

- ENDO, T., KUME, S., KINOMURA, N. & KOIZUMI, M. (1976). *Mater. Res. Bull.* **11**, 609–614.
- GRUNER, J. W. (1943). *Am. Mineral.* **28**, 497–506.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KINOMURA, N. (1973). *J. Am. Ceram. Soc.* **56**, 344–345.
- MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. (1975). *Acta Cryst.* **A31**, 245–249.
- MATHIESON, A. & WADSLEY, A. D. (1950). *Am. Mineral.* **35**, 99–101.
- MEGAW, H. D. (1968). *Acta Cryst.* **B24**, 149–153.
- MEGAW, H. D. (1973a). *Crystal Structures: A Working Approach*, p. 300. Philadelphia: W. B. Saunders.
- MEGAW, H. D. (1973b). *Crystal Structures: A Working Approach*, pp. 46–49. Philadelphia: W. B. Saunders.
- MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1020.
- MUKHERJEE, B. (1960). *Acta Cryst.* **13**, 164–165.
- MUKHERJEE, B. (1964). *Acta Cryst.* **17**, 1325.
- NORRISH, K. (1951). *Mineral. Mag.* **29**, 494–501.
- RINGWOOD, A. E., KESSON, S. E., WARE, N. G., HIBBERSON, W. & MAJOR, A. (1979). *Nature (London)*, **278**, 219–223.
- RINGWOOD, A. E. & REID, A. F. (1967). *Acta Cryst.* **23**, 1093–1099.
- ROLLETT, J. S. & CARRUTHERS, R. S. (1974). Private communications.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- SINCLAIR, W. & MCCLAUGHLIN, G. M. (1982). *Acta Cryst.* **B38**, 245–246.
- SINCLAIR, W., MCCLAUGHLIN, G. M. & RINGWOOD, A. E. (1980). *Acta Cryst.* **B36**, 2913–2918.
- TURNER, S. (1978). *High Resolution Electron Microscopy of Some Manganese Oxide and Silicate Minerals*. MS Thesis, Arizona State Univ.
- TURNER, S. & BUSECK, P. R. (1979). *Science*, **203**, 456–458.
- TURNER, S. & BUSECK, P. R. (1982). In preparation.
- VELDE, D. (1968). *Mineral. Mag.* **36**, 867–870.
- WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.
- YANCHUK, E. A. (1973). *Mineral. Sb. (Lvov)*, **27**, 26–38.
- YANCHUK, E. A. (1977). *Litol. Polezn. Iskop.* **6**, 144–149.
- YANCHUK, E. A. & POVARENENYKH, A. S. (1975). *Mineral. Sb. (Lvov)*, **29**, 9–21.
- ZHURAVLEVA, L. N., YURKINA, K. V. & RYABEVA, YE. G. (1978). *Dokl. Akad. Nauk SSSR*, **239**, 141–143.

Acta Cryst. (1982). **B38**, 1065–1070

The Structure of Silver Fluoride Iodide Hydrate $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$

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Abstract

$\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$ is monoclinic, space group $P2_1/n$, with $a = 7.4061$ (6), $b = 17.8298$ (32), $c = 9.3618$ (9) Å, $\beta = 91.278$ (8)°, $Z = 4$, and $D_m = 5.9$, $D_x = 6.17$ Mg m⁻³. The structure was determined from single-crystal X-ray diffractometer data. The refinement based on 2961 reflexions and anisotropic thermal parameters converged to a final R value of 0.039. Layers built up by Ag, I and F atoms are joined by a hydrogen-bond system containing four-membered $(\text{H}_2\text{O} \cdots \text{F})_2$ rings. The I atoms are rather unsymmetrically surrounded by seven or eight Ag atoms. Five of these describe a pentagon. These pentagons share edges to form layers, two per unit cell, also containing F atoms. Every Ag atom has six neighbours (two I, three F, and one F or one O atom), creating a distorted octahedron. Every F atom in the layer is surrounded by six Ag atoms in octahedral coordination. Two of the Ag–Ag distances are remarkably short – 2.92 and 2.98 Å respectively. The F atoms in the hydro-

gen-bond system have a tetrahedral environment of three Ag atoms and one O atom. The O–H \cdots F distances are short – 2.52, 2.55, 2.57 and 2.59 Å.

