Syntheses and Some Properties of Dioxygenyl Fluorometallate Salts

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Twelve dioxygenyl salts of complex fluorometallate anions have been prepared by a simple thermal method; seven of these compounds are new. The salts have been characterized by combinations of powder *X*-ray crystallography, Raman spectroscopy, and molecular beam mass spectroscopy. They fall into two classes: compounds of strongly oxidizing hexafluorides and compounds of strong fluoride-ion acceptors. Mass spectra provide evidence for the independent existence of AuF_5.

Dioxygenyl hexafluoroplatinate(v) was the first reported dioxygenyl salt, prepared by Bartlett and Lohmann initially by the action of PtF_6 on glass or silica,[1] and subsequently by the reaction of PtF_6 and O_2 and the fluorination of platinum and platinum salts in the presence of oxygen.[1,2] The salts O_2BF_4, O_2PF_6, O_2AsF_6, and O_2SbF_6 were later prepared by the action of O_2F_2 on the respective Lewis acids.[3,4] Photochemical [5] and thermal [6] oxyfluorination of AsF_5 and SbF_5 have also been used to prepare O_2AsF_6 and O_2SbF_6. Most recently, O_2AuF_6 has been characterized by Leary and Bartlett.[7]

From powder photographs, O_2PtF_6 was shown to be dimorphic, possessing both cubic and rhombohedral modifications.[2] Powder samples of the cubic phase were further studied by neutron diffraction [8] in an attempt to obtain a definitive O–O distance. This study confirmed many details of the cubic phase, a_0 = 10·03 Å, but disorder prevented an unequivocal determination of the O–O bond distance. Powder data [7] show O_2AuF_6 to be isomorphous with the rhombohedral form of O_2PtF_6. Young *et al.*[4] indexed O_2AsF_6 on the basis of a cubic cell, a_0 = 8·00 Å, but only with difficulty obtained a rough correlation of O_2SbF_6 with a cubic cell, a_0 = 10·71 Å. Shamir and Binenboym [5] confirmed this indexing of O_2AsF_6 (with a_0 = 8·10 Å), but indexed O_2SbF_6 with a smaller cubic cell, a_0 = 10·30 Å. While agreeing with the assignment of O_2AsF_6, Beal *et al.*[6] index their O_2SbF_6 as face-centred cubic, a_0 = 10·13 Å, isomorphous with $NOSbF_6$, a_0 = 10·19 Å.

More recently, McKee and Bartlett [9] and Stein [10] showed that the scatter in previously reported a_0 values for the antimony salt arose because some samples were authentic O_2SbF_6 (a_0 = 10·132 Å) and others were contaminated with $O_2Sb_2F_{11}$. The *X*-ray powder data for the latter compound could not be indexed properly and attempts to grow single crystals were singularly unsuccessful.

Some i.r. and Raman spectra of the various anions have been reported, but of special importance in identifying these salts is the characteristic vibration of the O_2^+ cation, close to the free ion value [11] of 1876 cm^{-1}. Shamir *et al.*[12] have observed intense Raman bands at 1858 and 1862 cm^{-1} for O_2AsF_6 and O_2SbF_6 solids but give data only for the AsF_6^- anion. For the transition

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[10] L. Stein, private communication.

[11] G. Herzberg, ' Molecular Spectra and Molecular Structure,' Van Nostrand, New York, 1950, p. 560.

[12] J. Shamir, J. Binenboym, and H. H. Claassen, *J. Amer. Chem. Soc.*, 1968, **90**, 6223.

metal compounds O_2PtF_6 [13] and O_2AuF_6,[7] bands ascribable to O_2^+ have been observed at 1837 and 1833 cm^{-1}, respectively. This vibration has also been observed in O_2BF_4 in the i.r. at 1866 and 1868 cm^{-1}, allowed by crystal fields.[14]

Little information is available about dioxygenyl salt vapours. Young *et al.*[4] have observed O_2^+ ions in the mass spectra of the vapours above O_2AsF_6 and O_2SbF_6 at room temperature, and O_2^+ plus ions characteristic of AsF_5 and SbF_5 on modest heating. Bartlett and Lohmann [1,2] reported O_2PtF_6 to sublime without decomposition at 90—130 °C.

