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Recent achievements in the synthesis and characterization of metal hexafluorantimonates and hexafluoroaurates

Zoran Mazej*

Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Abstract

The efforts to prepare new $MSbF_6/MSb_2F_{11}$ (A = In, Cu, Au, Hg) compounds were partly successful. Reaction between $InBF_4$ and excess SbF_5 in anhydrous hydrogen fluoride (aHF) yields a mixture of $InF_3{\cdot}3SbF_5$ and unidentified $SbF_3{\cdot}xSbF_5$. The attempts to synthesize $MSbF_6/MSb_2F_{11}$ salts (A = Au, Hg) by controlled reduction of $Au(SbF_6)_2$ or $Hg(SbF_6)_2$ solutions in aHF/SbF_5 by elemental hydrogen, resulted in the precipitation of metallic Au or $Hg_2(Sb_2F_{11})_2$. In the reaction of metallic Cu and deficit SbF_5, the synthesis of $CuSbF_6$ was achieved. $CuSbF_6$, like $CuAsF_6$, is a rare example of a Cu(I) compound in a pure fluorine environment.

Vibrational spectra of M(II) hexafluoroantimonates (M = Ni, Fe, Co, Cu, Cr, Pd, Ag) were reinvestigated. It was found that many of them originally assigned to $M(SbF_6)_2$ compounds, belong to their mixtures with oxonium salts $H_3OM(SbF_6)_3$, H_3OSbF_6, and/or $H_3OSb_2F_{11}$.

Reactions were studied between $MF_2/2AuF_3$ (M = Ni, Cu, Ag, Zn, Cd and Hg) and KrF_2 or UV-irradiated elemental fluorine in aHF as solvent at room temperature. On the basis of mass balances, Raman spectroscopy and X-ray powder diffraction analysis it can be concluded that the isolated solids have structures that can be considered in terms of an $M(AuF_6)_2$ formulation. Previously reported syntheses and characterization of $M(AuF_6)_2$ (M = Mg, Ca, Sr, Ba) were reinvestigated. In the case of M = Ba two different AuF_6^- salts were isolated.

Raman spectra of the majority of synthesized metal hexafluoroaurates (M = Ni, Cu, Ag, Zn, Cd, Hg, Mg and Ca) show more bands than expected for regular AuF_6^- anion, indicating that the salts obtained exhibit relatively strong cation–anion interactions. The Raman spectra of the remaining Sr and Ba salts show the presence of more regular AuF_6^- octahedra, indicating weak cation–anion interactions.

Keywords: Hexafluoroaurates; Hexafluoroantimonates; Fluorides; Transition metals; Alkali-earth metals

1. Introduction

Reactions of MF (M = Li, Na, K, Rb, Cs, Tl) with excess of SbF_5 in aHF yield $ASbF_6$ (M = Li, Na), ASb_2F_{11} (M = K, Rb, Cs, Tl) and ASb_3F_{16} (M = Cs) compounds [1]. The product of the reaction between $AgBF_4$ and excess of SbF_5 in aHF is also an $Sb_2F_{11}^-$ salt ($AgSb_2F_{11}$) [2]. Its vibrational spectra entirely match the reported vibrational spectra of β-$Ag(SbF_6)_2$, for which a formulation of a mixed valence Ag(I)/Ag(III) compound was incorrectly suggested [3]. In this paper the efforts to prepare other, presently unknown $MSbF_6/MSb_2F_{11}$ (M = In, Cu, Au, Hg) salts are reported.

Hexafluoroantimates of divalent transition metal cations are well known [3–6]. They are usually synthesized by reaction between corresponding metal difluoride and excess of SbF_5 in aHF. However, as found in our laboratory, their vibrational spectra and X-ray powder diffraction patterns were not always in agreement with those previously reported [4]. For that reason, a systematic study was made to clarify the observed disagreement. It was found that many of the previously reported vibrational spectra and X-ray powder diffraction patterns, originally assigned to $M(SbF_6)_2$ compounds [4], belong to $M(SbF_6)_2$ compounds contaminated with oxonium salts such as H_3OSbF_6 [7], $H_3OSb_2F_{11}$ [8] or $H_3OM(SbF_6)_3$ [9]. Because of the high sensitivity of $M(SbF_6)_2$ compounds to moisture, great care should be taken in the course of their preparation and characterization, in which any presence of moisture should be completely excluded. In this paper, novel vibrational spectra and X-ray powder diffraction patterns of $M(SbF_6)_2$ compounds are reported.

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* Tel.: +386 61 123 2125; fax: +386 61 123 2125.
E-mail address: zoran.mazej@ijs.si.

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Reactions between $MF_2/2AuF_3$ (M = Ni, Cu, Ag, Zn, Cd and Hg) starting mixtures and KrF_2 or ultraviolet photolyzed F_2 in aHF as solvent at room temperature were studied. New solid hexafluoroaurates were characterized by vibrational spectroscopy and X-ray powder diffraction analysis. Previously reported syntheses and characterization of $M(AuF_6)_2$ (M = Mg, Ca, Sr, Ba) compounds [10] were reinvestigated.

2. Results and discussion

2.1. Copper(I) hexafluoroantimonate

The efforts to prepare other unknown $MSbF_6/MSb_2F_{11}$ (M = In, Cu, Au, Hg) compounds were partly successful. Since corresponding MF monofluorides are not available (CuF and InF are not known, AuF was detected only as molecule [11,12] and HgF exists only as Hg_2F_2 with Hg_2^{2+} cation [13]), other routes were used to examine their preparation.

Reaction between $InBF_4$ and excess of SbF_5 in aHF yields a mixture of known $InF_3{\cdot}3SbF_5$ [14] and an unidentified phase of $SbF_3{\cdot}xSbF_5$.

When UV-light, dioxygen, hydrazinium difluoride or xenon are applied as reducing agents in aHF, the reduction of AuF_3 in aHF/SbF_5 went only in the best case to Au(II), but never further [15]. Controlled reduction of $Au(SbF_6)_2$ solution in aHF/SbF_5 by H_2 was tried. Immediately when elemental hydrogen came in close contact with a solution of $Au(SbF_6)_2$ in aHF/SbF_5, metallic Au started to precipitate and deposited on the reaction vessel wall.

When a solution of $Hg(SbF_6)_2$ in aHF/SbF_5 was treated by hydrogen, a white solid precipitated. A colourless solution was decanted and $Hg(SbF_6)_2$ (mostly) was recovered from it. The strongest bands in the Raman spectrum of the remaining white precipitate could be assigned to $Hg_2(Sb_2F_{11})_2$ [16]. The rest of them could not be identified.

