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Room Temperature Syntheses of AuF_6^- and PtF_6^- Salts, $Ag^+AuF_6^-$, $Ag^{2+}PtF_6^{2-}$, and $Ag^{2+}PdF_6^{2-}$, and an Estimate for $E(MF_6^-)$ [M = Pt, Pd]

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Solutions of AuF_4^- or PtF_6^{2-} salts, prepared from the metals at ∼20 °C, in liquid anhydrous hydrogen fluoride (aHF), made basic with alkali fluorides, are further oxidized by photodissociated F_2 (visible or near-UV light) to give AuF_6^- or PtF_6^- salts, including $O_2^+AuF_6^-$ (with O_2 in the F_2). Similar photochemical oxidation of PdF_6^{2-} salts does not occur. This new synthetic approach has provided $LiAuF_6$ and $LiPtF_6$ for the first time, each of which has the $LiSbF_6$ type ($R\bar{3}$) structure with (hexagonal cell): $LiAuF_6$, $a = 4.9953(9)$ Å, $c = 13.704(3)$ Å, $V/Z = 98.71(6)$ Å^3; $LiPtF_6$, $a = 5.0236(7)$ Å, $c = 13.623(2)$ Å, $V/Z = 99.25(5)$ Å^3. Interaction of AuF_6^- with Ag^+ gives $Ag^+AuF_6^-$ ($R\bar{3}$, $a = 5.283(3)$ Å, $c = 15.053(6)$ Å, $V/Z = 121.3(2)$ Å^3), whereas PtF_6^{2-} or PdF_6^{2-} stabilize Ag^{2+} as $Ag^{2+}Pt(Pd)F_6^{2-}$ ($R\bar{3}$; $AgPtF_6$: $a = 5.049(8)$ Å, $c = 14.46(2)$ Å, $V/Z = 106.4(5)$ Å^3; and $AgPdF_6$, $a = 5.00(4)$ Å, $c = 14.6(2)$ Å, $V/Z = 105(3)$ Å^3). New cubic modifications (probable space group $Ia3$) have been found for $AgMF_6$ (M, a value, Å): Ru, 9.653(10); Os, 9.7318(9); Ir, 9.704(2). The preference for $Ag^{2+}Pt(Pd)F_6^{2-}$ over $Ag^+Pt(Pd)F_6^-$ is attributed to a second electron affinity of $Pt(Pd)F_6$, $E(Pt(Pd)F_6^-) > 60$ kcal mol^{-1}.

Introduction

Recent work in these laboratories[1] showed that gold or the platinum metals, (except rhodium) are able to react at room temperature with F_2 in aHF, containing an alkali fluoride, to provide salts of AuF_4^- or MF_6^- (M = Ru, Os, Ir), or PtF_6^{2-}. This, and similar findings by Holloway and co-workers[2] for the preparation of ammonium salts of the platinum metal fluoroanions, gave broad and easy access to noble-metal fluorocomplexes, but neither AuF_6^- nor PtF_6^- were included, nor other related high oxidation-state salts such as AgF_4^- and NiF_6^{2-}. It was quickly found in these laboratories that photochemical excitation of the F_2 (sunlight or near-UV), the preparative conditions otherwise being similar, gave AuF_6^- or PtF_6^- salts. In addition, it was shown that even the difluorides AgF_2 and NiF_2, which are themselves insoluble in aHF, would react with the F atoms in basic aHF to give[3,4] salts of AgF_4^- and NiF_6^{2-}. Attempts to similarly prepare PdF_6^- salts have failed.

Although AuF_6^- and PtF_6^- salts were originally prepared at higher temperatures and fluorine pressure in nickel bombs[5,6] more than twenty-six years ago, this is the first time that the salts $LiAuF_6$ and $LiPtF_6$ have been prepared and structurally characterized. This paper gives a description of the syntheses of the AuF_6^- and PtF_6^- salts and compares the new $LiAuF_6$ and $LiPtF_6$ with other relatives of the third transition series. It also reports the new $Ag^+AuF_6^-$ salt which is contrasted structurally and chemically with $Ag^{2+}PtF_6^{2-}$ and $Ag^{2+}PdF_6^{2-}$. The latter salts were first reported but not structurally identified by Müller and Hoppe.[7] These $AgMF_6$ salts are compared structurally with others of the same stoichiometry.

The stabilization of Ag^{2+} by PtF_6^{2-} or PdF_6^{2-} indicates that the first ionization potential of these dianions is unusually high for MF_6^{2-} transition element species and an estimate of that energy, expressed as $E(MF_6^-)$, has been attempted.

Experimental Section

Materials. Anhydrous HF and fluorine were supplied by Matheson Gas Products (East Rutherford, NJ), Ag_2O by Lancaster Synthesis Inc. (99+%; Windham, NH) and Au by ROC/RIC (99.99%; Sun Valley, CA). Pd, Pt and Ir were supplied by Engelhard Corp. (East Newark, NJ), Os by Strem Chemicals (Newburyport, MA) and Ru from Johnson Matthey & Co. (London, UK). The alkali fluorides (Allied Chemical, B&A quality, Morristown, NJ) were dried at 150 °C under dynamic vacuum ($<10^{-6}$ Torr).

The noble metals were always used as fine powders. Ruthenium, osmium and iridium were heated (∼700 °C) under hydrogen, to minimize oxide coating, the metals being cooled in hydrogen and otherwise exposed only to dry argon or nitrogen. Otherwise, the metal powders were used as supplied.

AgF was prepared from Ag_2O through reaction with aHF. The AgF obtained in that way is orange in the solid state and dissolves in aHF yielding a colorless solution with no residue. To avoid photodecomposition it was stored in an FEP tube wrapped with Al foil. AgF_2 was synthesized by oxidation of AgF in aHF with F_2 at room temperature.

