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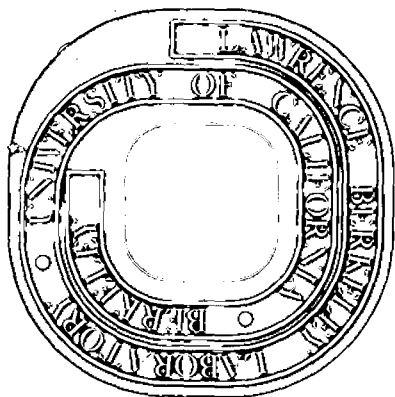
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[AuF₆]⁻ SALTS

Kevin Leary and Neil Bartlett

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A NEW OXIDATION STATE OF GOLD:
 THE PREPARATION AND SOME PROPERTIES OF $[\text{AuF}_6]^-$ SALTS

By Kevin Leary and Neil Bartlett*

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Summary Fluorination of AuF_3 in the presence of excess
 XeF_6 yields $[\text{Xe}_2\text{F}_{11}]^+[\text{AuF}_6]^-$. This salt interacts with
 CsF at 110° in vacuo with displacement of XeF_6 to yield
 CsAuF_6 .

Since gold hexafluoride promises¹ to be the most powerfully oxidizing
 hexafluoride of the third transition series, there is interest in a
 synthesis for that compound. Although the highest known established gold
 fluoride was AuF_3 ^{2,3}, a structurally ill-defined material $\text{AuF}_{3.6}$ has been
 obtained by the fluorination⁴, at 500° , of AuF_3 . Recently we recognized
 that the basic and solvent properties of xenon hexafluoride⁵ offered
 excellent conditions for the promotion of a higher gold oxidation state.
 The trifluoride (2mMoles), mixed with XeF_2 (12 mMoles) was heated, at
 400° , in gaseous F_2 (70 mMoles at 1000 p.s.i.) for several hours and
 cooled overnight to 20° , when excess fluorine and xenon hexafluoride
 were removed under vacuum. A macrocrystalline mass of pale yellow-green
 crystals was obtained (m.p. $145\text{--}150^\circ$). Analysis for xenon indicated the

empirical formula $F_{17}AuXe_2$. Found: Xe, $33.2 \pm 0.4\%$, $F_{17}AuXe_2$ requires 33.5%. This formulation is also supported by the crystallographic findings. Crystal Data: $F_{17}AuXe_2$, $M = 782.5$, orthorhombic, $a = 9.115(2)$; $b = 8.542(3)$; $c = 15.726(6)$; $V = 1224 \text{ \AA}^3$, $z = 4$, $D_c = 4.24 \text{ g cm}^{-3}$, space group $Pnma$ or $Pna2_1$. The volume of the unit cell, using Zachariason's criterion of 18 \AA^3 for each F atom⁶ 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 (frequencies in cm^{-1} and relative intensities in parentheses): 661(55), 600(40), 593(58), 586(78), 400(w), 356(w), 290(w), 223(20), 111(10), and 58(12). The italicized frequencies are attributable to the $[AuF_6]^-$ and the others show a marked similarity to the bands attributed by Bartlett and Wechsberg⁸ to the cation in the salt $[Xe_2F_{11}]^+[AsF_6]^-$. We therefore believe that the compound is the salt $[Xe_2F_{11}]^+[AuF_6]^-$. A full crystal structure analysis has been undertaken. The existence of quinevalent gold has, however, been established by the preparation of $CsAuF_6$ from the xenon salt.

A slight deficiency of CsF mixed with $[Xe_2F_{11}]^+[AuF_6]^-$ was heated under dry N_2 to 110° , 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-green solid remained. X-ray powder photographs established that $CsAuF_6$ is isomorphous with the other $CsMF_6$ noble metal salts.⁹ Crystal Data: $CsAuF_6$, $M = 443.9$ rhombohedral, $a = 5.24 \pm 0.01 \text{ \AA}$; $\alpha = 96.5 \pm 0.3^\circ$, $V = 141 \text{ \AA}^3$, $z = 1$, $D_c = 5.22 \text{ g cm}^{-3}$. Space group $R\bar{3}$. The Raman spectrum of the salt is compared with that of $CsAuF_4$ in the Table.

TABLE

Raman Spectra of CsAuF_6 and CsAuF_4
 (relative intensities in parentheses, frequencies in cm^{-1})

$[\text{AuF}_6]^-$ modes	CsAuF_6	CsAuF_4	$[\text{AuF}_4]^-$ modes
$\nu_1(a_{1g})$	595(66)	588(98)	$\nu_1(a_{1g})$
$\nu_2(e_g)$	520(28)	561(28)	$\nu_5(b_{2g})$
$\nu_5(f_{2g})$	224(25)	237(13) 230(14)	$\nu_3(b_{1g})$

The similarity of the vibrational spectra of AuF_6^- and AuF_4^- is reminiscent of the close similarity of the vibrational spectra of $[\text{Pd}(\text{Pt})\text{hal}_4]^{2-}$ salts to their related $[\text{Pd}(\text{Pt})\text{hal}_6]^{2-}$ salts¹⁰. 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}) in the bonding of two more F ligands to form the $[\text{AuF}_6]^-$ ion, does not change the strength of the Au-F bond.

In conformity with the antibonding- π character¹ of the low spin $d_{z^2}^6$ electron configuration of Au(V), the totally symmetric stretching frequency of $[\text{AuF}_6]^-$ is the lowest of the $[\text{MF}_6]^-$ 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.

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