylenediamine (DABCO·2HCl) and diaminoethane (en·2HCl) were precipitated by adding ice-cold concentrated hydrochloric acid to chilled solutions of the respective bases in ethanol. The resulting colorless crystals were pumped dry in a vacuum desiccator.

Analyses were carried out by Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Ethane-1,2-diammonium Aquapentachloroferrate(III), 1. When en·2HCl (2.05 g) dissolved in hot, concentrated hydrochloric acid was mixed with a filtered solution of iron(III) chloride (5.0 g, 2 molar equiv) in water and the resultant mixture allowed to concentrate slowly in a vacuum desiccator, dark orange-red crystals (5.43 g, 56% yield; mp 108−110 °C) of the ethylenediammonium aquapentachloroferrate(III) were obtained. These were filtered off and dried in vacuo. Anal. Calcd for $C_2H_{12}N_2Cl_5OFe$: C, 7.67; H, 3.87; N, 8.94; Cl, 56.58. Found: C, 7.3; H, 3.9; N, 8.6; Cl, 56.9.

The Mössbauer spectrum corresponds to a quadrupole split doublet with narrow line widths ($\Delta E = 0.32$ mm s^{-1}; $\delta = 0.52$ mm s^{-1}) at room-temperature.

Triethylenediammonium Chloride Tetrachloroferrate(III). When DABCO·2HCl (3.7 g) and iron(III) chloride (BDH, 3.2 g) were mixed in concentrated hydrochloric acid, bright yellow crystals precipitated immediately. These were filtered off and dried in vacuo (4.5 g, 68% yield). Anal. Calcd for $C_6H_{14}N_2Cl_5Fe$: C, 20.75; H, 4.07; N, 8.07; Cl, 51.03. Found: C, 20.8; H, 4.1; N, 8.1; Cl, 51.1.

The color of the compound and its narrow line width ($\Gamma = 0.28$ mm s^{-1}) singlet Mössbauer spectrum (isomer shift $\delta \sim 0.2$ mm s^{-1} relative to iron metal) clearly indicated that the material was the tetrahedral tetrachloroferrate double salt, DABCOH$_2$[FeCl$_4$]·Cl. It decomposed (darkened) above 120 °C.

Bis(triethylenediammonium) Trichloride Diaquatetrachloroferrate(III), 2. When the preceding yellow double salt was allowed to stand for several weeks in laboratory grade ethanol, the original color of the solid was observed to change to a distinct orange. This solid was filtered off and proved to be a mixture of orange and yellow crystals. The *orange* material (**2**) was carefully separated from the yellow by hand. Anal. Calcd for $C_{12}H_{32}N_4Cl_7O_2Fe$: C, 25.35; H, 5.68; N, 9.86; Cl, 43.65. Found: C, 23.4, 23.1; H, 5.2, 5.4; N, 9.0, 8.9; Cl, 43.9.

In an attempt to obtain larger quantities of the single, pure orange phase, **2**, via the interaction with ethanol, a sample of the freshly precipitated DABCO yellow double salt (3.0 g) was extracted in a Soxhlet apparatus using a 4:1 v/v ethanol−concentrated HCl mixture. In the early phases of this extraction, a bright yellow solution was obtained. When this solution was allowed to cool, distinctly orange needles grew around the thimble in the extraction vessel. These were carefully removed and dried in vacuo (0.87 g, 37% yield). Anal. Found: C, 25.0; H, 5.8; N, 9.7; Cl, 44.3, consistent with compound **2**.

The room-temperature Mössbauer spectrum of **2** corresponds to a broad ($\Gamma = 0.93$ mm s^{-1}) unresolved quadrupole doublet with an isomer shift, $\delta = 0.32$ mm s^{-1}, fully consistent with six-coordinate pseudo-octahedral high-spin Fe(III).

Variable-temperature Mössbauer spectra were recorded using equipment as previously described,[9] with α-iron foil being employed as the standard. The spectra were fitted to Lorentzians, using the program written primarily by Stone.[10] Ac susceptibility measurements were performed using a Lakeshore Cryotronics series 7000 susceptometer applying an ac field of 1 Oe at a frequency of 125 Hz.