Li_2PtF_6,[1] AuF_3,[8] SF_3MF_6[9] (M = Os, Ir), RuF_5,[10] $Ag(BiF_6)_2$,[11] K_2MF_6[1] (M = Pd, Pt), Cs_2PdF_6,[1] O_2AsF_6,[12] PdF_4,[13] $AgAsF_6$,[11] and $AgPF_6$[11] were prepared as previously described.

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Apparatus and Technique. A nickel vacuum line, fluorine handling equipment, and Teflon valves were used as previously described.[14] For all preparations two $^{1}/_{2}$- or 1-in. o.d. FEP tubes (CHEMPLAST Inc., Wayne, NJ), each sealed at one end and drawn down to $^{3}/_{8}$-in. o.d. at the other, were joined at right angles to a Teflon Swagelock T compression fitting. This assembly was joined to a Teflon valve by a small section of 3/8-in. o.d. FEP tubing drawn down to $^{1}/_{4}$-in. o.d. Such a reactor was connected to the vacuum line via an 1-ft. length of $^{1}/_{4}$-in. o.d. FEP tubing which facilitates the decantation of solutions from one arm to the other. The T reactors were evacuated, passivated with fluorine (2 atm) and evacuated again before use.

Anhydrous HF was condensed from the cylinder into a Teflon-valved reservoir FEP tube containing K_2NiF_6 (Ozark-Mahoning Pennwalt, Tulsa, OK) in order to destroy traces of water.

All solids were manipulated in the dry Ar atmosphere of a Vacuum Atmospheres Corp. DRILAB.

Preparations. General Comments for AMF_6 and A_2MF_6 Salts (A = Alkali). Preparations in aHF can make use of the high solubility of each alkali fluoride in this solvent,[15] the low solubility of the heavier alkali MF_6^- salts and the moderately good solubility of the $LiMF_6$. The reverse relationship holds for A_2MF_6 salts, where Li_2MF_6 are usually of low solubility and A = K, Cs of *much* higher solubility.

$LiPtF_6$ from Li_2PtF_6 and F_2. Li_2PtF_6 prepared from Pt, 2LiF, and F_2 in aHF at ~20 °C as previously described[1] is of low solubility in aHF (the statement[1] that it is "very soluble" should read *slightly soluble*). Li_2PtF_6 (427.6 mg, 1.324 mmol) was placed in one arm of the T reactor and aHF (5 mL) condensed on it. At ~20 °C some of the Li_2PtF_6 dissolved to yield a faintly yellow solution. Fluorine to 1500 Torr was added, and the reactor was placed (with agitation) in the sunlight. The color of the solution gradually intensified (repressurized with fluorine after 3 days), and after 9 days the bright yellow solution was decanted and all volatiles removed. The XRDP of the solid from the decantate (287.2 mg; 0.909 mmol) showed only the characteristic pattern of an $LiSbF_6$-type compound ($a = 5.0236(7)$ Å, $c = 13.623(2)$ Å; see Table S1); that of the residue (137.3 mg; 0.425 mmol) showed only Li_2PtF_6.

O_2AuF_6 from AuF_3 and F_2 (O_2 Contamination). An attempt to prepare AuF_5 directly from AuF_3 in aHF employing photo dissociation of F_2 did not succeed but produced O_2AuF_6 (via O_2, probably from a small leak). AuF_3 (680.2 mg; 2.678 mmol) in aHF (~13 mL) at ~20 °C was agitated with F_2 (6 mmol) and O_2 impurity, in an FEP T reactor, in the sunlight for 20 days. The bright yellow solution was decanted from unreacted AuF_3. The XRDP of the bright yellow solid from the decanted solution revealed that it was O_2AuF_6,[16,17] the residue being unreacted AuF_3.

$LiAuF_6$ ($CsAuF_6$) from AuF_3 and LiF (CsF). An FEP T reactor was loaded with AuF_3 (654.1 mg, 2.576 mmol for $LiAuF_6$; 463.0 mg, 1.823 mmol for $CsAuF_6$) in one arm and LiF (99.5 mg, 3.836 mmol) or CsF (450.3 mg, 2.964 mmol), respectively, in the other, and aHF (~2 mL) was condensed at −196 °C in each limb of each T reactor. The alkali fluoride was dissolved in the aHF at 20 °C, and the solution was poured onto the AuF_3 (itself insoluble in aHF) to produce a yellow solution of AuF_4^- over some undissolved AuF_3. F_2 was added to a total pressure of 1500 Torr, and each reactor was placed in the sunlight and agitated for 8 days. Much of the remaining AuF_3 dissolved within 1 day. After 4 days the reactor was repressurized with F_2 (1500 Torr) and replaced in the sunlight. In the case of the reaction to produce $LiAuF_6$ already after 1 day the color of the solution intensified to bright lemon yellow while in the case of $CsAuF_6$ the solution color faded because of the low solubility of that product, this solubility being further lowered by the common ion effect of the excess cesium fluoride. Four days later the reactor was re-attached to the vacuum line, the aHF was cooled to −196 °C, and the excess fluorine was pumped off. The solution of $LiAuF_6$ was separated from a small amount of residue (23.2 mg) by decantation, and all volatiles were removed. The XRDP of the solid obtained from the decanted solution (847.6 mg) showed an $LiSbF_6$-type pattern ($a = 4.9953(9)$ Å; $c = 13.704(3)$ Å; see Table S2). Decantation of the solution of excess CsF left a residue of $CsAuF_6$ (825.0 mg; 1.859 mmol), the XRDP of which was entirely that of $CsAuF_6$.[17]

$KAuF_6$ from Au, KF, and F_2. Au (62.7 mg, 0.318 mmol) and KF (21.6 mg, 0.372 mmol) were placed in one arm of an FEP T reactor, and aHF (~3 mL) was condensed at −196 °C. After being warmed to ~20 °C, the potassium fluoride dissolved and the reactor was pressurized with fluorine. Agitation overnight afforded a yellow solution of $KAuF_4$. The T apparatus was pressurized again with fluorine (1400 Torr) and agitated overnight under UV irradiation (low-pressure Hg lamp). All volatiles were removed under dynamic vacuum. The XRDP of the product showed the pattern of $KAuF_6$[17] with slight $KAuF_4$[18] impurity.

