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Crystal Structure of Copper Fluosilicate Hexahydrate*

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Contrary to earlier belief, copper fluosilicate hexahydrate (space group $R\bar{3}$) is not isomorphous with $NiSnCl_6.6H_2O$, having a primitive cell four times larger with $a=10{\cdot}998\pm0{\cdot}002$ Å, $\alpha=111°29'\pm3'$, $Z=4$. For the hexagonal cell, $a=18{\cdot}180$ (2) and $c=9{\cdot}857$ (2) Å. Using 592 independent X-ray data collected by a counter method, the structure has been refined to a conventional $R=0{\cdot}04$. The structure consists of two types of columns, both made up by alternate stacking of $Cu(H_2O)_6^{2+}$ and SiF_6^{2-} octahedra along the direction of the threefold axis, but while the SiF_6^{2-} octahedra are regular in both types of columns, $Cu(H_2O)_6^{2+}$ octahedra are regular in one with Cu–O = 2·074 (7) Å (one-fourth of the copper atoms) and tetragonally distorted in the other with Cu–O = 1·970 (7) Å (four neighbors) and 2·367 (7) Å (two neighbors) (three-fourths of the copper atoms).

In a previous communication (Ray, Zalkin & Templeton, 1973) we mentioned the diverse structures which exist for the fluosilicate hexahydrates of divalent metals, which earlier had been believed to be like the structure determined by Pauling (1930) for $NiSnCl_6.6H_2O$. In the present paper we describe the structure of $CuSiF_6.6H_2O$, which is significantly different from all the others.

Experimental

Copper fluosilicate was prepared by dissolving metallic copper in fluosilicic acid. On slow evaporation at room temperature (~23 °C), deep blue crystals of the hexahydrate appeared, which were recrystallized from aqueous solution. The crystals obtained were susceptible to rapid efflorescence on exposure to the atmosphere (relative humidity ~50%).

The specimen selected was of a prismatic habit, with both height and thickness ~0·2 mm. It was quickly sealed off in a quartz capillary, and a Laue photograph showed that it was unaffected by the brief exposure to air. The crystal, mounted nearly along the *c* axis, was transferred to a Picker FACS-I four-circle automatic diffractometer. A graphite monochromator was used, and a scintillation counter equipped with pulse-height discriminator served as the detector. Eleven Cu $K\alpha_1$ ($\lambda=1{\cdot}54051$ Å) reflections were successively centered on the aperture of the detector, and the corresponding angular settings were used for a least-squares refinement of the cell dimensions.

Intensity data were collected using Mo $K\alpha$ radiation, and a θ–2θ scan. The scan was started 0·8° below the $K\alpha_1$ peak, and continued to 0·8° beyond the $K\alpha_2$ peak for each reflection. Background was counted for 10 s at each end of the scan. Two standard reflections were checked at regular intervals. During the first attempt of data collection, the intensity of the standards diminished systematically due to slow change in the orientation of the crystal. During the collection of another data set, which was finally accepted as satisfactory, standards were checked every hour. Whenever perceptible change in the orientation of the crystal was apparent the orientation matrix was recalculated. This occurred at intervals of about six hours.

All of the reflections with positive l and $0° < 2\theta \leq 40°$ were thus scanned. In total, 1868 data were collected, of which 592 were independent; 235 of these had intensity less than the standard deviation, and were given zero weight in the least-squares refinement.

Structure factors and their standard deviations were derived as described by Fischer, Templeton & Zalkin (1970) with $p=0{\cdot}05$. No correction was made for absorption ($\mu=26{\cdot}1$ cm^{-1} for Mo $K\alpha$ radiation). We used the spherical hydrogen form factors of Stewart, Davidson & Simpson (1965) and form factors of other neutral atoms of Cromer & Waber (1965) with dispersion corrections of Cromer (1965).