This paper describes the syntheses, structures, mass spectra, and vibrational spectra of dioxygenyl salts with complex fluorometallate anions. In addition to those previously known, O_2RhF_6, O_2RuF_6, O_2BiF_6, $O_2Bi_2F_{11}$, $O_2Sb_2F_{11}$, O_2NbF_6, $O_2Nb_2F_{11}$, and $O_2Ta_2F_{11}$ are reported. $O_2^+NbF_6^-$, $O_2^+Nb_2F_{11}^-$, and NbF_5 were usually produced in the reactions of O_2 and F_2 with Nb. NbF_5 was easily removed and in a few attempts $O_2Nb_2F_{11}$ could be made free of O_2NbF_6. We were unable to synthesize or isolate the $O_2^+NbF_6^-$ salt in a pure form, however, and could identify it only as a contaminant in $O_2^+Nb_2F_{11}^-$. Our approach to the identification and characterization of the species considered has been to correlate *X*-ray powder diffraction data, Raman spectra, and mass spectra with already characterized systems, taking advantage of close relationships which exist.

EXPERIMENTAL

Syntheses.—The dioxygenyl salts $O_2^+MF_6^-$ for M = As, Sb, Bi, Ru, Rh, Au, and Pt and $O_2^+M_2F_{11}^-$ for M = Sb, Nb, and Ta were prepared by static heating of 0·004—0·008 mol samples of powdered M at 300—500 °C with *ca.* 5 atmos. of a 3 : 1 to 4 : 1 $F_2 : O_2$ mixture in a 260 cm^3 openable Monel reactor with a water cooled top for 10—89 h. Experimental parameters are summarized in Table 1 for specific reactions. Conversion of M was essentially complete in all cases although heating to 500 °C was found to be necessary for gold.

Antimony, niobium, and tantalum require special comments because the product favoured is the $O_2M_2F_{11}$ species. Pure O_2SbF_6 could be produced in the oxyfluorination of $O_2Sb_2F_{11}$ at a slightly reduced temperature. The conversion is easily monitored using the Raman technique because of the significantly different spectra obtained from the two compounds. The photochemical preparations [5] using arsenic and antimony yield O_2AsF_6 and $O_2Sb_2F_{11}$ exclusively.* Thermal preparations using Nb and Ta yield $O_2Nb_2F_{11}$ and $O_2Ta_2F_{11}$ although in the case of niobium, Raman data suggest that O_2NbF_6 is produced along with the more complicated salt. Attempts to prepare the individual O_2NbF_6 and $O_2Nb_2F_{11}$ salts in pure form were not successful. In some experiments $(O_2)_2TaF_7$ may have been formed but in general $O_2Ta_2F_{11}$ is the stable species.

The successful preparation of O_2BiF_6 appeared to be a strong function of temperature. At 400 °C a mixture of O_2BiF_6, $O_2Bi_2F_{11}$, and BiF_5 results from which BiF_5 could be removed by sublimation. At 375 °C pure O_2BiF_6 could be obtained.

TABLE 1

Reaction conditions and the dioxygenyl stretching frequencies

Compound	Temp./ °C	Time/ h	$F_2 : O_2 : M$ [a]	O_2^+ Wavenumber/ cm^{-1}
O_2PtF_6	280	11	10·6 : 2 : 1	1838 (1837) [b]
O_2AuF_6	500	89	8 : 2 : 1	1835 (1837) [c]
O_2RuF_6	300	14	8 : 2 : 1	1838
O_2RhF_6	300	15	8 : 2 : 1	1825 [d]
O_2AsF_6	450	16	3 : 1 : 1	1858 (1858) [e]
O_2SbF_6	150	21	25 : 6·3 : 1 [f]	1861
$O_2Sb_2F_{11}$	300	13	6 : 1·3 : 1	1864 (1862) [e]
O_2BiF_6	375	12	10·5 : 3·5 : 1	1847
$O_2Bi_2F_{11}$	400	12	10 : 3 : 1	1853
O_2NbF_6	330	12	10 : 3 : 1	*ca.* 1853
$O_2Nb_2F_{11}$				1858
$O_2Ta_2F_{11}$	375	12	9 : 3 : 1	1858