Attempted Fluorination (with UV Irradiation) of K_2PdF_6 and Cs_2PdF_6. Solutions of Cs_2PdF_6 or K_2PdF_6 in aHF, which were pressurized with F_2 (~1 atm), were irradiated with UV for extended periods (>24 h). The constant product weights and the negligible F_2 consumption indicated that oxidation had not occurred.

Synthesis of $Ag^{I}M^{V}F_6$ Salts (Table 1 Gives Quantities; M = Os, Ir, Au, Ru, Bi). The silver-containing salt (AgF or $AgBF_4$) was loaded into one tube of a passivated FEP T reactor inside the DRILAB. The appropriate noble metal salt ($LiAuF_6$, SF_3OsF_6, SF_3IrF_6, RuF_5) or bismuth fluoride, BiF_5, was placed in the other tube of the reactor. For the synthesis of $AgMF_6$ with M = Au, Os, Ir, Bi, aHF was condensed onto each of the reagents. Upon warming to room temperature, the salts dissolved completely affording colorless (AgF, $AgBF_4$, BiF_5, SF_3OsF_6, SF_3IrF_6) or yellow ($LiAuF_6$) solutions. As the respective AgF and $AgBF_4$ solutions were slowly poured onto the SF_3MF_6 (M = Os, Ir) and BiF_5 solution, there was vigorous gas evolution (SF_4 or BF_3) and a solid precipitated (orange $AgIrF_6$, colorless $AgOsF_6$, and light yellow $AgBiF_6$). For the synthesis of $AgRuF_6$ the AgF solution was poured slowly onto the dry RuF_5. $AgRuF_6$ formation was immediately evident as the green RuF_5 was replaced by an orange solid (in <1 min). For the synthesis of $AgAuF_6$, both limbs of the reactor were cooled to about −50 °C (methanol/dry ice), the AgF solution was poured into the other arm to precipitate an orange-brown solid (colorless supernatant), and the mixture was agitated at −50 °C for ~10 min.

All $AgMF_6$ salts were insoluble in aHF and were washed with it (typically three times). Volatiles were removed under dynamic vacuum. For $AgAuF_6$ the tube containing it was always kept at ~−50 °C. Because $AgRuF_6$ was photosensitive, the FEP storage tubes were wrapped in Al foil. The XRDP of the $AgMF_6$ salts gave a cubic unit cell for M = Ru, Os, Ir {M, a value, Å: Ru, 9.653(10); Os, 9.7318(9); Ir, 9.704(2); see Tables S3−S5}, a trigonal−rhombohedral one for $AgAuF_6$ {a = 5.283(3) Å, c = 15.053(6) Å; see Table S6} and a tetragonal one for $AgBiF_6$ {a = 5.079(2) Å, c = 9.552(3) Å; see Table S7}.[11]

Preparations of $AgPt(Pd)F_6$ (Table 1 Gives Quantities): (a) Interaction of $AgAsF_6$ with O_2PtF_6. The yellow solution over solid O_2PtF_6 in aHF was agitated, at ~20 °C, with the colorless slightly soluble $AgAsF_6$ until the solution color of PtF_6^- had almost disappeared, there being a deep-red insoluble residue. Decantation and washing (several times) provided yellow tinted crystalline O_2AsF_6 (XRDP showing only this). The yellow color probably comes from a small quantity (too small to give an XRDP) of O_2PtF_6. The XRDP of the deep-red insoluble product gave a pattern that was wholly indexed on the basis of a rhombohedral cell {hexagonal cell with a = 5.049(8) Å, c = 14.46(2) Å; see Table S8}.

(**b) Interaction of $Ag(BiF_6)_2$ with $K_2Pt(Pd)F_6$.** Interaction of solid $Ag(BiF_6)_2$ shaken slowly into a −50 °C solution of $K_2Pt(Pd)F_6$ produced a brown precipitate. Complete $Ag(BiF_6)_2$ transfer was ensured by washing over with two back-distillations of aHF. The brown precipitate was washed with aHF at ~20 °C (three times). An XRDP of this solid gave a rhombohedral-like pattern as observed in (a) but less crystalline

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Table 1. Summary of Reaction Weights for the Syntheses of $AgMF_6$ Salts[a]

	reactant 1	reactant 2	aHF (mL)	insol. product	decantate	
	$LiAuF_6$	AgF		$AgAuF_6$	$AgF(HF)_n/LiF(HF)_n$	
m_{obs}	**126.4**	**69.9**	**1**	**166.9**	**40.1**	
n_{obs}	(0.398)	(0.551)		(0.399)		
m_{calc}				167		
	SF_3IrF_6	AgF		$AgIrF_6$	$AgF(HF)_n$	SF_4↑
m_{obs}	**241**	**118**	**0.75**	**248**		
n_{obs}	(0.610)	(0.930)		(0.599)		
m_{calc}				252		
	SF_3OsF_6	AgF		$AgOsF_6$	$AgF(HF)_n$	SF_4↑
m_{obs}	**264**	**104**	**0.75**	**265**		
n_{obs}	(0.671)	(0.820)		(0.643)		
m_{calc}				277		
	RuF_5	AgF		$AgRuF_6$	$AgF(HF)_n$	
m_{obs}	**409**	**311**	**1.5**	**650**		
n_{obs}	(2.086)	(2.451)		(2.013)		
m_{calc}				674		
	BiF_5	$AgBF_4$		$AgBiF_6$	BiF_5	BF_3↑
m_{obs}	**347**	**206**	**1.0**	**467**		
n_{obs}	(1.142)	(1.058)		(1.084)		
m_{calc}				456		
	K_2PtF_6	$Ag(BiF_6)_2$		$AgPtF_6$	$KBiF_6/K_2PtF_6$	
m_{obs}	**292**	**524**	**2.6**	**333**[b]	**489**	
n_{obs}	(0.754)	(0.695)				
m_{calc}				290	503	23
	K_2PdF_6	$Ag(BiF_6)_2$		$AgPdF_6$	$KBiF_6/K_2PdF_6$	
m_{obs}	**316**	**752**	**2.3**	**357**[b]	**724**	
n_{obs}	(1.058)	(0.998)				
m_{calc}				328	722	18
	$KPtF_6$	AgF		$AgPtF_6$	$AgF(HF)_n/KF(HF)_n$	
m_{obs}	**61**	**43**	**1.5**	**79**[b]		
n_{obs}	(0.175)	(0.339)				
m_{calc}				73		
	O_2PtF_6	$AgAsF_6$		$AgPtF_6$	O_2AsF_6	
m_{obs}	**90.0**	**78.3**	**1**	**114.1**	**41.7**	
n_{obs}	(0.264)	(0.264)		(0.274)		
m_{calc}				110.0	58.3	

