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The Unsolvated Pentachloroferrate(III) Ion. X-ray Crystal Structure and Low-Temperature Magnetism of Tetramethylpiperazinium Pentachloroferrate(III)

Bruce D. James,* John Liesegang, and Margarita Bakalova

Faculty of Science and Technology, La Trobe University, Bundoora, Vic. 3083, Australia

William M. Reiff*

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

Brian W. Skelton and Allan H. White

Department of Chemistry, University of Western Australia, Nedlands, WA 6009, Australia

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Single-crystal X-ray diffraction study of the title compound, $C_8H_{20}Cl_5N_2Fe$, indicates crystallization in the monoclinic space group *C2/c*, $Z = 4$, with unit cell parameters $a = 15.56(1)$ Å, $b = 8.876(3)$ Å, $c = 12.487(6)$ Å, and $\beta = 115.61(6)°$, with a nearly ideal five-coordinate trigonal bipyramidal $[FeCl_5]^{2-}$ species in an ionic crystal lattice. A combination of ^{57}Fe Mössbauer spectroscopy and a.c. susceptometry confirms long-range magnetic order between 6 and 7 K with a 3-D antiferromagnetic ground state.

Introduction

The existence of equilibria which involve higher coordination number chloro complexes has been well established for many metals.[1] While the $FeCl_4^-$ ion dominates the chemistry of Fe(III) in hydrochloric acid solution,[2] the $[FeCl_6]^{3-}$ ion has been stabilized with large tripositive counterions,[3] and the binuclear $[Fe_2Cl_9]^{3-}$ species is formed with the cesium cation,[4] although other materials having $A_3Fe_2Cl_9$ stoichiometry have proved to be double salts of the $FeCl_4^-$ ion.[5] From aqueous media, the pentachloroferrate(III) species has only been isolated as the aqua complex $[FeCl_5(H_2O)]^{2-}$, which gives a series of interesting antiferromagnetic materials with alkali metal counterions[6] and a hydrogen-bond-containing aggregate with the ammonium cation.[7]

By the use of a nonaqueous medium (tetrahydrofuran/methanol), however, the $[FeCl_5]^{2-}$ ion was isolated first as the methanol solvate $[FeCl_5(CH_3OH)]^{2-}$ and then, after pumping, as the unsolvated species when precipitated with the diquaternized (dimethyl) cation obtained from diazabicyclo[2.2.2]-octane (DABCO).[8] Vibrational and Mössbauer spectroscopic measurements suggested that the $[FeCl_5]^{2-}$ ion was trigonal bipyramidal. Unfortunately, the methanol solvate is obtained in a poorly crystallized form *via* the reported synthesis and further pumping to yield the $[FeCl_5]^{2-}$ derivative results in a polycrystalline material. Creighton and Taylor[9] employed other large dipositive cations based on *N,N,N′,N′*-tetramethylethylenediamine to stabilize large halogeno dianions of various divalent metals (Co, Cu, Ni, Zn, Sn), and it was of interest to investigate their interactions with iron(III) chloride. By employing a THF/methanol solvent mixture in a system entirely analogous to that used for the DABCO derivative, we obtained well-formed crystals of the $[FeCl_5]^{2-}$ salts directly from slow evaporation, without any solid solvated intermediate. The results of the X-ray structure determination, variable-temperature Mössbauer spectroscopy, and a.c. susceptibility experiments for the *N,N,N′,N′*-tetramethylpiperazinium salt are reported here.

Experimental Section

The tetramethylpiperazinium (**I**) and tetramethylimidazolium (**II**) chloride salts were prepared from *N,N,N′,N′*-tetramethylethylenediamine as described previously.[9]

