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Publication Date

1973-06-01

Submitted to Acta Cryst.

LBL-1932
Preprint c. 2

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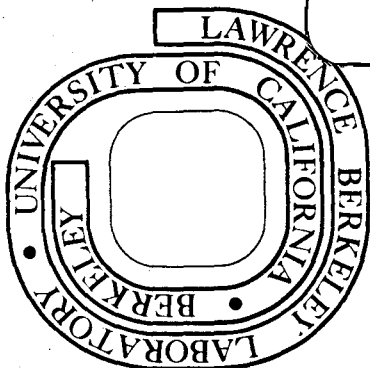
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Crystal Structures of the Fluosilicate Hexahydrates
of Cobalt, Nickel and Zinc*

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Of seven fluosilicate hexahydrates supposedly isomorphous with $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$, only $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ have the typical space group ($R\bar{3}$) and cell size ($a = 9.366(2), 9.313(3), 9.363(3)$; $c = 9.730(4), 9.623(2), 9.690(5)$ Å, respectively, for the hexagonal cell). These three crystal structures were refined with single-crystal X-ray diffraction data obtained by counter methods to conventional R values of 0.033, 0.022 and 0.018. The structures are essentially the same, and there is disorder of F between two positions unrelated by any symmetry element and with unequal occupancy. With either of the disordered sites, the $\text{M}(\text{H}_2\text{O})_6^{++}$ ($\text{M} = \text{Co}, \text{Ni}$ or Zn) and SiF_6^{--} octahedra are stacked alternately along the 3-fold axis in approximately CsCl-type packing. The hydrogen atoms take part in hydrogen bonds with O-F distances ranging from 2.68 to 2.88 Å. Other bond distances are $\text{Co-O} = 2.081$, $\text{Ni-O} = 2.047$, $\text{Zn-O} = 2.078$, $\text{Si-F (average)} = 1.676$ Å.

*Work done under the auspices of the U. S. Atomic Energy Commission.

Fluosilicate hexahydrates of several bivalent metals have been considered to be isomorphous with a large number of salts with the general formula MG_6LR_6 , where M is a bivalent metal, G may be water or ammonia, L is a quadrivalent element like Si, Sn, Ti or Zr, and R may be Cl, F or CN. These crystals have a rhombohedrally-distorted CsCl-type packing and similar cell dimensions, except for possible doubling of axes (Hassel, 1927 and 1931; Hassel & Richter-Salvesen, 1927).

Pauling (1930) determined a structure in space group $R\bar{3}$ for $NiSnCl_6 \cdot 6H_2O$, and this result has been widely regarded as typical for the entire series. The oxygen and chlorine atoms are arranged in nearly regular octahedra with identical orientations and dimensions, and this structure must be regarded as approximate at best. In a neutron-diffraction study of $FeSiF_6 \cdot 6H_2O$ Hamilton (1962) deduced the space group to be $R\bar{3}m$. Disorder was postulated to explain this enhancement of symmetry because it gave better agreement with the data than did the alternative of twinning of crystals of $R\bar{3}$ symmetry. The structure is a superposition of two components, each of symmetry $R\bar{3}$, related to each other by a mirror. The component structure resembles that determined by Pauling except

for significant differences in the dimensions and orientations of the two kinds of octahedra.

A phase transition occurs near 230°K in $\text{MnSiF}_6 \cdot 6\text{H}_2\text{O}$ (Tsujikawa & Couture, 1955) and near 250°K in $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ (Ray, 1964; Majumdar & Datta, 1965). While studying these transitions we became interested in the room-temperature structures of this series of salts and learned that they are remarkably diverse in spite of the close isomorphism in the sense of similar axial ratios. We have examined crystals of fluosilicate hexahydrates of Mg, Mn, Co, Ni, Cu and Zn with the result that all are different from the Fe salt and only the Co, Ni and Zn salts have the typical cell dimensions and space group. The Cu salt also exhibits space group $R\bar{3}$ but with a four-times larger cell. The Mn compound has a primitive hexagonal cell rather than a rhombohedral one, a fact also reported by Kodera, Torii & Osaki (1972). In our work at 23°C we observed crystals of the Mg salt to be of lower symmetry than trigonal, but twinned. Syoyami & Osaki (1972) discovered a transition at about 25° in this salt, with space group $R\bar{3}m$ above the transition. They determined the structure of the low-temperature form to be monoclinic, space group $P2_1/c$.