Table 1. Crystallographic Data

	1	**2**
formula	$C_2H_{12}Cl_5FeN_2O$	$C_{12}H_{32}Cl_7FeN_4O_2$
M_r	313.2	568.4
a (Å)	14.531(6)	16.378(3)
b (Å)	10.772(4)	7.3323(6)
c (Å)	6.888(2)	19.431(3)
V (Å^3)	1078.3(8)	2333.4(6)
space group	$P2_12_12_1$ (No. 19)	*Pnma* (No. 62)
Z	4	4
T (K)	295	295
λ (Å)	0.7107_3	0.7107_3
D_c (g cm^{-3})	1.92_9	1.61_8
$2\theta_{max}$, deg	60	50
μ(Mo Kα) (cm^{-1})	24.6	14.6
R^a	0.033^c	0.046
$R_w{}^b$	0.032^c	0.046

[a] $R = \sum\Delta|F|/\sum|F_o|$. [b] $R_w = (\sum w\Delta^2/\sum wF_o{}^2)^{1/2}$. [c] For the alternative hand 0.037, 0.036.

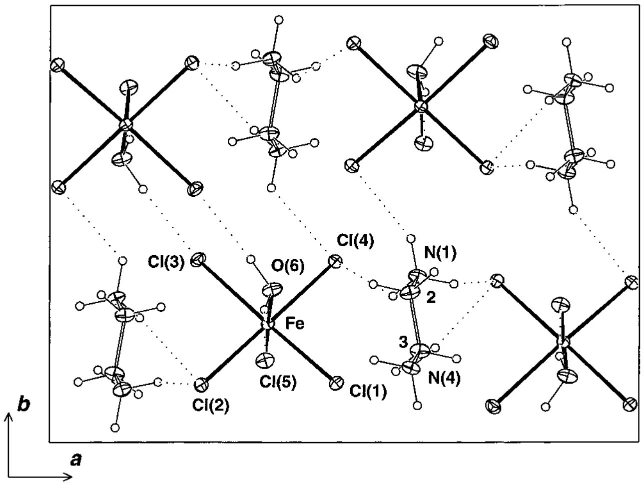

Figure 1. Unit cell contents of **1**, projected down *c*. Non-hydrogen atoms are shown with 20% thermal ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å. Carbon atoms are denoted by number only. Appended hydrogen atoms are denoted by the number of the parent, subscripted a, b, (c).

Structure Determinations. Unique room-temperature single counter diffractometer data sets were measured on capillary-mounted specimens ($2\theta/\theta$ scan mode, $2\theta_{max}$ as specified in Table 1; monochromatic Mo Kα radiation; specimen sizes 0.18 × 0.11 × 0.24 (**1**), 0.09 × 0.90 × 0.20 mm (**2**); $A^*_{min,\ max}$ 1.48, 1.65 (**1**), 1.14, 1.30 (**2**)) yielding 1793 (**1**), 2221 (**2**) independent reflections, 1295 (**1**), 1610 (**2**) with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at values estimated where possible in accord with difference map residues. Conventional R, R_w on $|F|$ at convergence are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being applied. Neutral atom complex scattering factors were employed,[11] computation using the XTAL 3.2 program system[12] implemented by S. R. Hall. Pertinent results are given in Figures 1 and 2 and the tables, and in the depositions.

For **2**, as modeled in space group *Pnma*, the majority of atoms lie in the crystallographic mirror planes normal to *b*, a plausible enough scenario for the heavy atoms of the structure, the structure refining smoothly in all respects, but a rather unlikely state of affairs for the cation, a more likely situation being one entailing disorder of the (CH$_2$)$_2$ bridge within the plane and, in concert, the pair of symmetry-related bridges to either side. The uncomfortable nature of this result was