[a] M = metalloid or metal atom. [b] Ref. 11. [c] Ref. 7. [d] This value (±5 cm^{-1}) was determined using 6471 Å excitation. [e] Ref. 10. [f] M = $O_2Sb_2F_{11}$.

X-Ray Powder Photographs.—*X*-Ray powder diffraction patterns of samples sealed under helium in 0·3 mm O.D. quartz capillaries were obtained with a 57·3 mm diameter Siemens powder camera. The film was mounted asymmetrically according to Straumanis. A Siemens Kristalloflex II *X*-ray generator was used to power a copper target tube run at 35 kV and 20 ma. A nickel filter removed Cu-K_β radiation.

Mass Spectra.—Mass spectra were obtained using a molecular beam mass spectrometer with a differentially pumped beam source chamber and a quadrupole mass analyser.[15] Samples were loaded into prefluorinated Monel cells in a Vacuum Atmospheres Corp. dry box under helium containing less than 1 part in 10^6 combined O_2 and H_2O. The Monel cells were fitted into small, electrically heated copper blocks. Effusion orifices of 0·010 in diameter were usually used with the beam source. Mass spectra were taken using 70 or 100 eV electrons at the lowest source temperatures giving adequate signal. When sample size permitted, spectra were also obtained at higher temperatures. Mass spectral data are summarized in Tables 2—4.

TABLE 2

Relative ion abundances for O_2MF_6 salts [a]

	70 eV Spectra			100 ev Spectra	
	Rh	Ru	Pt	Sb	Bi
Temperature/°C	25	27	33	129	103
O_2^+	100	100	100	14	100
M^+	49	6·1	24	8·7	7·1
MF^+	25	4·4	11	7·3	5·6
MF_2^+	26	3·8	10	11	11
MF_3^+	31	4·6	13	7·3	1·0
MF_4^+	40	6·4	15	100	20
MF_5^+	54	7·3	21	*	*
MF_6^+	16	0·91	12	*	*

* Ions not detected above noise level.

[a] All intensities are relative to the most intense peak = 100.

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* L. Stein has found that $O_2Sb_2F_{11}$, initially formed in the photolysis of SbF_5–O_2–F_2 mixtures, is converted into O_2SbF_6 on further reaction with O_2 and F_2. The final product is good quality O_2SbF_6, with a Raman spectrum and powder pattern similar to those reported here and in ref. 9.

[13] P. A. Bulliner, unpublished, quoted by N. Bartlett, *Angew. Chem. Internat. Edn.*, 1968, **7**, 433.

[14] K. R. Loos, V. A. Campanile, and C. T. Goetschel, *Spectrochim. Acta*, 1970, **26A**, 365.

[15] M. J. Vasile, G. R. Jones, and W. E. Falconer, *Internat. J. Mass Spectrometry and Ion Physics*, 1973, **10**, 457.

TABLE 3

Relative ion abundances for $O_2M_2F_{11}$ salts

	$O_2Nb_2F_{11}$ O_2NbF_6		$O_2Ta_2F_{11}$		$O_2Sb_2F_{11}$	
Temp./°C	38	61	58	87—100	77—85	127—134
O_2^+	9·0	1·3	100	0·62	16	4·1
M^+					20	11
MF^+		0·7			11	8·0
MF_2^+	4·3	4·0		3·3	50	13
MF_3^+	14	13·3	4·1	21	38	11
MF_4^+	100	100	24	100	100	100
MF_5^+						
MF_6^+						
$M_2F_9^+$	26·5	21·2		7·6	5·2	*
$M_3F_{14}^+$		0·3				*

* Not searched for.

