Journal of Fluorine Chemistry 132 (2011) 686–689

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

X-ray single crystal structures of $Hg(AuF_6)_2$ and $AgFAuF_6$

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ARTICLE INFO

Article history:
Received 18 February 2011
Received in revised form 28 March 2011
Accepted 29 March 2011
Available online 5 April 2011

Keywords:
Mercury
Gold
Silver
Hexafluoroaurates
Crystal structure

The authors dedicate this paper to Dr. Alain Tressaud on winning the 2011 ACS Award for Creative Work in Fluorine Chemistry.

ABSTRACT

$Hg(AuF_6)_2$ crystallizes at 200 K in the orthorhombic space group *Pbcn* (No. 60) with $a = 917.67(7)$ pm, $b = 971.59(8)$ pm, $c = 962.04(8)$ pm, and $Z = 4$. Mercury atoms are coordinated by eight fluorine atoms with six short and two long Hg–F contacts. HgF_8 polyhedra share their four vertices and two edges with six AuF_6 units forming a tridimensional framework.

The results of X-ray diffraction analysis on single crystals of $AgFAuF_6$ are in agreement with previously known powder X-ray diffraction data (Casteel et al, J. Solid State Chem. 96 (1992) 84–96). $AgFAuF_6$ crystallizes orthorhombic in the space group *Pnma* (No. 62), $a = 717.06(7)$ pm, $b = 761.67(7)$ pm, $c = 1013.61(10)$ pm at 200 K, $Z = 4$.

1. Introduction

Attempts to determine the crystal structures of known $M(AuF_6)_2$ (M = Mg, Ca, Sr, Ba, Ni, Cu, Ag, Zn, Cd, Hg) compounds [1] have been so far only partly successful. X-ray powder data indicate that $M(AuF_6)_2$ (M = Mg, Ni, Cu, Zn) are isostructural with corresponding hexafluoroarsenates and hexafluoroantimonates [1]. Only in the case of larger Cd^{2+} cation the crystal structure of $Cd(AuF_6)_2$ has been determined from the single crystal data [2]. An attempt to prepare single crystals of $Mg(AuF_6)_2$ resulted in the preparation of first example of a mixed oxidation state Au^{III}/Au^{V} ternary fluoride $[Mg(HF)AuF_4AuF_6]$ [2]. In the present paper, the crystal structure of $Hg(AuF_6)_2$ – a new structure type of $M^{II}(X^{V}F_6)_2$ compounds – is reported. The preparation of $Hg(AuF_6)_2$, its Raman spectrum and X-ray powder diffraction data have been previously reported [1].

In 1992, Casteel et al. reported the experimental synthesis conditions, the diffraction pattern and the magnetic susceptibility of $AgFAuF_6$ [3]. On the basis of the X-ray powder photographs it was concluded that $AgFAuF_6$ is isostructural with $AgFAsF_6$ [3]. Single crystal determination of the crystal structure of $AgAuF_6$, given in this paper, confirms their assumptions.

2. Results and discussion

The structural data of $Hg(AuF_6)_2$ and $AgFAuF_6$ are summarized in Table 1.

2.1. Crystal structure of $Hg(AuF_6)_2$

The known compounds with general formula $M^{II}(X^{V}F_6)_2$ adopt one of the four structural types [1,4,5]. The first and most common structural type is the $Ni(SbF_6)_2$-type [4] (Fig. 1a) where M^{2+} cations are sixfold co-ordinated by fluorine atoms. MF_6 octahedra share fluorine atoms with six XF_6 units on either side of the plane formed by the M atoms forming slabs. The structure can alternatively be described as derived from the $LiSbF_6$ type (ordered ReO_3), with ordered vacancies for half the cationic sites, i.e. $M_{0.5}\square_{0.5}XF_6$.

