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The Ferric Chloride α-Di-imine System. Part II. X-ray Structure Determination of 2,9-Di-CH_3-phenanthrolinium Tetrachloroferrate(III)

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The title compound, hereafter [2,9-di-CH_3-phen-H^+], is a novel example of a high-spin iron III complex that undergoes anti-ferromagnetic ordering at very low temperatures (~2 K) by virtue of close non-bonded chlorine–chlorine contacts and the exchange interaction of electron spin density delocalized to such chlorine ligands. In addition to a distorted tetrahedral ferric environment, the basic structure features included herein are highlighted by a *network of chlorine–chlorine contacts approaching the van der Waals radius.* More detailed structural results will be presented in a subsequent publication that includes correlations with zero and high field Mössbauer spectroscopy and magnetic susceptibility measurements of the cooperative ordering to as low as 1.5 K [1].

Experimental

[2,9-di-CH_3-phen H^+] [$FeCl_4^-$] was prepared as fine pale yellow needles from a mixture of glacial acetic acid, anhydrous ferric chloride and 2,9-di-methyl-phenanthroline hemihydrate. The crystals belong to monoclinic space group $C_{2/c}$ with a = 35.158(10), b = 20.857(8), and c = 7.068(2) Å, β = 96.33(5)°. The measured density of 1.58 gm/cm^3 compares well with the calculated density of 1.56 gm/cm^3 for 12 molecules per unit cell and a molecular weight of 405.923 grams for the formula $C_{14}H_{12}N_2Cl_4Fe$. The three-dimensional X-ray intensity data were collected on a Syntex $P2_1$ automated diffractometer using monochromatized Mo(Kα) radiation (λ = 0.71069 Å). Although, 2421 reflections were measured using the θ–2θ scan technique to a 2θ limit of 55°. 1271 intensities were larger than 1.25σ (I) and constitute the unique set to which Lorentz and polarization corrections were applied and which was used in the structure determination. Corrections for absorption were not made.

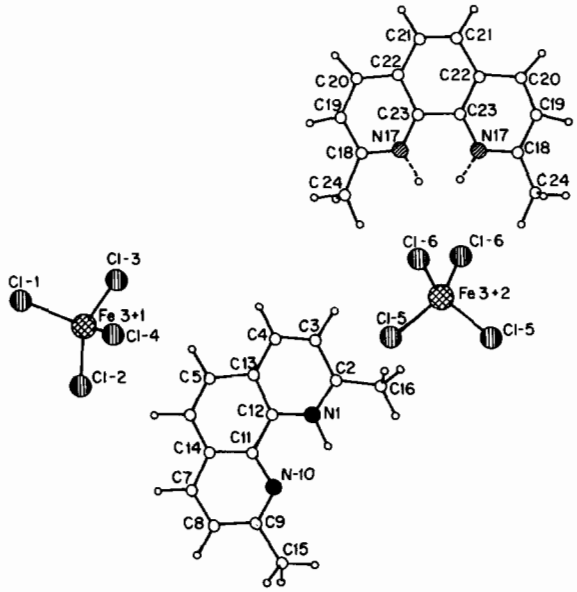

Fig. 1. Local structure.

Structure Solution and Refinement

The structure was solved by locating an iron atom in the three-dimensional Patterson synthesis and phasing the initial Fourier synthesis on this iron atom. From this Fourier map the positions of the four chlorine atoms were located and it became apparent that another iron atom was located at the special position 4e(0, y, ¼). Subsequent Fourier syntheses yielded the positions of the remaining non-hydrogen atoms.

Isotropic least-squares refinement of the non-hydrogen atoms converged at a residual of 0.153. The positions of the hydrogen atoms were calculated and included in the anisotropic refinement of all non-hydrogen atoms. The final residuals were R_w = 0.062 and R = 0.094, with the shift/error ratio for positional parameters below 0.2. The structure was solved and refined using the X-RAY 76 computer programs [2] and the atomic scattering factors were those of Cramer and Mann [3].