[a] ***n***, mmol in parentheses; ***m***, weights, in mg calculated and observed (observed in **bold** type). [b] These solids were not taken to dryness before they were washed with aHF, hence they were contaminated by (noncrystalline) adsorbed salts.

than it. The two patterns ($AgPdF_6$ and $AgPtF_6$) were nearly indistinguishable in line positions {a = 5.00(4) Å, *c* = 14.6(2) Å for $AgPdF_6$; see Table S9}.

(c) Interaction of AgF with $KPtF_6$. A solution of AgF in aHF was added to dry $KPtF_6$, and the mixture was agitated at ~20 °C (2 h). The red-brown product was washed (2×) with aHF to remove AgF excess. XRDP of the red-brown product showed a complex pattern akin to that of Ag_2SnF_6 with AgF_2 possibly also present. Fluorination of it in aHF at ~20 °C (1400 Torr of F_2) overnight produced a red-brown (aHF insoluble) product the XRDP of which was a combination of the pattern of rhombohedral-like $AgPtF_6$ (obtained in (a)) with that of AgF_2 {evidently the crystalline component (Ag_2PtF_6) had been fluorinated to AgF_2 and $AgPtF_6$}.

(d) Interaction of AgF_2 with PdF_4 in BrF_3/BrF_5. Interaction of AgF_2 with PdF_4 in BrF_3/BrF_5 at 90 °C followed by fluorination with F_2 at 250 °C gave a product the powder pattern of which showed the rhombohedral-like pattern of $AgPtF_6$ obtained in (a) together with some weak lines of an unidentified phase.

X-ray powder diffraction samples were prepared as previously described,[14] the X-ray diffraction pattern (XRDP) being recorded on film using Ni-filtered Cu Kα radiation (General Electric Co. precision camera, Straumanis loading). The program ERACEL[20] was used for the refinement of the lattice parameters which incorporates the Nelson-Riley extrapolation function.[21] The $AgMF_6$ salts (M = Os, Ir, Ru) show a cubic pattern similar to the one of O_2PtF_6[16,22] (*Ia*3) and the patterns were fully indexed on an *I* cubic unit cell with *Z* = 8 (see Table S3−S5). The observed line intensities match well with those calculated using the MF_6^- ion positional parameters from the single-crystal structure[16] of O_2PtF_6 with Ag atoms in $^1/_4$ $^1/_4$ $^1/_4$ (8a). These $AgMF_6$ salts were previously reported to adopt the $KNbF_6$ structure type,[23] however the cubic form (reported here for the first time) is always obtained from aHF solution. The same holds for $KSbF_6$. **$Ag^IAu^VF_6$** is isostructural with $LiSbF_6$ ($R\bar{3}$) and is so far the only $Ag^+MF_6^-$ salt of a second- or third-row transition series element known to adopt this structure type. The XRDP pattern (see Table S6) contained also lines of some $AgAuF_4$ impurity.[24] **$AgPtF_6$** and **$AgPdF_6$** are also isostructural with $LiSbF_6$ (see Table S8 and S9); however, they are to be formulated as $Ag^{II}M^{IV}F_6$ and not $Ag^IM^VF_6$. The possible departure from rhombohedral symmetry (that could arise from a Jahn−Teller distortion associated with Ag^{2+}) could be largely masked by the breadth of the lines. If so, the departure from rhombohedral symmetry must be subtle. There is a hint of small line splitting in the more crystalline samples of $AgPtF_6$ (obtained from the rather slow interaction of $AgAsF_6$ with O_2PtF_6). **$AgBiF_6$** (see Table S7) is isostructural with $KNbF_6$ (tetragonal, $P\bar{4}2m$) as previously reported for $AgMF_6$ (M = Os, Ir, Ru).[23]

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(24) Mayorga, S. Ph.D. Thesis, University of California at Berkeley, 1988; p 106; characterized by a tetragonal pattern with *a* = 5.798(3) Å, *c* = 10.806 Å, *V* = 363.2(5) Å^3, *Z* = 4.