Introduction

This work is part of a systematic structural investigation of compounds $\text{Ag}_n\text{X}_x\text{A}_y$ ($n > x$) with various counterions A and $X = \text{Cl}, \text{Br}, \text{or I}$. The investigations aim at a clarification of the coordination of the Ag atoms to the halide in these compounds where Ag is in excess over halide. Until now the detailed crystal structure is known only for a few compounds meeting these stoichiometric requirements. These compounds are Ag_2ClNO_3 (Persson, 1979a), Ag_2BrNO_3 (Persson & Holmberg, 1977), Ag_2INO_3 (Persson, 1979b), $\text{Ag}_3\text{I}(\text{NO}_3)_2$ (Birnstock & Britton, 1970), and $\text{Ag}_{13}\text{I}_9(\text{WO}_4)_2$ (Chan & Geller, 1977).

From the early work by Hayek (1936) and Lieser (1960) it should be possible to prepare an analogous

compound with fluoride as counterion *A*. From our recent investigation of solids formed in the system $\text{AgI}-\text{AgF}-\text{H}_2\text{O}$ it became evident that two solid hydrates meeting the general requirement $n > x$ can actually be prepared, *viz* $\text{Ag}_2\text{IF} \cdot \text{H}_2\text{O}$ (Holmberg & Persson, 1975) and $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$, which has been described as $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ in a preliminary report (Persson, 1977). The detailed structure of $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$ is described in this paper.

Experimental

A concentrated AgF solution was prepared by dissolution of Ag_2O in concentrated HF. The AgF solution was then saturated with AgI at about 323 K and after filtration single crystals of two different morphologies crystallized on cooling. The crystals so obtained appeared to be specimens of both $\text{Ag}_2\text{IF} \cdot \text{H}_2\text{O}$ and $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$. The crystals were colourless to soft yellow and were oval plates and more quadratic plates, respectively. Selected crystals of $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$ to be used in the present investigation could easily be separated by hand from the $\text{Ag}_2\text{IF} \cdot \text{H}_2\text{O}$ crystals due to the difference in morphology.

The ratio AgI to AgF was determined by chemical analysis to be 2:5. This was achieved by gravimetric analysis, yielding the AgI content, followed by an electrochemical determination of the residual Ag content and a subsequent recalculation in terms of AgF. The total content of Ag was also determined.

The results, which are given in Table 1, indicated that the compound has the stoichiometry $\text{Ag}_7\text{I}_2\text{F}_5 \cdot x\text{H}_2\text{O}$, where x falls in the range 2–2.5. Water analyses, based on coulometrically generated Karl Fischer reagent (Karlsson, 1972), were also performed (Table 1). The analyses all indicate the water content to be close to 2.5 water molecules per formula unit. (The structure analysis, however, gave no clear-cut support for this.) An approximate value of the density was determined by the displacement method in ligroin.

$\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$ is very sensitive to moisture and decomposes in air to AgI and AgF. During the data collection the crystal was kept in a glass capillary. The surface of the crystal darkened when exposed to light,

Table 1. Results of the chemical analyses with respect to Ag, AgI, AgF and H_2O content

	Ag (%)	AgI (%)	AgF (%)	H_2O (%)
Theoretical				
$\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$	66.25	41.19	55.65	3.16
$\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$	65.73	40.89	55.22	3.92
Experimental	65.72	40.83	55.23	3.94*
Water analysis (Karl Fischer)				4.09

* The residual after subtraction of the AgI and AgF contents.

Table 2. Additional crystal data, and details of the collection and reduction of intensity data, and of the least-squares refinement

FW	1149.1
Crystal size (mm)	$0.113 \times 0.050 \times 0.188$
Radiation (graphite-monochromated)	$\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
Take-off angle ($^\circ$)	3
$\Delta\omega$ ($^\circ$) (ω - 2θ scan)	$0.60 + 1.00 \tan \theta$
$\Delta\theta$ ($^\circ$)	3–30
Minimum number of counts in a scan	3000
Maximum recording time (s)	180
μ ($\text{Mo K}\alpha$) (mm^{-1})	15.76
Range of transmission factor	0.224–0.484
Number of measured reflexions	3744
Number of reflexions given zero weight	783
Number of independent reflexions used in the final refinements, m	2961
Number of parameters refined, n	163
$R = \sum F_o - F_c / \sum F_o $	0.039
$R_w = [\sum w(F_o - F_c)^2 / \sum F_o ^2]^{1/2}$	0.042
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	1.50
a (weighting function)	0.012
b (weighting function)	1.1
$g \times 10^{-4}$ (extinction)	0.038 (9)
Mosaic spread (seconds of arc)	154
Domain size (mm)	0.27×10^{-4}

but this had no serious effect on the X-ray intensities (see below).

