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The Hydrogen-Bonding System in Deuterated Copper Fluorosilicate Tetrahydrate: a Neutron Diffraction Study

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Abstract

The structure of copper hexafluorosilicate–deuterium oxide (1/4), $\text{CuSiF}_6 \cdot 4\text{D}_2\text{O}$, has been established by single-crystal neutron diffraction in order to describe the hydrogen-bonding system. It crystallizes in the monoclinic system, space group $P2_1/c$. The structure comprises SiF_6 and $\text{Cu}(\text{D}_2\text{O})_4\text{F}_2$ octahedra. A common F atom allows the formation of chains along the [101] direction; these chains are linked by hydrogen bonds.

Comment

Large crystals of the title compound with an estimated deuteration rate of 0.75 to 0.85 were prepared according to a technique described by Chevrier & Saint-James (1990). In spite of the fact that the method was the same as used to obtain deuterated hexahydrates such as $\text{CoSiF}_6 \cdot 6\text{D}_2\text{O}$ (Chevrier & Saint-James, 1990), $\text{MnSiF}_6 \cdot 6\text{D}_2\text{O}$ (Chevrier, 1991), $\text{MgSiF}_6 \cdot 6\text{D}_2\text{O}$ (Chevrier, 1992) and $\text{Mg}_{1-x}\text{Fe}_x\text{SiF}_6 \cdot 6\text{D}_2\text{O}$ (Chevrier, 1994), we arrived at the lower hydrate $\text{CuSiF}_6 \cdot 4\text{D}_2\text{O}$. The structure of the hydrogenated compound has been studied previously by X-ray diffraction using a Weissenberg camera (Clark, Fleming & Lynton, 1969), but the positional parameters of the H atoms were not obtained ($R = 0.083$). Therefore, we have used neutron diffraction to determine the position of all the atoms, especially the D atoms, and to understand the hydrogen bonding in all its details.

The final atomic coordinates of the non-H/D atoms do not differ fundamentally from the X-ray model (Clark, Fleming & Lynton, 1969), but the refinement of the D atoms leads to small corrections in their positions, of which the most important are $z(\text{F}1) = 0.4529(6)$, $z(\text{O}1) = -0.1203(7)$ and $z(\text{O}2) = 0.0790(7)$ (Table 1) compared to 0.4565(7), $-0.1224(8)$ and 0.0815(9), respectively, for the X-ray model.

In contrast to the hexahydrates, each Cu atom in the title compound is surrounded by only four D_2O molecules and two F atoms complete the octahedron.

This octahedron is very elongated, as seen from Table 2: the two equal Cu—O bond lengths [1.951(8) and 1.952(7) Å] should be compared with the Cu—F3 bond length (2.320 Å). The octahedron is also characterized by the O1—Cu—O2 plane, which is almost perpendicular to the $(10\bar{1})$ plane [$93.0(1)^\circ$].

The Si atom is coordinated by six fluorine atoms in the form of a far more regular octahedron: two Si—F bond lengths [1.693(6) and 1.693(7) Å] should be compared with the third Si—F3 bond length [1.658(10) Å] and with the average value obtained in the $\text{MSiF}_6 \cdot 6\text{D}_2\text{O}$ compounds (1.680 Å; Chevrier, 1992). Furthermore, the two equal Si—F bonds also define a plane perpendicular to $(10\bar{1})$ [$89.1(1)^\circ$]. The two types of octahedra are linked by a common F atom [the Cu—F3—Si angle is $153(4)^\circ$ and the angle between the planes O1—Cu—O2 and F1—Si—F2 is $26.1(3)^\circ$] and form chains parallel to the [101] direction. It is also noteworthy that F3 lies almost in the $(\bar{1}01)$ plane defined by the Cu atoms [$0.029(4)$ Å from the plane].