A solution of anhydrous ferric chloride (Merck), 2.7 g, in *ca.* 100 mL of tetrahydrofuran, was added through a filter to a solution of either **I**, 3.55 g, or **II**, 3.35 g, chloride salt in *ca.* 500 mL of dried ($CaSO_4$) methanol. Orange solutions were obtained from which dark red-orange (for **I**), mp 270 °C dec, or dark yellow (for **II**), mp 176−8 °C, crystals were obtained *via* slow evaporation of the solvent. A little dark powdery material also formed on evaporation, and this was filtered off prior to crystallization. The solutions are somewhat moisture sensitive, and crystallization is preferably carried out in a water-free atmosphere. Anal. (Campbell Microanalytical Laboratory, University of Otago, New Zealand). Found (calcd) for (**I**)$[FeCl_5]$: C, 25.42 (25.46); H, 5.28 (5.34); N, 7.25 (7.42); Cl, 48.07 (46.97). Found (calcd) for (**II**)$[FeCl_5]$: C, 22.99 (23.14); H, 5.55 (4.99); N, 7.65 (7.71); Cl, 48.58 (48.79). Both compounds displayed quadrupolar split Mössbauer signals at room temperature.

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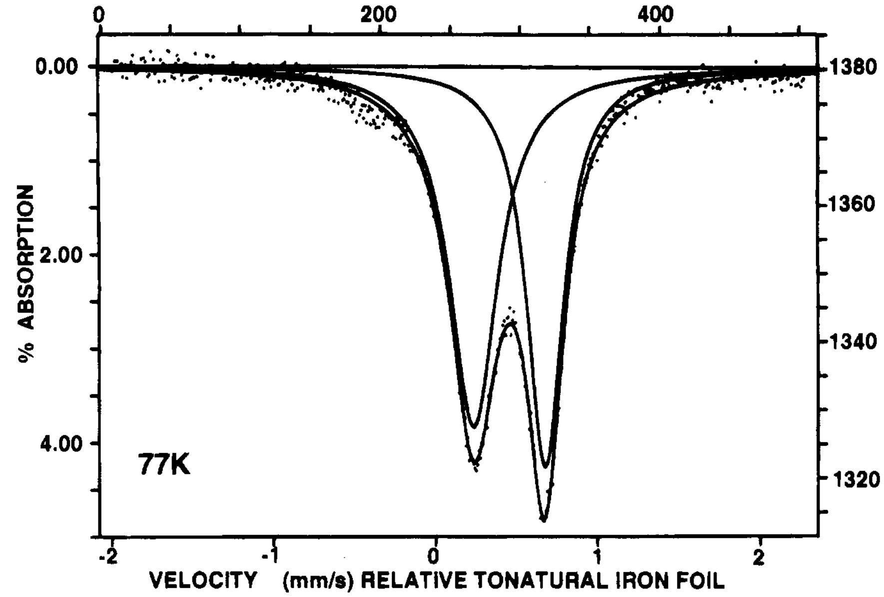

Figure 1. Mössbauer spectrum of (**I**)[$FeCl_5$] at 77 K.

Table 1. Crystallographic Data for (**I**)[$FeCl_5$]

chem formula	$C_8H_{20}Cl_5FeN_2$	space group	*C*2/*c* (No. 15)
fw	377.4	temp	22 °C
a	15.56(1) Å	radiation, λ	Mo Kα, 0.7107$_3$ Å
b	8.876(3) Å	ϱ(calc)	1.61 g cm^{-3}
c	12.487(6) Å	μ	1.7 mm^{-1}
β	115.61(6)°	R^a	0.042
V	1555 Å^3	$R_w{}^b$	0.045
Z	4		

[a] $R(F_o) = (\sum||F_o| - |F_c||)/(\sum|F_o|)$. [b] $R_w(F_o) = [\sum wA^2/\sum w|F_o{}^2|^2]^{1/2}$.

Variable-temperature Mössbauer spectra were recorded using equipment that was previously described.[10] α-Iron foil was employed as a standard. The spectra were fitted to Lorentzians, using the program written primarily by Stone.[11]

A.c. susceptibility measurements were performed using a Lakeshore Cryotronics Series 7000 susceptometer applying an a.c. field of 1 Oe at a frequency of 125 Hz.