The crystal structure of $Cd(AuF_6)_2$ represents a second type [2]. As in $Ni(SbF_6)_2$-type, divalent cations (i.e. Cd^{2+}) are coordinated by six fluorine atoms and the MF_6 (M = Cd) octahedra also share their vertices with six XF_6 (X = Au) units on either side of the plane formed by the M atoms (Fig. 1b). On that way $Ni(SbF_6)_2$- and $Cd(AuF_6)_2$-type show similar features. Both structures may be derived from hexagonal closed-packed array of fluorine atoms.

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doi:10.1016/j.jfluchem.2011.03.022

Table 1
Crystal data and structure refinement for $Hg(AuF_6)_2$ and $AgFAuF_6$.[a]

Formula	$HgAu_2F_{12}$	$AgAuF_7$
fw	822.52	437.824
Temp. (K)	200	200
a (pm)	917.67(7)	717.06(7)
b (pm)	971.59(8)	761.67(7)
c (pm)	962.04(8)	1013.61(10)
V (nm^3)	0.85775(12)	0.55360(9)
Z	4	4
D_{calcd} (g/cm^3)	6.369	5.253
λ (pm)	71.069	71.069
μ (mm^{-1})	52.145	30.073
Space group	*Pbcn*	*Pnma*
GOF indicator	1.348	1.281
$R1$; w$R2$ ($I > 2.00\sigma(I)$)	0.0844; 0.1647	0.0502; 0.1153

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $GOF = [\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$, where N_o is the no. of reflns and N_p is the no. of refined params.

However, M^{II} and X^V occupy the octahedral sites in a different manner, resulting in a layered structure, the $Ni(SbF_6)_2$ type sheet is illustrated by $Mn(SbF_6)_2$ in Fig. 1a, or three-dimensional framework $[Cd(AuF_6)_2]$ (Fig. 1b). The crystal structures of $Mn(AsF_6)_2$ [6] and $Pd(NbF_6)_2$ [7] are unique representatives of the third and the fourth type.

The crystal structure of $Hg(AuF_6)_2$ represents a fifth type. In the crystal structure of $Hg(AuF_6)_2$, mercury atoms, located on a special position 4*c* (rotating axis 2), are surrounded by 6 + 2 fluorine atoms in a distorted square anti-prismatic coordination (Fig. 2; Table 2). HgF_8 polyhedra share also four vertices and two edges with six AuF_6 units formning tri-dimensional framework (Figs. 3 and 4). There are three pairs of short Hg–F bonds (2 × 230(2) pm, 2 × 234(2) pm, 2 × 239(2) pm) and two elongated Hg–F contacts (2 × 251(2) pm). Fluorine atoms F3 and F5 (involved in the shortest Hg1–F3 and the longest Hg1–F5 bonds) are shared with the same AuF_6 moiety (Fig. 2). For comparison, in $Hg(AuF_4)_2$ and HgF_2, where Hg is also eightfold coordinated, Hg–F distances are equal to 236.0 pm [8] while the Hg–F bond lengths in HgF_2 are equal to 239.9 pm [9].

The AuF_6^- anions are distorted by interaction with Hg^{2+} cations (Fig. 2). Two of six fluorine atoms belonging to AuF_6 units are non-bridging (F_t) and four are bridging (F_b). The Au–F distances are noticeably different. The values of 186(2)–189(2) pm for Au–F_t bonds are shorter than that for Au–F_b ones (189(2)–192(2) pm). One of the Au–F_b bond distances (Au–F5) is significantly shorter (189(2) pm) than Au–F3, Au–F4 and Au–F6 (all are 192 pm), however, this difference is balanced by respective distances to the Hg atom as Hg–F5 is considerably longer (251(2) pm) than Hg–F3 (230(2) pm), Hg–F4 (234(2) pm) and Hg–F6 (239(2) pm). The Au–F bond lengths are comparable to Au–F distances in $Cd(AuF_6)_2$ (Au–F: 187.1–193.7 pm) [2].