Crystal data

$CuSiF_6.6H_2O$: deep blue prisms.
Hexagonal cell constants: $a=18{\cdot}180\pm0{\cdot}002$ Å, $c=9{\cdot}857\pm0{\cdot}002$ Å.
Rhombohedral cell constants calculated from the above: $a=10{\cdot}998\pm0{\cdot}002$ Å, $\alpha=111°29'\pm3'$.
Four formula units per rhombohedral cell.
Space group: $R\bar{3}$.
$D_m=2{\cdot}207$, $D_x=2{\cdot}215$ g cm^{-3}.

Determination of the structure

It was assumed that, as in other hexahydrated fluosilicates, this structure consists of columns, extending in

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the **c** direction, built up of alternating $Cu(H_2O)_6^{2+}$ and SiF_6^{2-} octahedra. But in this case the neighboring columns are not identical, and the cell dimensions are doubled in the plane normal to the threefold axis. Accordingly the Cu and Si atoms were given the following special positions in the hexagonal cell:

$$(0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})+$$

Cu(1) at $0,0,0$;
Cu(2) at $\tfrac{1}{2},0,0;\ 0,\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},0$;
Si(1) at $0,0,\tfrac{1}{2}$;
Si(2) at $\tfrac{1}{2},0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{1}{2};\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$.

Four independent atoms each of O and F were assigned general positions. Cu(1) with site symmetry $\bar{3}$, was surrounded by six equivalent O(1); each of the Cu(2), with site symmetry $\bar{1}$, was surrounded by O(2), O(3), O(4) and their centrosymmetric equivalents related by inversion through the position of the particular Cu(2). Similar labeling was adopted for Si and F.

A Patterson map indicated that while the oxygen octahedra surrounding Cu(1) and Cu(2) had the same orientation, there were two possible orientations for the corresponding SiF_6^{2-} octahedra. After some initial set-back in the matter of choice, all the O and F atoms were assigned satisfactory positions, so that least-squares refinement with isotropic temperature factors ended up with an $R=[\sum||F_o|-|F_c||/\sum|F_o|]$ value of 0·078. With anisotropic temperature factors for all the atoms, R dropped to 0·055.

A difference map was computed, and attempts were made to locate the hydrogen atoms. Although the map showed positive peaks at the expected positions of hydrogen atoms, the largest positive peaks seemed to be due to inadequate description of thermal motion. An attempt to refine the positions and thermal parameters of hydrogen atoms was unsuccessful. However, when the hydrogen atoms were held fixed in their calculated positions, varying only their common isotropic thermal parameter, further refinement reduced R to 0·040 (0·077 including zero-weighted data), $R_2=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$ to 0·043, and the goodness of fit to 1·12. In the last cycle, no parameter shifted more than 0·005σ.

The final coordinates and thermal parameters are given in Tables 1 and 2. The observed and calculated structure factors are listed in Table 3. Some interatomic distances and bond angles appear in Tables 4 and 5.

Table 1. *Fractional coordinates* ($\times 10^4$)

Estimated standard deviations of the least significant digits are in parentheses. Hydrogen coordinates were not refined.

	x	y	z
Cu(1)	0	0	0
Cu(2)	5000	0	0
Si(1)	0	0	5000
Si(2)	5000	0	5000
F(1)	795 (4)	703 (4)	4015 (5)
F(2)	4099 (4)	2068 (5)	2844 (6)
F(3)	2676 (4)	1747 (4)	2743 (7)
F(4)	3032 (5)	699 (4)	2253 (7)
O(1)	976 (4)	887 (4)	1207 (7)
O(2)	2522 (4)	4268 (4)	4453 (7)
O(3)	769 (5)	3357 (4)	4418 (7)
O(4)	1749 (5)	2381 (4)	4881 (7)
H(1)	920	820	2110
H(2)	1500	1000	960
H(3)	2350	4210	5330
H(4)	3010	4280	4430
H(5)	740	3820	4260
H(6)	330	2840	4640
H(7)	1500	2470	5600
H(8)	1440	1840	4600