Description of the Structure

The structure consists of discrete tetrachloroferrate anions [$FeCl_4^-$] as distorted tetrahedra and

TABLE I. Positional and Thermal Parameters.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0.1778(1)	0.1566(1)	0.4766(4)	3.98(19)	5.59(20)	6.31(22)	0.06(17)	−0.01(16)	−0.06(21)
Fe(2)	0.5000	0.1933(2)	0.2500	6.69(34)	5.47(33)	9.42(41)	0.00	1.47(31)	0.00
Cl(1)	0.1192(1)	0.1958(2)	0.4303(8)	4.92(34)	6.40(42)	8.56(46)	0.87(31)	−0.05(34)	−0.14(58)
Cl(2)	0.1777(1)	0.0654(2)	0.6258(9)	5.11(39)	7.32(43)	10.23(51)	−0.62(33)	−1.73(36)	1.97(42)
Cl(3)	0.2127(1)	0.2253(3)	0.6513(9)	6.39(39)	7.74(46)	10.34(53)	−0.90(35)	−1.54(38)	−0.58(42)
Cl(4)	0.1990(2)	0.1440(3)	0.2024(8)	7.91(45)	14.16(63)	7.43(47)	4.38(43)	1.57(39)	0.39(49)
Cl(5)	0.4517(2)	0.1317(3)	0.1566(10)	7.47(46)	14.75(75)	13.72(67)	−2.67(45)	−0.21(48)	−2.39(57)
Cl(6)	0.4853(2)	0.2532(4)	0.4767(15)	21.58(102)	16.65(84)	23.79(112)	0.02(72)	6.35(88)	−12.28(83)
N(1)	0.3893(4)	0.0154(7)	0.5765(21)	5.70(51)					
C(2)	0.4109(5)	0.0684(10)	0.6006(27)	5.38(60)					
C(3)	0.3929(6)	0.1291(10)	0.5795(29)	6.72(68)					
C(4)	0.3548(5)	0.1341(9)	0.5253(26)	5.28(61)					
C(5)	0.2915(5)	0.0741(9)	0.4356(28)	5.71(70)					
C(6)	0.2729(5)	0.0197(9)	0.4111(25)	4.48(57)					
C(7)	0.2745(5)	−0.0983(9)	0.4190(25)	4.21(55)					
C(8)	0.2952(6)	−0.1527(10)	0.4442(27)	6.67(65)					
C(9)	0.3347(5)	−0.1497(10)	0.5007(26)	5.72(62)					
N(10)	0.3519(4)	−0.0946(7)	0.5267(19)	3.82(44)					
C(11)	0.3309(5)	0.0412(9)	0.4967(25)	4.19(57)					
C(12)	0.3508(5)	0.0181(9)	0.5215(24)	4.10(55)					
C(13)	0.3333(5)	0.0788(8)	0.4966(25)	3.99(55)					
C(14)	0.2902(5)	−0.0395(9)	0.4374(25)	4.30(55)					
C(15)	0.3582(5)	−0.2094(10)	0.5337(28)	6.97(69)					
C(16)	0.4530(6)	0.0593(9)	0.6660(30)	7.75(73)					
N(17)	0.4626(4)	0.4175(7)	0.1858(21)	5.41(49)					
C(18)	0.4255(6)	0.4141(10)	0.1215(29)	6.40(68)					
C(19)	0.4064(5)	0.4705(10)	0.0821(28)	6.10(65)					
C(20)	0.4221(6)	0.5283(10)	0.1125(28)	6.01(66)					
C(21)	0.4817(4)	0.5911(8)	0.2205(28)	5.42(64)					
C(22)	0.4614(5)	0.5329(9)	0.1795(26)	4.97(58)					
C(23)	0.4796(4)	0.4746(8)	0.2134(23)	3.36(59)					
C(24)	0.4093(5)	0.3516(10)	0.0931(28)	7.47(70)					
H(1)	0.4030	−0.0318	0.5969	4.94					
H(3)	0.4095	0.1742	0.5972	6.71					
H(4)	0.3389	0.1814	0.5076	5.45					
H(5)	0.2754	0.1200	0.4137	5.70					
H(6)	0.2394	0.0193	0.3683	4.56					
H(7)	0.2421	−0.0990	0.3758	3.80					
H(8)	0.2788	−0.1959	0.4286	6.33					
H(151)	0.3895	−0.2144	0.5731	6.59					
H(152)	0.3466	−0.2387	0.6444	6.59					
H(153)	0.3542	−0.2399	0.4020	6.59					
H(161)	0.4673	0.0130	0.6852	6.84					
H(162)	0.4690	0.0846	0.5616	6.84					
H(163)	0.4597	0.0842	0.8018	6.84					
H(17)	0.4801	0.3742	0.2230	4.43					
H(19)	0.3763	0.4598	0.0166	6.33					
H(20)	0.4014	0.5656	0.0793	5.88					
H(21)	0.4654	0.6361	0.1916	6.08					
H(24)	0.4234	0.3048	0.1247	7.60					
H(242)	0.3826	0.3469	0.1664	7.60					
H(243)	0.3981	0.3458	−0.0624	7.60					

[a]Isotropic thermal parameters for hydrogen atoms are obtained by subtracting 1.0 from the U_{iso} of the respective heavy atom to which the hydrogen atom is bonded before final least squares refinement.

