Inorganica Chimica Acta, 64 (1982) L55–L57

Crystal Structure of Pyridinium Tetrachloroferrate(III) Sesqui (Pyridinium Chloride)

BRUCE D. JAMES, MARY B. MILLIKAN and MAUREEN F. MACKAY

Department of Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia

Received October 1, 1981

A compound with the formula $(C_5H_6N)_5Fe_2Cl_{11}$ (where $C_5H_6N^+$ = the pyridinium cation) was reported many years ago by Weinland and Kissling [1] in a study which included the syntheses of a number of chloroferrate(III) derivatives such as $(C_5H_6N)_3Fe_2Cl_9$ and $C_5H_6NFeCl_4$. Recently, we re-investigated some of these complexes in an attempt to characterize a crystalline compound of formula $(C_5H_6N)_2FeCl_5$ [2]. Since this latter might have been an interesting five-coordinate iron(III) complex, we attempted a crystal and molecular structure determination thereon. Although the sample was analyzed twice (in independent laboratories) and yielded satisfactory microanalytical data for the bulk mass having the formula $(C_5H_6N)_2FeCl_5$, the single crystal chosen for the diffractometer proved to be of composition $(C_5H_6N)_5Fe_2Cl_{11}$. Here we report the structure of this compound.

Experimental

The salt $(C_5H_6N)_2FeCl_5$ was prepared from $FeCl_3$, HCl and pyridine as previously reported [2] except that the stoppered solution was allowed to stand for *ca.* 3 hr. prior to being concentrated. This resulted in somewhat larger crystals being formed which tended to aggregate into clusters. *Anal.* Calculated for $C_{10}H_{12}N_2Cl_5Fe$: C, 30.54; H, 3.08; Cl, 45.07%. Found (two sets of microanalyses): C, 30.67 and 30.12; H, 3.23 and 3.45; Cl, 44.85 and 44.6%. (First set of data obtained by Alfred Bernhardt Laboratories, Elbach, Germany and the second by the Australian Microanalytical Service Division of Amdel, Melbourne).

Since the compound was moisture-sensitive, crystals were coated with sodium-dried paraffin oil before removal from a nitrogen-filled drybox. Single crystals were identified under a microscope and sealed in Lindemann glass capillaries. Considerable difficulty was encountered in finding crystals suitable for X-ray analysis and the crystal eventually selected for the intensity measurements was of poor quality. Crystals are orthorhombic, space group *Cmcm* (from systematic extinctions and the centrosymmetric system confirmed on refinement) with $a = 9.700(2)$, $b = 16.189(8)$, $c = 25.845(8)$; $U = 4058(2)$ Å^3; asymmetric unit $[FeCl_4^-]\cdot 2.5[C_5H_6N^+]\cdot 1.5[Cl^-]$, $Z = 8$, $M = 451.12$, $D_c = 1.48$ g cm^{-3}, $F(000) = 1816$; μ(Mo Kα) = 13.7 cm^{-1}. A crystal of approximate dimensions $0.65 \times 0.20 \times 0.15$ mm was employed for intensity measurements on a four-circle Rigaku-AFC diffractometer (graphite crystal monochromator, $\lambda = 0.71069$ Å). The data were recorded by an ω–2θ scan with a scan rate of 2° min^{-1}. Of the 1431 unique intensities measured to a 2θ maximum of 45°, only 270 for which $|F_o| > 8\sigma|F_o|$ were used in the refinement. The intensities were corrected for Lorentz and polarization factors but not for absorption. The sites of the Fe and Cl atoms were derived from Patterson maps and by direct method procedures. The C and N atom sites were located by difference and differentiation of the N atoms was based on their proximity to the adjacent Cl ions and the imposed crystallographic symmetry. Refinement with anisotropic temperature factors given to Fe and Cl and isotropic for C and N converged at $R = 0.069$. Hydrogen atoms were not included. The final atomic coordinates are given in Table I. The major calculations were carried out with the program SHELX-76 [3].

An authentic sample of $(C_5H_6N)_5Fe_2Cl_{11}$ for comparison was prepared by the method of Weinland and Kissling [1]. *Anal.* Calculated for $C_{25}H_{30}N_5Cl_{11}Fe_2$: C, 33.28, H, 3.35; N, 7.76; Cl, 43.22; Fe, 12.38%. Found: C, 33.47; H, 3.43; N, 7.94; Cl,

TABLE I. Atomic Fractional Coordinates; Fe, Cl($\times 10^4$), C, N($\times 10^3$).