Table 2 gives information concerning the crystal data, the collection of intensities, and the refinement. The method employed in data collection has been described elsewhere (Elding, 1976). Weissenberg photographs revealed the Laue class $2/m$ and the systematic absences $h0l$: $h + l = 2n + 1$ and $0k0$: $k = 2n + 1$. A single-crystal diffractometer (CAD-4) was used for data collection. The cell dimensions were improved by least-squares refinement of 39 reflexions (Danielsson, Grenthe & Oskarsson, 1976). The wavelength used for the determination of the cell dimensions was 0.70930 \AA . The intensities of three reflexions (310, 481, and 481) checked after every 100th measurement showed a small decrease ($<12\%$), and the intensities were scaled with the expression $Y = 1.00 - (0.671 \times 10^{-3})\bar{X}$, where \bar{X} is the total time in hours that the crystal had been exposed to X-radiation. The values of I and $\sigma_c(I)$, where $\sigma_c(I)$ is the standard deviation based on counting statistics, were corrected for Lorentz, polarization and absorption effects. The absorption correction was performed according to Busing & Levy (1957, 1967) using the numerical-integration method by Gauss. The crystal shape was described by eight planes.

Structure determination and refinement

The atomic positions of the I atoms and six out of seven Ag atoms were found using the *MULTAN* system of computer programs (Germain, Main &

Woolfson, 1971). In subsequent difference syntheses, the seventh Ag atom, the five F atoms, and two O atoms were revealed. The R value at this stage was 0.043. A difference synthesis showed a peak of height $3.9 \text{ e } \text{Å}^{-3}$, which might originate from a half-occupied O position, corresponding to the 2.5th water molecule as indicated by the chemical analyses.

Full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, was performed with weights $w = 1/[\sigma_c^2/(4F_o^2) + (aF_o)^2 + b]$; the values of a and b were chosen to make the average values $\langle w(|F_o| - |F_c|)^2 \rangle$ almost equal in different $|F_o|$ and $\sin \theta$ intervals. Two scale factors, and positional and anisotropic thermal parameters were refined (Table 2). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final refinement also included correction for extinction (Zachariasen, 1967) and anomalous dispersion by Ag and I. Only three reflexions had an extinction correction of 4–5% in $|F_o|$. In the last cycle the shift in the parameters for the nonhydrogen atoms was less than about 2% of the estimated standard deviations and the refinement was considered complete. The four H-atom positions of two of the water molecules could be located in a difference synthesis. The electron density of the peaks varied between 0.9 and $1.2 \text{ e } \text{Å}^{-3}$. The positional parameters were refined and the isotropic temperature factor was fixed to 3.0 Å^2 . The R value was reduced from 0.040 to 0.039. A final difference synthesis showed peaks of height $2.1 \text{ e } \text{Å}^{-3}$ or less in the vicinity of the heavy atoms; otherwise it was featureless.

Table 3. Positional and isotropic thermal parameters with estimated standard deviations

For non-hydrogen atoms $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	x	y	z	B_{eq}/B (Å^2)
Ag(1)	0.18255 (9)	0.21212 (4)	0.49992 (7)	2.78 (2)
Ag(2)	0.82933 (9)	0.28453 (6)	0.50147 (8)	3.84 (2)
Ag(3)	0.94382 (10)	0.16017 (4)	0.79394 (9)	3.42 (2)
Ag(4)	0.96388 (10)	0.16636 (5)	0.22064 (9)	3.64 (2)
Ag(5)	0.55880 (10)	0.15844 (6)	0.69402 (8)	3.97 (2)
Ag(6)	0.56935 (9)	0.16243 (5)	0.31257 (9)	3.43 (2)
Ag(7)	0.83727 (16)	0.48997 (7)	0.23660 (14)	6.47 (4)
I(1)	0.86952 (7)	0.10730 (3)	0.48787 (6)	2.16 (1)
I(2)	0.12311 (7)	0.38224 (3)	0.48381 (6)	2.37 (1)
O(1)	0.10989 (99)	0.53184 (56)	0.19527 (82)	4.83 (25)
O(2)	0.59309 (86)	0.45531 (39)	0.35555 (78)	2.90 (16)
O(3)	0.86256 (277)	0.46461 (136)	0.43211 (247)	7.2 (5)
F(1)	0.21393 (73)	0.71943 (36)	0.24651 (53)	3.49 (15)
F(2)	0.73922 (77)	0.28126 (40)	0.25370 (56)	3.95 (16)
F(3)	0.48605 (61)	0.73974 (32)	0.48296 (52)	3.11 (14)
F(4)	0.85117 (78)	0.40253 (34)	0.04001 (66)	3.90 (16)
F(5)	0.36817 (70)	0.56409 (34)	0.37566 (59)	3.39 (15)
H(11)	0.2393 (165)	0.5252 (80)	0.2672 (138)	3.0
H(12)	0.1512 (179)	0.5514 (79)	0.1149 (156)	3.0
H(21)	0.5152 (189)	0.4867 (80)	0.3752 (148)	3.0
H(22)	0.6047 (175)	0.4424 (76)	0.4543 (160)	3.0