When short wires of metallic Cu were treated with a less than equivalent amount of SbF_5 in aHF, orange-yellow crystals grew at both ends of the wires

$$\underset{n(\mathrm{cu}) \gg n(\mathrm{SbF_5})}{\mathrm{Cu} + \mathrm{SbF_5}} \xrightarrow[298\,\mathrm{K}]{\mathrm{aHF}} \mathrm{CuSbF_6} + \mathrm{SbF_3} \cdot x\mathrm{SbF_5} + \text{non-reacted Cu} \qquad (1)$$

The vibrational spectra on powdered samples, obtained by grinding selected single crystals, were consistent with the presence of regular SbF_6^- anion (Fig. 1), that is, the formation of $CuSbF_6$ salt. $CuSbF_6$, like $CuAsF_6$, is a unique example of a Cu(I) compound in a pure fluorine environment.

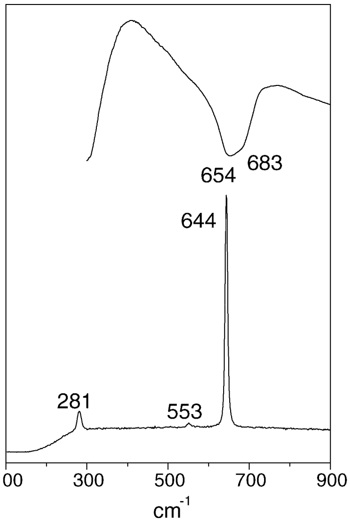


Fig. 1. Vibrational spectra of $CuSbF_6$.

2.2. Hexafluoroantimonates of divalent cations

Vibrational spectra and X-ray powder diffraction data of some M(II) hexafluoroantimonates (M = Ni, Fe, Co, Cu, Cr, Ag, Pd) [3,4] were reinvestigated. In Ref. [4] it was claimed that the Ni, Mg, Zn compounds and the Fe, Co, Cu compounds, together with $Sn(SbF_6)_2$, form two distinct structural triads, while the rest have structures which differ from each other and from those of the two triads [4].

Further investigations in our laboratory showed that, besides, the resulting $M(SbF_6)_2$ compounds are as sensitive to moisture as starting compound SbF_5. Traces of water could cause the desired $M(SbF_6)_2$ compounds to become contaminated with oxonium salts H_3OSbF_6 [7], $H_3OSb_2F_{11}$ [8] or $H_3OM(SbF_6)_3$ [9]. Although their amount is low, and they could not always be detected by X-ray powder diffraction analysis, their vibrational bands could dominate in the vibrational spectra of their mixtures with $M(SbF_6)_2$ salts.

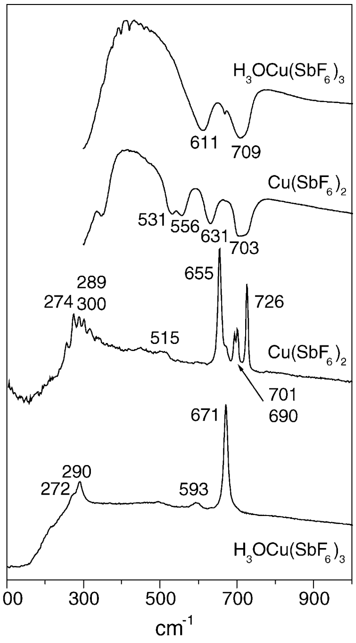


Fig. 2. Vibrational spectra of $Cu(SbF_6)_2$ and $H_3OCu(SbF_6)_3$ (Ref. [4] vibrational data of "$Cu(SbF_6)_2$"—IR: 703(vs), 676(s), 636(m, sh), 612(m, sh) 560(m, sh), 450(sh); Raman: 665(100), 594(15), 544(10), 287(30), 274(20)).

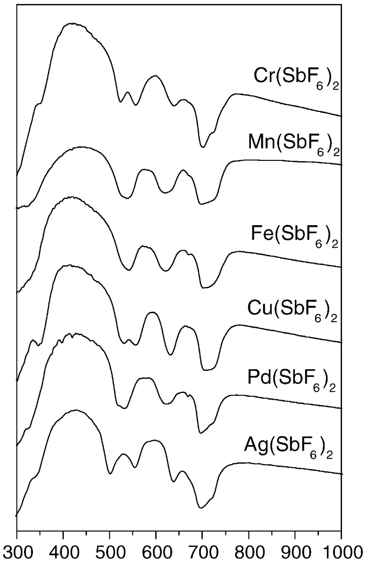


Fig. 3. Infrared spectra of M(SbF$_6$)$_2$ (M = Cr, Mn, Fe, Cu, Pd, Ag) compounds.

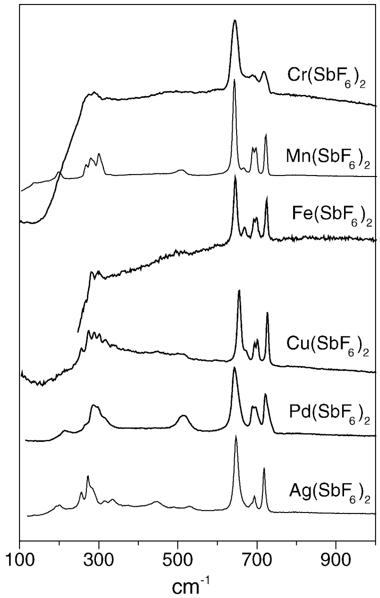


Fig. 4. Raman spectra of M(SbF$_6$)$_2$ (M = Cr, Mn, Fe, Cu, Pd, Ag) compounds.

As a typical example, the comparison of vibrational spectra of Cu(SbF$_6$)$_2$ obtained in this work and reported in [4] is shown. The reported infrared spectrum of Cu(SbF$_6$)$_2$ partly agrees with that obtained in this study. However the reported Raman spectrum of Cu(SbF$_6$)$_2$ is very similar to that of H$_3$OCu(SbF$_6$)$_3$ (Fig. 2).