The present paper describes the structures of the Co, Ni and Zn salts; they differ significantly from the structure reported by Pauling (1930) for $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$.

Experimental

The salts $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving respectively cobalt carbonate, nickel carbonate and metallic zinc in fluosilicic acid and slowly evaporating the filtered solutions. Crystals were selected from crops recrystallized from aqueous solution by slow evaporation.

The Co crystal selected for study was a hexagonal (almost triangular) prism of length 0.13 mm and maximum thickness 0.10 mm. The cell dimensions were derived from measurements of 2θ for $\underline{h}00$, $\underline{hh}0$ and $00\underline{l}$ reflections with a manual General Electric goniostat, using $\text{MoK}\alpha$ radiation ($\lambda = 0.70926 \text{ \AA}$ for α_1). The α doublet was resolved in each case. Intensity data were collected with Zr-filtered Mo radiation and a card-controlled General Electric automatic diffractometer which was equipped with a scintillation counter and pulse-height discriminator. The θ - 2θ scan technique was used with 2θ scanned at the rate of 1° min^{-1} , starting 0.6° below the α_1 peak and ending 0.6° beyond the α_2 peak, for all reflections with \underline{l} zero or positive and $2\theta < 70^\circ$. Background was counted for 10 sec each at 0.5° below the

start and 0.5° beyond the end of each scan. Four reflections were checked at regular intervals, and no systematic variation was observed. The measurements included 2666 reflections of which 721 were independent; 60 of these had observed intensity less than the estimated standard deviation.

The Ni crystal was of rhombohedral shape with height ~ 0.2 mm and maximum thickness ~ 0.2 mm. It showed all six faces of the form $\{01\bar{1}2\}$, three faces of the form $\{10\bar{1}1\}$, and four of the form $\{11\bar{2}0\}$. A computer-controlled Picker four-circle diffractometer with a scintillation counter and pulse-height discriminator was used for the diffraction experiments with $\text{CuK}\alpha$ radiation and an oriented-graphite monochromator. Cell dimensions were derived by least squares from measurements of twelve high-angle reflections ($\lambda = 1.54051 \text{ \AA}$ for α_1). Intensities were scanned as described above. The whole sphere of reciprocal space out to $2\theta = 162^\circ$, except for certain blind regions, was explored. Above 128° , the χ circle was in the parallel position. Standard reflections were checked periodically, and no systematic variation was observed. A total of 1873 reflections were measured, of which 298 were independent. Only 4 of these had intensity less than the standard deviation.

The Zn crystal was a regular hexagonal prism of height 0.10 mm and thickness 0.10 mm. Cell dimensions were derived by least squares from measurements of 24 high-angle reflections with the manual goniostat, the α -doublet being resolved in each case, and using $\text{CuK}\alpha$ radiation. Intensities were measured with the Picker diffractometer as described above, except that monochromatized $\text{MoK}\alpha$ radiation was used. The whole sphere out to $2\theta = 70^\circ$ was explored. No significant variation of standard reflections was observed.

Intensities of 726 independent reflections, of which 92 were less than the standard deviation, were obtained from 4336 reflections.

Linear absorption coefficients of the Co and Zn salts are respectively 20.4 cm^{-1} and 27.8 cm^{-1} for $\text{MoK}\alpha$ radiation. An estimation of absorption correction factors for the first case indicated less than 2% difference between maximum and minimum values, and the other case is comparable. No corrections were made for these two crystals. For the Ni compound, $\mu = 50.3 \text{ cm}^{-1}$ for $\text{CuK}\alpha$ radiation, and a correction was made by numerical integration. The correction factors ranged from 1.40 to 2.19, and they significantly improved the agreement for cases in which the same reflection was measured in both the "bisecting" and "parallel" positions of the χ circle.

Intensities were corrected for background, converted to structure factor magnitudes averaged for measurements of equivalent reflections, and assigned standard deviations which included contributions for counting statistics, excessive scatter, and systematic effects proportional to intensity as described by Fischer, Templeton & Zalkin (1970). The factor p for systematic effects was chosen as 0.05, 0.06 and 0.025 respectively for the Co, Ni and Zn salts.