Discussion

It is interesting to compare the present structure with that of $CoSiF_6.6H_2O$, as described in our previous communication (Ray *et al.*, 1973). The basic features in both the cases are the columns of alternating octahedra. In the cobalt compound we have two disordered positions unequally occupied by the fluorine atoms. In the present case, there is no disorder; instead, we have two very different types of column appearing alternately along the hexagonal *a* axis. The columns of the first type, containing Cu(1) and Si(1) atoms, have the $\bar{3}$ axes passing through them. The constituent $Cu(H_2O)_6^{2+}$ and SiF_6^{2-} octahedra are regular within the

Table 2. *Anisotropic thermal parameters* (Å²)

The form of the temperature factor is $\exp[-(B_{11}h^2a^{*2}+2B_{12}hka^*b^*+\ldots)/4]$.
The common isotropic thermal parameter for hydrogen refined to $B=3{\cdot}9\pm1{\cdot}0$ Å².

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	1·9 (1)	1·9	1·3 (2)	0·95	0	0
Cu(2)	2·1 (1)	2·2 (1)	1·81 (9)	1·14 (9)	0·00 (8)	−0·33 (8)
Si(1)	2·4 (3)	2·4	0·8 (3)	1·2	0	0
Si(2)	1·6 (2)	1·9 (2)	1·9 (2)	0·9 (2)	−0·3 (2)	−0·1 (2)
F(1)	2·3 (3)	3·4 (3)	2·1 (3)	1·1 (2)	0·7 (2)	0·5 (2)
F(2)	2·4 (3)	7·7 (4)	2·2 (3)	2·2 (3)	−0·8 (2)	−1·2 (3)
F(3)	3·3 (3)	6·8 (4)	3·3 (3)	3·4 (3)	0·0 (3)	−1·0 (3)
F(4)	6·5 (5)	3·1 (4)	6·7 (5)	1·7 (3)	−0·3 (4)	1·5 (3)
O(1)	2·6 (4)	3·8 (4)	1·6 (3)	1·2 (3)	−0·1 (3)	−0·0 (3)
O(2)	2·9 (4)	2·6 (4)	2·3 (4)	1·1 (3)	−0·4 (3)	−0·9 (3)
O(3)	3·5 (4)	1·7 (4)	4·3 (5)	1·5 (3)	0·8 (3)	−0·1 (3)
O(4)	4·5 (5)	2·9 (4)	2·3 (4)	2·3 (4)	0·2 (3)	−0·4 (3)

Table 3. *Observed and calculated structure factors*

Reflections marked with an asterisk had $I < \sigma(I)$ and were given zero weight.

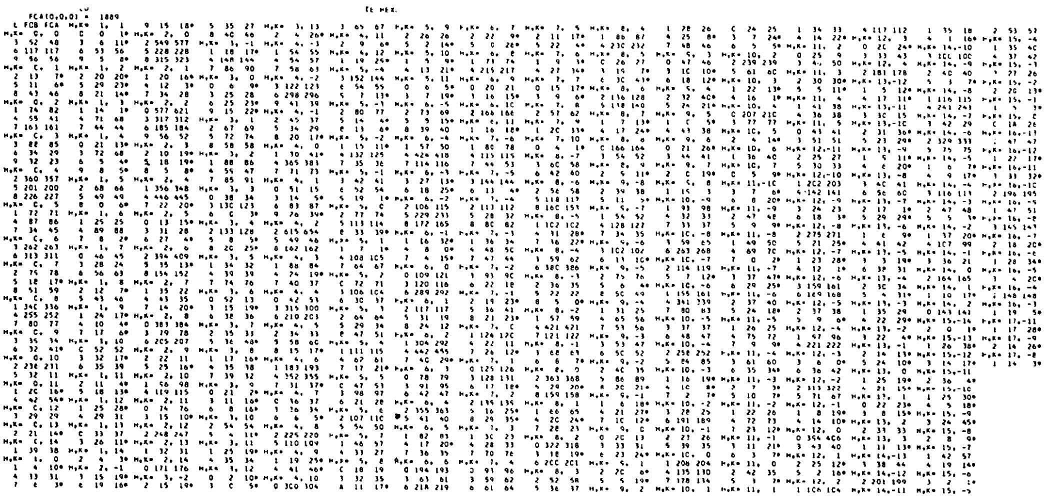

Table 4. *Interatomic distances* (Å)

Uncorrected distances are given, some followed within parentheses by values corrected for thermal motion assuming that the lighter atom rides on the heavier atom.

