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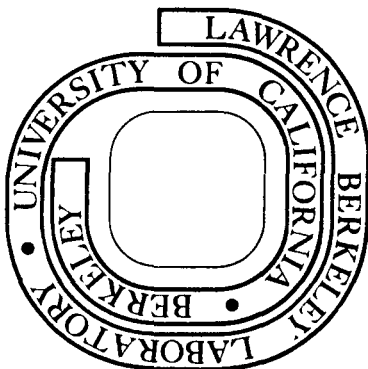
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THE DIOXYGENYL SALTS $O_2^+SbF_6^-$ AND $O_2^+Sb_2F_{11}^-$
AND THEIR CONVENIENT LABORATORY SYNTHESSES

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The first claim for the salt of formulation $O_2^+SbF_6^-$ was that of Young, et al.¹ These authors prepared their material by interaction of O_2F_2 with SbF_5 . A puzzling feature of this report, however, was the rather large cubic unit cell quoted, for which $a = 10.71 \text{ \AA}$, since in the previously characterized² platinum analogue $a = 10.032 \text{ \AA}$. In later papers Shamir and Binenboym described³ a photochemical synthesis for what was claimed to be $O_2^+SbF_6^-$ and Beal, et al. described⁴ a preparation from SbF_5 , F_2 , and O_2 which simply involved heating this mixture. The first authors presented no unambiguous evidence for the formulation $O_2^+SbF_6^-$, and quoted a cubic unit cell constant of 10.30 \AA , a value which, although more acceptable than that of Young, et al., still seemed rather high. Beal, et al. provided X-ray powder data to support a unit cell of 10.13 \AA , a value in much closer harmony with the cell parameter for the cubic $O_2^+PtF_6^-$ salt.² The X-ray powder data of Beal, et al. was, however, ascribed to a face-centered cell, whereas the full data (some of which was omitted from their tabulation) supported a body-centered cell with $a = 10.13 \text{ \AA}$. It is now clear that weak diffraction lines were omitted from their data. These represent (as discussed² by

Bartlett and Lohmann for the $O_2^+PtF_6^-$ case) diffraction by the light atom superlattice and are of crucial structural importance.

In their differential thermal analysis of $O_2^+SbF_6^-$ Nikitina and Rosolovskii recognized⁵ the existence of the $O_2^+Sb_2F_{11}^-$ salt as well as $O_2^+SbF_6^-$ and attempted a characterization of the two salts on the basis of X-ray powder data. Their data, however, is not that for the pure components $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$. Furthermore, Nikitina and Rosolovskii also failed to recognize $O_2^+SbF_6^-$ as an isomorph of $O_2^+PtF_6^-$.

Although the O_2^+ stretching frequency has been reported⁶ for what was stated to be the $O_2^+SbF_6^-$ salt, the anion spectra were not given.

The X-ray powder data given in Table I and the Raman spectrum shown in Fig. 1b characterize the $O_2^+SbF_6^-$ salt. The X-ray data establish that the compound is isomorphous with $O_2^+PtF_6^-$. The unit cell is cubic with $a = 10.132 \pm 0.002 \text{ \AA}$, $V = 1040 \text{ \AA}^3$, $z = 8$, $\frac{D}{C} = 3.418 \text{ g cm}^{-3}$. Since all observed reflections obey the conditions $\underline{h+k+l} = 2n$ and $\underline{0kl} \subset \underline{k(l)} = 2n$, the indicated space group is $Ia\bar{3}$ (#206)⁷ as established for O_2PtF_6 .^{2,8} The formula unit volume of 130 \AA^3 is 2.4 \AA^3 less than that found for $NO^+SbF_6^-$ by Bartlett and Jha.⁹ This is comparable to the PtF_6^- case where $V(NO^+PtF_6^-) = 129.5 \text{ \AA}^3$ and $V(O_2^+PtF_6^-) = 126.3 \text{ \AA}^3$. The close similarity of the intensities of the weak powder diffraction lines (oxygen and fluorine diffraction only), compared with those in the platinum relative,⁹ suggest an isostructural relationship. Comparison of the Raman spectrum with that of $O_2^+PtF_6^-$ (given in Fig. 1c) further supports the close structural similarity.

