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The Ferric Chloride-α-diimine System (I) Crystal Structure of Phenanthrolinium Tetrachlorophenanthrolineferrate(III), [phen H] [Fe(phen)Cl_4]

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In the course of a spectroscopic and magnetic susceptibility characterization study of a polycrystalline species formulated as phenanthrolinium pentachloroferrate, [phen H_2] [FeIII Cl_5], the occasion arose to isolate well defined single crystals of the salt, [phen H] [FeIII(phen)Cl_4]. In this letter we report the basic structural features of the pseudo-octahedral *anion* of this salt and briefly compare them to those observed for the related pseudo-octahedral *cation* in the salt [FeIII$(phen)_2Cl_2$] [$FeCl_4$].

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Experimental

[Phen H] [Fe(phen)Cl_4] belongs to the triclinic system (space group = P_T) with the following cell dimensions (Å): a = 8.690(1), b = 11.285(2), c = 12.790(2), α = 111.02°(1), β = 96.17°(1), γ = 93.68°(1), V = 1156.9 Å^3 and Z = 2 for a calculated density of 1.605 gmcm^{-3} and molecular weight of 559.087.

A Syntex $P2_1$ Automated diffractometer was used to determine cell dimensions and measure intensity data by the θ–2θ scan technique to a 2θ limit of 60°. The intensity data were corrected for Lorentz and polarization effects. 4365 of the 7034 intensities measured were considered observed ($I \geq 3\sigma(I)$), and were used in the structure determination.

Solution and Refinement of the Structure

The initial assumption of a noncentric space group (P_1) yielded a solution which could not be refined below 9.8%. The three dimensional Patterson synthesis permitted the location of the iron for the space group P_T. The non-hydrogen atoms were located for subsequent Fourier synthesis. A difference Fourier synthesis, after anisotropic refinement to a residual of 8.9%, yielded the positions of most of the hydrogen atoms including the proton of the uncoordinated phenanthroline molecule. At this point, all hydrogen atom positions were calculated and the final residual after anisotropic refinement of all nonhydrogen atoms was 7.7% with σ/Δ = 0.32.

Atomic scattering factors for the nonhydrogen atoms were taken from Cramer and Mann (1968) and those for hydrogen atoms from Stewart *et al.* (1965).

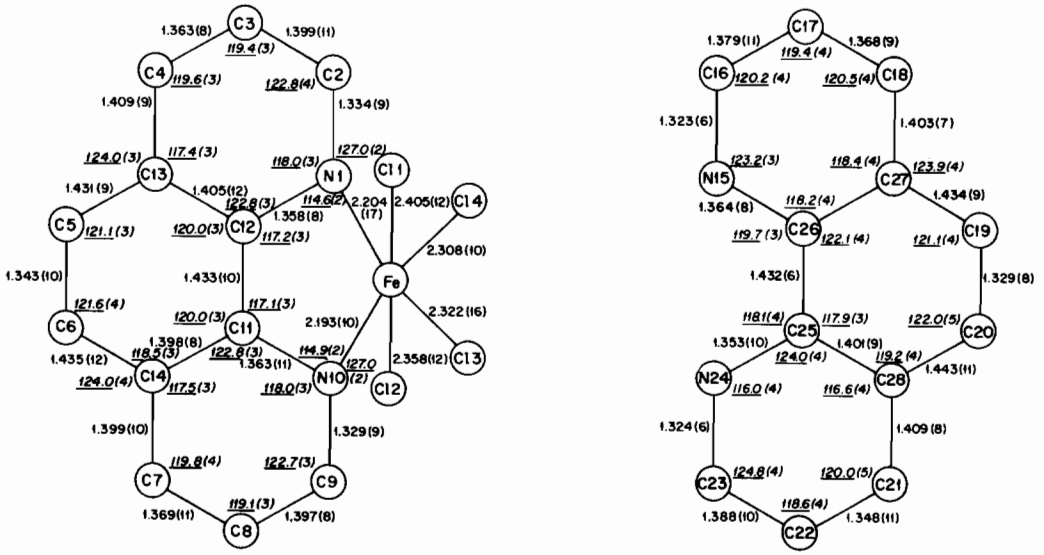

Fig. 1. Local bond distances and coordination environment for [phen H] [Fe(phen)Cl_4].