TABLE 4

Relative ion abundances for O_2AuF_6 at 212 °C

Monomer		Dimer		Trimer	
Ion	Rel. Int.	Ion	Rel. Int.	Ion	Rel. Int.
O_2^+	100	Au_2^+	5·8	$Au_3F_7^+$	0·46
Au^+	14	Au_2F^+	3·5	$Au_3F_8^+$	0·92
AuF^+	1·5	$Au_2F_2^+$	2·9	$Au_3F_9^+$	0·70
AuF_2^+	1·0	$Au_2F_3^+$	3·4	$Au_3F_{10}^+$	0·70
AuF_3^+	1·0	$Au_2F_4^+$	4·8	$Au_3F_{11}^+$	0·70
AuF_4^+	0·38	$Au_2F_5^+$	7·4	$Au_3F_{12}^+$	0·70
AuF_5^+		$Au_2F_6^+$	9·1		
		$Au_2F_7^+$	13		
		$Au_2F_8^+$	1·7		
		$Au_2F_9^+$	0·6		

Raman Spectra.—Attempts to obtain spectra of the highly coloured solid dioxygenyl salts with samples in Pyrex or amorphous quartz capillary tubes were unsatisfactory. Therefore, a special cell for use with highly corrosive solids and liquids was developed. This involved a modification of the spinning cell currently favoured for studying highly coloured samples.[16]

The cell is a partially threaded (24 t.p.i.) solid Teflon cylinder with a groove 0·10 in wide by 0·02 in deep. A sample was placed in the groove and capped with a 1 in O.D. × 0·02 in thick sapphire window. The threads were lubricated with a fluorocarbon grease prior to screwing on a brass retaining ring. The whole assembly was mounted on the shaft of an 1800 r.p.m. motor. The sample was illuminated with a laser so that the reflected beam was about 110° from the incident beam. Scattered light was focused onto the entrance slit of a monochromator with an *f*/8 lens.

Samples were illuminated with a Spectra-Physics 164-10 Argon ion laser using the 5145 Å (0·5—2·0 W) line, and in most cases also the 4880 Å line, with only aperture filtering of spurious plasma and laser lines. In special cases unidentified bands were checked on the anti-Stokes side of the laser to ensure that grating ghosts were not being observed. A Jarrell-Ash 25-100 double monochromator, a cooled ITT FW 130 photomultiplier tube, and a SSR photo count rate detection system were used to record Raman spectra.

IDENTIFICATION AND PROPERTIES

$O_2^+PtF_6^-$.—This crystalline, brick red powder gave an *X*-ray powder pattern in complete accord with that reported by Bartlett and Lohmann.[2] The Raman line observed in this sample at 1838 cm^{-1} is characteristic of the dioxygenyl stretching mode; the frequency is in close agreement with that previously reported.[9,13] The mass spectrum between room temperature and 100 °C showed O_2^+ as the most intense peak and a pattern characteristic of the cracking of PtF_6. No evidence for PtF_5 was obtained. After heating to 150 °C, no residue remained in the effusion cell. The observations further suggest the O_2PtF_6 prepared in this way is relatively uncontaminated

$O_2^+RuF_6^-$.—*X*-Ray powder data for this crystalline, red-orange powder gave a cubic cell with $a_0 = 10{\cdot}004 \pm 0{\cdot}003$ Å. The similarity of powder line intensities showed the compound to be isomorphous with the cubic phase of O_2PtF_6. The Raman frequency at 1838 cm^{-1} must be assigned to a dioxygenyl stretch of a salt of a strongly oxidizing transition metal hexafluoride. From room temperature to 50 °C, a mass spectrum paralleling that of O_2PtF_6 was observed, showing an O_2^+ peak and a fragment ion pattern characteristic of RuF_6. At 55 °C the metal containing portion of the mass spectrum began to change, and above 60 °C the pattern was dominated by the RuF_5 fragment ion pattern. Pentafluoride dimer was observed, and by 70 °C with slow heating, O_2^+ peaks had disappeared. Some contamination of the O_2RuF_6 sample by RuF_5 is probable, but the bulk of the RuF_5 results from thermal decomposition of the salt above 50 °C.