The conformations of the water molecules W1 [O1—D11 = 0.962(8), O1—D12 = 0.953(8) Å and D11—O1—D12 = $105.5(13)^\circ$] and W2 [O2—D21 =

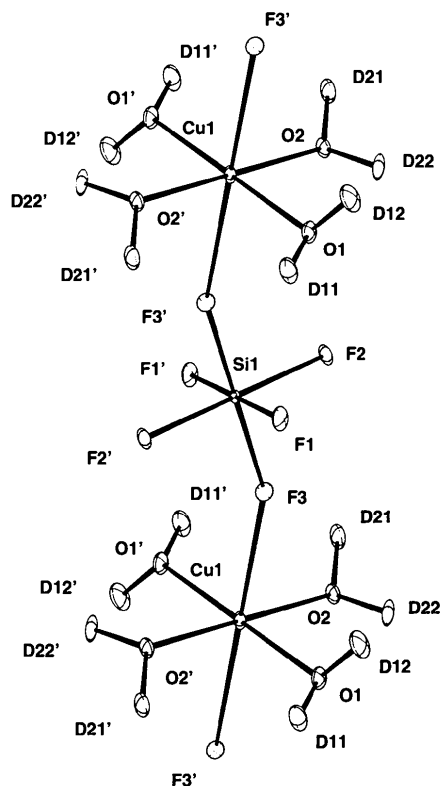


Fig. 1. A chain of $\text{CuF}_2(\text{D}_2\text{O})_4$ and SiF_6 octahedra along the [101] axis in $\text{CuSiF}_6 \cdot 4\text{D}_2\text{O}$ showing 90% probability displacement ellipsoids.

0.952 (10), O2—D22 = 0.957 (8) Å and D21—O2—D22 = 107.4 (15)°] are perfectly defined, as shown Tables 2 and 3, and the molecular planes form an angle of 56.5 (8)°. Furthermore, the W1 molecular plane contains O2 [maximum deviation from the mean least-squares plane: 0.012 (5) Å for O1; $\chi^2 = 9$].

The structure contains hydrogen bonds from W1 and W2 of one chain to the F atoms of six adjacent chains (Fig. 2). These define the two planes O1, D11, D12, F2ⁱⁱⁱ, F2^{iv} [maximum deviation from the mean least-squares plane: -0.040 (5) Å for D11; $\chi^2 = 98$] and O2, D21, D22, F1^v, F1^{vi} [maximum deviation from the mean least-squares plane: -0.029 (5) Å for D22; $\chi^2 = 48$] inclined at an angle of 54.8 (2)°. The hydrogen bonds are probably of the bent type (Table 3) and the distances between D and F lie between 1.720 (9) and 1.787 (9) Å. This means they are stronger than the bonds in the fluorosilicate hexahydrates [the average value from Chevrier & Saint-James (1990) and Chevrier (1991, 1992, 1994) is 1.838 Å], but are of the same order as the average value found in all H...F bonds (1.716 Å; Chiari & Ferraris, 1982).

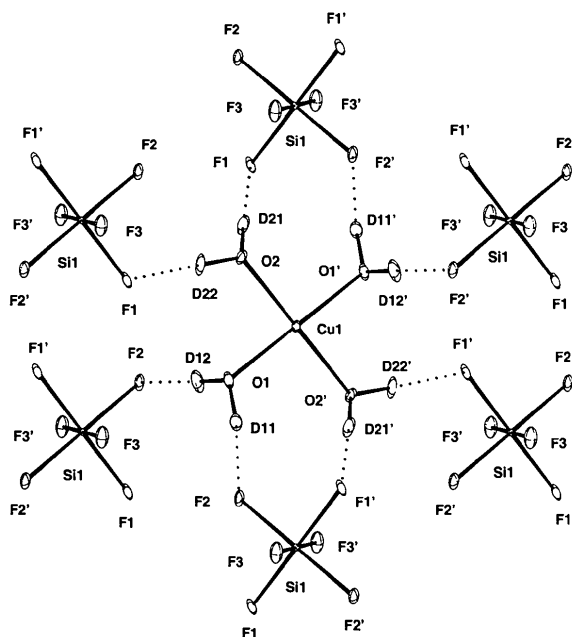


Fig. 2. The hydrogen-bonding scheme showing the interactions between the water molecules of one chain and the F-atom octahedra within other chains (90% probability displacement ellipsoids).

