

β -Alaninium Tetrachloroferrate(III)

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Abstract. $(\text{NH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{FeCl}_4 \cdot \text{C}_3\text{H}_8\text{NO}_2^+ \cdot \text{FeCl}_4^-$, monoclinic, $P2_1/c$, $a = 6.966$ (1), $b = 11.994$ (2), $c = 12.444$ (3) Å, $\beta = 91.01$ (1)°. $\rho_c = 1.822$ Mg m⁻³ with $Z = 4$. The FeCl_4^- anion shows only small distortions from tetrahedral coordination geometry ($\text{Fe}-\text{Cl}_{\text{av}} = 2.191$ Å). The β -alaninium cations dimerize through the carboxylic acid groups [$\text{O}-\text{H}\cdots\text{O} = 2.640$ (5) Å]. An internal $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond also exists.

Introduction. Orange-red needle crystals of $(\text{NH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{FeCl}_4$ are formed by the slow evaporation of a stoichiometric solution of β -alanine and ferric chloride in dilute HCl. A small crystal ($0.21 \times 0.18 \times 0.30$ mm) was mounted in a glass capillary with the crystallographic a axis parallel to the capillary axis. Systematic extinctions defined the unique monoclinic space group $P2_1/c$ ($l = 2n + 1$ for $h0l$ reflections and $k = 2n + 1$ for $0k0$ reflections). Intensity data were collected on an automated Picker four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. A θ - 2θ step-scan technique was utilized with 3 s steps of 0.05° over a base width of 1.6° . Background measurements of 20 s were made before and after each scan. Standard

deviations in intensity were calculated by $\sigma^2(I_o) = \text{TC} + \text{BC} + (0.03)^2 I_o^2$, where TC = total counts, BC = normalized background counts, and $I_o = \text{TC} - \text{BC}$. A total of 1490 reflections were collected in the scan range $5 \leq 2\theta \leq 50^\circ$, of which 1404 had $I > 3\sigma(I)$. Three standards monitored every 50 reflections show no systematic variation in intensity. Absorption corrections ($\mu = 2.459$ mm⁻¹) were made.

Fe and Cl positions were deduced from a Patterson function. C, N and O atoms were revealed on initial Fourier syntheses. Later Fourier syntheses, after least-squares refinement of the heavy-atom positions, revealed the locations of all H atoms. Full-matrix refinement [$w_{hkl} = 1/\sigma^2(F)$] with anisotropic thermal parameters for all non-hydrogen atoms yielded a final

Table 1. Final positional parameters for $(\text{NH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{FeCl}_4$ ($\times 10^4$; for H $\times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>
Fe	3983 (1)	7527 (1)	353 (1)
Cl(2)	2988 (2)	6584 (2)	1743 (1)
Cl(3)	1631 (3)	8600 (1)	-230 (1)
Cl(4)	4956 (2)	6459 (1)	-954 (1)
Cl(5)	6387 (3)	8563 (2)	918 (1)
O(6)	-273 (3)	-954 (3)	3895 (3)
O(7)	1278 (6)	669 (3)	4088 (3)
C(8)	2541 (10)	676 (5)	1964 (5)
C(9)	1135 (10)	-196 (5)	2340 (4)
C(10)	713 (8)	-123 (5)	3532 (4)
N	1770 (9)	1843 (5)	2114 (4)
H(81)	3 (14)	-18 (8)	204 (8)
H(82)	159 (13)	-107 (8)	230 (8)
H(91)	274 (14)	60 (8)	120 (8)
H(92)	409 (13)	58 (8)	243 (7)
HN(1)	59 (15)	204 (8)	181 (8)
HN(2)	268 (16)	224 (9)	200 (9)
HN(3)	158 (15)	209 (8)	276 (8)
HO	-94 (20)	-88 (10)	453 (10)

Table 2. Interatomic distances (Å) and angles (°) for $(\text{NH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{FeCl}_4$

Anion				
Fe-Cl(2)	2.190 (2)	Cl(2)-Fe-Cl(3)	108.59 (8)	
Fe-Cl(3)	2.196 (2)	Cl(2)-Fe-Cl(4)	113.06 (8)	
Fe-Cl(4)	2.187 (2)	Cl(2)-Fe-Cl(5)	106.85 (7)	
Fe-Cl(5)	2.192 (2)	Cl(3)-Fe-Cl(4)	109.69 (7)	
		Cl(3)-Fe-Cl(5)	109.58 (8)	
		Cl(4)-Fe-Cl(5)	109.00 (8)	
Cation				
N-C(8)	1.513 (9)	N-C(8)-C(9)	111.6 (5)	
C(8)-C(9)	1.513 (9)	C(8)-C(9)-C(10)	113.6 (5)	
C(9)-C(10)	1.519 (8)	C(9)-C(10)-O(6)	114.1 (5)	
C(10)-O(6)	1.296 (7)	C(9)-C(10)-O(7)	121.7 (5)	
C(10)-O(7)	1.235 (7)	O(6)-C(10)-O(7)	124.1 (5)	
C(8)-H(81)	0.97 (10)	H(81)-C(8)-H(82)	109 (7)	
C(8)-H(82)				
C(9)-H(91)	0.88 (10)	H(91)-C(9)-H(92)	105 (8)	
C(9)-H(92)				
Hydrogen-bonding contacts				
<i>A</i>	<i>B</i>	<i>A-H</i>	<i>B-H</i>	<i>A-B</i>
O(6)-HO-O(7) ^a		0.93 (9)	1.75 (9)	2.640 (6)
N-HN(3)-O(7)		0.95 (10)	2.39 (9)	2.857 (8)
N ^b -HN(1) ^b -Cl(3)		0.93 (10)	2.56 (8)	3.347 (6)
N-HN(2)-Cl(4)		0.80 (11)	2.63 (8)	3.399 (6)
N-HN(3)-Cl(5)		0.87 (10)	2.78 (8)	3.434 (6)
N-NH(1)-O(6) ^c		0.93 (10)	2.57 (9)	3.098 (8)