If M(II) hexafluoroantimonates (M = Cr, Mn, Fe, Cu, Ag, Pd) are not contaminated with oxonium salts, they have similar X-ray powder diffraction patterns (Table 3) and their vibrational spectra (Figs. 3 and 4, Table 1) also show very similar characteristics. Minor exceptions are the vibrational spectra of Ni and Co compounds. The strongest Raman band for M(SbF$_6$)$_2$ (M = Cr, Mn, Fe, Cu, Ag, Pd) is at ~650 cm^{-1}. In the Raman spectra of Ni(SbF$_6$)$_2$ (this work and [5]) the strongest band was always found at higher frequency at ~670 cm^{-1}. Co(SbF$_6$)$_2$ was a poor Raman scatterer and the spectrum obtained was of poor quality. Only a weak band at 670 cm^{-1} was observed. However its infrared spectrum closely resembles that of Ni(SbF$_6$)$_2$ (Fig. 5, Table 2). Even though some of the vibrational spectra of M(II) hexafluoroantimonates (M = Cr, Mn, Fe, Co, Ni, Cu, Ag, Pd) are not of the best quality, similar characteristics are noticeable. In all spectra, more bands are observed than would be expected for a regular SbF_6^- anion with O$_h$ symmetry. Bands in the region 500–560 cm^{-1} are typical for species where one fluorine bridges two different atoms, and can be readily assigned to M–F–Sb stretching modes. The bands in the region above 600 cm^{-1}, stronger than the stretching ones for bridging

Table 1
Vibrational spectra of M(SbF$_6$)$_2$ (M = Cr, Mn, Fe, Cu, Pd, Ag) compounds

Cr(SbF$_6$)$_2$		Mn(SbF$_6$)$_2$		Fe(SbF$_6$)$_2$		Cu(SbF$_6$)$_2$		Pd(SbF$_6$)$_2$		Ag(SbF$_6$)$_2$	
IR[a]	R	IR	R	IR	R	IR	R	IR	R	IR	R
724(sh)	719(30)	726(sh)	723(40)	712(sh)	724(70)	723(sh)	726(75)	722(sh)	722(60)	721(sh)	718(60)
702(vs)	695(20)	698(s)	698(25)	702(s)	700(40)	705(vs)	702(30)	697(vs)	697(40)	697(vs)	694(20)
	690(20)		690(25)		692(35)		694(25)		690(40)		687(15)
671(sh)		670(sh)	668(5)	671(sh)	669(20)	669(sh)		669(w)			
	644(100)		643(100)		645(100)		654(100)		644(100)		647(100)
639(m)		622(s)		621(m)		632(s)		622(m)		638(m)	
557(s)		537(s)		542(s)		557(s)		532(vs)		554(m)	530(5)
524(s)			509(5)		500(5)	531(s)	510(1)	519(s)	516(30)	502(s)	448(15)
							372(15)				335(5)
									314(sh)		315(2)
			302(20)		300(10)		303(25)		298(45)		
	290(15)		287(sh)				289(25)		286(50)		284(sh)
	276(10)		278(15)		282(20)		274(25)				273(45)
			268(10)		267(1)				265(sh)		256(25)
							256(1)				
			199(6)						216(10)		200(5)

[a] Intensities are given in parenthesis; w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

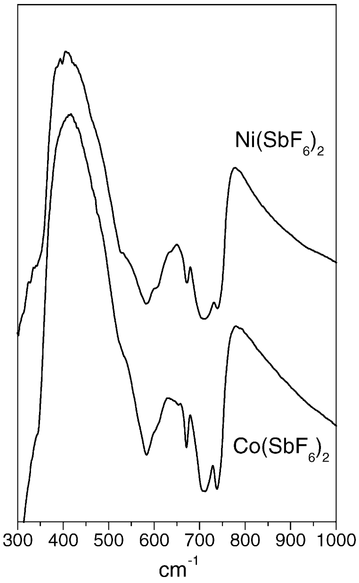


Fig. 5. Infrared spectra of Ni and Co hexafluoroantimonates.

Table 2
Infrared spectra of Ni and Co hexafluoroantimonates

Co(SbF$_6$)$_2$	Ni(SbF$_6$)$_2$	
IR[a,b]	IR[b]	IR[c]
738(s)	739(s)	740(vs)
712	713(vs, br)	716(s)
707(s)	704(vs, br)	708(s)
673(m)	672(ms)	673(ms)
656(w)	639(vw)	615(sh)
615(sh)	608(sh)	568(sh)
583(m)	582(s)	583(s)
521(sh)	526(sh)	521(m)

[a] Intensities are given in parenthesis; vw = very weak, ms = medium strong, s = strong, vs = very strong, sh = shoulder, br = broad.

[b] This work.

[c] Ref. [5].

fluorine atoms, can be assigned to Sb–F$_{\text{terminal}}$ stretching modes. Bands below 400 cm^{-1} are assigned to deformation and lattice modes.

The vibrational spectra of M(SbF$_6$)$_2$ (M = Cr, Mn, Fe, Co, Ni, Cu, Pd, Ag) confirm strong interactions between cation and anion via fluorine bridging, consistent with the highly

Table 3
X-ray powder diffraction patterns of the divalent transition metal hexafluoroantimonates[a]

Cr(SbF$_6$)$_2$		Mn(SbF$_6$)$_2$		Fe(SbF$_6$)$_2$		Co(SbF$_6$)$_2$		Ni(SbF$_6$)$_2$[b]		Cu(SbF$_6$)$_2$		Pd(SbF$_6$)$_2$		Ag(SbF$_6$)$_2$	
d	*I*/*I*$_0$	*d*	*I*/*I*$_0$	*d*	*I*/*I*$_0$	*d*	*I*/*I*$_0$	*d*	*I*/*I*$_0$	*d*	*I*/*I*$_0$	*d*	*I*/*I*$_0$	*d*	*I*/*I*$_0$
4.683	60	4.673	50			4.636	30	4.593	20	4.581	40	4.775	10	4.764	10
								4.416	20			4.491	10	4.238	10
4.256	100	4.228	90	4.270	60	4.210	50	4.208	80	4.181	60	4.199	70	3.954	90
3.858	60					3.942	10								
										3.799	70				
3.742	70	3.742	100	3.734	100	3.721	100	3.712	100	3.644	100	3.737	100	3.699	100
3.667	70							3.595	40					3.583	10
								3.320	10					3.323	5
								3.231	20						
2.792	50	2.755	50	2.745	50	2.728	40	2.714	60	2.758	50	2.756	60	2.834	50
2.699	30									2.716	50				
										2.654	50				
2.569	30	2.559	10	2.571	10	2.564	10	2.558	40	2.550	40	2.547	40	2.536	10
								2.434	10						
		2.375	10			2.388	10	2.377	10						
2.308	10					2.323		2.316	10						
2.244	30	2.246	50	2.238	50	2.243	50	2.229	60	2.241	20	2.248	40	2.228	10
2.212	10					2.176	10	2.175	10	2.188	30			2.142	10
2.159	10									2.123	20				
2.120	30	2.123	10	2.104	10	2.110	10	2.104	30	2.089	10	2.106	40	2.105	20
1.938	20					1.929	10			1.906	10			1.969	10
1.875	10	1.884	10	1.877	10	1.872	40	1.860	60	1.870	10	1.874	10	1.853	5
1.836	20	1.815	10							1.841	20				
1.799	30									1.817	40				
1.734	10	1.740	40	1.729	40	1.718	70	1.704	80	1.748	30	1.724	70	1.748	10
1.709	10									1.718	30				
1.689	10									1.681	30				
1.644	10	1.641	20			1.667	10	1.656	30	1.666	10	1.621	10	1.694	10
1.623	20			1.625	40	1.629	10	1.624	40	1.604	10				