A CDC-6600 computer was used for the calculations. Refinement by least squares was done with a full-matrix program which minimizes $R_2^2 = \sum w(\Delta F)^2 / \sum w|F_o|^2$, where $w = [\sigma(F)]^{-2}$. Temperature factors were of the form $\exp(-B\lambda^{-2}\sin^2\theta)$ if isotropic or $\exp(-\sum\sum B_{ij}b_i b_j h_i h_j / 4)$ if anisotropic, where b_i is the magnitude of the i th reciprocal axis. Neutral-atom form factors of Cromer & Waber (1965) were used for atoms other than hydrogen, for which the values of Stewart, Davidson & Simpson (1965) were used. Anomalous dispersion corrections (Cromer, 1965) were, for $\text{MoK}\alpha$, Co: $0.37 + i 1.06$, Zn: $0.33 + i 1.54$, Si: 0.09 ; for $\text{CuK}\alpha$, Ni: $-3.20 + i 0.67$, Si: $0.23 + i 0.36$.

Crystal Data

$\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$: reddish pink hexagonal prisms.

Hexagonal cell: $\underline{a} = 9.366(2)$, $\underline{c} = 9.730(4)$ Å, $\underline{Z} = 3$.

Rhombohedral cell: $\underline{a} = 6.306(3)$ Å, $\alpha = 95^\circ 55(4)'$, $\underline{Z} = 1$.

Space group: $R\bar{3}$; $\underline{D}_m = 2.07$, $\underline{D}_x = 2.08$ g cm⁻³.

$\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$: apple green rhombohedra.

Hexagonal cell: $\underline{a} = 9.313(3)$, $\underline{c} = 9.623(2)$ Å, $\underline{Z} = 3$.

Rhombohedral cell: $\underline{a} = 6.261(2)$ Å, $\alpha = 96^\circ 6(5)'$, $\underline{Z} = 1$.

Space group: $R\bar{3}$; $\underline{D}_m = 2.12$, $\underline{D}_x = 2.13$ g cm⁻³.

$\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$: colorless hexagonal prisms.

Hexagonal cell: $\underline{a} = 9.363(3)$, $\underline{c} = 9.690(5)$ Å, $\underline{Z} = 3$.

Rhombohedral cell: $\underline{a} = 6.297(3)$ Å, $\alpha = 96^\circ 3(6)'$, $\underline{Z} = 1$.

Space group: $R\bar{3}$; $\underline{D}_m = 2.12$, $\underline{D}_x = 2.13$ g cm⁻³.

Determination of the Structure

The structure was determined in much the same way in each case, but we give more details for the Co salt.

Atoms were assigned coordinates similar to those of one of the lower symmetry ($R\bar{3}$) components of $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ (Hamilton, 1962). With isotropic temperature factors,

least-squares refinement reduced the conventional

$R = \sum |\Delta F| / \sum |F_o|$ to 0.16. With anisotropic temperature

factors, \underline{R} was reduced to 0.11, but \underline{B}_{11} and \underline{B}_{22} for \underline{F}

were unusually high. A Fourier synthesis of $\Delta \underline{F}$ showed

two prominent but unequal peaks, one on each side (in the same x - y plane) of the assumed position of \underline{F} . The only satisfactory explanation of this was the assumption of a disordered model. Fractional atoms, referred to as $F(1)$ and $F(2)$, were assigned to these two positions with occupation factors adding to unity. With equal occupancy, \underline{R} was reduced to 0.07; with $F(1)/F(2) = 1/2$, $\underline{R} = 0.05$. Serious discrepancies remained between \underline{F}_o and \underline{F}_c for the $00l$ reflections. A ΔF map at this stage showed clearly the positions of the two hydrogen atoms. Introduction of these atoms with isotropic temperature factors removed the above discrepancies and reduced \underline{R} to 0.033. Trial of various values of the occupation factors yielded the best fit with $F(1)/F(2) = 0.43/0.57$: $\underline{R} = 0.033$ (excluding data where $I < \sigma(I)$), $\underline{R} = 0.038$ (all data), $R_2 = 0.038$, estimated standard deviation of an observation of unit weight = 1.03. In the last cycle no parameter shifted more than 3% of its standard deviation.

In the case of $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ we introduced an empirical extinction correction: $F_o' = F_o(1 + 1.3 \times 10^{-7} I)$, where F_o' is the corrected structure factor. The correction factor was 1.43 for the strongest reflection, 110 , and exceeded 1.13 for only three other reflections. With occupancy factors $F(1)/F(2) = 0.33/0.67$, $\underline{R} = 0.022$ (with

or without the four zero-weighted data), $R_2 = 0.040$, and the standard deviation of an observation of unit weight = 1.33. In the last cycle, no parameter shifted more than 1% of its standard deviation. Slight variation of the occupancy ratio did not result in any significant improvement.