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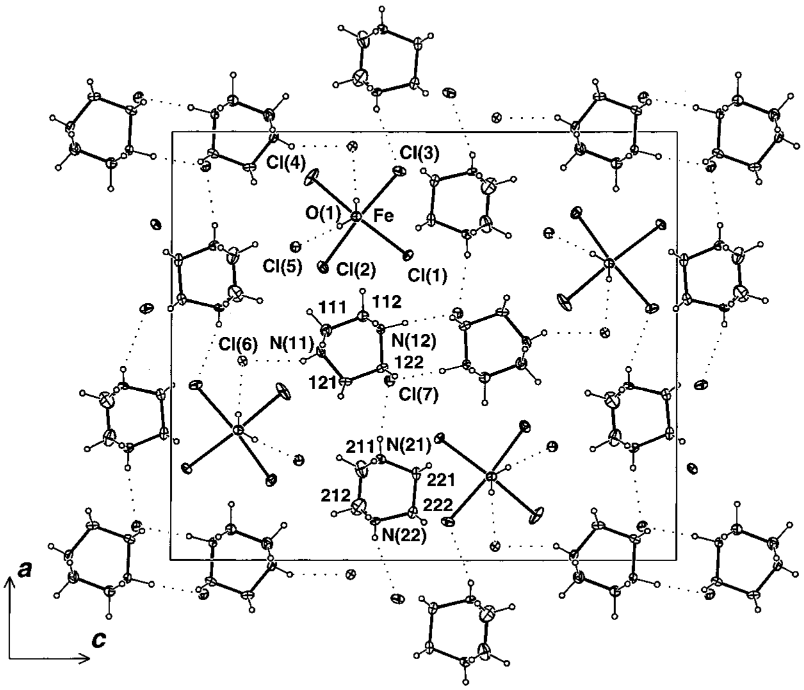

Figure 2. Unit cell contents of **2**, projected down *b*.

Table 2. Anion Geometry, **1**[a,b]

atom	*r*	Cl(2)	Cl(3)	Cl(4)	Cl(5)	O(6)
Cl(1)	2.377(2)	88.98(6)	170.48(6)	88.88(6)	94.85(6)	84.3(1)
Cl(2)	2.372(2)		89.49(6)	173.43(6)	93.05(6)	87.6(1)
Cl(3)	2.375(2)			91.59(6)	94.62(6)	86.3(1)
Cl(4)	2.336(2)				93.33(6)	86.0(1)
Cl(5)	2.329(2)					178.9(1)
O(6)	2.180(4)					

[a] *r* is the Fe−X distance (Å); other entries in the matrix are the angles subtended by the relevant atoms at the head of the row and column (deg). [b] In the cation, N(1)−C(2), C(2)−C(3), C(3)−N(4) are 1.474(7), 1.480(7), 1.479(7) Å, respectively; angles subtended at C(2,3) are 111.2(4)°, 111.9(4)°, with the N−C−C−N torsion −178.6(5)°.

Table 3. Anion Geometry, **2**[a]

atom	*r*	Cl(2)	Cl(3)	Cl(4)	O(1)
Cl(1)	2.381(2)	89.09(7)	85.50(7)	176.47(8)	92.9(1)
Cl(2)	2.324(2)		174.59(7)	94.45(8)	89.8(1)
Cl(3)	2.374(2)			90.97(8)	90.5(1)
Cl(4)	2.380(2)				87.1(1)
O(1)	2.049(4)				174.2(2)[b]

[a] Presentation as in Table 2. [b] O(1) −Fe−O(1) (x, $^5/_2 - y$, z).

reflected in rather erratic behavior among the associated displacement parameters, not assisted by the rather weak data obtained from a relatively fragile specimen. In this context, the possibility of lower symmetry was explored, inherently fruitlessly. This being the case, a full hemisphere of data was measured (9360 reflections to $2\theta_{max} = 50°$), merging to an orthorhombic array ($R_{int} = 0.047$), indicative that any lower symmetry perturbation was minor, if not negligible. Accordingly, refinement proceeded on the premise of orthorhombic symmetry, attempts to refine/resolve disordered components of the cation being inherently unfruitful, as were attempts at refinement in the non-centrosymmetric space group $Pn2_1a$. The *Pnma* model is accordingly presented, with appropriate caveats in respect of the model adopted for the cation. The hydrogen-bonded hydrogen atoms on N and O were refined in (x, y, z, U_{iso}) for **1** and **2**.

Results and Discussion

For the ethylenediammonium salt **1**, selected pertinent bond distances and angles are given in Table 2, while details of the cell packing are shown in Figure 1. Similar data for the derivative **2** are given in Table 3, with the packing diagram in Figure 2.

The ethylenediammonium salt **1** extends the well-known highly stable aquapentachloroferrate(III) series by providing an organic dication stabilization of the Fe(III) moiety in another ionic aggregate similar to that of the ammonium salt.[13] It is clear that the dimensions of neither the cation nor the anion are at all unusual, although the Fe−OH$_2$ and the Fe−Cl distance trans to it are both rather longer in this compound than those in the ammonium salt [Fe−O, 2.180(4) Å vs 2.110 Å; Fe−Cl, 2.375(2) Å vs 2.323 Å] and comparable with those also established for the cesium salt.[14] Regardless of the lengthening of Fe−OH$_2$, the Cl(equatorial)−Fe−O angles in all compounds are less than 90°, perhaps a consequence of steric crowding here, since in **2**, the trans pair of Fe−O(H$_2$) are much shorter.