[a] Up to date the crystal structures of M(SbF$_6$)$_2$ (M = Ag: triclinic, $P\bar{1}$, with $a = 522.4(1)$ pm, $b = 546.7(2)$ pm, $c = 877.9(2)$ pm, $\alpha = 75.78(2)^\circ$, $\beta = 89.02(2)^\circ$, $\gamma = 62.29(2)^\circ$ and $z = 1$ [4]; Pd: triclinic, $P\bar{1}$ with $a = 884.3$ pm, $b = 557.5$ pm, $c = 512.3$ pm, $\alpha = 117.3^\circ$, $\beta = 89.8^\circ$, $\gamma = 105.5^\circ$ and $z = 1$ [18]; Mn: triclinic, $P\bar{1}$, with $a = 517.3(2)$ pm, $b = 554.9(2)$ pm, $c = 888.2(2)$ pm, $\alpha = 73.98(3)^\circ$, $\beta = 89.17(2)^\circ$, $\gamma = 62.54(2)^\circ$ and $z = 1$ [17]) have been determined using single crystal data.

[b] Ref. [5].

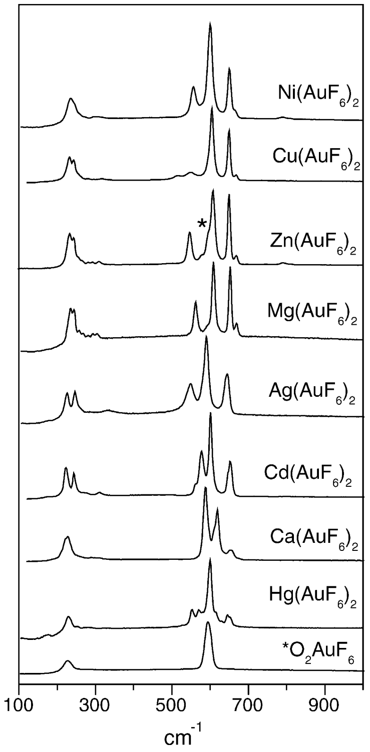


Fig. 6. Raman spectra of $M(AuF_6)_2$ (M = Ni, Cu, Zn, Mg, Ag, Cd, Ca, Hg) and O_2AuF_6.

distorted SbF_6 octahedra found in the known single crystal structures of $M(SbF_6)_2$ (M = Mn [17], Ag [4] and Pd [18]) compounds.

The small differences in the X-ray powder patterns of the divalent transition metal hexafluoroantimonates (Table 3) are probably the consequence, not only of slight differences in their crystal structures, but of the fact that metal(II) hexafluorantimonates, when isolated from aHF solution, are usually of low crystallinity and consequently yield very poor X-ray powder diffraction patterns.

2.3. *Hexafluoroaurates of divalent cations of transition metals*

New hexafluoroaurates of M = Ni, Cu, Ag, Zn, Cd, Hg were prepared by the reaction between KrF_2 or ultraviolet photolyzed F_2 and $MF_2/2AuF_3$ starting mixtures in aHF as solvent at room temperature:

$$MF_2 + 2AuF_3 + nF_2 \xrightarrow[298\,K]{aHF,\,UV} M(AuF_6)_2 \quad (M = Ni, Cu, Zn, Cd) \tag{2}$$

$$MF_2 + 2AuF_3 + nKrF_2 \xrightarrow[298\,K]{aHF} M(AuF_6)_2 \quad (M = Ni, Cu, Ag, Zn, Cd, Hg) \tag{3}$$

The final masses of the isolated products were in agreement with an 1:2 MF_2:AuF_5 molar ratio.

In some cases, a weak band at 1834 cm^{-1} was observed in the Raman spectra. Its position is typical of the O_2^+ cation in O_2AuF_6 [19]. This indicated that traces of O_2AuF_6 were also formed, even though they could usually not be detected by X-ray powder diffraction analysis. The presence of oxygen can be attributed to impure MF_2 or to slow diffusion of O_2 trough the wall of the FEP reaction vessel. Contaminated solid O_2AuF_6 products were redissolved in aHF and traces of O_2AuF_6 decomposed. The released AuF_5 is not stable in aHF at room temperature and, in aHF, is reduced to insoluble orange AuF_3 [20]. No band due to O_2^+ could be observed in the Raman spectra of solids recovered from decanted solutions.

Table 4
Raman spectra of $M(AuF_6)_2$ (M = Ni, Cu, Zn, Mg, Ag, Cd, Hg, Ca)

$Ni(AuF_6)_2$	$Cu(AuF_6)_2$	$Zn(AuF_6)_2$	$Mg(AuF_6)_2$	$Ag(AuF_6)_2$	$Cd(AuF_6)_2$	$Hg(AuF_6)_2$	$Ca(AuF_6)_2$
665(sh)[a]	669(5)	669(10)	669(20)				
650(50)	648(55)	650(95)	652(90)	646(50)	651(40)	653(sh)	652(15)
					647(sh)	645(15)	
							617(70)
						615(sh)	610(sh)
600(100)	602(100)	608(100)	609(100)	590(100)	600(100)	600(100)	586(100)
		578(sh)		579(sh)	576(55)	571(25)	
556(30)	549(10)	547(45)	562(50)	549(30)	561(15)	553(25)	
	513(5)						
				335(5)			
307(5)	316(2)	309(5)	304(5)		309(3)		308(1)
		293(2)	294(5)				
	279(1)	281(2)	282(2)		276(1)		287(1)
			268(3)				
			257(10)			254(5)	
244(sh)	242(20)	243(40)	243(35)	245(20)	243(20)		
235(25)	231(30)	233(45)	235(40)			229(25)	228(30)
				224(22)	222(25)		220(sh)
	179(1)				175(3)	177(5)	176(3)

[a] sh = shoulder.