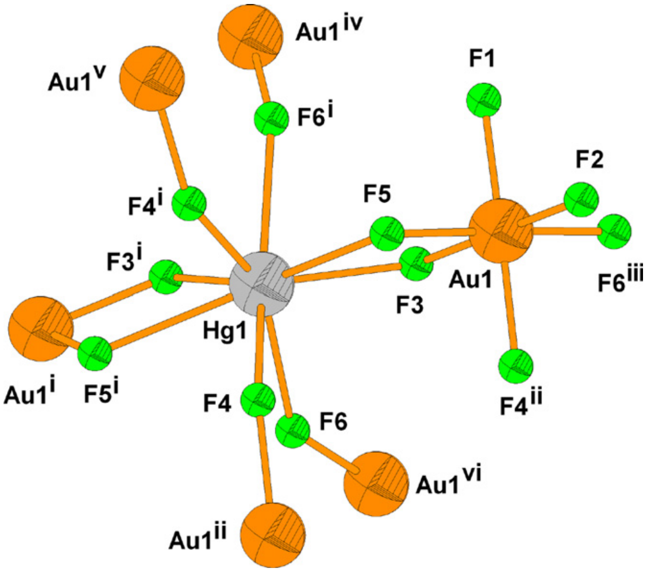

Fig. 2. Coordination of Hg and Au atoms in the crystal structure of $Hg(AuF_6)_2$. Symmetry codes used to generate equivalent atoms correspond to those in Table 2.

Table 2
Selected bond lengths (pm) in $Hg(AuF_6)_2$.

Hg1–F3, Hg1–F3^i	230(2)	Au1–F1	186(2)
Hg1–F4, Hg1–F4^i	234(2)	Au1–F2	189(2)
Hg1–F6, Hg1–F6^i	239(2)	Au1–F5	189(2)
Hg–F5, Hg–F5^i	251(2)	Au1–F4^{ii}	192(2)
		Au1–F3	192(2)
		Au1–F6^{iii}	192(2)

Symmetry codes used to generate equivalent atoms: (i) $-x, y, 1/2-z$; (ii) $-x, -y, -z$; (iii) $1/2+x, 1/2-y, -z$; (iv) $1/2-x, 1/2-y, 1/2+z$; (v) $x, -y, 1/2+z$; (vi) $1/2-x, 1/2-y, -z$.

2.2. Crystal structure of $AgFAuF_6$

An attempt to prepare single crystals of $Ag(AuF_6)_2$ resulted in the synthesis of single crystals of $AgFAuF_6$ instead. As expected on the basis of X-ray powder photographs of the solid [3], $AgFAuF_6$ is isostructural to $AgFAsF_6$ [10]. The structure consists from $(Ag{-}F)_n^{n+}$ one dimensional chains linked to $[AuF_6]^-$ anions (Fig. 5). Selected bond lengths and angles for $AgFAuF_6$ are provided in Table 3.

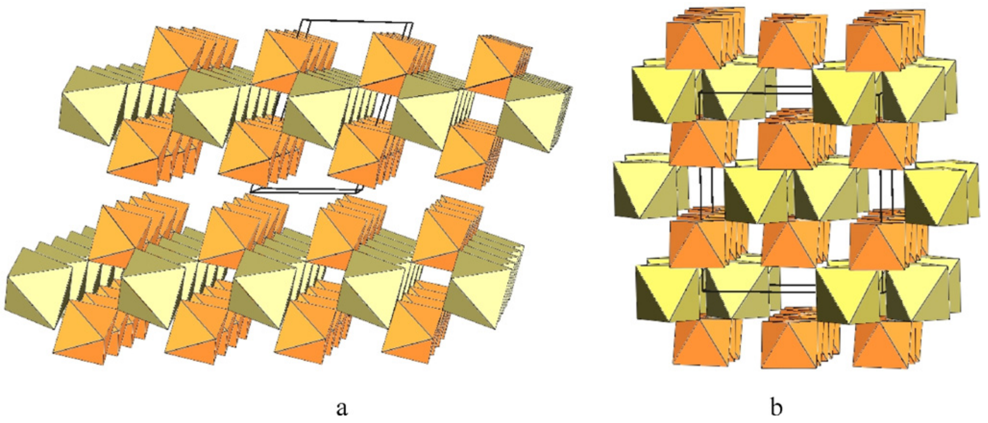

Fig. 1. (a) Packing of slabs in $Mn(SbF_6)_2$ (view along *a*-axis) [5] (example of the $Ni(SbF_6)_2$-structural type) and (b) three-dimensional framework in $Cd(AuF_6)_2$ (view along *b*-axis) [2]. Orange octahedra (dark) represent X^VF_6 (X = Sb, Au) units.

