ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 7, pp. 512–516. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 7, pp. 427–431.

Refinement of the Molecular Structure of Ammonium Pentachloroaquaferrate $(NH_4)_2[FeCl_5(H_2O)]$

O. V. Koval'chukova[a, b], **S. B. Strashnova**[a, *], **A. N. Utenyshev**[c], **and P. V. Strashnov**[d]

[a] *Peoples Friendship University, Moscow, Russia*
[b] *Kosygin State University, Moscow, Russia*
[c] *Sechenov State Medical University, Moscow, Russia*
[d] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991 Russia*
**e-mail: sstrashnova@mail.ru*

Received July 26, 2018; revised December 20, 2018; accepted December 26, 2018

Abstract—The crystal structure of ammonium pentachloroaquaferrate $(NH_4)_2[FeCl_5(H_2O)]$ is refined (CIF file CCDC no. 1831198). Compounds $(A)_x[FeCl_5(H_2O)]$, where A is an organic or inorganic anion ($x = 1, 2$), crystallize in the orthorhombic crystal system. The geometry and structural parameters of the $[FeCl_5(H_2O)]^{2-}$ anion are nearly independent of the counterion nature.

Keywords: X-ray diffraction analysis, iron complexes, aquaferrate complexes

DOI: 10.1134/S1070328419060022

INTRODUCTION

The compounds belonging to the class of segnetoelectrics exhibit simultaneously the segnetoelectric and (anti)ferromagnetic properties in the same phase and attract special attention in the recent time [1–5]. Their spin structures are usually complicated and noncollinear. Such phenomena as circulation, electric polarization rotation or suppression, magnetization, and others can occur in these compounds depending on the magnetic field strength and direction, which is interesting both from the viewpoint of fundamental physics and as a possibility to use similar materials for manufacturing systems of information storage and sensors.

Binary oxides of transition metals, for example, $LnMnO_3$ (Ln = Tb, Dy), $Ni_3V_2O_8$, $LiCu_2O_2$, $MnWO_4$, etc. [6], and some non-oxide materials ($CuCl_2$, $K_3Fe_5F_{15}$) [7, 8] are traditionally classified as segnetoelectrics. In the recent years, the segnetoelectric properties were found for the compounds of the erythrocerite type with the general formula $A_2[FeX_5(H_2O)]$, where A is the alkaline metal or ammonium cation, and X is the halide ion [1, 9]. These compounds are isolated during hydrolysis as the predominant form of iron(III) ions in acidified solutions: tetrachloroferrate ions [10]. The high spin number of the iron cation (d^5) and the high-spin state of the central ion ($S = 5/2$) result in a low magnetic anisotropy [11]. This fact has attracted attention of researchers since the 1990s [12–14], and interest in such compounds is being actively continued nowadays [1, 9, 15].

Pentachloroaquaferrate has first been synthesized as early as in 1947 by the evaporation of solutions containing a mixture of iron(III) and ammonium chlorides [16]. The unit cell parameters were determined and the structure of the compound was proposed in 1948 [17]. The crystal structure of $(NH_4)_2[FeCl_5(H_2O)]$ was solved in 1978 [18] and then refined [19]. However, the pentachloroaquaferrate structure is absent from the structural databases and, hence, we can consider this problem once more.

EXPERIMENTAL

Ammonium pentachloroaquaferrate $(NH_4)_2[FeCl_5(H_2O)]$ was obtained as orange-red crystals of the byproduct in the synthesis of the iron(III) complex with 4-(2-(1,5-dimethyl-3-oxo-2-phenylpyrazolidinyl)hydrazono)-3-methyl-1-phenylpyrazolone-5 (HL). The synthesis was carried out by the slow mixing on heating of equal volumes of equimolar alcohol solutions of the initial ligand and iron(III) chloride. The hot mother liquor was neutralized with a 10% aqueous solution of ammonia, cooled to room temperature, and kept for 2 h. Then the precipitate was filtered off, and single crystals of $(NH_4)_2[FeCl_5(H_2O)]$ were separated under a microscope from the polycrystalline complex.