In the otherwise straightforward refinement of the structure of $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ we were confronted with the interesting fact that in this centric space group ($R\bar{3}$) different values of the coordinates must be assigned to identical structures if opposite choices are made for the positive direction of the unique axis. By chance, the same choice was made for the Co and Ni crystals, but the opposite choice for the Zn crystal. Thus the Zn structure was determined without the knowledge that it was so nearly the same as the others. The coordinates and indices had to be transformed by the matrix

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

to yield the results reported here. No meaningful improvement was gained when the occupancy ratio was changed from $F(1)/F(2) = 0.33/0.67$, and with this ratio $R = 0.018$ excluding reflections with $I < \sigma(I)$, $R = 0.023$ (all reflections), $R_2 = 0.021$, standard deviation of an observation of unit weight = 1.07. In the last cycle no parameter shifted by more than 4% of its standard deviation.

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

Discussion

Except for minor numerical details the three salts have the same crystal structure. An unusual feature of this structure, for which we have no satisfactory explanation, is the disorder of F between two sites, unrelated by any symmetry element and with unequal occupancy factors. The distances between alternate sites are 0.71, 0.60 and 0.66 Å, respectively, in the Co, Ni and Zn salts. We assume that all the F atoms in a particular SiF_6^{2-} ion are in the same type of site because otherwise there would be unsatisfactory F-F distances. According to this model, the disorder involves two orientations of the fluosilicate ion about 30° apart with respect to rotation about the 3-fold axis. The F atoms are at the corners of regular or nearly regular octahedra; for the F(1) sites in the Ni and Zn compounds the octahedra are regular within the experimental accuracy, while in the other cases there is a slight elongation in the direction of the 3-fold axis of two to four standard deviations. All six results are within about one standard deviation of an average shape with $\text{F-Si-F} = 89.7^\circ$, as is also the result found by Hamilton (1962) for the Fe salt.

The water molecules are also at the corners of nearly regular octahedra, but these octahedra are not so consistent in shape. In the Zn salt the octahedron is regular, while for Co it is elongated and for Ni it is compressed, but by amounts which change bond angles only about half a degree. Hamilton (1962) observed a greater elongation ($O-Fe-O = 88.6(3)^\circ$) in the Fe salt.

These octahedra are packed according to a rhombohedrally-distorted CsCl-type structure. The densest packing is in columns of alternate cations and anions along the 3-fold axis (Fig. 1). Three hydrogen bonds connect each pair of adjacent octahedra in a column, while one hydrogen bond connects an octahedron to each of its six neighboring octahedra in other columns. This topology of hydrogen bonding is the same for either F site and is also the same as that which Hamilton (1962) deduced for each component of his structure. It would not exist in the Pauling (1930) structure because in that arrangement each O would have two equidistant F neighbors in the same column (Fig 2). This latter arrangement permits closer packing of spherical atoms, but provides too many acceptors for hydrogen bonds. Any rotation of one kind of octahedron relative to the other makes one neighbor closer than the other, with a rotation of 60° giving the maximum difference. In the

$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ structure, the oxygen atoms are twisted about 40° from the Pauling (1930) structure, in each component of the disorder model. In the present structures it is the fluorine atoms which are twisted, F(1) about 50° and F(2) about 20° .

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Table 1. Coordinates and thermal parameters, with estimated standard deviations in parentheses

For atoms with site symmetry $\bar{3}$, $B_{11}=B_{22}=2B_{12}$; $B_{13}=B_{23}=0$.

(a) $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$		x	y	z		
Co		0	0	0		
Si		0	0	1/2		
F(1)		.1536(4)	.1356(4)	.4001(3)		
F(2)		.1673(3)	.0679(3)	.3997(2)		
O		.1745(2)	.1860(2)	.1247(1)		
H(1)		.187(4)	.172(4)	.212(3)		
H(2)		.191(3)	.278(4)	.114(2)		
	B_{11} or B_{22}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2.00(1)	2.00	1.45(2)	1.00	0	0
Si	1.88(2)	1.88	1.35(3)	.94	0	0
F(1)	3.1(1)	4.0(1)	2.16(8)	.5(1)	.46(8)	.5(1)
F(2)	2.30(7)	4.9(1)	2.58(7)	1.42(8)	.60(5)	.23(9)
O	3.84(6)	3.52(4)	2.26(4)	.94(4)	-.66(4)	-.28(3)
H(1)	4.6(6)					
H(2)	4.3(6)					