Table 2. Trigonal Unit Cells for the Rhombohedral ($R\bar{3}$) $LiMF_6$ Salts of the Second and Third Transition Series[31]

	$LiNbF_6$	*$LiMoF_6$*[a]	$LiRuF_6$	$LiRhF_6$
a/Å	5.304(2)	*5.190*	5.0751(4)	5.0161(6)
c/Å	13.576(4)	*13.585*	13.543(1)	13.547(2)
c/*a*	2.560(2)	*2.618*	2.6685(4)	2.7007(8)
V/*Z*	110.3(2)	*105.6*	100.70(3)	98.40(4)

	$LiTaF_6$	*$LiWF_6$*[a]	*$LiReF_6$(?)*[a,b]	$LiOsF_6$	$LiIrF_6$	$LiPtF_6$	$LiAuF_6$
a/Å	5.3120(7)	*5.234*	5.057 (?)	5.1007(5)	5.061(1)	5.0236(7)	4.9953(9)
c/Å	13.609(2)	*13.606*	13.735 (?)	13.608(2)	13.622(3)	13.623(2)	13.704(3)
c/*a*	2.5619(8)	*2.600*	2.716 (?)	2.6679(7)	2.692(2)	2.7118(8)	2.743(2)
V/*Z*	110.85(4)	*107.6*	101.4 (?)	102.20(4)	100.67(7)	99.25(5)	98.71(6)

[a] These data were taken from Kemmit et al.[23]; all other cell parameters were obtained in this work from XRDP taken with Cu Kα radiation (Ni filter), the indexing being carried out with the program ERACEL which refines lattice parameters applying a Nelson−Riley extrapolation function. [b] Eight out of 23 lines in the powder pattern of the compound could not be indexed on the basis of a rhombohedral unit cell; the authenticity of the compound is therefore doubtful.

Magnetic measurements were carried out using a Superconducting Quantum Interference Device (SQUID) as previously outlined.[25] The temperature dependence of the magnetic susceptibility was measured for $AgPdF_6$ and $AgAuF_6$. **$AgPdF_6$** was found to be a Curie−Weiss paramagnet with $\Theta = 4.4$ K, $\mu = 1.80\ \mu_B$. This value is lower than the one previously reported[7] ($\mu = 1.97\ \mu_B$). This can be attributed to some diamagnetic contamination (adsorbed $KBiF_6$) of the sample measured here. **$AgAuF_6$** was found to be diamagnetic. The magnetic properties of $AgOsF_6$ ($\mu = 2.95\ \mu_B$), $AgIrF_6$ ($\mu = 1.24\ \mu_B$), and $AgRuF_6$ ($\mu = 3.91\ \mu_B$) have been reported previously,[11,26] indicating that Ag^+ and M^{5+} (M = Os, Ir, Ru) are present in these compounds.

Results and Discussion

Since AuF_4^- and PtF_6^{2-} can be made from the elements[1,2] at 20 °C, in aHF made basic with good F^- donors, it is evident from the present work that similar conditions will produce AuF_6^- and PtF_6^- if the F_2 is photodissociated. In practice it is often more convenient to make the quinquevalent salts starting from the AuF_4^- and PtF_6^{2-} precursors, but in some cases (e.g. $KAuF_6$) the synthesis can be conveniently managed in one step with high yield since the $KAuF_6$ is of modest solubility compared to KF (and $KAuF_4$) contaminant, which are therefore readily removed, in aHF solution, by decantation from the precipitated $KAuF_6$ salt.

The easy addition of fluorine (as F atoms) to AuF_4^- to generate AuF_6^-

$$\mathrm{AuF_4}^-_{\mathrm{(solv)}} + 2\mathrm{F}_{\mathrm{(solv)}} \rightarrow \mathrm{AuF_6}^-_{\mathrm{(solv)}} \tag{1}$$

stands in contrast to the failure[14] to similarly prepare AgF_6^- even using the excellent F atom source, KrF_2. This facile oxidation of Au(III) is attributable to the weaker binding of the d orbital electrons of the gold, because of the tighter binding of s orbital electrons resulting from the high nuclear charge at the gold nucleus (a relativistic effect). This relativistic effect[27,28] is much less significant for silver, where the high effective nuclear charge, at least in Ag(III), causes the 4d orbital electrons to be tightly held. This is seen especially in the small size of the $4d_{z^2}$ electron pair of Ag(III) compared[29] with Au(III), the latter formula unit volume being 5 Å^3 bigger than the former.

Although the remaining valence electrons of PtF_6^{2-} constitute a weakly antibonding set of t_{2g}^6 symmetry, which has highly favorable exchange energy,[30] the F atoms in aHF solution break this configuration and efficiently generate PtF_6^-:

$$\mathrm{PtF_6}^{2-}_{\mathrm{(solv)}} + \mathrm{F}_{\mathrm{(solv)}} \rightarrow \mathrm{PtF_6}^-_{\mathrm{(solv)}} + \mathrm{F}^-_{\mathrm{(solv)}} \tag{2}$$

The analogous reaction with PdF_6^{2-}, however, does not occur. Evidently as with Ag(III) the tighter binding of the 4d electrons relative to 5d electrons causes Pd(V) to be inaccessible, at least by this route. The decrease in formula-unit volume with increase in atomic number for the set of $LiMF_6$ salts, given in Table 2, is much more marked in the second transition series than in the third, and clearly indicates that the effective nuclear charge builds up more, with atomic number, across the second than across the third transition series.

The dt_{2g}^6 valence electron configuration of AuF_6^- is so stable toward oxidation that the powerful one-electron oxidizer Ag(III) in acidified aHF is unable to release AuF_6, although that same reagent generates PtF_6, RuF_6, and RhF_6 in high yields from their MF_6^- salts.[32] This stability of AuF_6^- is in agreement with the large electron affinity, $E(AuF_6)$, calculated by Miyoshi and Sakai[33] of 9.56 eV. The higher nuclear charge of gold must be the most important factor in the greater oxidation resistance of AuF_6^- relative to PtF_6^- the ionization potential of which[34−36] ($= E(PtF_6)$) is ∼ 8 eV, but the more favorable exchange energy of the dt_{2g}^6 configuration of Au(V) relative to the dt_{2g}^5 configuration of Pt(V) must also contribute. The tighter binding of all electrons in AuF_6^- versus PtF_6^- is seen in the smaller effective volume of the former (see Table 2).