For $(NH_4)_2[FeCl_5(H_2O)]$ (*FW* = 287.20)

Anal. calcd., %	Fe, 19.45	N, 9.75	Cl, 61.72	H, 3.51
Found, %	Fe, 19.53	N, 9.81	Cl, 61.98	H, 3.48

Table 1. Selected crystallographic data and refinement parameters for compound **I**

Parameter	Value
FM	287.20
Crystal system	Orthorhombic
Space group	*Pnma*
a, Å	13.581(3)
b, Å	9.925(2)
c, Å	6.9498(14)
Z	4
ρ_{calcd}, g/cm^3	2.036
V, Å^3	936.8(3)
$F(000)$	572
Scan range, deg	2.99–31.42
Ranges of indices	$-19 \le h \le 12$, $-14 \le k \le 11$, $-9 \le l \le 4$
Number of measured/independent reflections	3283/1483
R_{int}	0.0181
Reflections with $I > 2\sigma(I)$	1312
Number of refined parameters	64
GOOF	1.057
R_1, wR_2 for $I > 2\sigma(I)$	0.0274, 0.0674
R_1, wR_2 for all data	0.0322, 0.0719
Residual electron density (min/max), e Å^{-3}	−1.042/0.479

X-ray diffraction analysis of the orange-red rhombic crystals of $(NH_4)_2[FeCl_5(H_2O)]$ 0.560 × 0.085 × 0.50 mm in size was carried out on a KM4 automated diffractometer (KUMA DIFFRACTION, Poland) ($\lambda(MoK_\alpha)$ = 0.71073 Å, graphite monochromator, $\omega/2\theta$ scan mode) at 120.0(1) K. The structure was solved by a direct method [20]. The positional and temperature parameters of non-hydrogen atoms were refined in the anisotropic approximation by full-matrix least squares [21]. The positions of hydrogen atoms were revealed from the difference Fourier syntheses and refined with restraints by the riding model. All calculations were performed using the SHELXTL program package [22]. The main crystallographic data and experimental characteristics for compound **I** are presented in Table 1.

The crystallographic data for the structure of compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1831198; www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The general view of ammonium pentachloroaquaferrate is presented in Fig. 1. The Fe atom lies on the *m* plane. The coordination polyhedron of the central Fe(III) cation is a distorted octahedron, and its coordination sphere contains five chloride anions and one water molecule. The Fe–O and Fe–Cl(1) axial bond lengths are 2.098(2) and 2.3221(8) Å, respectively. The lengths of four equatorial Fe–Cl bonds are not equivalent. Three of these bonds (Fe–Cl(2), Fe–Cl(3), and Fe–Cl(3a)) are somewhat longer (2.3930(8)–2.3919(6) Å), which can be due to the participation of both atoms in stronger hydrogen bonds with the hydrogen atoms of the ammonium cations. The fourth bond Fe–Cl(4) is substantially shorter (2.3494(8) Å). The bond angles between the bonds in the coordination polyhedron $FeCl_5O$ range from 85.58(1)° to 94.416(13)°, and the angles involving the O and Cl(2) atoms are smaller than 90°.

The water molecule participates in the weak intermolecular hydrogen bond with the Cl(3) atom ($1 - x$, $-y$, $1 - z$): O(1)···Cl(3) 3.178(4) Å, H(*w*)···Cl(3) 2.38 Å, angle O(1)H(*w*)Cl(3) 177°. The ammonium cation is involved in two weak intermolecular bonds with the Cl(2) ($1 - x$, $-y$, $1 - z$) and Cl(4) (x, y, z) atoms: N(1)···Cl(2) 3.289(4) Å, H(3)···Cl(2) 2.76 Å, angle N(1)H(3)Cl(2) 132.0° and N(1)···Cl(4) 3.290(4) Å, H(2)···Cl(4) 2.79 Å, angle N(1)H(2)Cl(4) 126.3°. The packing fragment of the

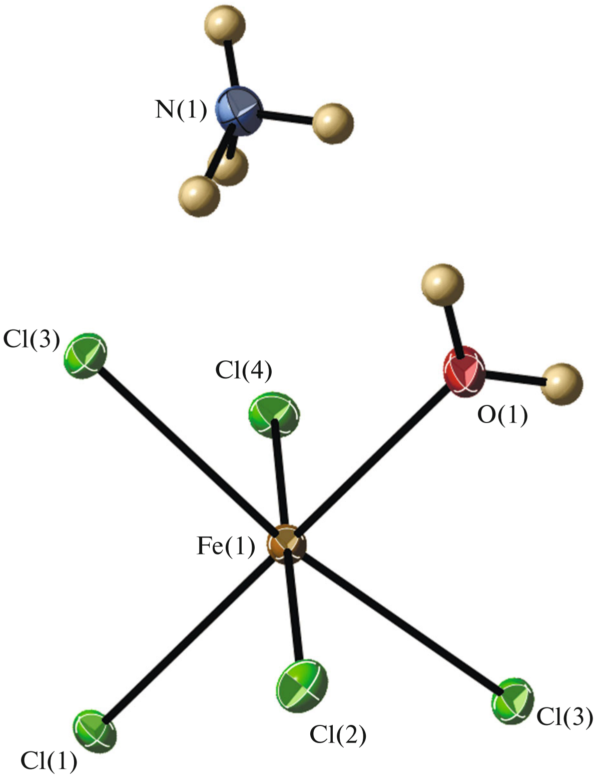

Fig. 1. Molecular structure of $(NH_4)_2[FeCl_5(H_2O)]$. Thermal ellipsoids of 50% probability.