In the cesium compound, the octahedral $[FeCl_5(H_2O)]^{2-}$ ions are linked together into layers perpendicular to *b* by O−H···Cl hydrogen bonds, these interactions being assisted by the Cs···Cl and Cs···O interactions.[14b] In the ammonium salt, the anion displays considerable irregularity caused by both N−H···Cl and O−H···Cl hydrogen bonds. In the present array (Figure 1), interactions H(6a,b)···Cl(5) (x, y, $1 + z$), Cl(3) ($^1/_2 - x$, $1 - y$, $^1/_2 + z$) are 2.3, 2.4 Å (est.); while H(1a,b,c)(4a,c)···Cl(2) ($^1/_2 + x$, $^1/_2 - y$, $1 - z$), Cl(4), Cl(1) ($1 - x$, $^1/_2 + y$, $^3/_2 - z$), Cl(2) ($^1/_2 + x$, $^1/_2 - y$, $2 - z$), Cl(4) ($1 - x$, $y - {}^1/_2$, $^3/_2 - z$) are 2.6, 2.6, 2.5, 2.4, 2.6 Å (est.), respectively.

Some low-temperature Mössbauer spectra for **1** are shown in Figure 3. For the paramagnetic temperature regime, narrow line width, small quadrupole doublet spectra ($\delta = 0.52$, $\Gamma = 0.35$, $\Delta E = 0.53$ mm s^{-1} at 77 K; and $\delta = 0.49$, $\Gamma = 0.31$, $\Delta E = 0.56$ mm s^{-1} at 4.6 K) are observed. These values are similar to those found in the $M_2FeCl_5{\cdot}H_2O$ series (M = K, Rb, Cs,

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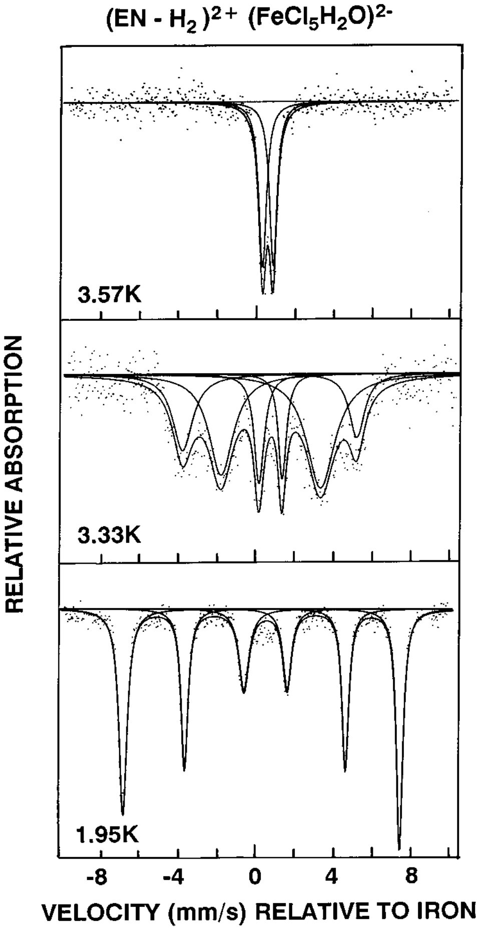

Figure 3. Mössbauer spectra of **1** in the vicinity of T_{critical}.

NH_4).[15] The isomer shift values are typical of six-coordinate high-spin Fe(III), while the observed *small electric field gradient* is expected for a local C_{4v} symmetry coordination chromophore. The Mössbauer spectra below ca. 3.6 K exhibit resolved magnetic hyperfine splitting over a very small (~0.3 K) temperature interval. This behavior is typical of the onset of long range 3D magnetic order, with 3.3 K < T_{critical} < 3.57 K. The internal hyperfine field at 1.95 K is ~45 T, fairly typical of magnetically ordered $[FeCl_6]^{3-}$ and $[FeCl_5(H_2O)]^{2-}$ chromophores with little zero point spin reduction effects but some covalency reduction of H_n.