A normal probability plot of $R(i) = \delta|F_o(i)| - |F_c(i)|/\sigma|F_o(i)|$ versus the values expected for a normal distribution (Abrahams & Keve, 1971) was performed. The intercept and slope of the least-squares line fitted to all data in the range $|\delta R(i)| < 6$ are 0.09 and 1.38 respectively. The positive intercept may indicate a small overestimation of weak intensities (Persson & Holmberg, 1977). The value of the slope indicates that $\sigma(|F_o|)$ is underestimated by about 40%. It is, however, still in good agreement with the value of the estimated standard deviation of an observation of unit weight ($S = 1.50$, Table 2). All computations were made on the Univac 1108 computer in Lund. Final positional and isotropic thermal parameters are given in Table 3.*

Description of the structure

A stereoview of the unit cell is given in Fig. 1. Selected interatomic distances and angles are listed in Table 4. The structure consists of layers, containing Ag, I, and F atoms, in the ac plane, joined by a partial ring system of $O \cdots F$ hydrogen bonds. These hydrogen bonds are created by the water O atoms and some of the F atoms that are not situated in the layers mentioned above. The layers are formed by Ag–I polyhedra with seven or eight Ag atoms at the corners and an I atom located at an approximately central position. The polyhedra are linked together by shared edges. Three of the five F

* Lists of structure factors, anisotropic thermal parameters and root-mean-square components of thermal displacement along the ellipsoid axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36462 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

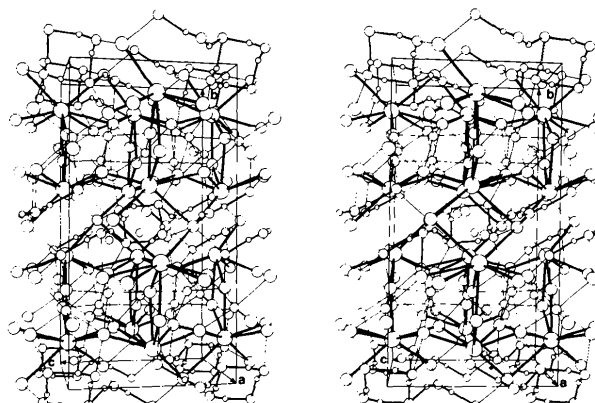


Fig. 1. A stereoscopic pair of drawings showing the contents of the unit cell. The largest circles are I, the next largest are Ag, and the third largest circles represent F and O atoms. The H-atom positions are represented by the smallest circles. Figs. 1–4 have been drawn by the program ORTEP II (Johnson, 1971).

atoms are also situated within these layers. They are octahedrally coordinated to six Ag atoms.

The Ag-to-I coordination in $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$ cannot be described in terms of a simple polyhedral arrangement of Ag atoms around the I atoms. The two I atoms have seven or eight nearest neighbours – all Ag atoms. Each of the I atoms has six Ag atoms on one side and five of these define a distorted pentagon. The largest deviation of an Ag atom from the least-squares Ag_5 plane is 0.32 and 0.40 Å for the I(1) and I(2) pentagon, respectively. The axis described by the Ag–I bond to the sixth Ag atom is almost perpendicular, 92.7 and 89.8° for I(1) and I(2) respectively, to the

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations

Symmetry code

(i)	$1+x, y, z$	(ii)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(iii)	$-1+x, y, z$	(iv)	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
(v)	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	(vi)	$1-x, 1-y, 1-z$
(vii)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	(viii)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
(ix)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	(x)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(xi)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	(xii)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
(xiii)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	(xiv)	$1-x, 1-y, z$
(xv)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	(xvi)	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
(xvii)	$2-x, -y, 1-z$	(xviii)	$-x, 1-y, 1-z$
(xix)	$x, y, 1+z$	(xx)	$x, y, -1+z$