Experimental

The title compound was prepared according to the procedure described by Chevrier & Saint-James (1990) and mounted in an argon-filled aluminium container.

Crystal data

CuSiF₆·4D₂O
M_r = 285.7

Neutron radiation
 $\lambda = 1.520 (2) \text{ \AA}$

Monoclinic
P2₁/c
a = 5.33 (2) Å
b = 9.60 (5) Å
c = 7.18 (5) Å
 $\beta = 105.16 (1)^\circ$
V = 354 (8) Å³
Z = 2
D_x = 2.679 Mg m⁻³
D_m not measured

Cell parameters from 17 reflections
 $\theta = 12.5\text{--}36.5^\circ$
 $\mu = 0.0683 \text{ mm}^{-1}$
(estimated)
T = 296 K
Prism
4.00 × 3.50 × 3.00 mm
Blue

Data collection

Four-circle 6T2 diffractometer at the Orphee reactor
Unique set between 45 and 120° 2 θ . ω scans between 2 $\theta = 2$ and 45°, ω - θ scans between 2 $\theta = 45$ and 60°, and ω -2 θ scans between 2 $\theta = 60$ and 120°
Absorption correction: none
759 measured reflections

571 independent reflections
433 observed reflections [$F^2 > 2.5\sigma(F^2)$]
R_{int} = 0.046
 $\theta_{\text{max}} = 60.0^\circ$
h = -4 → 6
k = -10 → 10
l = -8 → 2
2 standard reflections
frequency: 120 min
intensity decay: <0.5%

Refinement

Refinement on F²
R = 0.0647
wR = 0.0465
S = 5.713
433 reflections
101 parameters
w = 1/σ²(F²)
(Δ/σ)_{max} = 0.00007

$\Delta\rho_{\text{max}} = 0.65 \text{ fm \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.75 \text{ fm \AA}^{-3}$
Extinction correction: type II anisotropic (Coppens & Hamilton, 1970)
Extinction coefficient: G_{eq} = 0.113 (5)
Atomic scattering factors from Delapalme (1985)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U _{eq}
Cu	0	0	0	0.0176 (9)
Si	1/2	0	1/2	0.0083 (13)
F1	0.7311 (7)	0.1050 (4)	0.4529 (6)	0.0274 (11)
F2	0.3893 (8)	0.1334 (4)	0.6110 (5)	0.0255 (10)
F3	0.2981 (7)	0.0471 (4)	0.2921 (5)	0.0305 (11)
O1	0.1260 (8)	0.1582 (5)	-0.1203 (7)	0.0257 (12)
O2	-0.2393 (7)	0.1269 (5)	0.0790 (7)	0.0236 (12)
D11	0.2204 (10)	0.1406 (5)	-0.2153 (8)	0.0361 (15)
D12	0.2198 (11)	0.2301 (6)	-0.0398 (8)	0.0414 (17)
D21	-0.2500 (10)	0.1226 (5)	0.2092 (10)	0.0364 (15)
D22	-0.2427 (10)	0.2232 (5)	0.0437 (7)	0.0336 (16)

Table 2. Selected geometric parameters (Å, °)

Cu—O1	1.951 (8)	Si—F3	1.658 (10)
Cu—O2	1.952 (7)	O1—D11	0.962 (8)
Cu—F3	2.320 (13)	O1—D12	0.953 (8)
Si—F1	1.693 (6)	O2—D21	0.952 (10)
Si—F2	1.693 (7)	O2—D22	0.957 (8)
O1—Cu—O2	88.3 (5)	F1—Si—F3	89.6 (6)
O1—Cu—O2 ⁱ	91.7 (7)	F1—Si—F3 ⁱⁱ	90.4 (7)
O1—Cu—F3	90.8 (8)	F2—Si—F3	89.6 (8)
O1—Cu—F3 ⁱ	89.2 (6)	F2—Si—F3 ⁱⁱ	90.4 (6)

O2—Cu—F3	87.8 (6)	D11—O1—D12	105.5 (13)
O2—Cu—F3 ⁱ	92.2 (8)	D21—O2—D22	107.4 (15)
F1—Si—F2	90.3 (6)	Cu—F3—Si	153 (4)
F1—Si—F2 ⁱⁱ	89.7 (7)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 1 - z$.