$(NH_4)_2[FeCl_5(H_2O)]$ molecules with hydrogen bonds is presented in Fig. 2.

Since the segnetomagnetic and segnetoelectric properties of the samples can be determined by distortions of the crystal structure, it seemed of interest to compare the changes in the characteristics of the $[FeCl_5(H_2O)]^{2-}$ anion and the crystallographic characteristics of the samples depending on the nature of the outer-sphere cation (size, nature, and the possibility of participating in hydrogen bond formation). The crystal structures containing the pentachloroaquaferrate anion and potassium, rubidium, cesium, ammo-

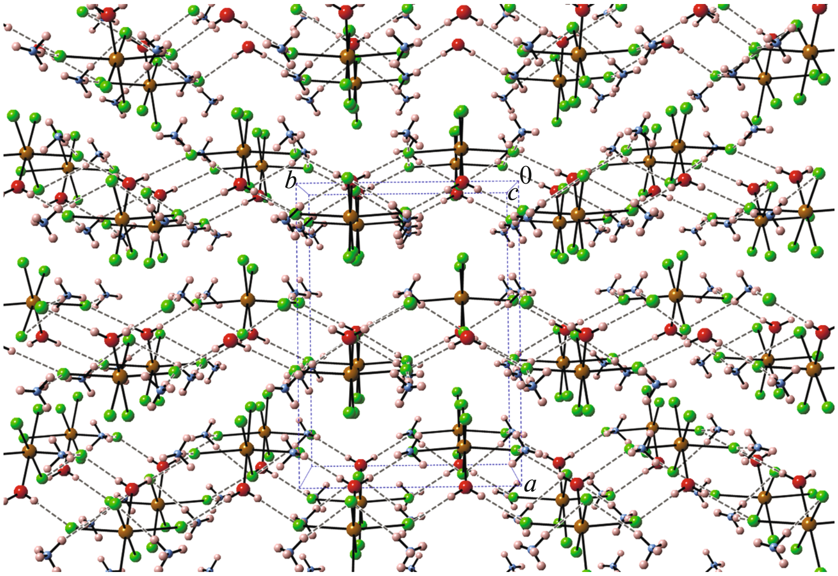

Fig. 2. Packing fragment of $(NH_4)_2[FeCl_5(H_2O)]$ in the crystal. Hydrogen bonds are shown by dashed lines.

Table 2. Comparative structural characteristics of some compounds containing anion $[FeCl_5(H_2O)]^{2-}$

Compound	Space group	Crystal lattice parameters (*a*, *b*, *c*), Å	Bond length, Å		Bond angles, deg	Reference
			Fe–Cl	Fe–O		
$K_2[FeCl_5(H_2O)]$	*Pnma*	13.5862(9) 9.7087(5) 7.0177(5)	2.324(1) 2.392(1) 2.355(1) 2.369(1)	2.078(4)	86.5(0)–93.5(0)	[23]
$Rb_2[FeCl_5(D_2O)]$	*Pnma*	13.8015(2) 9.9049(1) 7.0783(1)	2.321(5) 2.394(4) 2.356(4) 2.378(2)	2.035(7)	85.55(9)–94.45(9)	[23]
$Cs_2[FeCl_5(H_2O)]$	*Cmcm*	7.426(4) 17.306(7) 8.064(2)	2.379(1) 2.379(1) 2.379(1) 2.379(1) 2.888(2)	2.176(7)	85.7(1)–94.3(1)	[24]
$(H_3O)_2[FeCl_5(H_2O)]$	*Pcmn*	7.038(1) 9.926(3) 13.720(8)	2.352(1) 2.328(1) 2.383(1) 2.394(1)	2.107(4)	85.59(2)–94.41(2)	[25]
$(NH_4)_2[FeCl_5(H_2O)]$	*Pnma*	13.706(2) 9.924(1) 7.024(1)	2.3828(8) 2.390(1) 2.323(1) 2.350(1)	2.110(4)	85.60(2)–94.40(2)	[18]
$(NH_4)_2[FeCl_5(H_2O)]$	*Pnma*	13.760(1) 9.960(1) 7.060(1)	2.396(2) 2.333(2) 2.363(2) 2.390(1) 2.390(1)	2.119(5)	85.59(4)–94.41(3)	[19]
$(NH_4)_2[FeCl_5(H_2O)]$	*Pnma*	13.581(3) 9.925(2) 6.9498(14)	2.3221(8) 2.3494(8) 2.3919(6) 2.3930(8)	2.098(2)	85.582(14)–94.416(13)	This work
$(DienH_3)$ $[FeCl_5(H_2O)]Cl$*	*Pna*2_1	30.0352(6) 6.2551(1) 7.4881(1)	2.4037(5) 2.3460(5) 2.3257(5) 2.4450(5) 2.3151(5)	2.146(2)	80.38(4)–94.13(2)	[9]