Because of their strong oxidizing nature no infrared spectra could be taken and the characterization of new Au(V) salts was restricted to Raman spectroscopy and X-ray powder diffraction analysis. However, the Raman spectroscopy provides a qualitative indication of the degree to which the octahedral AuF_6^- anion interacts with its counterion, which is indicated by the increased number of anion bands observed when the anion is distorted by fluorine bridge formation with the cation (cited from Ref. [19]).

Raman spectra (Fig. 6, Table 4) of isolated $M(AuF_6)_2$ salts (M = Ni, Cu, Ag, Zn, Cd, Hg; including Mg and Ca—see Section 2.4) show more bands than expected for regular AuF_6^- anion, indicating that the salts obtained have relatively strong cation–anion interactions.

Raman spectra of the Ni, Cu, and Zn compounds, together with Mg salt, suggest that the products are structurally related. This is consistent with their similar X-ray powder diffraction patterns (Table 5), which resemble those of the corresponding $M(SbF_6)_2$ compounds.

Raman spectra and X-ray powder diffraction patterns of Ag and Cd compounds have similar features and differ from those of M = Ni, Cu, Zn and Mg.

The remaining $Hg(AuF_6)_2$ and previously known Ca salt (see Section 2.4) have X-ray powder diffraction patterns (Table 5) and Raman spectra (Fig. 6, Table 4) which differ from each other and from those of M = Ni, Cu, Zn, Mg and M = Ag, Cd.

2.4. Hexafluoroaurates of alkali-earth metals

Previously reported syntheses and characterization of hexafluoroaurates of Mg, Ca, Sr and Ba [10] were reinvestigated. Corresponding $MF_2/2AuF_3$ starting mixtures (M = alkali-earth metal) were exposed to KrF_2 or UV-

Table 5
X-ray powder diffraction data of $M(AuF_6)_2$ (M = Ni, Cu, Zn, Mg, Ag, Cd, Hg)

$Ni(AuF_6)_2$		$Cu(AuF_6)_2$		$Zn(AuF_6)_2$		$Mg(AuF_6)_2$		$Ag(AuF_6)_2$		$Cd(AuF_6)_2$		$Hg(AuF_6)_2$	
d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
												6.326	20
		4.857	10					4.836	90	4.875	80		
4.599	60	4.591	50	4.624	40	4.630	50	4.624	10				
								4.328	100	4.351	90		
4.087	100	4.131	100	4.163	90	4.167	100					4.179	70
												3.957	80
3.817	10	3.861	10	3.899	40							3.840	80
		3.729	50										
3.633	100	3.634	90	3.682	100	3.675	90					3.626	60
								3.324	50			3.293	80
								3.238	90	3.258	100	3.2011	20
								3.130	80			3.074	20
								3.037	10				
												2.844	10
		2.751	20									2.776	10
2.676	70	2.675	20	2.715	60	2.698	50					2.707	10
2.501	10	2.515	10	2.523	20	2.539	20	2.517	30	2.529	70	2.595	30
2.315	20	2.315	10	2.335	10	2.323	10	2.430	10	2.454	50		
2.194	50	2.213	10	2.220	40	2.207	70	2.271	30	2.252	80		
2.118	10	2.184	20	2.144	10	2.162	10	2.176	30	2.193	30		
								2.132	20	2.142	80		
2.056	30	2.060	30	2.076	20	2.090	20	2.070	40			2.087	50
								2.029	40	2.004	80	2.053	10
								1.997	40			1.989	50
								1.935	50			1.919	20
1.816	20	1.863	10	1.843	10	1.847	10					1.8838	50
1.786	10	1.809	10	1.805	10	1.796	10						
								1.779	90	1.772	80	1.751	10
								1.722	90			1.730	10
1.685	80	1.679	20	1.702	40	1.700	70	1.687	10			1.669	10
		1.629	10	1.642	30	1.647	10	1.646	30	1.659	20		
								1.626	60	1.641	20		
1.586	10	1.584	20	1.606	10	1.605	20	1.578	40	1.572	80		
								1.551	40	1.537	80		
								1.521	50				
		1.503	10	1.490	10	1.501	10	1.492	10				
		1.479	10	1.473	10	1.479	10	1.462	20	1.460	70		
1.490	10	1.463	10	1.455	10	1.455	10	1.445	20				

Table 6
X-ray powder diffraction data of $M(AuF_6)_2$ (M = Ca, Sr, Ba)

$Ca(AuF_6)_2$		$Sr(AuF_6)_2$[a]		$Sr(AuF_6)_2$[b]		$Ba(AuF_6)_2$[a] (type A)		$Ba(AuF_6)_2$[b] (type B)	
d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
7.470	30								
								5.666	30
								4.931	50
4.744	40	4.767	90	4.779	90	4.780	30		
4.361	40							4.411	30
		4.278	20	4.302	60				
4.184	100			4.091	60				
		3.850	10	3.866	60				
						3.703	60		
				3.494	10	3.497	100	3.488	100
3.349	10	3.374	100	3.377	100				
3.232	70			3.212	20			3.283	20
		3.176	20			3.153	50	3.139	10
						2.940	30	2.980	20
								2.859	10
2.764	80	2.754	10	2.769	20			2.740	20
								2.633	20
2.507	80			2.537	10			2.472	20
2.343	90	2.397	30	2.402	30	2.411	40	2.397	20
2.307	90	2.324	30	2.328	10	2.313	10	2.268	30
				2.283	10				
2.220	10	2.200	10	2.196	30	2.152	30	2.159	40
2.138	10			2.143	10				
2.099	10	2.092	80	2.094	80	2.028	100	2.019	50
				2.052	10				
				1.994	10				
2.006	20	1.956	90	1.959	90	1.973	10	1.979	30
1.922	10			1.922	10			1.949	20
		1.919	10	1.886	10			1.903	20
1.853	60			1.843	20	1.865	30	1.837	20
1.807	30	1.784	20	1.794	20			1.809	10
1.769	60					1.746	20	1.749	10
1.727	60	1.695	30	1.705	20			1.722	10
1.668	50	1.664	30	1.677	20				
1.655	50								
1.625	10					1.611	40	1.629	10
1.594	30							1.605	10
		1.585	10	1.581	20	1.588	20	1.567	10
1.539	70							1.546	30
								1.529	20
1.502	20	1.500	50	1.505	50			1.511	20