The X-ray crystal structure determination was performed on a crystal of (**I**)[$FeCl_5$] with dimensions 0.20 × 0.14 × 0.16 mm which had been sealed in a Lindemann glass capillary. A unique data set was measured to $2\theta_{max} = 65°$ ($2\theta/\theta$ scan mode). A total of 2812 independent reflections were obtained, 1831 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction and solution of the structure by Patterson methods. Anisotropic thermal parameters were used for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals on $|F|$ at convergence, R, R_w (statistical weights derived from the relationship $\sigma^2(I) = \sigma^2(I)_{diff} + 0.00004\sigma^4(I)_{diff}$) are quoted. Neutral-atom complex scattering factors were used; for computations the XTAL program system was used,[12] implemented by S. R. Hall.[13] Selected crystallographic data are given in Table 1.

Results and Discussion

Unlike the quaternized DABCO[$FeCl_5$] derivative, the $[FeCl_5]^{2-}$ salts of cations **I** and **II** crystallize readily from the solvent mixture without coordination of either methanol or THF to the Fe(III) center. Both salts are easily handled in dry conditions.

Table 2. Non-Hydrogen Positional and Isotropic Displacement Parameters

atom	*x*	*y*	*z*	U_{eq}, Å$^{2\,a}$
Fe(1)	$^1/_2$	0.30544(6)	$^1/_4$	0.0303(2)
Cl(1)	$^1/_2$	0.5627(1)	$^1/_4$	0.0581(5)
Cl(2)	0.33107(5)	0.30539(9)	0.16358(7)	0.0382(3)
Cl(3)	0.50467(6)	0.1825(1)	0.41133(8)	0.0540(4)
N(1)	0.2278(2)	0.3500(3)	0.3958(2)	0.0313(9)
C(11)	0.3124(2)	0.4536(3)	0.4278(3)	0.039(1)
C(12)	0.1551(2)	0.3887(4)	0.2728(3)	0.042(1)
C(2)	0.1819(2)	0.3689(3)	0.4796(3)	0.037(1)
C(3)	0.2440(2)	0.3125(3)	0.6025(3)	0.033(1)

[a] The expression for the equivalent isotropic thermal parameter is $U_{eq} = (\sum_i\sum_j U_{ij}a_i{}^*\cdot a_j{}^*\cdot a_i\cdot a_j)/3$

The well-defined quadrupolar split Mössbauer spectra obtained at room temperature [for **I**, $\delta = 0.21$, $\Delta = 0.42$ mm s^{-1}; for **II**, $\delta = 0.312$, $\Delta = 0.50$ mm s^{-1}] and at 77 K (Figure 1) indicated that the Fe(III) centers were in environments containing nonsymmetric electric fields, thus negating any suggestion that these compounds might have been some kind of double salts involving the $FeCl_4^-$ or $[FeCl_6]^{3-}$ ions. The data were also consistent with the room-temperature results obtained on the quaternized DABCO derivative [$\delta = 0.27$, $\Delta = 0.34$ mm s^{-1}][14] and conform to the expected ^{57}Fe isomer shift trend,[8] namely $\delta(FeCl_4^-) < \delta(FeCl_5^{2-}) < \delta(FeCl_6^{3-})$. In addition, the infrared spectrum of (**I**)[$FeCl_5$] contained strong bands around 330 and 260 cm^{-1} (the latter an asymmetric envelope), which may be assigned, as previously,[8] to the e′ and a$_2$″ modes of the $[FeCl_5]^{2-}$ ion in essentially D_{3h} symmetry.

Non-hydrogen atomic coordinates for (**I**)[$FeCl_5$] are given in Table 2, and the packing in the crystal is shown in Figure 2. The cations are disposed about crystallographic inversion centers, while each anion lies with one of the equatorial Fe−Cl bonds coincident with a 2-fold axis. The material is clearly an ionic aggregate, with no abnormal interionic contacts. The most significant feature is the structure of the $[FeCl_5]^{2-}$ ion (Figure 3), which can be seen to be almost perfectly trigonal bipyramidal. The axial Fe−Cl distances (Fe−Cl(2) = 2.371(2) Å) are slightly longer than the equatorial (Fe−Cl(1,3) = 2.283(2), 2.264(1) Å), as expected. These distances compare with 2.3926-