Ag(1 ⁱ)–I(1)	2.978 (1)	F(1)–Ag(1 ^{iv})	2.451 (5)
Ag(2)–I(1)	3.176 (1)	F(1)–Ag(2 ^v)	2.388 (5)
Ag(3)–I(1)	3.055 (1)	F(1)–Ag(3 ^{vi})	2.470 (6)
Ag(4)–I(1)	2.816 (1)	F(1)–Ag(4 ^{vii})	2.579 (6)
Ag(5)–I(1)	3.170 (1)	F(1)–Ag(5 ^{viii})	2.801 (6)
Ag(6)–I(1)	2.905 (1)	F(1)–Ag(6 ^{ix})	2.385 (6)
Ag(7 ^h)–I(1)	3.316 (1)	F(2)–Ag(1 ^{xv})	2.406 (5)
Ag(1)–I(2)	3.068 (1)	F(2)–Ag(2)	2.401 (5)
Ag(2 ⁱⁱ)–I(2)	2.795 (1)	F(2)–Ag(3 ^{iv})	2.459 (6)
Ag(3 ⁱⁱⁱ)–I(2)	3.092 (1)	F(2)–Ag(4)	2.664 (7)
Ag(4 ^v)–I(2)	3.433 (1)	F(2)–Ag(5 ^{vii})	2.670 (6)
Ag(5 ^{vi})–I(2)	2.839 (1)	F(2)–Ag(6)	2.532 (7)
Ag(6 ^{viii})–I(2)	3.212 (1)	F(3)–Ag(1 ^{xv})	2.602 (5)
Ag(7 ^{vii})–I(2)	3.478 (1)	F(3)–Ag(2 ^{vi})	2.383 (5)
Ag(7 ⁱⁱⁱ)–I(2)	3.648 (1)	F(3)–Ag(3 ^v)	2.569 (5)
Ag(3 ^{iv})–O(2 ^{xiii})	2.399 (7)	F(3)–Ag(4 ^{xv})	2.348 (5)
Ag(6 ^{ix})–O(1 ^{xv})	2.679 (10)	F(3)–Ag(5 ^{vi})	2.474 (5)
Ag(7 ⁱⁱⁱ)–O(1 ⁱ)	2.194 (8)	F(3)–Ag(6 ^{vii})	2.629 (5)
Ag(7 ⁱⁱⁱ)–O(2)	2.235 (7)	F(4)–Ag(1 ^{viii})	2.422 (6)
Ag(1 ⁱ)–Ag(2)	2.917 (1)	F(4)–Ag(5 ^{vii})	2.350 (6)
Ag(1 ⁱ)–Ag(4)	3.152 (1)	F(4)–Ag(7)	2.413 (6)
Ag(3)–Ag(5)	2.982 (1)	F(5)–Ag(4 ^{xv})	2.394 (6)
Ag(3 ⁱⁱⁱ)–Ag(6)	3.300 (1)	O(1)···F(5)	2.588 (9)
Ag(4)–Ag(6)	3.065 (1)	O(1)···F(4 ^{xvii})	2.516 (10)
Ag(4 ^v)–Ag(5)	3.213 (1)	O(2)···F(5 ^v)	2.550 (9)
Ag(5 ^{vi})–Ag(7)	3.143 (2)	O(2)···F(5)	2.566 (9)
Ag(6 ^{viii})–Ag(7)	3.188 (2)	O(1)···F(4 ⁱⁱⁱ)	3.313 (11)
I(1)–I(1 ^{xviii})	4.290 (1)	O(1)–H(11)	1.16 (13)
I(1)–I(2 ^{vii})	5.024 (1)	O(1)–H(12)	0.89 (14)
I(1)–I(2 ^{xiii})	5.030 (1)	O(2)–H(21)	0.83 (14)
I(1)–I(2 ⁱ)	5.250 (1)	O(2)–H(22)	0.96 (15)
I(2)–I(2 ^{viii})	4.591 (1)	F(5)–H(11)	1.54 (13)
		F(5)–H(21)	1.76 (14)
		F(5)–H(22 ^{vi})	1.60 (15)
		F(4)–H(12 ^{xv})	1.67 (14)

Table 4 (cont.)