$O_2^+AuF_6^-$.—This crystalline, golden-yellow powder gave an *X*-ray powder pattern identical to that found by Leary and Bartlett,[7] isomorphous with the low temperature rhombohedral modification [2] of O_2PtF_6. A characteristic dioxygenyl stretching frequency of 1835 cm^{-1} was found, as previously observed.[7] The anion frequencies for AuF_6^- ($\nu_1 = 594$, $\nu_5 = 227$ cm^{-1}) agree closely with those observed by Leary and Bartlett [7] for O_2AuF_6 and $CsAuF_6$. We do not observe a band at 530 cm^{-1} reported by them for ν_2. On heating, O_2^+ ions were first observed mass spectrometrically below 100 °C. At 125—150 °C, O_2^+ persisted and Au^+ ions were then observed, followed at the same temperature by a series of AuF_x^+ fragments. At 175 °C, ions containing two Au atoms were seen, and at 200°, F_2^+ was observed. A substantial amount of gold coloured residue, probably AuF_3, remained in the effusion cell after the spectrum had disappeared at 225 °C.

The spectra of Au containing fragments are more representative of pentafluoride patterns than those of hexafluorides observed for O_2PtF_6, O_2RuF_6, and O_2RhF_6. The relative involatility of O_2AuF_6 requires taking mass spectra at temperatures where decomposition almost certainly occurs. The Raman and powder *X*-ray data suggest the O_2AuF_6 samples as formed are reasonably pure.

$O_2^+RhF_6^-$.—This very deep red, rather sticky compound gave *X*-ray powder reflections observable at low angles only. The pattern appears to contain extra lines from an impurity, probably RhF_5. This compound is isostructural with the rhombohedral salts; unit cell dimensions derived from the powder pattern are $a_0 = 5{\cdot}05 \pm 1$ Å and $\alpha = 97 \pm 1°$. The very deep colour of this material precluded a usable Raman spectrum; extensive decomposition of the sample occurred upon Ar ion laser irradiation. The room temperature mass spectrum contained O_2^+ and fragment ions of RhF_6. No evidence of RhF_5 was seen until *ca.* 100 °C.

$O_2^+AsF_6^-$.—White powders were obtained both thermally and photochemically. *X*-Ray powder data were consistent with the previously reported cubic cell with $a_0 = 8{\cdot}08$ Å. The Raman spectrum contained a vibration at 1858 cm^{-1}

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[16] W. Keifer and H. J. Bernstein, *Appl. Spectroscopy*, 1971, **25**, 609.

and an anion spectrum identical to that previously reported.[12]

$O_2^+SbF_6^-$ *and* $O_2^+Sb_2F_{11}^-$.—Thermal and photochemical preparations result in fluffy white powders which were identified as $O_2Sb_2F_{11}$. This compound was converted to O_2SbF_6 by further heating at 300 °C at a high $(4F_2 + O_2) : O_2Sb_2F_{11}$ ratio (see Table 1). The two compounds are easily distinguished by their O_2^+ stretching frequencies (O_2SbF_6, $\nu = 1861$ cm^{-1}; $O_2Sb_2F_{11}$, $\nu = 1864$ cm^{-1}). The anion spectra are also significantly different and details are given elsewhere.[9] *X*-Ray powder patterns of the two compounds are also quite different. The simpler O_2SbF_6 compound had an easily indexable powder pattern (cubic, $a_0 = 10{\cdot}13$ Å) but the pattern for $O_2Sb_2F_{11}$ was much more complicated and could not be readily indexed. McKee and Bartlett discuss this problem in more detail.[9]