The X-ray powder data for $O_2^+Sb_2F_{11}^-$ given in Table II have not been indexed and all attempts to grow single crystals have failed. The

Raman spectrum given in Fig. 1a again gives clear evidence of the O_2^+ ion (in the band at 1865 cm^{-1}) and the anion spectrum shows relationship to the SbF_6^- spectrum. The anion spectrum is in fact simpler than in $XeF^+Sb_2F_{11}^-$ (ref. 11) and $XeF_3^+Sb_2F_{11}^-$ (ref. 12).

It may be that the anion in $O_2^+Sb_2F_{11}^-$ possesses a linear bridge and that the O_2^+ species are symmetrically placed about the anion. This would account for the absence of features in the Raman spectrum attributable to bridge stretching. In the $XeF^+Sb_2F_{11}^-$ and $XeF_3^+Sb_2F_{11}^-$ salts the bridge angles are 150° (ref. 13) and 155° (ref. 14), respectively, and the salts show Raman bands attributable to bridge stretch at 482 (ref. 11) and 487 cm^{-1} (ref. 12), respectively. In $BrF_4^+Sb_2F_{11}^-$ where the bridge angle is not significantly deviant from linearity,¹⁵ this Raman feature is not observed.¹² The presence of a band at 470 cm^{-1} in the infrared spectrum of $O_2^+Sb_2F_{11}^-$ indicates that the strength of the bridge bond on the anion is not much different from that in the other salts, and coupled with the absence of its counterpart in the Raman, argues for a linear anion.

Experimental

$O_2^+Sb_2F_{11}^-$ was prepared by irradiation of a fluorine, oxygen, and antimony pentafluoride mixture contained in a Pyrex bulb provided with a Kel-F tipped Whitey valve joined to the bulb through a Kovar seal. A 450 watt Hanovai ultraviolet lamp was used at a distance of 6 inches; irradiations lasted 12-16 hours. A stoichiometry appropriate for the reaction $O_2 + \frac{1}{2}F_2 + 2SbF_5 \rightarrow O_2Sb_2F_{11}$ was found to be best; thus 69.0 mmoles

SbF₅ with 34.5 mmoles O₂ and 17.3 mmoles F₂ in a 5 liter flask were quantitatively converted to O₂Sb₂F₁₁ in 12 hours. In irradiations where an excess of F₂ and O₂ over that required for O₂Sb₂F₁₁ formation prevailed, O₂⁺SbF₆⁻ was also observed in the product. Use of excess SbF₅ necessitated the removal of this material from the product but this approach does provide pure O₂⁺Sb₂F₁₁⁻.

O₂SbF₆ was prepared by heating O₂Sb₂F₁₁ in a dynamic vacuum at 110°. At that temperature, the SbF₅ is removed slowly and at an approximately constant rate. If removal of SbF₅ is halted at a weight corresponding to loss of one mole of SbF₅ per mole of O₂Sb₂F₁₁, the material which remains provides the X-ray powder pattern and the Raman spectrum assigned to O₂⁺SbF₆⁻. The O₂⁺SbF₆⁻ salt itself is unstable under those preparative conditions, but O₂⁺Sb₂F₁₁⁻ decomposes to O₂⁺SbF₆⁻ at a greater rate. It is therefore essential to monitor the rate of loss of SbF₅ so that SbF₅ removal may be halted when the last of the Sb₂F₁₁⁻ salt has decomposed. The conversion of 5.55 mmoles O₂Sb₂F₁₁ to 5.54 mmole O₂SbF₆ required 282 hours at 110°. O₂Sb₂F₁₁ may be converted to O₂SbF₆ more rapidly under vacuum at higher temperatures, but the yield is lower; e.g., at 160° the conversion of 0.76 mmoles O₂Sb₂F₁₁ to 0.49 mmoles O₂SbF₆ was complete in only 3 hrs., the loss of material being due to thermal decomposition. X-ray powder photography and Raman spectroscopy revealed that removal of SbF₅ from O₂⁺Sb₂F₁₁⁻ was associated with the appearance of O₂⁺SbF₆⁻. No phases other than O₂⁺SbF₆⁻ and O₂⁺Sb₂F₁₁⁻ were indicated.

$O_2Sb_2F_{11}$ was also prepared from O_2SbF_6 . The 1:1 salt (1.75 mmole) was placed in a Pyrex tube with excess SbF_5 (2-3 ml), under 300 mm of nitrogen pressure. The tube was brought to 125° and shaken. A clear solution was not obtained, but care was taken to break up the clumps of solid by agitating the mixture to a white slurry. The mixture was cooled to room temperature before unreacted SbF_5 was removed under vacuum. The white solid which remained was shown by X-ray and Raman spectra to be $O_2Sb_2F_{11}$ and the weight corresponded to 1.61 mmoles.