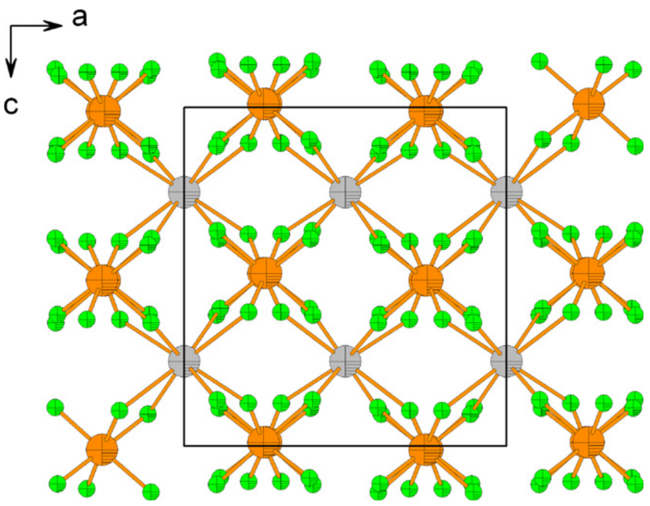

Fig. 3. View along *b*-axis of the crystal structure of $Hg(AuF_6)_2$.

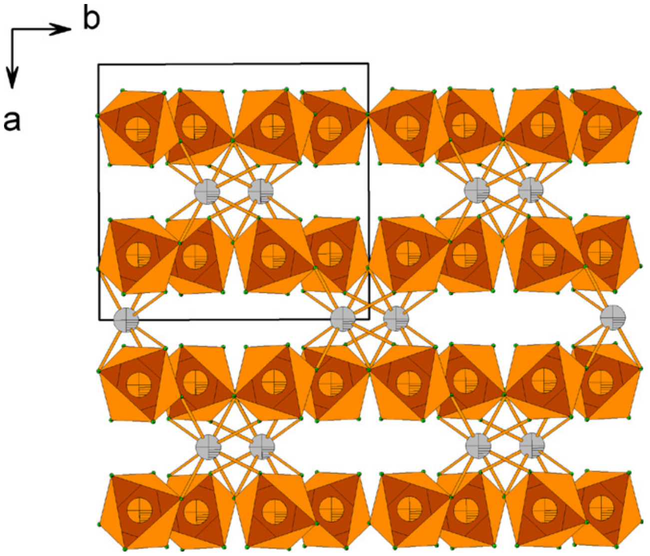

Fig. 4. View along *c*-axis showing the formation of channels in the crystal structure of $Hg(AuF_6)_2$.

Five fluorine atoms from four AuF_6^- anions form the planar pentagonal environment of silver atoms, and two F1 bridges complete Ag pentagonal bi-pyramidal surrounding (Fig. 6). The Ag–F$_b$ distances in $(Ag–F)_n^{n+}$ chains are equal to 198.9(4) pm and 201.9(4) pm, respectively (Fig. 6) and Ag–F–Ag angle is 144°. The corresponding Ag–F$_b$ intra-chain distances in $AgFAsF_6$ are equal to 199.5(5) pm and 200.4(5) pm and Ag–F–Ag angle to 143.3° [10].

Table 3
Selected bond lengths (pm) and angles (°) in $AgFAuF_6$.