These facile syntheses of AuF_6^- and PtF_6^- in aHF provide for the preparation of a wide variety of salts of which the $LiMF_6$ are new. It is also of interest that even $O_2^+AuF_6^-$ is preparable with this approach using O_2/F_2 mixtures with AuF_3 in aHF. It is plausible that the photochemistry generates[37] O_2F, which although a weak base in aHF is nevertheless able to generate

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O_2^+ salts. The previously observed[37] rapid low-temperature oxidation of AuF_4^- by O_2^+ or O_2F in aHF indicate that AuF_6^- would be quickly made by either of these oxidizers.

Because the AuF_6^- has a filled subshell, dt_{2g}^6, it has a poor electron affinity, $E(AuF_6^-)$, since an added electron must be placed in an antibonding σ orbital (e_g*). This is in marked contrast to PtF_6^-, where an additional electron (to give PtF_6^{2-}) enters the t_{2g}^5 set, filling it, and in the process enhancing the exchange energy for that set by ∼50%. These effects explain the oxidation of Ag^+ by PtF_6^- and the stabilization of Ag^{2+} by PtF_6^{2-} or PdF_6^{2-} and the inability of AuF_6^- to oxidize Ag^+ to Ag^{2+}:

$$AuF_6{}^-{}_{(solv)} + Ag^+{}_{(solv)} \rightarrow Ag^+AuF_6{}^-{}_{(c)} \qquad (3)$$

$$Pt(Pd)F_6{}^{2-}{}_{(solv)} + Ag^{2+}{}_{(solv)} \rightarrow Ag^{2+}Pt(Pd)F_6{}^{2-}{}_{(c)} \qquad (4)$$

The reactions in eq 4 are especially remarkable since the Ag^{2+} ion in aHF is able to oxidize[32] O_2 to O_2^+ and Xe to Xe(II) salts.[38] Interaction of $O_2^+PtF_6^-$ with $AgAsF_6$ to give $Ag^{2+}PtF_6^{2-}$

$$AgAsF_{6(c)} + O_2{}^+{}_{(solv)} + PtF_6{}^-{}_{(solv)} \rightarrow Ag^{2+}PtF_6{}^{2-}{}_{(c)} + O_2{}^+{}_{(solv)} + AsF_6{}^-{}_{(solv)} \qquad (5)$$

establishes that PtF_6^- is a potent oxidizer. The failure to oxidize PdF_6^{2-} with F atoms, in the same way as for PtF_6^- from PtF_6^{2-}, implies that the unknown PdF_6^- should be an even more powerful oxidizer than PtF_6^-. Although the magnetic properties of $AgPt(Pd)F_6$ do not discriminate between $Ag^+MF_6^-$ and $Ag^{2+}MF_6^{2-}$, since each possesses one unpaired electron, (the $Ag^+MF_6^-$ in the dt_{2g}^5 configuration of the anion, the $Ag^{2+}MF_6^{2-}$, in the d^9 configuration of the cation) there can be no doubt that the appropriate formulation is the latter one. The unit cell size and chemistry establish that the formulation is $Ag^{2+}Pt(Pd)F_6^{2-}$. For $AgAuF_6$, its diamagnetism and unit cell (see Table 3) show unambiguously that it is $Ag^+AuF_6^-$.

Data for the $LiMF_6$ salts of the second and third transition series, given in Table 2, show that the AuF_6^- has the smallest effective MF_6^- volume of the third transition series. Evidently because effective nuclear charge increases more with increasing atomic number in the second than in the third transition series, the effective volume of $LiRhF_6$ is smaller,[31] and it is the last of that series, PdF_6^- and AgF_6^- being unknown. All other known $LiEF_6$ salts adopt the rhombohedral variant of the (6:6 coordinate) NaCl type arrangement (which is named from the $LiSbF_6$ structure[39]). This is essentially a hexagonal *close-packed* array of F ligands containing ordered arrangements of E and Li in octahedral holes. The structure can be attributed to the small, hard, and highly polarizing Li^+ strongly attracting, octahedrally, six F ligands of surrounding MF_6^-. The smallest EF_6^- (PF_6^-) results in a formula unit volume,[23] V_{FU}, of only 88 $Å^3$ for $LiPF_6$, whereas for the largest anion represented so far in this structure type,[31] TaF_6^-, $V_{FU}(LiTaF_6) = 111$ $Å^3$. This gives an approximate estimate for the sizes of the anions since the Li^+ can be taken to contribute very little to the cell volume in each case. This is not so for the Na^+ ion in the $NaEF_6$ salts, which also for the most part adopt the same $LiSbF_6$ structure, or cubic relatives (*Pa*3 or *Fm*3*m*), all variants of 6:6 coordination. Generally, for any given $LiSbF_6$ lattice E, $V_{FU}(NaEF_6)$ exceeds $V_{FU}(LiEF_6)$ by ∼20 $Å^3$, this being a measure of how much larger Na^+ is than the octahedral hole in the approximately close-packed F ligand array. Since Ag^+ is similar in size to Na^+, it might, therefore, have been expected that the $AgEF_6$ salts would also have adopted 6:6 coordination throughout the series, but as the data in Table 3 show, this is not the case.