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—D11...F2 ⁱ	0.962 (8)	1.720 (9)	2.676 (12)	172.2 (6)
O1—D12...F2 ⁱⁱ	0.953 (8)	1.787 (9)	2.740 (12)	178.8 (6)
O2—D21...F1 ⁱⁱⁱ	0.952 (10)	1.786 (14)	2.737 (18)	177.0 (6)
O2—D22...F1 ^{iv}	0.957 (8)	1.764 (10)	2.718 (14)	173.7 (5)

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$.

The rate of deuteration of the crystals was obtained from the occupation parameters of the D-atom sites, which were constrained to the same value: we obtained 0.749 (9), which leads to a deuteration rate of 0.839 (3). From the coordinates obtained by Clark, Fleming & Lynton (1969) and with the D atoms located from a difference synthesis, the structure was refined by the full-matrix least-squares method based on F^2 . Using a type II anisotropic extinction correction (Coppens & Hamilton, 1970), the coefficients z_{11} , z_{22} , z_{33} , z_{23} , z_{13} and z_{12} ($z_{ij} = W'_{ij} \times 10^{-4}$) obtained were 0.0063 (9), 0.0070 (11), 0.0201 (41), -0.0057 (15), -0.0010 (9) and -0.0002 (5), respectively, which leads to values of 0.230, 0.187 and 0.096 μm for the principal axes of the ellipsoid of the average crystallite shape.

The computer programs used were *SHELXL93* (Sheldrick, 1993) and *ORXFLS4* (Busing, Martin, Levy, Brown, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1977) on PC and *CI-XP* computers.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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La₃(Si₂O₇)Cl₃

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Abstract

The crystal structure of trilanthanum trichloride pyrosilicate, La₃(Si₂O₇)Cl₃, has been determined. The main building units are La(1)Cl₄O₅, La(2)Cl₅O₅ and La(3)Cl₃O₆ polyhedra, and Si₂O₇ pyrosilicate groups.

Comment

The structures of the lanthanum chloride silicates La₃(SiO₄)₂Cl (Gravereau, Es-Sakhi & Fouassier, 1988) and La₃(SiO₄)Cl₅ (Gravereau, Es-Sakhi & Fouassier, 1989) have been determined previously. These compounds show interesting luminescent properties.

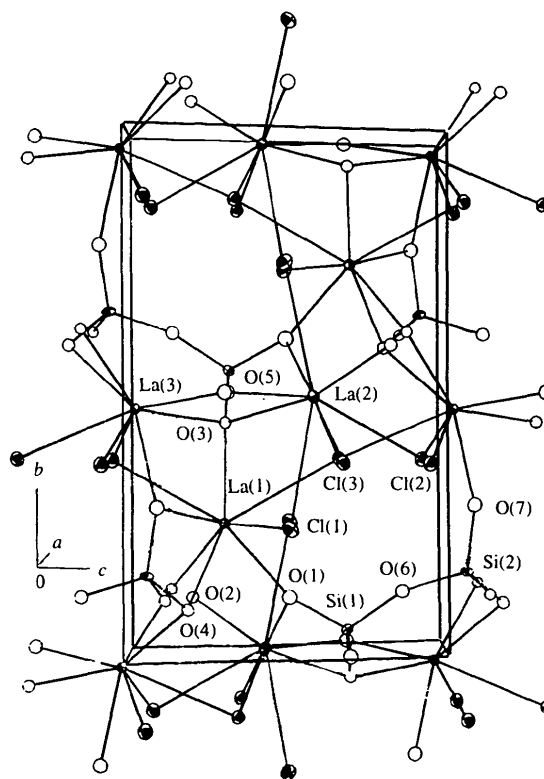


Fig. 1. The crystal structure of La₃(Si₂O₇)Cl₃ with ellipsoids at the 50% probability level.