A New Oxidation State of Gold: The Preparation and some Properties of $[AuF_6]^-$ Salts

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Summary Fluorination of AuF_3 in the presence of excess XeF_6 yields $[Xe_2F_{11}]^+[AuF_6]^-$; this salt interacts with CsF at 110 °C *in vacuo* with displacement of XeF_6 to yield $CsAuF_6$.

SINCE gold hexafluoride promises[1] to be the most powerfully oxidizing hexafluoride of the third transition series, its synthesis is of interest. Although the highest known established gold fluoride was AuF_3,[2,3] a structurally illdefined material $AuF_{3\cdot6}$ has been obtained by the fluorination,[4] at 500 °C, of AuF_3. Recently we recognized that the basic and solvent properties of xenon hexafluoride[5] offered excellent conditions for the promotion of a higher gold oxidation state. The trifluoride (2 mmol), and XeF_2 (12 mmols) were heated (400 °C), in gaseous F_2 (70 mmols at 1000 p.s.i.) for several hours and cooled overnight to 20 °C, when the excess of fluorine and xenon hexafluoride were removed under vacuum. A macrocrystalline mass of pale yellow–green crystals was obtained (m.p. 145–150°). Analysis for xenon indicated the empirical formula $F_{17}AuXe_2$. This was supported by the crystal data: $F_{17}AuXe_2$, $M = 782\cdot5$, orthorhombic, $a = 9\cdot115(2)$, $b = 8\cdot542(3)$, $c = 15\cdot726(6)$, $V = 1224$ Å^3, $z = 4$, $D_c = 4\cdot24$ g cm^{-3}, space group *Pnma* or *Pna*2$_1$. The volume of the unit cell, using Zachariason's criterion of 18 Å^3 for each *F* atom[6] indicates a total of 68 per unit cell. Furthermore, the compound is isomorphous with $[Xe_2F_{11}]^+[MF_6]^-$ (M = Ru, Ir, Pt).[7] The Raman spectrum of the compound shows the following bands: 661(55), 600(40), 593(58), *586*(78), 400(w), 356(w), 290(w), *223*(20), 111(10), and 58(12) cm^{-1}. The italicized frequencies are attributable to the $[AuF_6]^-$ and the others show a marked similarity to the bands attributed by Bartlett and Wechsberg[8] to the cation in the salt $[Xe_2F_{11}]^+$-$[AsF_6]^-$. The compound is therefore $[Xe_2F_{11}]^+[AuF_6]^-$. A full crystal structure analysis has been undertaken. The existence of quinquevalent gold has, however, been established by the preparation of $CsAuF_6$ from the xenon salt.

TABLE. *Raman spectra of* $CsAuF_6$ *and* $CsAuF_4$ (*relative intensities in parentheses, frequencies in* cm^{-1})

$[AuF_6]^-$ modes	$CsAuF_6$	$CsAuF_4$	$[AuF_4]^-$ modes
$\nu_1(a_{1g})$	595(66)	588(98)	$\nu_1(a_{1g})$
$\nu_2(e_g)$	520(28)	561(28)	$\nu_4(b_{2g})$
$\nu_5(f_{2g})$	224(25)	237(13) 230(14)	$\nu_3(b_{1g})$

A slight deficiency of CsF mixed with $[Xe_2F_{11}]^+[AuF_6]^-$ was heated under dry N_2 to 110 °C, at which temperature XeF_6 evolved. The XeF_6 displacement: $CsF + [Xe_2F_{11}]^+[AuF_6]^- \rightarrow 2XeF_6 + CsAuF_6$, was completed under vacuum, (the slight excess of xenon complex sublimed out of the reactor) and a pale yellow solid remained. *X*-Ray powder photographs established that $CsAuF_6$ is isomorphous with the other $CsMF_6$ noble metal salts.[9] *Crystal data:* $CsAuF_6$, $M = 443\cdot9$ rhombohedral, $a = 5\cdot24 \pm 0\cdot01$ Å; $\alpha = 96\cdot5 \pm 0\cdot3°$, $V = 141$ Å^3, $z = 1$, $D_c = 5\cdot22$ g cm^{-3}. Space group $R\bar{3}$. The Raman spectrum of the salt is compared with that of $CsAuF_4$ in the Table. The similarity of the vibrational spectra of AuF_6^- and AuF_4^- is reminiscent of the close similarity of the vibrational spectra of $[Pd(Pt)(hal)_4]^{2-}$ salts to their related $[Pd(Pt)(hal)_6]^{2-}$ salts.[10] Since the symmetric stretching frequencies of AuF_4^- and AuF_6^- are almost identical it is evident that the involvement of the non-bonding Au^{III} valence-electron pair (usually represented as $d_{z^2}{}^2$) in the bonding of two more F ligands to form the $[AuF_6]^-$ ion, does not change the strength of the Au–F bond.

In conformity with the antibonding-π character[1] of the low spin $d_{t_{2g}}{}^6$ electron configuration of Au^V, the totally symmetric stretching frequency of $[AuF_6]^-$ is the lowest of the $[MF_6]^-$ species in the series:[11] OsF_6^-, 690; IrF_6^-, 672; PtF_6^-, 647; AuF_6^-, 595 cm^{-1}.

The preparation of AuF_6 will be attempted by electrolysis of the molten xenon salt.

Added in proof. Fluorination of $CsAuF_4$ has yielded $CsAuF_6$ directly. Also, $O_2 + F_2$ has given $O_2^+[AuF_6]^-$.

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