Ag(1 ⁱ)–Ag(4)–Ag(6)	104.39 (3)	Ag(1 ⁱ)–I(1)–Ag(4)	65.84 (2)
Ag(4)–Ag(6)–Ag(5)	108.86 (1)	Ag(4)–I(1)–Ag(6)	64.76 (3)
Ag(6)–Ag(5)–Ag(3)	105.73 (1)	Ag(6)–I(1)–Ag(5)	71.93 (3)
Ag(5)–Ag(3)–Ag(1 ⁱ)	104.91 (1)	Ag(5)–I(1)–Ag(3)	57.20 (2)
Ag(3 ⁱⁱⁱ)–Ag(1)–Ag(4 ⁱⁱⁱ)	109.33 (3)	Ag(3)–I(1)–Ag(1 ⁱ)	69.33 (2)
		Ag(2)–I(1)–Ag(7 ⁱⁱ)	127.64 (3)
Ag(2 ⁱⁱ)–Ag(6)–Ag(4)	103.26 (1)	Ag(2 ⁱⁱ)–I(2)–Ag(6 ^v)	71.07 (2)
Ag(6)–Ag(4)–Ag(3 ^{xv})	105.40 (1)	Ag(6 ^v)–I(2)–Ag(4 ^v)	54.81 (2)
Ag(4 ^{xv})–Ag(3)–Ag(5)	109.15 (1)	Ag(4 ^v)–I(2)–Ag(3 ^{iv})	75.32 (2)
Ag(3)–Ag(5)–Ag(2 ⁱ)	102.46 (1)	Ag(3 ^{iv})–I(2)–Ag(5 ^{vi})	60.18 (3)
Ag(5 ^{vi})–Ag(2)–Ag(6 ^{ix})	110.82 (1)	Ag(5 ^{vi})–I(2)–Ag(2 ⁱⁱ)	77.46 (3)
		Ag(1)–I(2)–Ag(7 ^{vii})	126.97 (3)
H(11)–O(1)–H(12)	103 (10)	Ag(1)–I(2)–Ag(7 ⁱⁱⁱ)	129.22 (3)
H(21)–O(2)–H(22)	90 (13)	Ag(7 ⁱⁱⁱ)–I(2)–Ag(7 ^{vi})	99.81 (3)
F(5 ^v)–H(22)–O(2)	170 (13)		
F(5)–H(21)–O(2)	167 (14)		
F(4 ^{xviii})–H(12)–O(1)	158 (13)		
F(5)–H(11)–O(1)	147 (12)		

Ag_5 plane. The remaining Ag atoms are located on the other side of the plane at longer distances (Figs. 2 and 3). The pentagons are linked to form chains by shared edges along *c*. Two such chains are joined to double layers *via* the sixth Ag atom [Ag(2) and Ag(1) in Figs. 2 and 3]. Ag(2) participates in the Ag–I bond perpendicular to the Ag_5 pentagon around I(1) and is also a member of the Ag_5 pentagon around I(2) in another chain. Ag(1) joins I(2)-centred pentagons with I(1)-centred ones in an analogous way. Those F atoms which do not participate in the hydrogen-bond system are located inside these double layers.

The distances between I(1), I(2) and the surrounding Ag atoms range from 2.80 to 3.65 Å with an average value of 3.07 Å if the longest one is excluded. The shortest Ag–I distances are of the same order of magnitude as those in $\beta\text{-AgI}$ (2.814 Å; Burley, 1963). The mean Ag–I distance in $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2 \cdot 5\text{H}_2\text{O}$ is slightly longer than that for other compounds containing Ag in excess over I, e.g. Ag_2INO_3 [$\overline{\text{Ag}-\text{I}} = 3.001$ Å; Persson, 1979b], and $\text{Ag}_3\text{I}(\text{NO}_3)_2$ [$\overline{\text{Ag}-\text{I}} = 2.938$ Å;

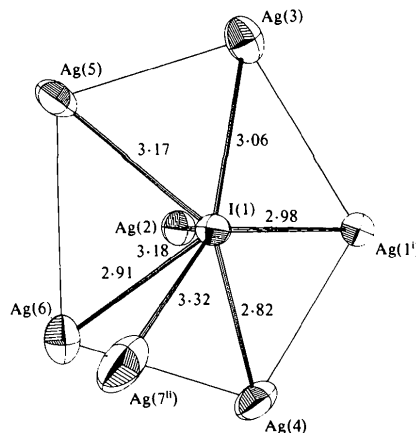


Fig. 2. The environment of the I(1) atoms. Distances are in Å.

Birnstock & Britton, 1970]. In both these structures the I atom is coordinated to six Ag atoms describing trigonal prisms. The higher coordination number in $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$ has to be considered, and it may explain the observed increase in the central-atom–ligand-atom distances.

The Ag–O distances between Ag(7), situated between the Ag(1)–Ag(6), I, F layers, and the water O atoms are short, 2.19 and 2.24 Å respectively, while the Ag(7)–I distances are long, 3.32–3.65 Å. This may indicate a weak interaction between Ag(7) and I depending on a strong interaction between Ag(7) and the water O atoms.

The atoms Ag(1)–Ag(6) are all approximately octahedrally surrounded by two I and three F atoms and one F or one O atom from the hydrogen-bond system. The Ag(7) atom also has six nearest neighbours which describe a distorted octahedron with three I, one F and two O atoms at the corners. The Ag environments can be seen in Fig. 1.