Ag1–F1	198.8(4)	Au1–F5	182.5(6)
Ag1–F1^{i}	201.9(4)	Au1–F4	190.4(3)
Ag1–F2	233.4(4)	Au1–F4^{v}	190.4(3)
Ag1–F4	234.9(3)	Au1–F3^{iii}	191.1(3)
Ag1–F4^{ii}	234.9(3)	Au1–F3^{iv}	191.1(3)
Ag1–F3	245.3(3)	Au1–F2^{iv}	194.2(4)
Ag1–F3^{ii}	245.3(3)	Ag1–F1–Ag1^{vii}	144.0(3)

Symmetry codes used to generate equivalent atoms: (i) $3/2-x, 1/2-y, 1/2-z$; (ii) $3/2-x, y, z$; (iii) $-1/2+x, 1/2-y, -1/2+z$; (iv) $-1/2+x, 1-y, -z$; (v) $1/2-x, y, z$; (vi) $1-x, 1/2-y, -1/2+z$; (vii) $3/2-x, -1/2+y, 1/2-z$, (viii) $1+x, y, z$; (ix) $1-x, 1/2-y, -z$; (x) $1/2+x, 1-y, -z$.

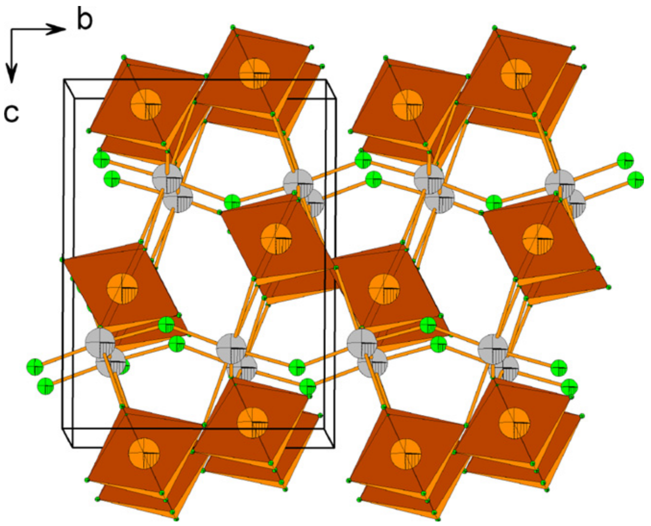

Fig. 5. Packing of $(Ag–F)_n^{n+}$ chains in $AgFAuF_6$.

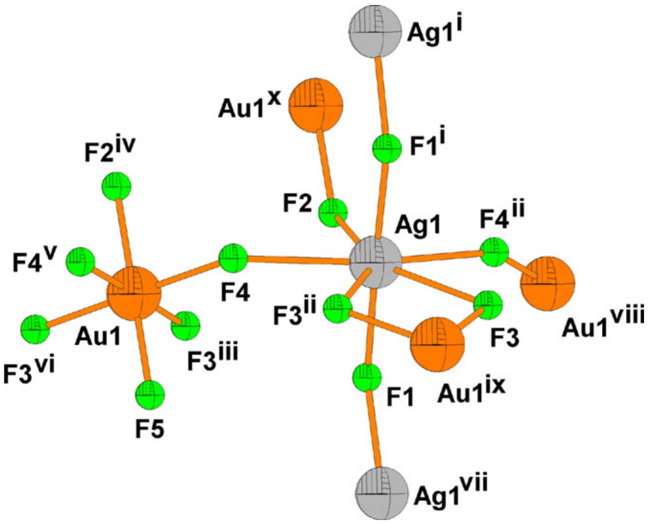

Fig. 6. Coordinations of Ag and Au atoms in the crystal structure of $AgFAuF_6$. Symmetry codes used to generate equivalent atoms correspond to those in Table 3.

The remaining five Ag–F(–AuF$_5$) bond contacts are significantly elongated and are in the range 233.4(4)–243.5(3) pm (239.4–243.9 pm in $AgFAsF_6$). The longest two contacts involve a pair of symmetrically related F3 atoms bonded to the same AuF_6. Each AuF_6 units consist from a single non-bridging (Au–F$_t$ = 182.5(6) pm) and five bridging fluorine atoms (Au–F$_b$: 190.4(3)–194.2(4) pm).