The critical temperature is somewhat lower than the values found for the salts of the corresponding group IA complexes, whose Néel temperatures range from 14.06 K (potassium salt[16]) to 6.25 K (cesium[14a]), with the ammonium salt having $T_{\text{Néel}} =$ 6.87 K.[16] It seems reasonable to correlate the substantially lower critical temperature of the present ethylenediammonium compound with its large bulk and concomitant enhanced magnetic dilution of the solid material (the shortest Fe···Fe distance is 6.888(2) Å) although this is by no means the only or necessarily the most important factor affecting the value of T_{critical}.

Compound **1** exhibits a gradual decrease of the effective moment, μ, from ~5.3 μ_B near 80 K to ~1.7 μ_B at 1.5 K indicating *dominant antiferromagnetic exchange interactions* as found in the $M_2[FeCl_5(H_2O)]$ (M = alkali metal) analogues. The local symmetry of **1**, axial C_{4v}, is such that *if* the sole cause of the observed moment decrease was axial single ion zero field splitting, the limiting low-temperature value of μ is expected[17] to approach $\sqrt{19}$ (or 4.36) μ_B, considerably in excess of that observed. From the susceptibility data of Figure 4, it is apparent that one is approaching a *very broad* antiferromagnetic maximum in χ' likely resulting from *unresolved* 3D and lower D *antiferromagnetic* spin correlation effects. However, it is clear from the Mössbauer spectra that **1** orders (3-dimensionally) at ~3.4 K. Thus, one concludes from the absence of an out-of-phase signal, χ'', that the magnetic ground state of **1** is uncanted antiferromagnetic, again similar to the alkali metal analogues. This possibility has to be considered in that overt canting of antiferromagnetic sublattices is allowed[1] for the non-centrosymmetric space group ($P2_12_12_1$) of **1**.

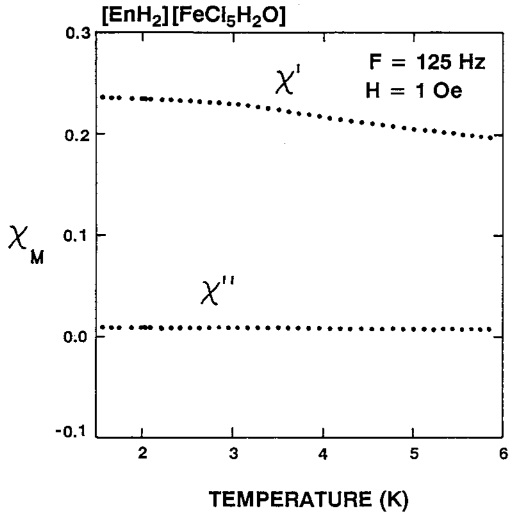

Figure 4. In-phase (χ') and out-of-phase (χ'') components of the ac susceptibility for **1** in the vicinity of T_{critical}.

For compound **2**, the color of the material and the intense, broad O−H stretching mode in the infrared spectrum initially suggested that it might be a double salt based on the well-known aquapentachloroferrate(III) anion, i.e., of the type $(DABCOH_2)_2[FeCl_5(H_2O)]\cdot 2Cl\cdot H_2O$. However, it proved to be an unusual ionic double salt, containing both chloride and the *trans*-diaquatetrachloroferrate(III) anions (Figure 2).

Although the distorted octahedral *trans*-diaquatetrachloro ligand field arrangement (Table 3) is known for other transition metals (e.g., for Mn(II)[15]), it had been recognized only recently for Fe(III).[8] The compound is also related to the complex $(DABCOH_2)_2[CuCl_3(H_2O)_2]Cl_3\cdot H_2O$, but that material was crystallized from dilute HCl[19] while the extraction procedure used in this (Fe) case, largely involving ethanol in the presence of only limited amounts of available water, is presumably particularly conducive to restricting the usual ligand lability in the high-spin ferric system. However, the light orange complex is quite stable, once isolated. The anion does not well approximate D_{4h} symmetry, the O(1)−Fe−O(1′) angle being 174.2(2)° (Table 3). The Cl(1)−Fe−Cl(3) angle is closed somewhat from the regular 90°, with the opposite angle Cl(2)−Fe−Cl(4) opening a little to compensate. The Fe−O(1) distances (2.049(4) Å) are somewhat shorter than those in the aquapentachloroferrate(III) ions, indicating the effect of water ligands trans to each other, in comparison with water trans to a chloride group. Hydrogen bonding in the lattice is limited to a few strong interactions between the water and protonated amine