* Dien is diethylenetriamine.

nium, hydroxonium, and diethylenetriammonium cations were chosen for comparison (Table 2).

As can be seen from the data in Table 2, the compounds crystallize in the orthorhombic crystal system in all the presented cases, and the symmetry somewhat decreases with an increase in the counterion size. An analysis of the bond lengths and bond angles in the $[FeCl_5(H_2O)]^{2-}$ anion suggests that its geometry, structural parameters, and the degree of distortion are almost independent of the nature of the counterion.

FUNDING

This work was supported by the Peoples Friendship University (project no. 5-100).

REFERENCES

1. Ackermann, M., Brüning, D., Lorenz, T., et al., *New J. Phys.*, 2013, vol. 15, p. 123001.
2. Kimura, T., Goto, T., Shintani, H., et al., *Nature*, 2003, vol. 426, p. 55.
3. Fiebig, M., *J. Phys. D: Appl. Phys.*, 2005, vol. 38, p. R123.
4. Spaldin, N.A. and Fiebig, M., *Science*, 2005, vol. 309, p. 391.
5. Cheong, S.-W. and Mostovoy, M., *Nature Mater.*, 2007, vol. 6, p. 13.
6. Kimura, T., Lawes, G., Goto, T., et al., *Phys. Rev.*, 2005, vol. 71, p. 224425.
7. Kimura, T., Sekio, Y., Nakamura, H., et al., *Nature Mater.*, 2008, vol. 7, p. 291.
8. Seki, S., Kurumaji, T., Ishiwata, S., et al., *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, vol. 82, p. 064424.
9. James, B.D., Mrozinski, J., Klak, J., et al., *Z. Anorg. Allg. Chem.*, 2007, vol. 633, p. 974.
10. Luter, M.D. and Wertz, D.L., *J. Phys. Chem.*, 1981, vol. 85, p. 3542.
11. Carlin, R.L., *Magnetochemistry*, Berlin: Springer, 1986.
12. Zora, J.A., Seddon, K.R., Hitchcock, P.B., et al., *Inorg. Chem.*, 1990, vol. 29, p. 3302.
13. Shaviv, R., Lowe, C.B., Zora, J.A., et al., *Inorg. Chim. Acta*, 1992, vols. 198–200, p. 613.
14. Shaviv, R. and Carlin, R.L., *Inorg. Chem.*, 1992, vol. 31, p. 710.
15. Wyrzykowski, D., Warnke, Z., Kruszynski, R., et al., *Transition Met. Chem.*, 2006, vol. 31, p. 765.
16. Lindqvist, I., *Arkiv Kemi. Mineral. Geol. A*, 1947, vol. 24, p. 1.
17. Bellanca, A., *Period. Mineral.*, 1948, vol. 17, p. 59.
18. Figgis, B.N., Raston, C.L., Sharma, R.P., and White, A.H., *Aust. J. Chem.*, 1978, vol. 31, p. 2717.
19. Lacková, D., Ondrejkovičová, I., and Koman, M., *Acta Chim. Slovaca*, 2013, vol. 6, p. 129.
20. Sheldrik, G.M., *SHELX-86. Program for the Crystal Structure Determination*, Cambridge: Univ. of Cambridge, 1986.
21. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
22. Sheldrick, G.M., *SHELXTL. Version 6.14. Structure Determination Software Suite*, Madison: Brucker AXS, 2000.
23. Gabas, M., Palacio, F., Rodriguez-Carvajal, J., and Visser, D., *J. Phys.: Condens. Matter*, 1995, vol. 7, p. 4725.
24. Greedan, J.E., Hewitt, D.C., Faggiani, R., and Brown, I.D., *Acta Crystallogr., Sect. B: Sruct. Crystallogr. Cryst. Chem.*, 1980, vol. 36, p. 1927.
25. Søtofte, I. and Nielsen, K., *Acta Chem. Scand. A*, 1981, vol. 35, p. 821.

Translated by E. Yablonskaya