TABLE I. Atomic parameters in Fractional Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^2$) with e.s.d. s. Temperature Factor: $\exp[-2\pi^2(U11(ha^*)^2 + \ldots + 2U12(hka^*b^*) + \ldots]$.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe^{3+}	2775(1)	3359(1)	2037(1)	311(3)	290(3)	308(3)	2(2)	97(2)	107(2)
Cl1	4741(1)	2831(1)	3221(1)	391(6)	394(5)	342(5)	75(4)	91(4)	141(4)
Cl2	953(1)	3629(1)	658(1)	346(5)	486(6)	427(6)	29(4)	59(4)	242(5)
Cl3	3079(1)	5505(1)	3198(1)	487(6)	292(5)	446(6)	36(4)	142(4)	75(4)
Cl4	835(1)	2584(1)	2798(1)	386(6)	476(6)	398(6)	−60(4)	130(4)	184(5)
N1	2884(3)	1486(3)	704(2)	308(16)	294(16)	325(16)	−5(13)	47(13)	106(13)
C2	2017(4)	394(3)	523(3)	327(20)	333(21)	435(22)	−49(17)	35(17)	148(18)
C3	2031(4)	−711(3)	−431(3)	409(22)	259(19)	491(24)	−30(17)	−40(19)	89(18)
C4	2960(4)	−687(3)	−1218(3)	423(23)	330(21)	400(22)	68(17)	−27(18)	57(18)
C5	4944(5)	563(4)	−1816(3)	539(25)	455(24)	320(21)	144(20)	114(18)	65(19)
C6	5864(4)	1653(4)	−1587(3)	474(24)	561(26)	367(22)	119(21)	186(18)	169(20)
C7	6830(4)	3884(4)	−268(3)	334(21)	523(25)	427(22)	61(18)	125(17)	264(20)
C8	6728(4)	4876(3)	718(3)	297(20)	439(23)	446(22)	−51(17)	30(17)	230(19)
C9	5620(4)	4740(3)	1393(3)	319(19)	328(20)	329(19)	−28(16)	0(15)	119(16)
N10	4661(3)	3677(3)	1126(2)	290(15)	303(15)	271(15)	17(12)	57(12)	127(13)
C11	4791(4)	2679(3)	159(3)	274(18)	296(18)	279(18)	45(14)	52(14)	125(15)
C12	3826(4)	1511(3)	−72(3)	286(18)	303(19)	287(18)	42(15)	29(14)	116(15)
C13	3901(4)	446(3)	−1056(3)	356(21)	378(21)	316(19)	88(17)	25(16)	118(17)
C14	5847(4)	2746(3)	−574(3)	317(20)	388(21)	321(19)	72(16)	80(16)	171(17)
N15	2791(3)	3105(3)	5302(2)	423(18)	372(18)	337(17)	30(14)	131(14)	113(15)
C16	2719(4)	4314(4)	5425(3)	494(24)	414(23)	376(22)	−23(19)	73(18)	175(19)
C17	1812(5)	5055(4)	6168(3)	516(26)	388(23)	529(26)	80(20)	68(21)	134(21)
C18	1008(4)	4535(4)	6792(3)	347(22)	524(26)	436(24)	62(19)	65(18)	55(20)
C19	319(5)	2651(5)	7314(3)	494(26)	744(33)	453(25)	−47(24)	202(20)	194(24)
C20	441(5)	1433(5)	7159(4)	543(28)	810(35)	548(28)	−117(25)	166(22)	382(27)
C21	1442(5)	−652(5)	6103(4)	636(31)	642(32)	588(30)	−148(25)	−81(24)	397(26)
C22	2310(6)	−1299(4)	5317(4)	795(35)	421(26)	678(33)	−49(24)	−131(27)	240(25)
C23	3080(5)	−650(4)	4753(4)	626(30)	458(26)	570(28)	86(22)	21(23)	132(23)
N24	3015(4)	570(3)	4913(3)	541(22)	422(20)	486(21)	63(17)	104(17)	158(17)
C25	2137(4)	1208(4)	5700(3)	336(21)	451(23)	342(21)	−45(18)	−17(17)	159(18)
C26	2014(4)	2528(3)	5895(3)	306(19)	447(22)	280(19)	−32(16)	45(15)	154(17)
C27	1099(4)	3259(4)	6676(3)	334(21)	529(25)	325(20)	−01(18)	69(16)	142(19)
C28	1325(4)	654(4)	6329(3)	429(24)	566(27)	425(23)	−128(20)	−36(19)	276(21)

The least-squares refinements were carried out using the X-RAY 76 crystallographic computer program system (Stewart, 1976).