[a] Prepared by photochemical reaction [Eq. (4)].
[b] Prepared by KrF_2 [Eq. (5)].

irradiated, with F_2 in aHF as a solvent at room temperature:

$$MF_2 + 2AuF_3 + nF_2 \xrightarrow[298\,K]{aHF,\,UV} M(AuF_6)_2 \quad (M = Mg, Ca, Sr, Ba) \tag{4}$$

$$MF_2 + 2AuF_3 + nKrF_2 \xrightarrow[298\,K]{aHF} M(AuF_6)_2 \quad (M = Mg, Ca, Sr, Ba) \tag{5}$$

For each of the metals (M = Mg, Ca, Sr) the X-ray powder diffraction patterns (Tables 5 and 6) and vibrational spectra (Table 4, Figs. 6 and 7) of the corresponding isolated $M(AuF_6)_2$ salts were identical, regardless of synthetic path used (Eqs. (4) and (5)).

Barium proved to be a special case. Raman spectra (Fig. 8) and X-ray powder diffraction data (Table 6) of the isolated products, prepared by KrF_2 or UV-irradiated F_2 (Eqs. (4) and (5)), differ from each other and from those of Ca and Sr salts.

Additional experiments were carried out (Scheme 1). In the first, the solid product of photochemical reaction, i.e. $Ba(AuF_6)_2$—type A (Eq. (4)), was redissolved in aHF and treated with excess KrF_2. The Raman spectrum and X-ray powder diffraction pattern of the isolated solid corresponded to those of type B of $Ba(AuF_6)_2$.

In the second experiment, aHF was condensed onto solid $Ba(AuF_6)_2$—type B at 77 K. The reaction vessel was allowed to warm to room temperature and a clear yellow solution was obtained. After 10 min of intensive stirring,

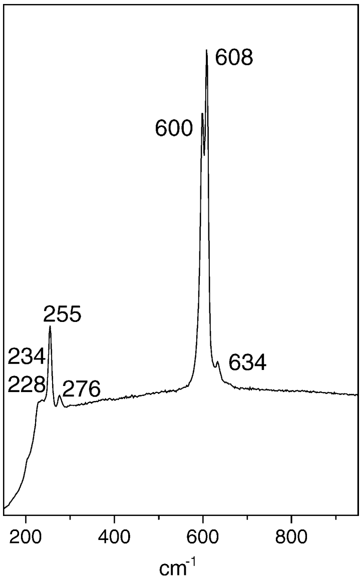


Fig. 7. Raman spectrum of $Sr(AuF_6)_2$.

volatiles were pumped away and the whole procedure was repeated. The Raman spectrum and X-ray powder diffraction analysis of the isolated solid showed that $Ba(AuF_6)_2$—type B was converted back to $Ba(AuF_6)_2$—type A. No vibrational bands belonging to O_2^+—or to KrF^+—salts could be detected in the Raman spectra of either type of $Ba(AuF_6)_2$. The presence of O_2^+—or KrF^+—by-products (i.e. O_2AuF_6 or $KrFAuF_6$) could be excluded.

In recent years it was found that compounds of the type $M(XF_6)_2$ (M = alkali-earth metal, X = As, Sb) can bind XeF_2, yielding a new type of coordination compound (i.e.: $M(XeF_2)_n(XF_6)_2$ [21–24]). It could be speculated that some KrF_2 are bound on $Ba(AuF_6)_2$ in the case of the type B compound. A report that alkali-earth metal hexafluoroaurates react with KrF_2 and form room temperature stable "clathrates" can be found in the literature [25]. There it was claimed that their Raman spectra showed an increase in the vibrational frequency of the Kr–F bond (up to 35 cm^{-1} shift) compared with KrF_2 (462 cm^{-1}), and a splitting of the vibrational band. Unfortunately, this preliminary report was never confirmed. In the Raman spectrum of $Ba(AuF_6)_2$ (type B), prepared by reaction between $BaF_2/2AuF_3$ mixture and KrF_2 in aHF, no vibrational bands which could be assigned to KrF_2 have been observed.

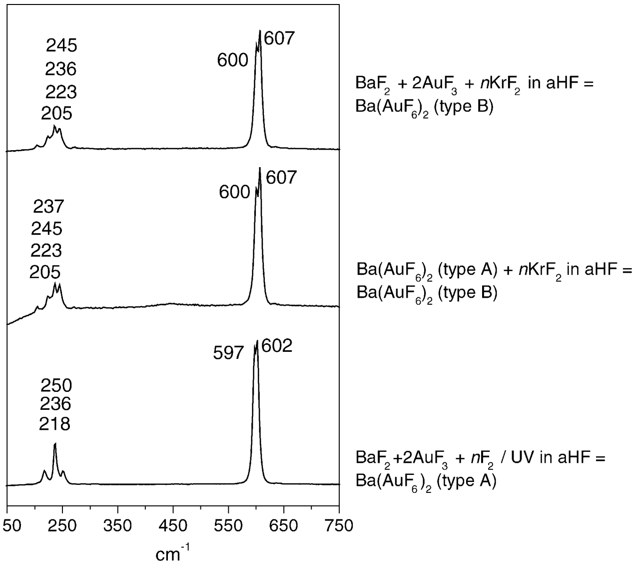
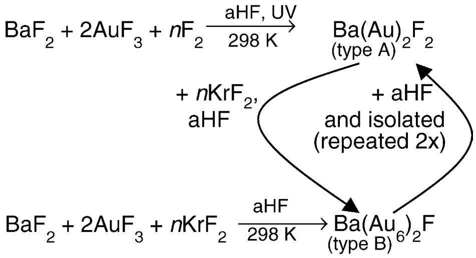


Fig. 8. Raman spectra of $Ba(AuF_6)_2$ (types A and B).



Scheme 1.

The other explanation for the existence of two different phases of $Ba(AuF_6)_2$ could be that one type is pure $Ba(AuF_6)_2$ compound, while the other is $Ba(HF)_n(AuF_6)_2$ compound. Many examples of HF containing compounds have been reported in recent years (i.e. $M(HF)_2(SbF_6)_2$, M = Mg, Ca [26]; $Ca(HF)(AsF_6)_2$ [27]).