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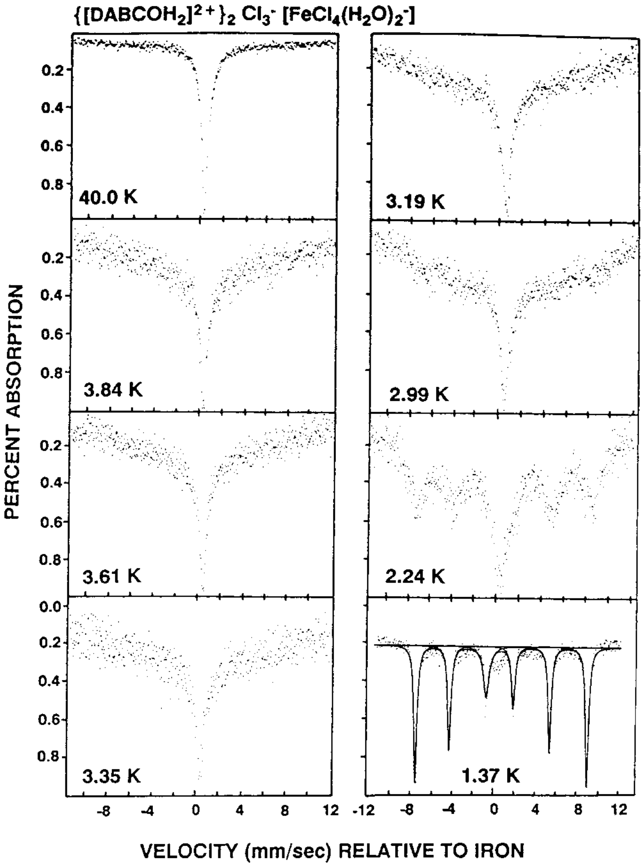

Figure 5. Mössbauer spectra of **2** at 40 K and in the vicinity of T_{critical}.

hydrogen atoms at quite short distances: H(1a)···Cl(6) ($^1/_2 + x$, $^3/_2 - y$, $^1/_2 - z$), 2.41(5); H(1b)···Cl(5), 2.32(6); H(11)···Cl(6), 2.34(8); H(12)···Cl(7) ($1 - x$, $y - {}^1/_2$, $1 - z$), 2.06(7); H(21)···Cl(7) (x, $y - 1$, z), 2.27(7); H(22)···Cl(3) ($x - 1$, $y - 1$, z), 2.50(8) Å, as shown in Figure 2. (The whole array in space group *Pnma* has a mirror plane normal to the direction of projection, *b*.) Nevertheless, these interactions are apparently of sufficient strength to lead to antiferromagnetic exchange and the long-range ordering of **2**.

The ambient temperature Mössbauer spectrum of **2** consists of a very broad ($\Gamma = 0.93$ mm/s) resonance that substantially further broadens ($\Gamma = 1.50$ mm s^{-1}) on cooling to 77 K. The absence of a resolved quadrupole doublet for **2** relative to **1** was rather unexpected in view of the fact that the principal component of the electric field gradient tensor for *trans*-MA_4B_2 (nominal D_{4h}) is $4(b - a)$ while that for MA_5B (C_{4v}) is $2(b - a)$ where a and b are the partial quadrupole splittings (in this case of the chloride and water ligands, respectively) in a point charge model calculation.[20,21] Hence, other things being equal, the ratio of their quadrupole splittings (**2**/**1**) should be 2:1. An acceptable, unconstrained Lorentzian fit to the Mössbauer spectrum of **2** at 77 K was possible using a broadened quadrupole doublet with $\delta = 0.45$, $\Delta E = 0.29$, and $\langle\Gamma\rangle = 1.45$ mm s^{-1}. It seems possible that the effective symmetry of the $[FeCl_4(H_2O)_2]^-$ units is too low and/or the local bonding is sufficiently covalent that an ionic point charge calculation of the electric field gradient is inappropriate for these systems.