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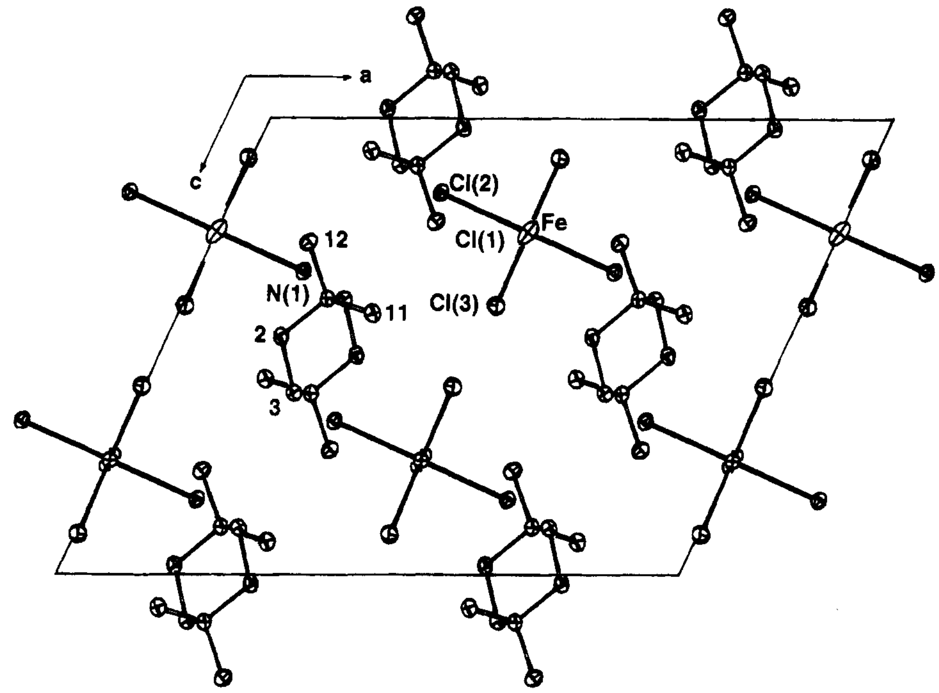

Figure 2. Packing diagram for the structure of (I)[FeCl$_5$], showing atom labeling.

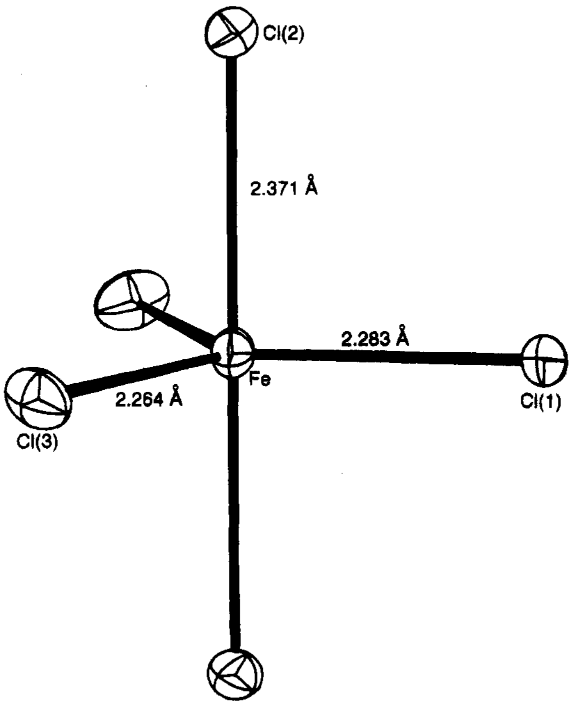

Figure 3. Structure of the [FeCl$_5$]$^{2-}$ anion.