(b) $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$

	x	y	z
Ni	0	0	0
Si	0	0	1/2
F(1)	.1610(8)	.1258(8)	.3999(7)
F(2)	.1681(3)	.0647(3)	.3981(3)
O	.1772(2)	.1830(1)	.1218(1)
H(1)	.181(3)	.164(3)	.209(3)
H(2)	.184(3)	.262(3)	.116(2)

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	1.79(3)	1.79	1.34(4)	.895	0	0
Si	1.71(3)	1.71	1.22(5)	.855	0	0
F(1)	2.9(2)	4.4(3)	2.0(2)	-.6(2)	.6(1)	.1(2)
F(2)	2.20(7)	3.8(1)	2.46(9)	1.22(9)	.49(5)	-.1(1)
O	3.02(5)	2.17(5)	2.20(6)	.88(4)	-.48(4)	-.15(4)
H(1)	4.2(5)					
H(2)	4.3(6)					

(c) $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$

	x	y	z
Zn	0	0	0
Si	0	0	1/2
F(1)	.1555(4)	.1326(4)	.4001(3)
F(2)	.1676(2)	.0685(2)	.3992(2)
O	.1766(1)	.1853(1)	.1240(1)
H(1)	.184(2)	.169(2)	.202(2)
H(2)	.192(2)	.274(2)	.117(2)

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn	1.968(9)	1.968	1.49(1)	.984	0	0
Si	1.68(1)	1.68	1.23(2)	.84	0	0
F(1)	2.8(1)	3.8(1)	2.08(8)	.2(1)	.52(7)	.53(9)
F(2)	2.25(4)	4.56(8)	2.36(4)	1.33(5)	.59(3)	.14(5)
O	3.47(4)	2.35(3)	2.18(3)	.95(3)	-.62(2)	-.21(2)
H(1)	4.0(4)					
H(2)	4.3(4)					

Table 2. Observed and calculated structure factors

Data where $I < \sigma(I)$ are marked with an asterisk.

(Table to be reproduced photographically.)

TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COBALT FLUOSILICATE MERMOPYRITE

Table with columns for h, k, l, F_obs, and F_calc for Cobalt Fluosilicate Mermopyrite. The table lists structure factor data for various reflections, including observed and calculated values.

TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR NICKEL FLUOSILICATE MERMOPYRITE

Table with columns for h, k, l, F_obs, and F_calc for Nickel Fluosilicate Mermopyrite. The table lists structure factor data for various reflections, including observed and calculated values.

TABLE OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ZINC FLUOSILICATE MERMOPYRITE

Table with columns for h, k, l, F_obs, and F_calc for Zinc Fluosilicate Mermopyrite. The table lists structure factor data for various reflections, including observed and calculated values.

Table 3. Interatomic distances, Å

Values in parentheses are corrected for thermal motion, assuming that the lighter atom rides on the heavier atom. Distances involving disordered positions F(1) and F(2) are designated by (1) and (2) respectively.

(a) $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$

Co - O		$2.081 \pm .001$	(2.092)
Si - F	(1)	$1.674 \pm .001$	(1.695)
	(2)	$1.678 \pm .002$	(1.697)
O - H(1)		$0.874 \pm .026$	(0.888)
O - H(2)		$0.805 \pm .032$	(0.822)

(b) $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$

Ni - O		$2.047 \pm .001$	(2.055)
Si - F	(1)	$1.671 \pm .006$	(1.701)
	(2)	$1.683 \pm .003$	(1.698)
O - H(1)		$0.862 \pm .029$	(0.881)
O - H(2)		$0.709 \pm .026$	(0.737)

(c) $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$

Zn - O		$2.078 \pm .001$	(2.088)
Si - F	(1)	$1.671 \pm .003$	(1.693)
	(2)	$1.680 \pm .003$	(1.698)
O - H(1)		$0.778 \pm .020$	(0.790)
O - H(2)		$0.775 \pm .020$	(0.797)

Table 4. Distances involved in hydrogen bonds

F_{||} and F_⊥ refer respectively to bonds approximately parallel and perpendicular to the 3-fold axis.