Table 3. Comparison of $Ag^+AuF_6^-$ and $Ag^{2+}[Pt(Pd)F_6]^{2-}$ with some $Ag^+EF_6^-$ Salts

	CsCl-type (8:8) arrangement		NaCl-type (6:6) arrangement	
	$Ag^IRu^VF_6$[c]	[d]	**$Ag^{II}Pd^{IV}F_6$**[a]	
color	orange		brown	
SG	*Ia*3		$R\bar{3}$	
a (Å)	9.653(10)		5.00(4)	
c (Å)			14.6(2)	
V/*Z* ($Å^3$)	112.4(4)		105(3)	
	$Ag^IOs^VF_6$[c]	**$Ag^IIr^VF_6$**[c]	**$Ag^{II}Pt^{IV}F_6$**	**$Ag^IAu^VF_6$**
color	white	orange	brown	brown
SG	*Ia*3	*Ia*3	$R\bar{3}$	$R\bar{3}$
a (Å)	9.7318(9)	9.704(2)	5.049(8)	5.283(3)
c (Å)			14.46(2)	15.053(6)
V/*Z* ($Å^3$)	115.21(4)	114.23(8)	106.4(5)	121.3(2)
	$AgBiF_6$	**$AgSbF_6$**	**$AgAsF_6$**	**$AgPF_6$**
color	light yellow	white	white	white
SG	$P\bar{4}2m$	*Ia*3	*Pa*3	*Pa*3
a (Å)	5.079(2)	9.857(5)[2)]	7.773(7)	7.563(4)
c (Å)	9.552(3)			
V/*Z* ($Å^3$)	123.2(2)	119.7(2)	117.4(5)	108.2(2)

[a] The XRDP of $AgPdF_6$ was broad-lined and weak, and nearly indistinguishable from that of $AgPtF_6$. The V_{FU} is certainly close to the one of $AgPtF_6$. [b] The lattice parameters were recalculated from ref 40. [c] The cubic modification (probable SG *Ia*3) was obtained for the first time. Previously a tetragonal $KNbF_6$-type structure has been reported for those compounds.[23] [d] $AgRhF_6$ has been reported to be black; however, no structural information was given.[7]

For the closed-shell, group 15 $AgEF_6$ salts, there is a switch in structure type,[23,41] the smaller anions PF_6^- and AsF_6^- adopting NaCl-type structures, and the larger (SbF_6^- and BiF_6^-), variants of the CsCl structure type. The cubic forms reported here for $AgMF_6$ (M = Ru, Os, Ir) are new, these having been previously described as having the $KNbF_6$ structure type.[23] The data for the second and third transition series $AgEF_6$ salts show that the switch from NaCl to CsCl type is even more subtly correlated with anion size, since $AgRuF_6$ and $AgIrF_6$ both adopt CsCl type lattices, whereas $AgAuF_6$ has a $LiSbF_6$ structure (i.e., NaCl relative), even though the V_{FU} of the $LiEF_6$ relatives (see Table 2) differ by no more than 2 $Å^3$. Comparing $V_{FU}(AgAuF_6) = 121$ $Å^3$ with $V_{FU}(LiAuF_6) = 99$ $Å^3$, each of which adopts the NaCl-like $LiSbF_6$ structure, we see that the Ag^+ is ∼22 $Å^3$ larger than the Li^+ in effective volume (a value close to that already noted earlier for Na^+). A similar comparison of the CsCl-type lattice $V_{FU}(AgRuF_6) = 112$ $Å^3$ with that of the NaCl type $V_{FU}(LiRuF_6) = 101$ $Å^3$ shows that the $AgRuF_6$ lattice is ∼11 $Å^3$ more closely packed than if it had adopted the NaCl-type lattice. This better packing provided by the $AgMF_6$ of CsCl-type structure holds in general for cations of the size of Ag^+ or larger. An aspect of the closer packing of the CsCl type arrangement is that it places the nearest like-charged ions closer together than does the NaCl arrangement. This is illustrated well by the cubic $AgRuF_6$ structure (smallest V_{FU} of all salts of CsCl-type structure) in which the nearest RuF_6^- are 4.83 Å apart,

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whereas in LiRuF$_6$ the closest interionic distance of like ions[42] is 5.075 Å. Even in the smallest NaCl-type LiEF$_6$ (LiPF$_6$), the closest like-ion distance[23] is 4.921 Å. It is probable that EF$_6^-$ ions in cubic or rhombohedral CsCl-type cells cannot be placed much closer than they are in AgRuF$_6$ since their repulsive interactions would then become severe. When the symmetry is tetragonal, as in the AgBiF$_6$ cell, the octahedra can be stacked more efficiently, each with a 4-fold axis parallel to the a,b plane and a super imposed octahedron at right angles, such that the two F$^-$ ligands, of one octahedral edge, pack tetrahedrally with the like F ligands of the octahedron packing closely with it (above and below z). This requires 4_2 axes parallel to z. For octahedrally close-packed spheres of radius r the ideal c axis for such an arrangement would be $(4 + 2\sqrt{2})r$.

For unmeshed octahedral EF$_6^-$ species, they are thinnest when measured along a 3-fold axis. Such symmetry is appropriate for the packing of the octahedra in cubic or rhombohedral lattices. For an octahedral collection of spherical F$^-$ ligands of radius r, the separation of one 3-fold set of F nuclei from the other is $2r\sqrt{2}/\sqrt{3}$. For the total effective thickness of the octahedral cluster in the 3-fold axis direction, we must add $2r$. Therefore this effective thickness is $2r(1 + \sqrt{2}/\sqrt{3})$. If the thickness is 4.83 Å, as in AgRuF$_6$, we have $r = 1.33$ Å. This is slightly less than the commonly accepted value[43] (1.36 Å) for the van der Waals radius for the F$^-$ ligand. Clearly, MF$_6^-$ closest distances less than 4.83 Å, would signify strong repulsion. Indeed, in AuF$_6^-$, where the effective nuclear charge is high enough to raise the ionization potential[33] ~1 eV higher than in the ruthenium ion,[35] the AuF$_6^-$ as a whole must be effectively smaller than RuF$_6^-$. But at this point the repulsive interactions of AuF$_6^-$ (which would surely be placed less than 4.83 Å apart in a CsCl-type lattice) seem to render that arrangement less favorable than the less well packed NaCl structure. As is indicated in Table 3, this structure has a closest AuF$_6^-$ interionic distance of 5.283(3) Å. The larger EF$_6^-$ are associated with lower effective nuclear charge at E (e.g., Ta(v)), and this in turn must mean that the F ligands of the larger anions are more electron rich and polarizable, i.e. much softer than in the AuF$_6^-$ ion. In any case, in the CsCl type structures with large anions, the like ions are further apart than 4.83 Å, the separation distance being (at least approximately) the anion diameter.