The mass spectra of O_2SbF_6 showed no dimer ions at a limit of 1 part in 100 of the SbF_4^+ ion. The O_2^+ and SbF_4^+ peaks occurred at nearly equal intensities from 50 to 80 °C. Above 85 °C, the SbF_4^+ became dominant. In contrast, the mass spectrum of $O_2Sb_2F_{11}$ always showed a dominant SbF_4^+ ion. Inspection of Tables 2 and 3 shows that, at comparable temperatures, the ratio of the intensities SbF_4^+ to O_2^+ is larger in the spectrum of $O_2Sb_2F_{11}$ than in the spectrum of O_2SbF_6, as expected. A weak dimer ion occurred in the spectrum of $O_2Sb_2F_{11}$, but trimer could not be detected. The abundance of the dimer ion is significantly less than in the spectrum of SbF_5.[17]

$O_2^+BiF_6^-$.—This fluffy white powder had a simple *X*-ray powder pattern which could be indexed on the basis of a cubic unit cell with $a_0 = 10{\cdot}255 \pm 0{\cdot}005$ Å. The O_2^+ stretching frequency occurred at 1847 cm^{-1} in the Raman spectrum and at lower frequencies the spectrum was completely in accord with that expected for an octahedral BiF_6^- species ($\nu_1 = 591$, $\nu_2 = 549{,}512$, $\nu_5 = 253{,}237$ cm^{-1}) in which the degeneracies of the ν_2 and ν_5 fundamentals were removed. The O_2^+ stretching frequency associated with $O_2^+Bi_2F_{11}^-$ occurred at 1853 cm^{-1} but in no case was this compound isolated in pure form nor was any attempt made to synthesize it specifically. Presumably the reaction, $O_2BiF_6 + BiF_5 \longrightarrow O_2Bi_2F_{11}$ would proceed quantitatively at modest temperatures.

In the mass spectrum, O_2^+ was first observed at a source temperature of 30 °C. At 100 °C, the O_2^+ ion was still dominant, with the next most intense peak being BiF_4^+. A search for the dimeric ion $Bi_2F_9^+$ showed it to be absent at about 1 part in 100 of the BiF_4^+ peak. Contamination due to BiF_5 is therefore highly unlikely, and conditions in the effusion source were apparently unfavourable for the polymerization of BiF_5 monomer that results from the thermal degradation of O_2BiF_6.

$O_2^+Nb_2F_{11}^-$ *and* $O_2^+NbF_6^-$.—The major product formed in the thermal reaction was $O_2^+Nb_2F_{11}^-$ despite repeated attempts to prepare the simple $O_2^+NbF_6^-$. In all syntheses, the product was initially contaminated with an excess of NbF_5 which could be readily identified by its characteristic Raman spectrum[18] and by the fact that it could be completely removed by sublimation.

The Raman spectrum consisted of a characteristic O_2^+ stretching frequency at 1858 cm^{-1} and a complicated anion spectrum at lower frequencies which is qualitatively similar to that reported earlier by Gillespie and Landa[19] for $Cs^+Nb_2F_{11}^-$. The two most intense peaks occur at 759 and 685 cm^{-1} in $O_2^+Nb_2F_{11}^-$. In our purest sample of $O_2^+Nb_2F_{11}^-$ there was no evidence of NbF_5 or $O_2^+NbF_6^-$. The spectrum of the NbF_6^- species was available from our unpublished results on $NO^+NbF_6^-$ ($\nu_1 = 686$, $\nu_2 = 584{,}554$, $\nu_5 = 291{,}273$ cm^{-1}). Samples of $O_2^+Nb_2F_{11}^-$ containing $O_2^+NbF_6^-$ impurities could be identified by the O_2^+ stretching frequency at 1853 cm^{-1} corresponding to the $O_2^+NbF_6^-$ species. In addition, the intensity ratio of the 759—685 cm^{-1} bands in $O_2^+Nb_2F_{11}^-$ is lower because of the contribution to the latter by the ν_1 fundamental of the NbF_6^- species. From a detailed comparison of the relative intensities, band widths, and frequencies of the complete Raman spectra we are reasonably confident in our ability to synthesize and purify $O_2^+Nb_2F_{11}^-$ but we have been unable to prepare a pure sample of $O_2^+NbF_6^-$. The two compounds are easily distinguishable, however, by their O_2^+ stretching frequencies. The *X*-ray powder pattern for $O_2^+Nb_2F_{11}^-$ was complex and was not readily indexed.