(a) $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$

O	- F	(1) 2.711 ± .003	(2) 2.888 ± .003
H(1)	- F	(1) 1.861 ± .026	(2) 2.037 ± .029
O	- F _⊥	(1) 2.721 ± .004	(2) 2.759 ± .003
H(2)	- F _⊥	(1) 1.961 ± .031	(2) 1.957 ± .033

(b) $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$

O	- F	(1) 2.718 ± .007	(2) 2.863 ± .004
H(1)	- F	(1) 1.862 ± .031	(2) 2.017 ± .031
O	- F _⊥	(1) 2.683 ± .007	(2) 2.782 ± .003
H(2)	- F _⊥	(1) 2.021 ± .028	(2) 2.082 ± .027

(c) $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$

O	- F	(1) 2.710 ± .004	(2) 2.868 ± .002
H(1)	- F	(1) 1.948 ± .020	(2) 2.104 ± .021
O	- F _⊥	(1) 2.713 ± .003	(2) 2.766 ± .002
H(2)	- F _⊥	(1) 1.979 ± .020	(2) 1.995 ± .021

Table 5. Bond angles, deg(a) $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$

O-Co-O			89.4 ± 0.1
O-Co-O'			90.6 ± 0.1
F-Si-F	(1)	89.6 ± 0.2	(2) 89.6 ± 0.2
F-Si-F'	(1)	90.4 ± 0.2	(2) 90.4 ± 0.2
H(1)-O-H(2)			108.7 ± 3.0
O-H(1)---F	(1)	163.7 ± 1.0	(2) 162.7 ± 1.0
O-H(2)---F	(1)	157.0 ± 1.0	(2) 174.0 ± 0.8
F---O---F	(1)	110.7 ± 0.1	(2) 123.5 ± 0.1

(b) $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$

O-Ni-O			90.5 ± 0.1
O-Ni-O'			89.5 ± 0.1
F-Si-F	(1)	90.1 ± 0.4	(2) 89.4 ± 0.2
F-Si-F'	(1)	89.9 ± 0.4	(2) 90.6 ± 0.2
H(1)-O-H(2)			107.4 ± 3.0
O-H(1)---F	(1)	171.9 ± 1.0	(2) 166.4 ± 0.7
O-H(2)---F	(1)	155.6 ± 1.0	(2) 169.5 ± 0.7
F---O---F	(1)	111.5 ± 0.2	(2) 123.1 ± 0.1

(c) $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$

O-Zn-O			89.9 ± 0.1
O-Zn-O'			90.1 ± 0.1
F-Si-F	(1)	89.8 ± 0.2	(2) 89.6 ± 0.1
F-Si-F'	(1)	90.2 ± 0.2	(2) 90.4 ± 0.1
H(1)-O-H(2)			108.1 ± 2.6
O-H(1)---F	(1)	166.3 ± 0.7	(2) 167.0 ± 0.5
O-H(2)---F	(1)	157.8 ± 0.7	(2) 170.8 ± 0.6
F---O---F	(1)	110.9 ± 0.1	(2) 123.2 ± 0.1

Figure Captions

Fig. 1. Two neighboring columns in the structure of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$. Fluorine atoms are shown in (a) according to the F(1) positions and in (b) according to F(2).

Fig. 2. Relative orientation of oxygen atoms on the top face of a water octahedron and halogen atoms on the bottom face of the adjacent octahedron in (a) $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$ (Pauling, 1930), (b) $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ (Hamilton, 1962) and (c) $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ (this study). The numbers indicate values of the z coordinates ($\times 100$), and broken circles indicate the alternate sites according to the disorder models.