An additional problem in clarifying Ba(II)/Au(V)/F-chemistry, is the discrepancy between the results of characterization (vibrational and X-ray powder diffraction analysis) obtained in this study and those previously claimed [10]. Mg, Ca, Sr and Ba hexafluoroaurates studied in this work have Raman spectra which differ from those of previously reported [10], not only in the positions of observed bands but also in their number. The Raman spectra of $Mg(AuF_6)_2$ and $Ca(AuF_6)_2$ compounds, obtained in this study, show particularly noticeable differences. They have more bands than previously reported [10], indicating relatively strong cation–anion interactions. $Sr(AuF_6)_2$ and both types of $Ba(AuF_6)_2$ compounds show the presence of more regular AuF_6^- octahedra.

The X-ray powder diffraction pattern of $Ca(AuF_6)_2$ reported in this work only partly matches the literature data [10]. Although the Raman spectrum of $Ba(AuF_6)_2$ (type B), prepared by reaction between $BaF_2/2AuF_3$ mixture and KrF_2 in aHF, differs from that reported [10], its X-ray powder diffraction pattern is in agreement with that reported by the same authors.

3. Conclusion

The previously reported X-ray single crystal analyses and the X-ray powder diffraction patterns indicate that three

Table 7
Known structural types of $M(XF_6)_2$ compounds determined by single crystal diffraction analyses (*) and by the comparison of X-ray powder diffraction patterns

X^V	M^{II}										
	Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pd	Ag	Au
As	Refs. [9,28][a]		Ref. [29][*,b]	Refs. [9,30][a]	Refs. [9,28][a]	Refs. [9,28][a]			Ref. [31][*,a]		
Sb	Refs. [4,9][a]	This work and Ref. [4][a]	Ref. [17][*,a]	This work[a]	This work and Ref. [30][a]	Ref. [5][a]	This work and Ref. [30][a]	Refs. [4,9,30][a]	Ref. [18][*,a]	Ref. [4][*,a]	Ref. [32][*,a]
Bi						Ref. [33][a]				Ref. [34][*,a]	
Au	This work[a]					This work[a]	This work[a]	This work[a]			–
Nb									Ref. [35][*,c]	Ref. [36][*,a]	
Ta										Ref. [36][*,a]	

[a] $Ni(SbF_6)_2$-type.
[b] $Mn(AsF_6)_2$-type.
[c] $Pd(NbF_6)_2$-type.

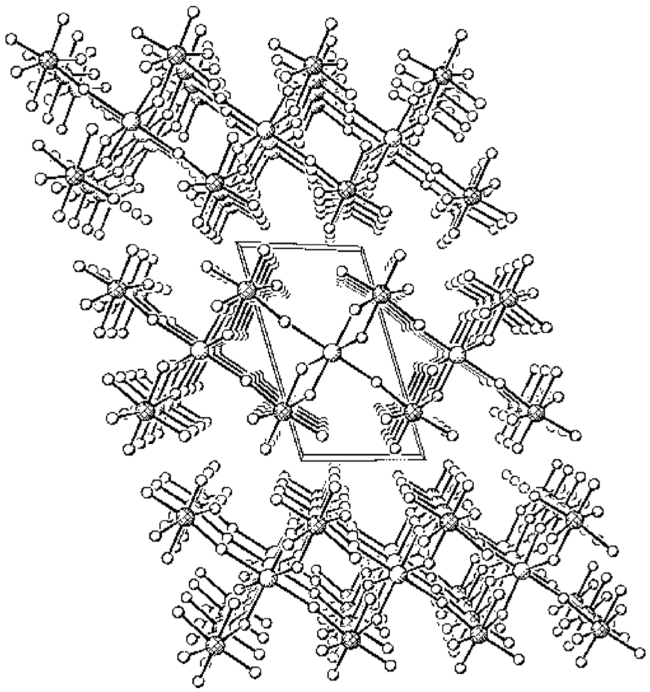


Fig. 9. Layered $Ni(SbF_6)_2$-structural type (small light spheres: F; large light spheres: M^{II}; large hatched spheres: X^V).

structural types are adopted by most of the known compounds with general formula $M^{II}(X^VF_6)_2$ (Table 7) [4,5,9,17,18,28–36].

The most common structural type is the $Ni(SbF_6)_2$-type (Fig. 9) where M atoms are in an octahedral environment of fluorine, and MF_6 octahedra are connected through their vertices to six XF_6 units on either side of the plane formed by the M atoms. There are only van der Waals contacts of fluorine atoms between neighbouring slabs and the network can be derived from the $CdCl_2$ type. 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. $M_{0.5}\square_{0.5}XF_6$.

There are probably slight differences between the crystal structures of different $M(XF_6)_2$ compounds crystallizing in $Ni(SbF_6)_2$-type due to the size and polarizing power of the cation. From single crystal diffraction analyses it is known that $Mn(SbF_6)_2$ and $M(XF_6)_2$ (M = Ag, Au, X = Sb, Bi) are isostructural to $Ni(SbF_6)_2$. However, Mn(II) is six-fold coordinated in $Mn(SbF_6)_2$, in contrast to the similar Ag and Au compounds in which, due to the Jahn–Teller effect, octahedra around the metal are so distorted that coordination around Ag^{II} and Au^{II} is better described as square-planar rather than octahedral.

Crystal structures of $Mn(AsF_6)_2$ [29] and $Pd(NbF_6)_2$ [35] differ from each other and from that of $Ni(SbF_6)_2$-type. $Mn(AsF_6)_2$ constitutes the rare example of an Mn(II) compound where Mn(II) shows the unusually high coordination number eight in a pure fluorine environment.

X-ray powder diffraction patterns of Ag, Cd and Hg hexafluoroaurates differ from those of the three types of crystal structures of $M(XF_6)_2$ compounds previously described. However, the X-ray powder diffraction patterns of Ag and Cd salt resemble each other. The $M(AuF_6)_2$ (M = Ca, Sr, Ba) salts reported in this work have X-ray powder diffraction patterns which differ from each other, and from those of $M(AuF_6)_2$ (M = Ni, Cu, Ag, Zn, Cd, Hg, Mg). On the basis of the results obtained in this study, it is still unclear if the compounds reported in [10] are pure $M(AuF_6)_2$ salts or not. Also, the correctness of all previously reported crystal structures of $M(XF_6)_2$ (M = Mg, Ca, Sr, Ba, X = As, Sb, Au) compounds, determined from X-ray powder diffraction data [10,37,38], is also in question.