(3) Å in [Co(NH$_3$)$_6$][FeCl$_6$][15] and 2.185(5) Å in the FeCl$_4^-$ groups of (pyH)$_3$Fe$_2$Cl$_9$.[16] The "unperturbed" Fe–Cl distances in the [FeCl$_5$(H$_2$O)]$^{2-}$ ion are 2.350(1) Å.[7] The Cl–Fe–Cl angles are very close to 120° in the equatorial plane (Cl(1)–Fe–Cl(3) = 2 × 118.81(3)°; Cl(3)–Fe–Cl(3) = 122.39(5)°) and 90° between the axial and equatorial positions (Cl(2)–Fe–Cl(1) = 90.01(2)°; Cl(2)–Fe–Cl(3) = 90.45(4)°). These structural results confirm those deductions made previously[8] for the [FeCl$_5$]$^{2-}$ ion from spectroscopic measurements. Also, this determination is the first unambiguous crystallographic characterization of a pentacoordinate iron(III) complex which has five identical unidentate ligands. The pentaazidoferrate(III) complex reported earlier,[17] although also clearly trigonal bipyramidal, contained significant disorder in the nitrogen atom positions.

The relatively long Fe••Fe distances in [FeCl$_6$]$^{3-}$ derivatives have led to magnetic order taking place only at very low temperatures (*e.g.* ~0.9 K for [Co(NH$_3$)$_6$][FeCl$_6$]).[18] On the other hand, there has been considerable recent interest in magnetic interactions which occur in FeCl$_4^-$ derivatives.[16,19] In this context, it was of interest to investigate whether magnetic ordering occurs for (I)[FeCl$_5$]$^{2-}$, the shortest Fe••Fe distance distance being 7.135(3) Å in this case. Preliminary DSC measurements had not indicated any structural phase transitions from room temperature down to 100 K.

The temperature dependence of the Mössbauer spectra is given in Figure 4, in which initial hyperfine splitting is obvious at 6.5 K. On the basis of these spectra, 6.5 K < T_{critical} < 7.1 K. This result is consistent with the value of T_{critical} suggested by the temperature dependence of the a.c. susceptibility (*vide infra*). The value of the internal hyperfine field corresponding to the fully resolved spectrum of 4.5 K is 39 T. This is somewhat less than values ranging from 45 to 50 T which are typical of high-spin Fe(III) with chloro ligands, even with consideration of some reduction in value owing to covalency effects,[20] and suggests that the material is not fully magnetically saturated at 4.5 K. The quadrupolar shift $S_1 - S_2$ of the inner four transitions of the latter spectrum relative to the outer pair is +0.43 mm s^{-1}. This reflects the quadrupole splitting, ΔE = 0.44 mm s^{-1} apparent for the paramagnetic phase spectrum at lower velocity sweep (compare Figures 1 and 4). For an axially

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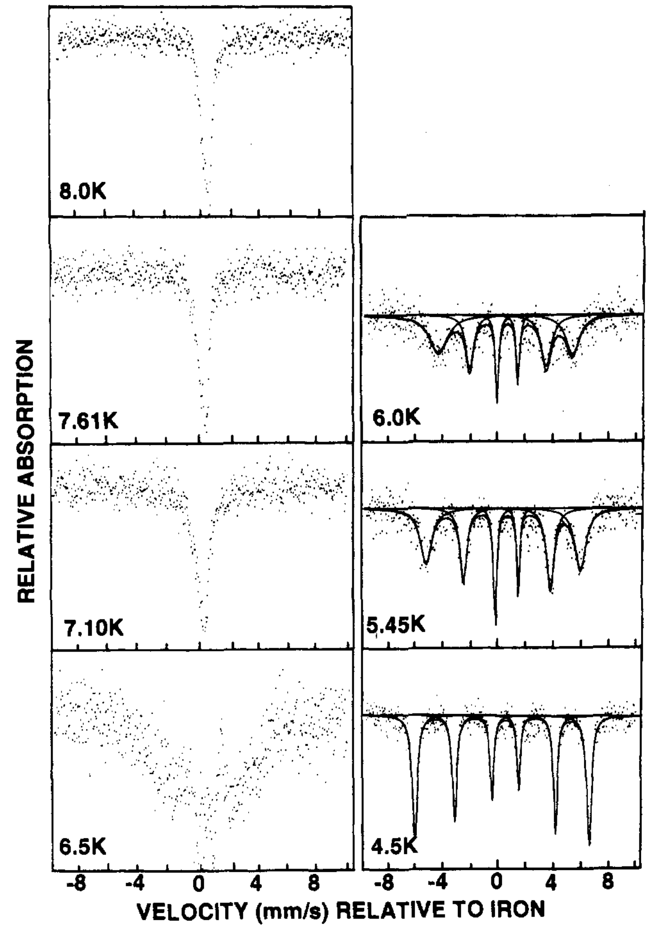