The mass spectrum of this mixture showed NbF_5 evolution at a lower temperature than O_2 evolution. At 36 °C NbF_4^+ and $Nb_2F_9^+$ could be detected easily, while O_2^+ rose above background at 40 °C. The oxygen signal persisted throughout the remainder of the measurements. Table 3 shows the detection of $Nb_3F_{14}^+$, which must result from the gas phase reaction of NbF_5 monomers or NbF_5 and Nb_2F_{10} in the effusion source, since the Raman spectra showed conclusively that NbF_5 was absent in the solid phase.

$O_2^+Ta_2F_{11}^-$.—Paralleling the behaviour reported for niobium, $O_2Ta_2F_{11}$ appears to be the species formed in the oxyfluorination of tantalum. No evidence for the formation of O_2TaF_6 could be found although for some syntheses there were indications in the Raman spectra that the formation of $(O_2^+)_2TaF_7^{2-}$ occurred. The evidence is not particularly persuasive, however, and we report data only on $O_2Ta_2F_{11}$. The anion spectrum is qualitatively similar to that observed for $O_2^+Nb_2F_{11}^-$ with the most intense peaks at 749 and 699 cm^{-1}. The spectrum is drastically different from that observed for a compound previously considered to be $CsTa_2F_{11}$.[19] We have not studied the spectrum of the latter compound, however, and accordingly do not comment on the observed spectral differences. The O_2^+ stretching frequency occurs at 1858 cm^{-1}, the same value as that reported for $O_2^+Nb_2F_{11}^-$. The *X*-ray patterns are too complex to be indexed.

The mass spectra for $O_2Ta_2F_{11}$ show that at 58 °C the O_2^+ ion dominates the spectra, and the $Ta_2F_9^+$ ion is absent. However, in the temperature range of 87—100 °C the TaF_4^+ ion dominates the spectrum, while the relative intensity of the O_2^+ ion has dropped by an order of magnitude. The dimeric ion is also evident in the latter temperature range. There was no evidence of the trimer ion $Ta_3F_{14}^+$ at about one part in 10^4 of the MF_4^+ peak, indicating the absence of the pentafluoride.

Raman Spectra.—Observation of the vibrational bands associated with the O_2^+ cations was the most important aspect of the Raman spectra of the dioxygenyl salts in so far as this feature was used as a criterion for successful synthesis.

The dioxygenyl frequencies are listed in Table 1. For the dioxygenyl salts, agreement with previous work is excellent. For all except O_2RhF_6, the presence of the O_2^+ cation is clear. The deeply coloured rhodium salt decomposed too rapidly in the argon laser beam to give

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[17] M. J. Vasile and W. E. Falconer, *Inorg. Chem.*, 1972, **11**, 2282 and references quoted therein.

[18] I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958.

[19] R. J. Gillespie and B. Landa, *Inorg. Chem.*, 1973, **12**, 1383.

interpretable results. An O_2^+ stretching frequency could be observed using a Krypton ion laser, although the intensity and accuracy of the measurement is lower than the others. The stretching frequencies fall into two sets. The dioxygenyl salts of those transition metals that would form strongly oxidizing hexafluorides (Pt, Au, and Ru) have their frequencies at about 1835 cm^{-1}. Those elements that form pentafluorides with strong affinities for F^-, *viz.* the main group elements, niobium, and tantalum, have frequencies above 1850 cm^{-1}. In cases where O_2MF_6 and $O_2M_2F_{11}$ species are formed, the dioxygenyl stretching frequency for the former always occurs a few wavenumbers below that for the latter (Table 1). The difference is small but easily measurable.