3. Conclusions

The crystal structures of two AuF_6^- salts are determined from single crystal X-ray diffraction data. The crystal structure of $Hg(AuF_6)_2$ represents the fifth crystal structural type type for the $M^{II}(X^{V}F_6)_2$ compounds. In this structural type, the M^{2+} cations are coordinated by eight fluorine atoms. The MF_8 polyhedra share four vertices and two edges with six XF_6 units and thus form the three dimensional framework. $AgFAuF_6$ is isostructural to $AgFAsF_6$ [10] and consists of $(Ag–F)_n^{n+}$ chains connected by $[AuF_6]^-$ anions.

4. Experimental

4.1. Apparatus and reagents

Volatile materials (anhydrous HF, F_2) were handled in an all PTFE vacuum line equipped with PTFE valves. The manipulation of the non-volatile materials was done in a dry box (M. Braun). The residual water in the atmosphere within the dry-box never exceeded 1 ppm. The reactions were carried out in FEP (tetrafluoroethylene–hexafluoropropylene) reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE valves and PTFE coated stirring bars. Prior to their use all reaction vessels were passivated with elemental fluorine. $Hg(AuF_6)_2$ and $Ag(AuF_6)_2$ were prepared as described previously [1]. Fluorine was used as supplied (Solvay). Anhydrous HF (Fluka, Purum) was treated with K_2NiF_6 (Ozark Mahoning) for several hours prior to use. A 400 W medium pressure mercury lamp (Baird and Tatlock, London, Type 400 LQ) was used as the UV source.

4.2. Preparation of single crystals of $Hg(AuF_6)_2$ and $AgFAuF_6$

$M(AuF_6)_2$ (M = Hg, Ag) (approximately 100 mg) was placed into the wider tube of the T-shaped reaction vessel. Anhydrous HF (4 ml) and elemental fluorine (2–3 bar) were added and exposed to UV light over the night. $Hg(AuF_6)_2$ dissolved only partly, yielding yellow solution, while $Ag(AuF_6)_2$ dissolved completely yielding turquoise-green solution. Those solutions were decanted into the narrower arm of the reaction vessel. During three weeks, the crystals were grown with a small temperature gradient of 10 K (running tap water-ambient temperature). Majority of the single crystals isolated from $Hg(AuF_6)_2$/aHF solution were $Hg(AuF_6)_2$, only a few of them were O_2AuF_6. Single crystals from $Ag(AuF_6)_2$/aHF solution corresponded to $AgFAuF_6$ and one more phase which could not be identified.

Selected orange and green crystals of $Hg(AuF_6)_2$ and $AgFAuF_6$, respectively, were isolated and immersed in perfluorinated oil (ABCR, FO5960) in the dry-box, selected under microscope, and transferred into the cold nitrogen stream of the diffractometer.

4.3. X-ray structure determinations

Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromatized Mo$K\alpha$ radiation at 200 K. Data were treated using the Rigaku CrystalClear software suite package [11]. Both structures were determined by direct methods using SIR-92 [12] program (TeXan crystallographic software package of Molecular Structure Corporation [13]) and refined with SHELXL-97 [14] software implemented in program package WinGX [15]. A reproducible merohedral twinning of all checked $Hg(AuF_6)_2$ crystals and, consequently, it turned out to be impossible to apply an appropriate absorption correction, resulted in a rather poor quality of obtained data. After unsuccessful attempts of anisotropic refinement, the thermal parameters of fluorine atoms were finally refined in isotropic mode. The figures were prepared using DIAMOND 3.1 software [16].

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition numbers CSD-422687 for $Hg(AuF_6)_2$ and CSD-422686 for $AgFAuF_6$, respectively.

Acknowledgements

The authors gratefully acknowledge the Slovenian Research Agency (ARRS) for the financial support of the present study within the research program: P1-0045 Inorganic Chemistry and Technology.

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