(*a*) Distances in octahedra.

Cu(1)–O(1)	2·074 ± 0·007	(2·083)
Cu(2)–O(2)	1·970 ± 0·007	(1·978)
Cu(2)–O(3)	1·970 ± 0·007	(1·978)
Cu(2)–O(4)	2·367 ± 0·007	(2·374)
Si(1)—F(1)	1·679 ± 0·005	(1·690)
Si(2)—F(2)	1·674 ± 0·006	(1·704)
Si(2)—F(3)	1·659 ± 0·006	(1·684)
Si(2)—F(4)	1·663 ± 0·006	(1·705)

(*b*) Distances involved in hydrogen bonds (arranged according to the serial number of the hydrogen atom involved).

O(1)—F(1)	2·79 ± 0·01
O(1)—F(2)	2·71 ± 0·01
O(2)—F(2)	2·78 ± 0·01
O(2)—F(4)	2·69 ± 0·01
O(3)—F(3)	2·99 ± 0·01
O(3)—O(4)	2·84 ± 0·01
O(4)—F(3)	2·97 ± 0·01
O(4)—F(1)	2·78 ± 0·01

Table 5. *Bond angles* (°)

O(1)—Cu(1)—O(1)	90·4 ± 0·4
O(1)—Cu(1)—O(1)	89·6 ± 0·4
O(2)—Cu(2)—O(3)	89·0 ± 0·4
O(2)—Cu(2)—O(4)	87·7 ± 0·3
O(3)—Cu(2)—O(4)	91·3 ± 0·3
F(1)—Si(1)—F(1)	89·9 ± 0·3
F(1)—Si(1)—F(1)	90·1 ± 0·3
F(2)—Si(2)—F(3)	89·8 ± 0·4
F(2)—Si(2)—F(4)	89·0 ± 0·4
F(3)—Si(2)—F(4)	90·0 ± 0·4
F(1)···O(1)···F(2)	109·6 ± 0·3
F(2)···O(2)···F(4)	106·4 ± 0·3
F(3)···O(3)···O(4)	124·5 ± 0·3
F(3)···O(4)···F(1)	110·2 ± 0·3

experimental limits, and oriented in the same way as the corresponding octahedra in $CoSiF_6.6H_2O$, with the fluorine in the position with lower occupancy. The neighboring column, containing Cu(2) and Si(2), both with site symmetry $\bar{1}$, is very different. While the SiF_6^{2-} octahedron is still almost regular, there is a distinct tetragonal distortion in the $Cu(H_2O)_6^{2+}$ octahedron. This is very significant, because previously $CuSiF_6.6H_2O$, like the other hexahydrated fluosili-

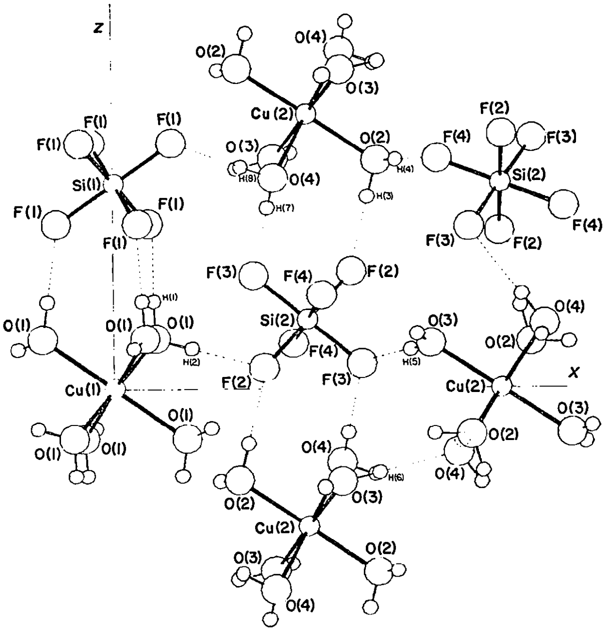

Fig. 1. Structure of $CuSiF_6.6H_2O$: orthogonal projection on the *xz* plane.