The three F atoms situated in the Ag layers described above are each the centre of an octahedron with Ag atoms at all corners. Two chains, formed by octahedra with shared corners in the axial direction, run along *c*. These chains are joined by an octahedron with its axial direction perpendicular (along *a*) to that of the chains. This octahedron shares two triangular faces with each chain which it joins.

The H atoms belonging to O(1) and O(2) could be located, and the positions in the hydrogen-bond system can be seen in Fig. 4. One of the water molecules, O(2), is part of a four-membered ring system also involving an F atom, $(\text{H}_2\text{O} \cdots \text{F})_2$. This F atom is hydrogen bonded to three water O atoms, two O(2) and one O(1). The O \cdots F distances are 2.55 and 2.57 Å within the ring and 2.52, 2.59 Å for the O \cdots F bonds not participating in the four-membered-ring. These O \cdots F distances are short compared to those normally found in metal fluoride hydrates (Simonov & Bukvetsky, 1978). Because of the large number of heavy atoms in

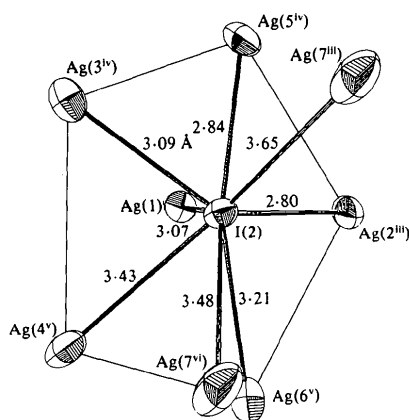


Fig. 3. The environment of the I(2) atom. Distances are in Å.

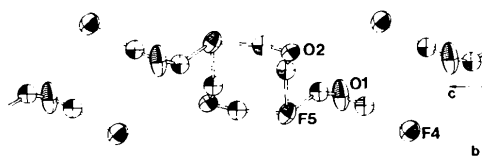


Fig. 4. The hydrogen-bond system.

the structure there are large uncertainties in the H-atom positions, determined by X-ray diffraction, and thereby in the O–H and F \cdots H distances. The O–H distances vary between 0.83 and 1.16 Å with an average value of 0.97 Å and an e.s.d. of 0.14 Å. The H–O–H angles are 90 and 103° with an e.s.d. of about 10°. The F \cdots H distances range from 1.54 to 1.76 Å. The formation of a ring system of hydrogen bonds as in $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$ has also been found in $\text{Te}(\text{OH})_6 \cdot 2\text{CsF} \cdot 2\text{H}_2\text{O}$ (Allmann & Rius, 1978), where the O \cdots F distances are 2.62 and 2.73 Å within the $(\text{H}_2\text{O} \cdots \text{F})_2$ rings and 2.51 Å outside the rings. The O in the latter, short O \cdots F bond belongs to a hydroxide group. Another example of such four-membered rings is shown by the structure of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ (Abrahams & Prince, 1962), where the O–H \cdots F distance is 2.645 Å (neutron diffraction). Even six-membered $(\text{H}_2\text{O} \cdots \text{F})_3$ rings have been observed, e.g. in $[\text{Cr}(\text{H}_2\text{O})_6]_3\text{F}_3 \cdot 3\text{H}_2\text{O}$ with O \cdots F distances of 2.64 and 2.65 Å (W. Massa, unpublished; cited by Allmann & Rius, 1978).

Among the O and F atoms which are involved in the $(\text{H}_2\text{O} \cdots \text{F})_2$ ring system in $\text{Ag}_7\text{I}_2\text{F}_5 \cdot 2.5\text{H}_2\text{O}$, F(4), F(5) and O(2) have tetrahedral environments of three Ag and one O, one Ag and three O, and two Ag and two F, respectively. The O(1) environment can also be described as a tetrahedron of two Ag and two F atoms, but the O(1) atom is moved towards one of the triangular faces. The O(1)–Ag and O(1)–F distances are 2.18, 2.68 and 2.52, 2.59 Å respectively.

Finally, it should be observed that there are two remarkably short Ag–Ag distances in the structure, 2.917 and 2.982 Å (Table 4). A preliminary literature survey reveals that such short interionic Ag^I distances [close to the Ag–Ag distance in metallic silver, 2.889 Å (Straumanis & Riad, 1965)] are surprisingly frequent in crystalline compounds containing silver in the formal oxidation state +I. A further discussion of the Ag₂²⁺ pairs will be advanced in a forthcoming paper on the structure of $\text{Ag}_2\text{IF} \cdot \text{H}_2\text{O}$.