Figure 4. Variation in the Mössbauer spectrum of (I)[FeCl$_5$] between 8.0 and 4.5 K.

symmetric electric field gradient tensor

$$S_1 - S_2 = -\Delta E(3\cos^2\theta - 1)$$

where ΔE is the quadrupole splitting of the paramagnetic phase and θ is the angle between V_{zz} (the principal component of the EFG tensor) and the internal hyperfine field and therefore presumably also the easy axis of magnetization of the ordered state. Thus, assuming that V_{zz} is in fact positive, as is reasonable in view of the crystallographic data (*i.e.* measurably longer axial Fe(III)−Cl bonds *vs* equatorial), one calculates $\theta = 90°$. This implies that the easy axis is located in the *bc* plane of the monoclinic unit cell (Figure 2). The low-temperature magnetic ordering observed here is similar to that observed earlier in the DABCO derivative, for which $T_{\text{critical}} \sim 7.5$ K for the $[\text{FeCl}_5]^{2-}$ complex.[14]

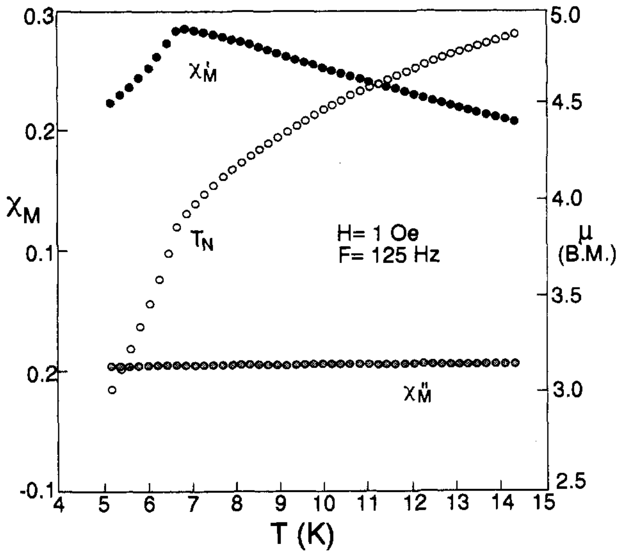

Figure 5. Variation in the components of the a.c. susceptibility (filled circles) and of μ_{eff} (open circles) with temperature between 4 and 15 K.

Previous static d.c. (Faraday) susceptibility studies on the DABCO[FeCl$_5$] derivative for H_0 varying from 0.03 to 0.3 T indicated highly field-dependent behavior and a "weakly ferromagnetic" 3-D ground state.[14] A.c. study (125 Hz, 1 Oe) of the present piperazinium compound clearly indicates a 3-D antiferromagnetic ground state. Thus, there is a broad maximum in χ_M *vs* T (Figure 5) centered at 6.9 K (inflection point corresponding to $T_{\text{Néel}} \sim 6.6$ K) with no out-of-phase absorption ($\chi''_M = 0$) in this temperature range. The basic antiferromagnetic nature of (I)[FeCl$_5$] and $T_{\text{Néel}} \sim 6.6$ K are further confirmed in the plot of μ_{eff} *vs* T, which shows a steadily decreasing moment and an obvious change of slope below ~6.5 K. The true nature of the magnetic ground state of the DABCO cation derivative with the $[\text{FeCl}_5]^{2-}$ anion and its CH$_3$OH and H$_2$O adducts is the subject of further a.c. susceptibility studies.[21]

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Supplementary Material Available: Tables giving crystallographic data and details of the structure determination, bonds lengths and angles, atomic anisotropic thermal parameters, and hydrogen positional and isotropic displacement parameters (4 pages). Ordering information is given on any current masthead page.

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