The continued broadening with decreasing temperature ($\Gamma = 1.6$ mm s^{-1} at 4.6 K) and gradual development of winglike structure in the spectral baselines (Figure 5) are reminiscent of slow paramagnetic relaxation (primarily spin−spin in this case) at least above ~2.0 K. This is likely the result of small negative single ion zero field splitting and a degree of magnetic self-dilution,[22] the shortest Fe···Fe distance being 7.332(2) Å. However, the limiting zero field Mössbauer spectra for the extremes of *infinitely slow* paramagnetic relaxation versus *long-range cooperative magnetic order* (at saturation) are essentially identical in appearance. In this context, it is clear that the *resolved* magnetic hyperfine splitting of **1** occurs over a much smaller temperature interval than for **2**, consistent with the 3D order of the former. Thus, in the absence of detailed susceptibility results (vide infra), it is difficult to decide unequivocally (on the basis of Mössbauer spectroscopy alone) whether **2** is magnetically ordered or not. Finally, we note that the Mössbauer spectrum at 1.37 K exhibits a small but definite quadrupolar shift (−0.33 mm s^{-1}) which when considered as a small perturbation on the larger nuclear Zeeman splitting effect results in an internal hyperfine field H_n ca. 49 T. This value for the *trans*-Cl_4O_2 coordination of **2** is to be compared to the "all oxygen" coordinated $FeNH_4(SO_4)_2{\cdot}12H_2O$, anhydrous $Fe_2(SO_4)_3$, and $Fe(acetylacetonate)_3$ for which $H_n = 58$, 55, and 53 T, respectively,[22−24] and 44 T for the Cl_5O chromophore of **1**. Thus, with increasing oxygen content in the coordination environment ("increasing ionicity"), one sees, at least qualitatively, the expected *lessening* of covalency reduction of H_n.[24]

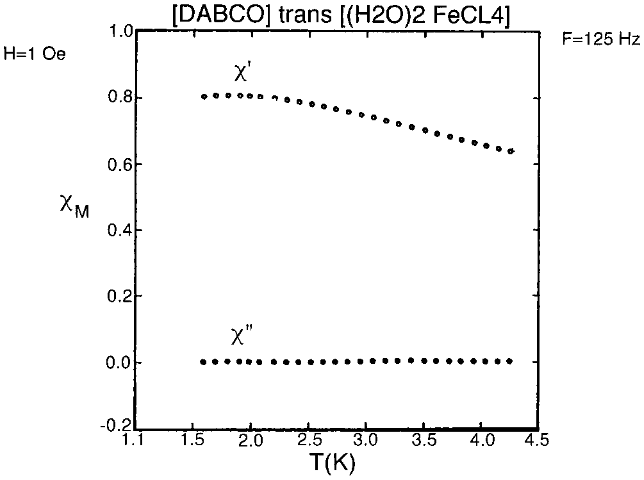

Figure 6. In-phase (χ') and out-of-phase (χ'') components of the ac susceptibility for **2** in the vicinity of T_{critical}.

Magnetic interaction between adjacent complex ferric anions of **2** is likely articulated by successive water molecules, H(1a,b)···O(1) (x, $y - 1$, z) 2.93(6), 3.08(7) Å, and appears to be reflected in the ac susceptibility results now considered.

Most of the comments concerning the low-temperature susceptibility and moment behavior of **1** apply to **2** save that its limiting low-temperature moment (~3.1 μ_B at ~1.5 K) is somewhat larger than that observed for **1** (1.7 μ_B), clearly suggesting *stronger antiferromagnetic exchange* for the latter. Perhaps consistent with this observation is the indication that the antiferromagnetic maximum (Figure 6) in χ' versus T for **2** has shifted to ≤2 K, i.e., ~1.5 K below that for **1**. It is also the case that if **2** has the same (centric) space group at these

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temperatures that it has at 298 K, it cannot have a canted magnetic ground state.[1]

Conclusion

It is clear from this investigation that a careful synthetic approach using large organic cations has led to *a nontrivial extension of high-spin iron(III) chemistry* in the isolation of **2**. The remaining member of this series yet to be isolated and characterized is the *cis*-$[FeCl_4(H_2O)_2]^-$ anion. It is to be hoped that further systematic studies along these lines will be equally fruitful, perhaps resulting in the isolation of the latter or interesting new higher nuclearity iron(III) or mixed-valence iron clusters. Such systems based on the high-spin d^5 (Mn(II) or Fe(III)) have been of considerable recent interest in the context of quantum tunneling of magnetization.[25,26]

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Supporting Information Available: Graphical representations of the detailed temperature variation of the magnetic moments of compounds **1** and **2**. Crystallographic files for each of **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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