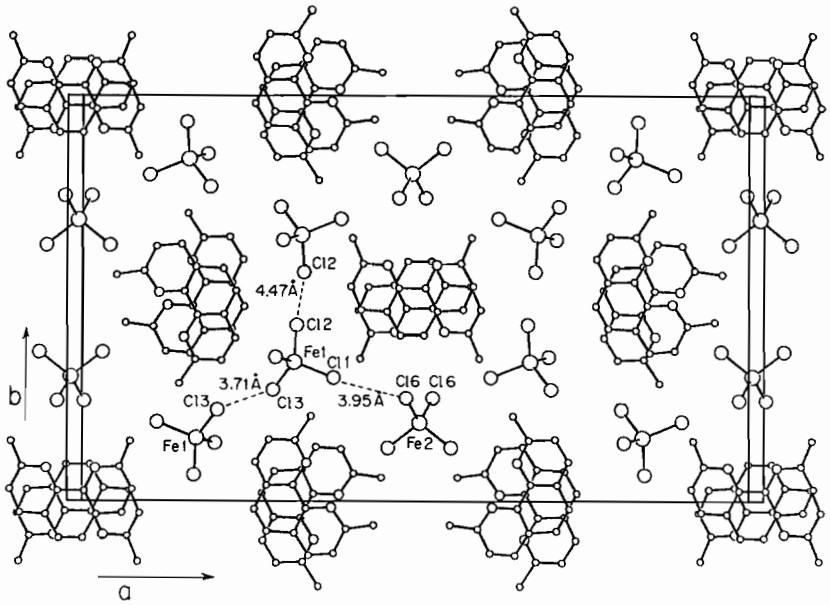

Fig. 2. Packing structure.

TABLE II. Distances and Angles Around the Iron Atoms.

Fe(1)–Cl(1)	2.208(6) A
Fe(1)–Cl(2)	2.173(6)
Fe(1)–Cl(3)	2.181(6)
Fe(1)–Cl(4)	2.167(7)
Fe(2)–Cl(5)	2.174(7)
Fe(3)–Cl(6)	2.138(10)
Fe–Cl(Average) = 2.174 A	
	Angle in degrees
Cl(1)–Fe(1)–Cl(2)	110.2(2)
Cl(1)–Fe(1)–Cl(3)	107.4(2)
Cl(1)–Fe(1)–Cl(4)	108.6(2)
Cl(2)–Fe(1)–Cl(3)	109.4(2)
Cl(2)–Fe(1)–Cl(4)	110.3(3)
Cl(3)–Fe(1)–Cl(4)	111.0(3)
Cl(5)–Fe(2)–Cl(6)	109.1(3)
Cl(5)–Fe(2)–Cl(5)'	107.6(3)
Cl(5)–Fe(2)–Cl(6)'	111.2(3)
Cl(6)–Fe(2)–Cl(6)'	108.6(4)
Cl–Fe–Cl(Average) = 109.3°	

essentially planar 2,9-dimethyl-1,10-phenanthrolinium cations. Each asymmetric unit contains one $FeCl_4^-$ anion in a general position and one in a special position (*vide supra*) with a two-fold axis of symmetry passing through the iron atom. These anion charges are balanced by one [2,9-di-CH_3-phen H^+] cation in a general position and one at the special position such that the two-fold symmetry axis bisects the phenanthroline moiety.

The local structure including hydrogen ions is depicted in Fig. 1 while the packing is given in Fig. 2. It is possible to identify short contact distances in the *a* and *c* directions between the distorted $FeCl_4^-$ tetrahedra. The magnetic implications of these short contact distances (3.71 Å in *a* and 3.89 Å in *c*) have been studied and will be discussed elsewhere.

Table I gives the observed positional parameters while Table II contains the pertinent bond lengths and bond angles at the ferric sites. The latter are similar to those observed in previous studies [4, 5] of the tetrachloroferrate anion and are not remarkable.

Acknowledgements

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References

1 W. M. Reiff and E. H. Witten, to be submitted for publication.
2 'The X-ray System' – version of 1976 J. M. Stewart, Editor. Technical report T.R. – 446 of the Computer Science Center, U. of Maryland, College Park, Maryland.
3 D. Cramer and J. Mann, *Acta Cryst., A24,* 321 (1968).
4 R. R. Richards and N. W. Gregory, *J. Phys. Chem., 69,* 239 (1965).
5 B. Zaslow and R. E. Rundle, *J. Phys. Chem. 61,* 490 (1957).