	X/a	*Y/b*	*Z/c*	*U*(Å^2)
Fe	0000	1313(5)	596(3)	0.08(1)
Cl(1)	0000	2469(9)	1016(9)	0.13(2)
Cl(2)	0000	318(10)	1154(6)	0.12(1)
Cl(3)	1852(10)	1258(6)	135(3)	0.12(1)
Cl(4)	2881(15)	4454(8)	2500	0.11(1)
Cl(5)	5000	1591(11)	2500	0.08(1)
N(1)	500	343(3)	170(2)	0.12(2)
C(2)	389(4)	322(3)	153(2)	0.12(2)
C(3)	386(4)	266(3)	109(2)	0.14(2)
C(4)	500	238(4)	85(3)	0.12(2)
N(5)	000	460(3)	−162(2)	0.11(2)
C(6)	119(4)	483(2)	−139(1)	0.10(1)
C(7)	120(4)	522(2)	−92(1)	0.09(1)
C(8)	000	549(3)	−68(2)	0.10(2)
N(9)	000	109(4)	250	0.13(3)
C(10)	111(5)	149(3)	250	0.08(2)
C(11)	129(6)	236(3)	250	0.12(2)
C(12)	000	280(4)	250	0.08(3)

43.00; Fe, 11.93%. (Microanalysis by Alfred Bernhardt Laboratories; Fe by colorimetry-phenanthroline method).

Results and Discussion

The structure consists of discrete tetrachloroferrate(III) and chloride anions together with pyridinium cations, all of which lie at special positions. This confirms the nature of the compound as a double salt of pyridinium tetrachloroferrate(III) and pyridinium chloride as suggested previously [2].

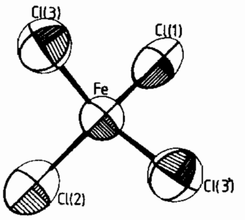

Fig. 1. The $FeCl_4^-$ anion with thermal ellipsoids scaled to 40% probability.

TABLE II. Distances (Å) and Angles (degrees) in the $FeCl_4^-$ Anion.

Fe–Cl(1)	2.16(2)	Cl(1)–Fe–Cl(2)	108.0(8)
Fe–Cl(2)	2.16(2)	Cl(1)–Fe–Cl(3)	108.2(5)
Fe–Cl(3)	2.16(1)	Cl(2)–Fe–Cl(3)	109.7(4)
Cl(1)····Cl(2)	3.50(2)	Cl(3)–Fe–Cl(3')	112.7(2)
Cl(1)····Cl(3)	3.50(2)		
Cl(2)–Cl(3)	3.53(2)		
Cl(3)–Cl(3')	3.59(2)		

The geometry about the Fe atom in the complex anion, which has exact *m* symmetry, is distorted tetrahedral. The Fe–Cl bond lengths are 2.16(2) Å, and while one of the Cl–Fe–Cl angles is 112.7(2)°, and so is significantly greater than the standard tetrahedral value, the others only range between 108.0(8) and 109.7(4)° (see Table II). The intramolecular Cl····Cl distances range from 3.50(2) to 3.59(2) Å. Similar dimensions have been reported for two $[FeCl_4]^-$ anions which have exact S_4 symmetry; in $[AsPh_4][FeCl_4]$, the Fe–Cl bond length is 2.18(1) Å and the Cl–Fe–Cl angles 106.95(5) and 114.6(1)° [4], whereas in $[FeCl_2(DMSO)_4]FeCl_4$, distortion from tetrahedral geometry is not so appreciable, the Fe–Cl bond length being 2.162(5) Å and the Cl–Fe–Cl angles 108.1(3) and 112.2(3)° [5]. Two of the pyridinium ions in the title compound have site symmetry *m* and one has site symmetry *mm*.

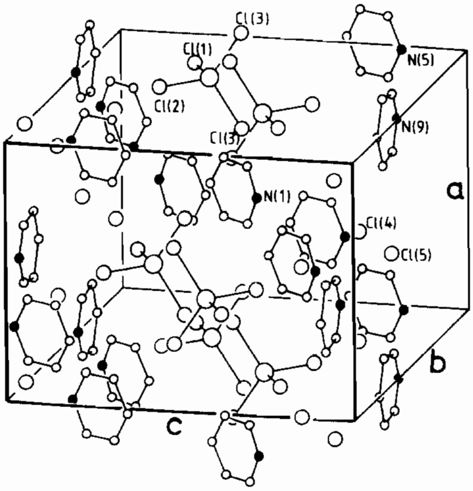

Fig. 2. The crystal packing.

