

## Short Communication

### The Crystal Structure of Oxonium Aquapentachloroferrate(III)

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As part of an investigation of benzotriazole complexes<sup>1–3</sup> an attempt to prepare an iron benzotriazole compound was made. Unfortunately, benzotriazole did not coordinate to iron, and instead the present complex was precipitated.

Orange crystals of  $(\text{H}_3\text{O})_2[\text{FeCl}_5(\text{H}_2\text{O})]$  were precipitated by mixing  $1.5 \times 10^{-4}$  mol iron(III) chloride hexahydrate in 4 ml 2 M hydrochloric acid and  $3 \times 10^{-3}$  mol benzotriazole in 4 ml acetone. Determination of the possible space groups and the data collection were carried out as described in Ref. 1. The dimensions of the crystal were  $0.08 \times 0.05 \times 0.03$  mm. The structure was solved by Patterson technique.<sup>4</sup> The references to the atomic scattering factors and the refinement technique are those used

in Ref. 1. However, the atomic scattering factor for the oxonium ion was calculated<sup>5</sup> as  $f_{\text{H}_3\text{O}^+} = f_{\text{O}} + 2f_{\text{H}} \sin(4\pi rs)/4\pi rs$ , where  $r = 1.00 \text{ \AA}$  and  $s = \sin \theta/\lambda$ . Thus, the hydrogen atoms in  $\text{H}_3\text{O}^+$  are not located. The space group *Pcmm* was assumed in all calculations. The refinement confirms that this choice is correct. Crystal data and *R*-values are listed in Table 1. The final positional parameters with standard deviations are listed in Table 2. Lists of thermal parameters and observed and calculated

Table 2. Final atomic coordinates  $\times 10^4$ . The estimated standard deviations  $\times 10^4$  are given in parentheses. The values of the hydrogen atom are multiplied by  $10^3$ .

Atom	x	y	z
Fe	6896(1)	2500	3837(1)
Cl1	4280(2)	2500	2770(1)
Cl2	8982(1)	2500	2520(1)
Cl3	6761(1)	106(1)	3952(1)
Cl4	9531(2)	2500	4941(1)
O	5023(6)	2500	5035(3)
$\text{H}_3\text{O}^+$	1597(4)	4992(3)	3585(2)
H	456(6)	189(4)	528(3)

Table 1. Crystal data.

<i>M</i>	289.2
$\mu(\text{MoK}\alpha)(\text{cm}^{-1})$	29.2
Crystal system	orthorhombic
<i>a</i> (Å)	7.038(1)
<i>b</i> (Å)	9.926(3)
<i>c</i> (Å)	13.720(2)
Space group	<i>Pcmm</i>
<i>D</i> <sub>c</sub> (g/cm <sup>3</sup> )	2.00
<i>Z</i>	4
Total number of reflections	1627
Number of independent observations	965
$[I \geq 2\sigma(I)]$	
$R = \frac{\sum   F_o  -  F_c  }{\sum  F_c }$	0.031
$R_w = \frac{\left[ \frac{\sum w( F_o  -  F_c )^2}{\sum w F_o ^2} \right]^{1/2}}$	0.038

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations.

Atoms	Distance or angle
Fe–Cl1	2.352(1)
Fe–Cl2	2.328(1)
Fe–Cl3	2.383(1)
Fe–Cl4	2.394(1)
Fe–O	2.107(4)
O–H	0.76(4)
Cl1–Fe–Cl2	90.61(5)
Cl1–Fe–Cl3	90.58(2)
Cl1–Fe–O	89.77(12)
Cl2–Fe–Cl3	94.41(2)
Cl2–Fe–Cl4	90.13(5)
Cl3–Fe–Cl4	89.36(2)
Cl3–Fe–O	85.59(2)
Cl4–Fe–O	89.49(11)

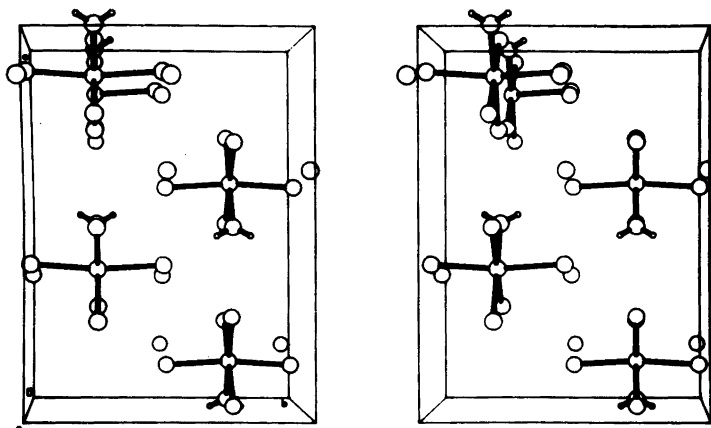


Fig. 1. Stereo view along the  $a$ -axis of the structure.

structure factors may be obtained from the authors on request.

*Description and discussion of the structure.* Bond lengths and bond angles with estimated standard deviations are listed in Table 3. The compound is built from  $\text{H}_3\text{O}^+$  and  $[\text{FeCl}_5(\text{H}_2\text{O})]^{2-}$  ions. The Fe atom, which lies on a mirror plane, has a distorted octahedral coordination to one O atom and five Cl atoms, the O atom and three of the Cl atoms being positioned on the mirror plane (Fig. 1). The structure is isostructural with  $(\text{NH}_4)_2[\text{FeCl}_5(\text{H}_2\text{O})]$ .<sup>6</sup> The Cl–Cl distances in the complex fall within the range of 3.327–3.457 Å. The Cl–O distances are 3.152 Å and 3.175 Å. The shortest distances from the  $\text{H}_3\text{O}^+$  ion are 3.304(3) Å to Cl4( $1-x, \frac{1}{2}+y, 1-z$ ), 3.308(3) Å to Cl1 and 3.364(3) Å to Cl2( $-\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$ ). The shortest distances from O in  $\text{H}_2\text{O}$  are 3.193(3) Å to Cl3( $1-x, -y, 1-z$ ) and Cl3( $1-x, \frac{1}{2}+y, 1-z$ ). Thus, the strongest hydrogen-bonding interactions are between the complex ions, while the hydrogen-bonding interactions described by the  $\text{H}_3\text{O}^+$ –Cl distances are somewhat weak compared with those found in other compounds.<sup>7</sup>

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1. Søjtofte, I. and Nielsen, K. *Acta Chem. Scand. A* 35 (1981) 733.
2. Søjtofte, I. and Nielsen, K. *Acta Chem. Scand. A* 35 (1981) 739.
3. Søjtofte, I. and Nielsen, K. *Acta Chem. Scand. A* 35 (1981) 747.

4. Stewart, J. M., Kundell, F. A. and Baldwin, J. C. *The X-Ray System, Version of 1975*, University of Maryland, College Park 1975.
5. Zachariasen, W. H. *Theory of X-Ray Diffraction in Crystals*, Dover Publications, New York 1967, p. 223.
6. Lindquist, I. *Ark. Kemi, Mineral. Geol. A* 24 (1946) No. 1.
7. Olovsson, I. and Jönsson, P.-G. *The Hydrogen Bond II*, North-Holland, Amsterdam 1976, p. 440.

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