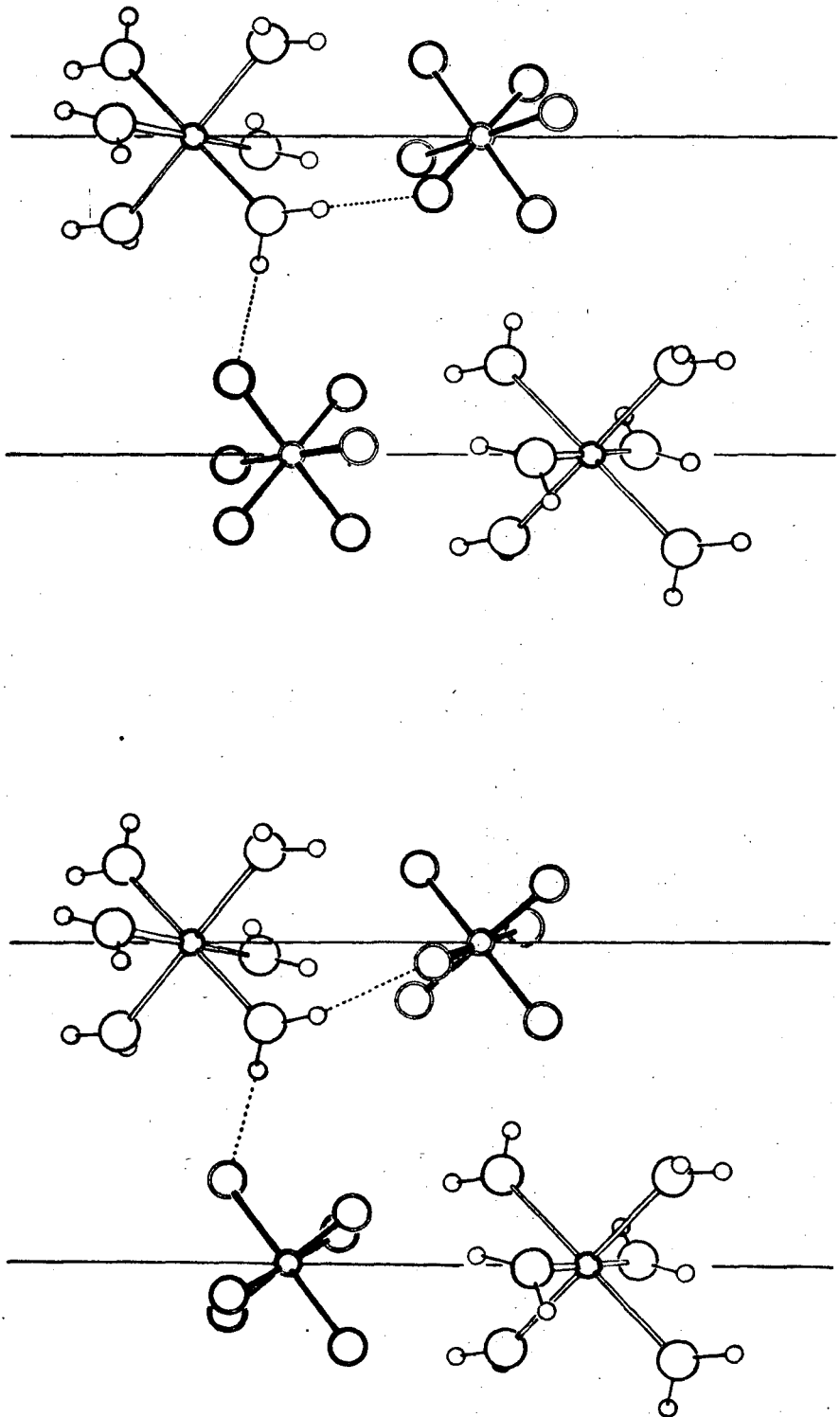
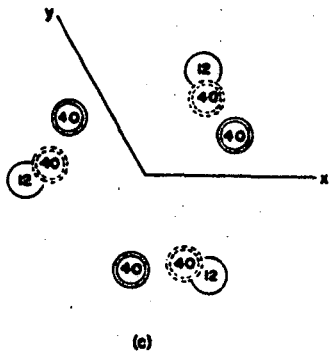
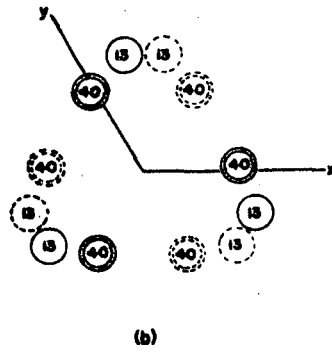
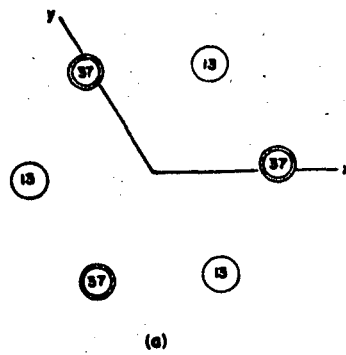


Fig. 1.

XBL 696-619



○.○ : Oxygen

⊙.⊙ : Halogen

XBL 704-678

Fig. 2.

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