The present study has indicated that the nature of the counterion *A* in compounds $\text{Ag}_n\text{X}_x\text{A}_y$ ($n > x$) may have a profound influence on the coordination of Ag to I for the case $\text{I} = \text{X}$. This is clear from a comparison with, for example, $\text{Ag}_3\text{I}(\text{NO}_3)_2$ and Ag_2INO_3 . In these compounds the Ag-to-I coordination geometry can be described by distorted trigonal Ag₆ prisms.

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References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- ABRAHAMS, S. C. & PRINCE, E. (1962). *J. Chem. Phys.* **36**, 50–55.
- ALLMANN, R. & RIUS, J. (1978). *Acta Cryst.* **A34**, S167.
- BIRNSTOCK, R. & BRITTON, D. (1970). *Z. Kristallogr.* **132**, 87–98.
- BURLEY, G. (1963). *J. Chem. Phys.* **38**, 2807–2812.
- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457–464.
- CHAN, L. Y. Y. & GELLER, S. (1977). *J. Solid State Chem.* **21**, 331–347.
- DANIELSSON, S., GRENTHE, I. & OSKARSSON, Å. (1976). *J. Appl. Cryst.* **9**, 14–17.
- ELDING, I. (1976). *Acta Chem. Scand. Ser. A*, **30**, 649–656.
- GERMAN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HAYEK, E. (1936). *Monatsh. Chem.* **68**, 29–32.
- HOLMBERG, B. & PERSSON, K. (1975). *Acta Cryst.* **A31**, S65.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- KARLSSON, R. (1972). *Talanta*, **19**, 1639–1644.
- LIESER, K. H. (1960). *Z. Anorg. Chem.* **305**, 133–137.
- PERSSON, K. (1977). Abstract PII 79. 4th European Crystallographic Meeting, Oxford.
- PERSSON, K. (1979a). *Acta Cryst.* **B35**, 1432–1435.
- PERSSON, K. (1979b). *Acta Cryst.* **B35**, 302–306.
- PERSSON, K. & HOLMBERG, B. (1977). *Acta Cryst.* **B33**, 3768–3772.
- SIMONOV, V. I. & BUKVETSKY, B. V. (1978). *Acta Cryst.* **B34**, 355–358.
- STRAUMANIS, M. E. & RIAD, S. M. (1965). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **233**, 964–967.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1982). **B38**, 1070–1074

Structure du Perrhénate de Gadolinium–Sodium Tétrahydraté $\text{GdNa}(\text{ReO}_4)_4 \cdot 4\text{H}_2\text{O}$

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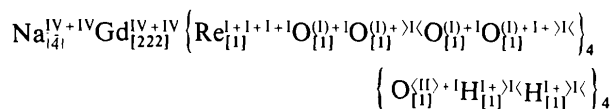
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Abstract

The tetragonal salt $\text{GdNa}(\text{ReO}_4)_4 \cdot 4\text{H}_2\text{O}$ crystallizes in space group $P4n2$, with $Z = 2$, $a = b = 12.483(5)$, $c = 5.728(4)$ Å; $d_m = 4.68 \pm 0.05$, $d_x = 4.662$ Mg m⁻³. The crystal structure was refined using three-dimensional X-ray data (collected on an automatic four-circle diffractometer at room temperature with Mo $K\alpha$ radiation) to $R = 0.0402$ for 1605 F_o , with full corrections for absorption and anomalous dispersion for cations. The coordination formula is:



* Auteur auquel toute correspondance doit être adressée.

Introduction

L'étude des systèmes $\text{Ln}(\text{ReO}_4)_3\text{-MReO}_4$ ($\text{Ln} = \text{La}$ à Lu ; $M = \text{Na}, \text{K}, \text{Ag}$) a mis en évidence un perrhénate double, $\text{MLn}(\text{ReO}_4)_4$. Tous ces composés sont sensibles à l'humidité. Des tétrahydrates $\text{MLn}(\text{ReO}_4)_4 \cdot 4\text{H}_2\text{O}$, tous isotopes, sont identifiés pour $\text{Ln} = \text{Eu}$ à Lu (Aït Ali Slimane, Silvestre & Freundlich, 1978). Ce travail concerne la détermination de la structure cristalline de la phase $\text{GdNa}(\text{ReO}_4)_4 \cdot 4\text{H}_2\text{O}$.

Les monocristaux sont obtenus à partir d'une solution aqueuse de perrhénate de gadolinium–sodium à 323 K. Ils sont incolores et transparents. Leur forme est parallélépipédique et leurs dimensions peuvent dépasser $4 \times 4 \times 10$ mm. Le cristal utilisé a pour dimensions approximatives $68 \times 54 \times 209$ µm. Il est allongé selon le paramètre c . Sa morphologie a été observée au goniomètre optique (Fig. 1). Les faces