Mass Spectra.—Cracking patterns for the O_2MF_6 compounds are presented in Table 2 and those for the $O_2M_2F_{11}$ compounds are given in Table 3. The gross features correlate with the groupings of compounds based on the Raman spectra. For salts of those metals that form strongly oxidizing hexafluorides, *viz.* O_2RhF_6, O_2RuF_6, and O_2PtF_6, the mass spectra show O_2^+ ions as the most intense peak plus a distribution of fragment ions similar to that obtained from the related hexafluoride which include relatively intense doubly charged ions M^{2+}, MF^{2+}, MF_2^{2+}, MF_3^{2+}, intense MF_5^+ ions, and weak parent ions MF_6^+. For dioxygenyl salts of those elements that form pentafluorides with strong affinities for F^-, the mass spectra show O_2^+, in some cases F_2^+, and a fragment ion pattern extremely similar to that of the corresponding pentafluoride including in some cases the presence of oligomers. The ratios of dimer to monomer observed in the spectra of the simple O_2MF_6 salts of Sb and Ru were significantly below the values obtained for the corresponding pentafluorides. In contrast, the relative amounts of dimers observed in the spectra of the more complex $O_2M_2F_{11}$ salts of Nb and Ta were close to those obtained for the pentafluorides, which provides further evidence that the stoicheiometry of the latter samples are as claimed.

The mass spectrum of O_2AuF_6, Table 4, should fall into the first group, since if AuF_6 were to exist, it would certainly be a sufficiently powerful oxidizer to ionize O_2. The unique pattern is, however, much closer to that of a pentafluoride than a hexafluoride, particularly with respect to the high abundances of dimeric and trimeric species. The spectrum differs from that of other pentafluorides by the unusually low intensities of the MF_3^+ and MF_4^+ ions. Instability of the AuF_5 moiety at the temperature and electron energy used to obtain the spectra may be responsible for this effect.

The observation of abundant fragment ions containing two or three gold atoms requires AuF_5 vapour at sufficient pressures in the effusion source to yield association into neutral dimers and trimers. It is highly unlikely that these associated species can result from ion–molecule reactions of degradation products in the ion source.[15] We therefore conclude that O_2AuF_6 decomposes in the effusion source to give AuF_5, and that AuF_5 exists as a stable molecule.

DISCUSSION

The dioxygenyl salts that have now been characterized fall into two groups: those that form with metal hexafluorides that will oxidize molecular oxygen, and those that form with powerful fluoride ion acceptors. O_2BF_4 [3,14,20,21] is the only example of this latter class not having a hexafluoro anion. All known examples of this class have the common property that the formal oxidation state of the anion central atom is the highest allowed by the valence electrons of the neutral atom. It is probable that additional dioxygenyl salts could be prepared with strong F^- acceptor molecules of potentially higher valent transition metals under conditions which do not oxidize the metals to stable hexafluorides. Further examples of the first class would be contingent upon finding conditions to stabilize additional transition metals to the right of Rh and Au in the Periodic Table as fluorides in the pentavalent state. O_2CrF_6 or O_2MnF_6 are possibilities in the first transition series.

The vibrational frequency of O_2^+, readily observed by Raman scattering, provides a facile diagnostic of compounds of this type in which charge nearly equivalent to an electron is transferred to form the cation. The salts formed by strongly oxidizing hexafluorides have O_2^+ frequencies furthest removed from the free ion value [11] of 1876 cm^{-1}, indicating a small covalent contribution to the stability of this class. It must be remembered that the observations are not for free molecules, but for crystalline solids in which the free molecular properties may be strongly perturbed.

The volatility of the first class of these compounds is surprisingly high, O_2RhF_6 being readily sublimed at room temperature, and all providing sufficient vapour pressure (*ca.* 2—5 Torr) for mass spectral studies with modest heating. This shows that the molecular units are themselves stable, not requiring additional stabilization from the crystals. This is a direct reflection of the large electron affinities of the respective fluorides. Molecules of the second type appear to decompose to yield the observed mass spectra.

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