Although the XRDP of the (rapidly) precipitated AgPt(Pd)F$_6$ is broad-lined and of heavy background, the pattern is unmistakably akin to that of AgAuF$_6$, but of cell size much closer to that of PdPtF$_6$. Indeed direct comparison of XRDP patterns of AgPt(Pd)F$_6$ (which were nearly the same in diffraction-line placement) with those of AgAuF$_6$ and PdPtF$_6$ immediately indicated that the platinum and palladium salts belonged to the family of M^{2+}MF$_6^{2-}$ $R\bar{3}$ materials.[44] The formula unit volume derived from the indexing of each of the patterns was ~106 Å^3, which is slightly larger than that[45] of PdPtF$_6$ (104 Å^3), in harmony with the greater antibonding effect of the d^9 configuration of Ag^{2+} compared to that of the d^8 of Pd^{2+}. Although there could be a Jahn–Teller distortion arising from the d^9 configuration this, if it occurs, must be sufficiently subtle to be masked by the broadening of the lines (as a consequence of small crystallite size; in more crystalline samples of AgPtF$_6$ a possible line splitting could be present, in which case the true symmetry must be lower than the rhombohedral symmetry assumed here). The pattern is convincingly indexable on the basis of a LiSbF$_6$ type rhombohedral cell. It is clear that if the material were Ag$^+$PtF$_6^-$ the formula unit volume should be slightly larger than that of AgAuF$_6$, just as LiPtF$_6$ is ~0.4 Å^3 larger than LiAuF$_6$ (see Table 2), i.e., $V_{\mathrm{FU}}(\mathrm{Ag^+PtF_6^-}) \approx 122$ Å^3. The simple explanation for the observed formula unit volume, of ~106 Å^3 (which will not be significantly different if the symmetry is lower), is the formulation Ag^{2+}Pt(Pd)F$_6^{2-}$, in which the Coulomb attraction is four times greater than in Ag$^+$AuF$_6^-$, or what might have been Ag$^+$Pt(Pd)F$_6^-$. The Ag^{2+}Pt(Pd)F$_6^{2-}$ formulation is also in harmony with the failure of these materials to combine with fluorine. The Ag$^+$MF$_6^-$ salts (M = As, Ru, Ir) and Ag$^+$BF$_4^-$, all add fluorine easily to form AgF$^+$ salts[11,25] (AgPF$_6$ gives AgF$_2$ and PF$_5$, and AgOsF$_6$ gives AgF$_2$ and OsF$_6$). The salt AgF$^+$AuF$_6^-$ has also been prepared previously in these laboratories[25] and is isostructural with[46] AgF$^+$AsF$_6^-$.

It is of interest that each of PtF$_6^-$ and RuF$_6^-$ is able to stabilize[6,16,47] O$_2^+$. The salts have similar unit cells[6,16,47] and stability with respect to dissociation. In harmony with these similarities the electron affinity of RuF$_6$ should be close to that of PtF$_6$[34−36] which is ~8 eV. It might have been expected, therefore, that the second electron affinity would also have nearly the same value for both ions. But RuF$_6^{2-}$ does not stabilize Ag^{2+}. The close structural relationship of AgRuF$_6$ to AgIrF$_6$ (each has a CsCl-type cell, such as would also be expected for Ag$^+$PtF$_6^-$) and its reported magnetic behavior[11,26] establish that the ruthenium salt is Ag$^+$RuF$_6^-$. This must signify a smaller second electron affinity for RuF$_6$ than for PtF$_6$, since the unit cells of the AgMF$_6$ salts of the same charge must be similar, as is the case for a variety[1,48] of RuF$_6^-$ compared with PtF$_6^-$, and RuF$_6^{2-}$ compared with PtF$_6^{2-}$ salts. The lattice energetics of the ruthenium and platinum relatives must therefore be similar.[49] Consequently, it is plausible to assign the greater second electron affinity of PtF$_6$ to the favorable exchange energy benefit when dt$_{2g}^5$ becomes dt$_{2g}^6$. In the conversion of the ruthenium dt$_{2g}^3$ to dt$_{2g}^4$ there is no increase in exchange energy.

The preference of the formulation Ag^{2+}PtF$_6^{2-}$ to that of Ag$^+$PtF$_6^-$ requires that the electron affinity of PtF$_6^-$, E(PtF$_6^-$), and the lattice energy benefit provided by Ag^{2+}PtF$_6^{2-}$ relative to Ag$^+$PtF$_6^-$ must exceed the ionization enthalpy for conversion of Ag$^+$ to Ag^{2+}. The last term[50] is 496 kcal mol^{-1}. The lattice enthalpy[49] for Ag$^+$PtF$_6^-$ based on the anticipated formula unit volume is −139 kcal mol^{-1}. On the basis of the observed volume for Ag^{2+}PtF$_6^{2-}$ (of ~106 Å^3) and assuming that the lattice energy of A^{2+}B^{2-} is four times that of A$^+$B$^-$, the lattice energy is estimated to be 575 kcal mol^{-1}. The change in lattice energy is therefore ~436 kcal mol^{-1}. Therefore E(PtF$_6^-$) is required to be >60 kcal mol^{-1} for such an oxidation to occur. This approaches the electron affinity of a fluorine atom,[51] E(F) = 78.4 kcal mol^{-1}. It is clear, however, that E(PdF$_6^-$) must be even larger than E(PtF$_6^-$).

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Supporting Information Available: Tables S1−S9, listing measured and calculated $1/d^2$ as well as the respective estimated and calculated intensities and (*hkl*) values. This material is available free of charge via the Internet at http://pubs.acs.org.

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