For a definitive determination of the crystal structure of $M(AuF_6)_2$ (M = Ag, Cd, Hg, Ca, Sr, Ba) compounds, the proper way for preparing their corresponding single crystals should first be found. This will not be a simple task because, in the case of similar $M(XF_6)_2$ (M = Mg, Ca, Sr, Ba, X = As, Sb) compounds, the single crystals obtained from corresponding solutions in aHF, have not been $M(XF_6)_2$ salts but new coordination compounds of the type $M(HF)_n(XF_6)_2$ [26,27]. In the case of M = Au and X = Sb the crystal structures of $Au(SbF_6)_2$, [32] and $[Au(HF)_2](SbF_6)_2{\cdot}2HF$ [15] are already known.

4. Experimental details

4.1. Apparatus and reagents

Volatile materials (BF_3, SbF_5, aHF) were handled in an all Teflon vacuum line equipped with Teflon 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 reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with Teflon valves and Teflon coated stirring bars. Reaction vessels combined from two FEP tubes in a T-shape manner and equipped with Teflon valve were used in some experiments. Prior to their use all reaction vessels were passivated with elemental fluorine. Fluorine was used as supplied (Solvay, 99.98%). Anhydrous HF (Fluka, Purum) was treated with K_2NiF_6 for several hours prior to use. MF_2 (M = Fe, Co, Ni, Cu, Zn, Mg, Ca, Sr, Ba) were used as supplied. AgF_2 and HgF_2 were prepared by reaction of $AgNO_3$ or $HgCl_2$ with elemental fluorine in a nickel reactor at high temperature. CdF_2 was prepared by pressure fluorination of $CdCl_2{\cdot}H_2O$ with elemental fluorine in aHF in an FEP reaction vessel [39]. $InBF_4$ was prepared from a piece of metallic In wire and excess of BF_3 as described previously [40]. AuF_3 was prepared from metallic gold wires and BrF_3 as described [41]. SbF_3 (Alfa Aesar, 99%) was treated with aHF in order to remove possible traces of Sb_2O_3. SbF_5 was prepared by high temperature fluorination of SbF_3 by elemental fluorine in a flow reaction. KrF_2 was synthesized as described [42].

4.2. Instrumentation

Infrared spectra were taken on a Perkin-Elmer FTIR 1710 spectrometer on powdered samples between AgCl windows in a leak tight brass-cell. Raman spectra were recorded on a Renishaw Raman Imaging Microscope System 1000, with He–Ne laser with wavelength 632.8 nm. X-ray powder diffraction patterns were obtained using the Debye–Scherrer technique with Ni-filtered Cu Kα radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry box. Intensities were estimated visually.

4.3. Synthesis

4.3.1. General procedure

In a glove box, starting materials were loaded into an FEP reaction vessel aHF—and, when necessary, SbF_5 or KrF_2—were condensed onto solid reactants at 77 K, which were then brought to room temperature. Fluorine was added when needed. The reaction mixtures were vigorously agitated and after some time volatiles were pumped away. Isolated products were characterized by mass balance, vibrational spectroscopy, and X-ray powder diffraction patterns (XRPD-pattern).

4.3.2. Attempts to prepare new fluoroantimonates of monovalent cations

aHF and excess SbF_5 were added onto $InBF_4$. After 3 days, volatiles were pumped away. The Raman spectrum of the isolated white solid have bands (707(100), 657(95), 316(10), 269(40), 221(5)) which could be assigned to $InF_3{\cdot}3SbF_5$. The rest (670(70), 656(80), 633(100), 571(10), 530(5), 290(20)) belong to a by-product, probably $SbF_3{\cdot}xSbF_5$ compound.

A solution of $Au(SbF_6)_2$ in aHF/SbF_5 was prepared as reported [32]. A dark metallic precipitate formed immediately after the solution came in contact with hydrogen. The lines in XRPD-pattern of the isolated solid could be assigned to Au metal.

HgF_2 was dissolved in aHF acidified with a large excess of SbF_5. A clear colourless solution was obtained. With slow addition of hydrogen, a white precipitate formed. After some time, the clear colourless solution was decanted. From Raman spectroscopy, the white product recovered from the solution contains mainly $Hg(SbF_6)_2$; the strongest bands in the Raman spectrum of the white precipitate (670(sh), 660(100), 288(25), 195(20)) could be assigned to $Hg_2(Sb_2F_{11})_2$ [16].

A reaction mixture containing metallic Cu-wires (10 mmol), SbF_5 (3 mmol) and aHF (3 ml) was prepared. After 1 week yellow-orange crystals formed at the each end of all the Cu-wires. The vibrational spectra (Fig. 1) on powdered samples obtained by grinding selected single crystals were in agreement with the formation of $CuSbF_6$ salt.

4.3.3. Hexafluoroantimonates and hexafluoroaurates of divalent cations

$M(SbF_6)_2$ compounds were prepared from the corresponding difluorides and an excess of SbF_5 in aHF as previously described [4], and/or by fluorination of $MF_2/nSbF_3$ ($n \geq 2$) mixtures by elemental F_2 in aHF at room temperature. $Pd(SbF_6)_2$ was prepared from Pd metal, SbF_5 and F_2 in aHF as previously described for $Pd(AsF_6)_2$ [31].

Hexafluoroaurates were prepared from the corresponding MF_2/AuF_3 (0.3 mmol/0.6 mmol) starting mixtures and elemental fluorine (∼4 bar) or KrF_2 (∼3 mmol) in aHF (3–5 ml) at room temperature. When elemental fluorine was used, the reaction mixtures were exposed to UV-light (1–2 days). For M = Mg, Ca, Sr, Ba, Cd all syntheses were determined to be complete when clear yellow solutions were obtained. Products of reactions, where M = Ni, Cu and Zn, were only sparingly soluble or, where M = Ag and Hg, almost insoluble in aHF. In this case the syntheses were determined to be complete when undissolved solid in the bottom of the reaction vessel turned from orange (colour of AuF_3) to yellow (M = Ni, Cu, Zn, Hg) or turquoise green (M = Ag). Volatiles were pumped away at room temperature. Isolated solid products were yellow (from canary to dark yellow) except green $Ag(AuF_6)_2$. Final masses of isolated solids corresponded to MF_2:AuF_5 = 1:2 molar ratios, indicating the formal composition $M(AuF_6)_2$ of isolated products. Raman spectra and X-ray powder diffraction patterns of isolated solids have been taken.

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