Coordinates transformed by: (a) $x, -y, 1 - z$; (b) $-x, 1 - y, 1 - z$; (c) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

conventional R value ($= \sum |F_o| - |F_c| / \sum |F_o|$) of 0.058 and a weighted R value [$= \sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2$] of 0.058. The standard error of an observation of unit weight was 1.42. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Final positional parameters are given in Table 1 and pertinent distances and angles listed in Table 2.* Computer programs used were part of a local computer library (Anderson, 1971; Caputo, 1976).

Discussion. The structure consists of discrete FeCl_4^- anions and dimeric β -alaninium cations, as shown in Fig. 1. The anion shows only small distortions from idealized T_d symmetry. The average Fe—Cl distance is 2.191 Å, with the range of distances (2.187–2.196 Å) being statistically significant. There is no readily apparent correlation between these variations and the relatively weak N—H...Cl hydrogen bonds (see below). Similar statements hold for the Cl—Fe—Cl angles, which span the range 106.85–113.06°. The Cl thermal parameters are approximately 50% larger than those of the atoms in the β -alaninium ion. Thus, as shown by the thermal ellipsoids in Fig. 1, the FeCl_4^- anion is undergoing rather large torsional oscillations. Again, this is an indication that the N—H...Cl hydrogen bonding is weak. However, we note that the Fe—Cl distances reported here are significantly longer than reported distances in $\text{Ph}_4\text{AsFeCl}_4$ (Cotton & Murillo, 1975) and $\text{PCl}_4\text{FeCl}_4$ (Kistenmacher & Stucky, 1968) of 2.182 (1) and 2.185 (2) Å respectively. Some weakening of the Fe—Cl bonds due to the hydrogen bonding thus presumably does occur.

The cations dimerize through pairs of short O(6)—H...O(7) hydrogen bonds of 2.640 (6) Å. The C—O distance of 1.235 (7) Å involving the carbonyl O(7) atom, is considerably shorter than the distance of 1.296 (7) Å to the hydroxyl O(6) atom. Each β -alaninium cation is locked into a nearly planar conformation by an internal N—H...O(7) hydrogen bond of 2.857 (8) Å. This hydrogen bonding ties the dimer

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33908 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

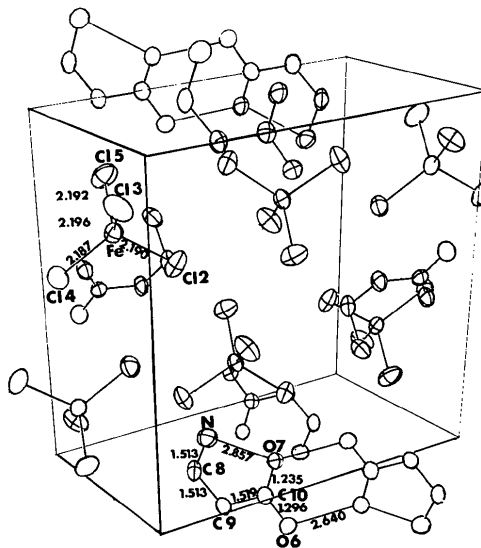


Fig. 1. The structure of β -alaninium tetrachloroferrate(III). Thermal ellipsoids of atoms outside the unit cell, included for connectivity purposes, are shown without ellipses. The b axis is vertical, the a axis is into the page.

together in a rather rigid structure with low amplitudes of thermal vibration for the constituent atoms.

The remaining hydrogen bonds are rather weak. Three short N...Cl contacts exist, but only one, to Cl(4), has a nearly linear N—H...Cl hydrogen bond. A bifurcated hydrogen bond exists from the N atom to Cl(3) and O(6), the latter being an interdimer interaction. Similarly, the short N—Cl(5) contact is part of a bifurcated bond shared with the intradimer N—H...O(7) bond.

References

- ANDERSON, D. N. (1971). PhD Thesis, Washington State Univ., USA.
 CAPUTO, R. E. (1976). PhD Thesis, Washington State Univ., USA.
 COTTON, F. A. & MURILLO, C. A. (1975). *Inorg. Chem.* **14**, 2467–2469.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KISTENMACHER, T. J. & STUCKY, G. D. (1968). *Inorg. Chem.* **7**, 2150–2155.