The crystal packing is illustrated in Fig. 2. Viewed along [010], the structure is seen to consist of layers containing $[FeCl_4^-]$ ions sandwiched between pyridinium ions which alternate with sheets containing both Cl^- and pyridinium ions. One short distance of 2.98(3) Å between N(5) and Cl(5), which is significantly less than the sum of their van der

TABLE III. The X-ray Powder Pattern of $(C_5H_6N)_5Fe_2Cl_{11}$ and a Comparison of the Strongest Lines with those Calculated from Single Crystal Data.

Powder Pattern[a] for $(C_5H_6N)_5Fe_2Cl_{11}$:

12.90(ms), 12.28(w), 8.35(s), 7.63(w), 6.94(ms), 6.05(m), 4.75(s), 4.39(s), 4.16(m), 3.91(s), 3.72(vw), 3.45(s), 3.31 (vw), 3.22(ms), 2.99(ms), 2.87(m), 2.63(vw), 2.40(w), 2.24(wv), 2.12(vw), 1.99(vw), 1.66(vw).

d-spacing (calc)[b] (Å)	d-spacing (obs) (Å) ± 0.05	possible *hkl*
12.85	12.90	002
8.35	8.35	110
6.99	6.94	112
6.09	6.05	113
4.86, 4.73	4.75	020, 130
4.38, 4.34, 4.28	4.39	115, 025, 006
4.14, 4.11	4.16	113, 221
3.88, 3.87	3.91	204, 042
3.45	3.45	044
3.21, 3.21, 3.19	3.22	008, 206, 045
2.99	2.99	313
2.85	2.87	314

[a] Using a Philips 57.3 mm radius camera and Ni-filtered CuKα radiation. w, weak; m, moderate; s, strong. [b] From formula $d(hkl) = \dfrac{abc}{(h^2b^2c^2 + k^2c^2a^2 + l^2a^2b^2)^{1/2}}$

Waals radii (3.2 Å), is indicative of hydrogen bonding (*cf.* N····Cl distance of 2.95 Å in pyridinium chloride [6]). The nitrogen atoms of the other two $C_5H_6N^+$ ions each have two close approaches with Cl^- ions. Both N(1) and N(9) lie 3.36 Å from two Cl(4) ions which are related by the *m* symmetry. In addition N(1) lies 3.36 Å from Cl(2) of the $[FeCl_4^-]$ anion. No other approaches of less than 3.63 Å are observed between N and Cl atoms.

In order to confirm that the crystal used for data collection was identical to that of an authentic sample of $(C_5H_6N)_5Fe_2Cl_{11}$, the X-ray powder pattern of the latter* was compared with that which was calculated from the intensity measurements observed from the single crystal. The results (Table III) indicate that a reasonable fit for the strongest lines of the powder pattern has been achieved.

Since both $(C_5H_6N)_5Fe_2Cl_{11}$ and $(C_5H_6N)_2FeCl_5$ are double salts, it is perhaps not surprising that a small amount of the former can be found in a batch of the latter. In any event, the planar nature of the pyridinium ion and its propensity for engaging in hydrogen bonding appear to make it an unlikely candidate for stabilizing a genuine $FeCl_5^{2-}$ species.

References

1 R. F. Weinland and A. Kissling, *Z. Anorg. Allgem. Chem., 120,* 209 (1922).
2 M. B. Millikan and B. D. James, *J. Inorg. Nucl. Chem., 43,* 1175 (1981).
3 G. M. Sheldrick. SHELX-76. A program for crystal structure determination. Univ. of Cambridge, England (1976).
4 F. A. Cotton and C. A. Murillo, *Inorg. Chem., 14,* 2467 (1975).
5 M. J. Bennett, F. A. Cotton and D. L. Weaver, *Acta Cryst., 23,* 581 (1967).
6 C. Rerat, *Acta Cryst., 15,* 427 (1962).

---

*The compound is extremely hygroscopic and so the packing of the Lindemann glass capillary was carried out in the drybox. Despite this, it was found to be very difficult to grind the compound to an even particle size, and the powder patterns obtained, whilst consistent- and significantly different from that reported for $(C_5H_6N)_2FeCl_5$ [2] - were of only moderate quality.