Description of the Structure

The final positional and thermal parameters are given in Table I. A labelled drawing is presented in Fig. 1. The iron atom is octahedrally coordinated to four chlorine atoms and two nitrogen atoms of a phenanthroline molecule. The negative charge of the Fe(III) complex is opposed by a phenanthrolinium ion. The bond angles and bond lengths are given in Table II and Figs. 1 and 2. Inspection of these values does not reveal structurally significant deviations. The average Fe–Cl bond length is 2.348(43) Å and there are no significant interactions below the expected Van der Waal's contacts.

This structure exemplifies the ability of iron(III) to form an octahedral complex with a single 1,10-phenanthroline ligand and four chloride ions. Goodwin and McPartlin (1977) have previously reported on the structure of the *cis* dichlorobis(1,10-phenanthroline)iron(III) tetrachloroferrate(III) cation, where the octahedrally bonded iron atom complexes to two chloride ions and two 1,10-phenanthroline ligands. While the Fe–N bond lengths do not differ significantly, (between $Fe(phen)Cl_4^-$ and $Fe(phen)_2Cl_2$), we observe a distinct lengthening of the Fe–Cl bond lengths in the present anion. In particular, the trans chlorine atoms have Fe–Cl bond lengths which are somewhat longer than those for the chlorine atoms *trans* to nitrogen atoms of the 1,10-phenanthroline ligand (see Fig. 1). These Fe–Cl bond distances are all longer than the 2.252(4) Å and 2.231(4) Å distances as reported by Goodwin and McPartlin. This lengthening of the Fe–Cl bond is probably the result of increased crowding of the coordination sphere of the pseudo-octahedral anion. The tetrahedral Fe(III)–Cl bond lengths have been observed to be 2.19 Å (Goodwin and McPartlin) and 2.17 Å, Veidis, Reiff, Brennan, Garafalo and Witten (1979).

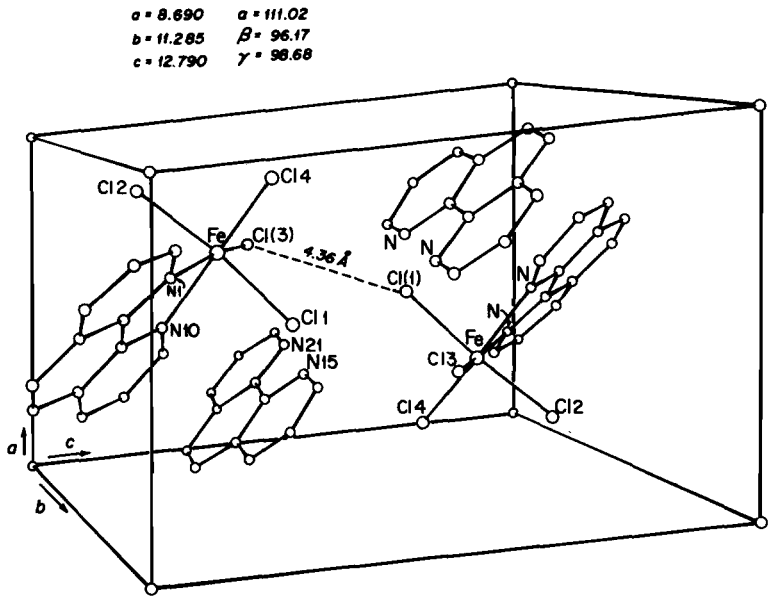

Fig. 2. Packing diagram for [phen H][Fe(phen)Cl_4].

TABLE II. Bond Angles and Bond Distances Around the Iron Atom.

X-M-X	Angle (°)
Cl1-Fe-Cl2	171.68(3)
Cl1-Fe-Cl3	93.19(4)
Cl1-Fe-Cl4	90.79(4)
Cl1-Fe-N1	88.32(8)
Cl1-Fe-N10	86.21(8)
Cl2-Fe-Cl3	94.03(4)
Cl2-Fe-Cl4	91.95(4)
Cl2-Fe-N1	83.67(8)
Cl2-Fe-N10	89.52(8)
Cl3-Fe-Cl4	100.53(4)
Cl3-Fe-N1	165.87(9)
Cl3-Fe-N10	91.09(7)
Cl4-Fe-N1	93.50(8)
Cl4-Fe-N10	168.15(7)
N1-Fe-N10	74.97(10)

Acknowledgements

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