cates, was supposed to be isomorphous with $NiSnCl_6.6H_2O$, with one formula unit per rhombohedral unit cell, and consequently, the water octahedron surrounding the Cu^{2+} ion was considered trigonally distorted. With such assumption, Bleany & Ingram (1950) used mixed crystals of $CuSiF_6.6H_2O$ and $ZnSiF_6.6H_2O$ in their study of paramagnetic resonance, and Abragam & Pryce (1950) gave theoretical interpretation of the results thus obtained, assuming that the Cu^{2+} ion was subjected to a ligand field of trigonal symmetry. The Cu:Zn ratio in the mixed crystal used in the experiment has not been mentioned in the paper of Bleaney & Ingram. Assuming that the Cu^{2+} ion concentration was very low, it is quite probable that the structure of the mixed crystal resembled that of $ZnSiF_6.6H_2O$, and consequently the Cu^{2+} ions may indeed have been in a ligand field with trigonal symmetry. In that case, there should be no objection to the said studies, except that the results obtained do not relate to the actual ligand field in $CuSiF_6.6H_2O$. A careful study of paramagnetic resonance with the 'undiluted' salt would then be worthwhile. It would also be interesting to prepare mixed crystals with different Cu:Zn ratio, and find out for what maximum concentration of Cu^{2+} the structure resembles that of $ZnSiF_6.6H_2O$.

Fig. 1 shows a portion of the structure in orthogonal projection on the *xz* plane. One of each kind of hydrogen atom is identified. The bonds O(1)···F(1) and O(1)···F(2) follow the same pattern as in $CoSiF_6.6H_2O$. But while each of F(1), F(2) and F(3) takes part in two hydrogen bonds, F(4) seems to participate in only one; there appears an O(3)···O(4) bond instead. This makes the hydrogen bond configuration in this case rather different than that in $CoSiF_6.6H_2O$, where each F atom participates in two hydrogen bonds.

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A Neutron Diffraction Study of Potassium and Rubidium Hydrogen Oxydiacetate. The Dynamics of Their Hydrogen Bonds

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The crystal structures of $KHO(CH_2COO)_2$ and $RbHO(CH_2COO)_2$ have been investigated by neutron diffraction to obtain information about the hydrogen-bond systems in these compounds. The structures were refined to $R=0{\cdot}036$ and $R=0{\cdot}030$, respectively. The positions of the heavy atoms are in agreement with earlier X-ray investigations. Both compounds consist of hydrogen oxydiacetate chains crosslinked by the alkali metal ion. The hydrogen bond (O–H···O) in the potassium compound is asymmetric and of length 2·476 (2) Å. The angle O–H···O is 174·2 (3)° and the covalent O–H bond length 1·152 (3) Å. In the rubidium compound the bond is symmetric. Its length is 2·449 (3) Å and the angle O···H···O is 175·0 (4)°. Analysis of the thermal motion parameters of the acid hydrogen atom indicates that, in $RbHO(CH_2COO)_2$, it vibrates anharmonically in a broad, single, and symmetric potential-energy well. The asymmetric O–H stretching frequency is less than 1000 cm^{-1} in both compounds.

Introduction

In a study of the hydrogen-bond system in the alkali hydrogen salts of oxydiacetic acid the crystal and molecular structures of $MHO(CH_2COO)_2$, M=Na, K, and Rb, have been determined from X-ray intensities (Albertsson, Grenthe & Herbertsson, 1973*a*, *b*). The compounds are hereafter denoted NaHOXY, KHOXY and RbHOXY, respectively. NaHOXY and KHOXY are isostructural and crystallize in the monoclinic space group $P2_1/c$ but RbHOXY is tetragonal with space group $I\bar{4}2d$. Both types of structures contain chains of