The preparative technique for X-ray powder diffraction and Raman samples has been previously described, as has the equipment used.¹² Long exposure times were required to obtain a suitable powder pattern for $O_2^+Sb_2F_{11}^-$, but the 25 lines reported in Table II unambiguously fingerprint that compound. The Raman spectra have been intensity corrected for non-linear sensitivity of the phototube. For the antimony salts the exciting line was the $5145 \text{ \AA} \text{ Ar}^+$ line and for the deep red platinum salt the $6741 \text{ \AA} \text{ Kr}^+$ line.

Infrared spectra from $4000\text{-}400 \text{ cm}^{-1}$ were recorded on a Perkin-Elmer 237 Infracord spectrophotometer. The powdered solids were pressed between AgCl windows in an all Kel-F cell. O_2SbF_6 shows only one broad band in the region examined, at $660\text{-}670 \text{ cm}^{-1}$, characteristic of the ν_3 mode of the SbF_6^- ion. $O_2Sb_2F_{11}$ shows three bands, centered at 677, 652, and 470 cm^{-1} .

Acknowledgments

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TABLE I

X-Ray Powder Data for $O_2^+SbF_6^-$

(Cubic: $a = 10.132 \pm 0.002 \text{ \AA}^*$, $V = 1040 \text{ \AA}^3$, $z = 8$, $D_c = 3.418 \text{ g/cm}^3$, Space group $Ia\bar{3}$, Cu $K\alpha$ radiation Ni filter).

$d\text{\AA}$	$1/d_{obs}^2$	$1/d_{calc}^2$	h k l	I/I _o
5.091	.0385	.0390	2 0 0	8
3.595	.0772	.0779	2 2 0	10
2.915	.1175	.1169	2 2 2	5
2.697	.1371	.1364	3 2 1	2
2.534	.1556	.1558	4 0 0	4
2.389	.1751	.1753	4 1 1	2
2.260	.1957	.1948	4 2 0	5
2.159	.2144	.2143	3 3 2	3
2.067	.2339	.2338	4 2 2	7
1.980	.2550	.2533	4 3 1	1
1.785	.3138	.3117	4 4 0	5
1.685	.3520	.3507	4 4 2, 6 0 0	5
1.597	.3919	.3896	6 2 0	5
1.521	.4322	.4286	6 2 2	5
1.461	.4685	.4676	4 4 4	2
1.430	.4891	.4871	5 4 3	< 1
1.401	.5095	.5065	6 4 0	4
1.374	.5294	.5260	6 3 3, 7 2 1, 5 5 2	1
1.351	.5480	.5455	6 4 2	5
1.283	.6070	.6040	7 3 2, 6 5 1	1
1.265	.6257	.6234	8 0 0	1
1.226	.6650	.6624	8 2 0, 6 4 4	4

* Cell dimension obtained from an extrapolation using the Nelson-Riley function.

TABLE I Continued

θ dA	$1/d^2_{\text{obs}}$	$1/d^2_{\text{calc}}$	h k l	I/I _o
1.192	.7047	.7014	8 2 2, 6 6 0	4
1.160	.7435	.7403	6 6 2	3
1.131	.7827	.7793	8 4 0	3
1.104	.8212	.8182	8 4 2	3
1.077	.8623	.8572	6 6 4	3
1.033	.9371	.9351	8 4 4	2
1.012	.9759	.9741	10, 0, 0; 8 6 0	2
.9926	1.015	1.013	10, 2, 0; 8 6 2	4
.9738	1.054	1.052	10, 2, 2; 6 6 6	3
.9396	1.132	1.130	10, 4, 0; 8 6 4	4
.9240	1.171	1.169	10, 4, 2	3
.8945	1.249	1.247	8 8 0	1
.8811	1.287	1.286	10, 4, 4; 8 8 2	3
.8681	1.326	1.325	10, 6, 0; 8 6 6	3
.8556	1.365	1.364	10, 6, 2	3
.8438	1.404	1.403	12, 0, 0; 8 8 4	3
.8324	1.443	1.442	12, 2, 0	2
.8215	1.482	1.481	12, 2, 2; 10, 6, 4	4
.8006	1.560	1.558	12, 4, 0	2
.7910	1.598	1.597	12, 4, 2; 10, 8, 0; 8 8 6	6
.7816	1.637	1.636	10, 8, 2	4

TABLE II

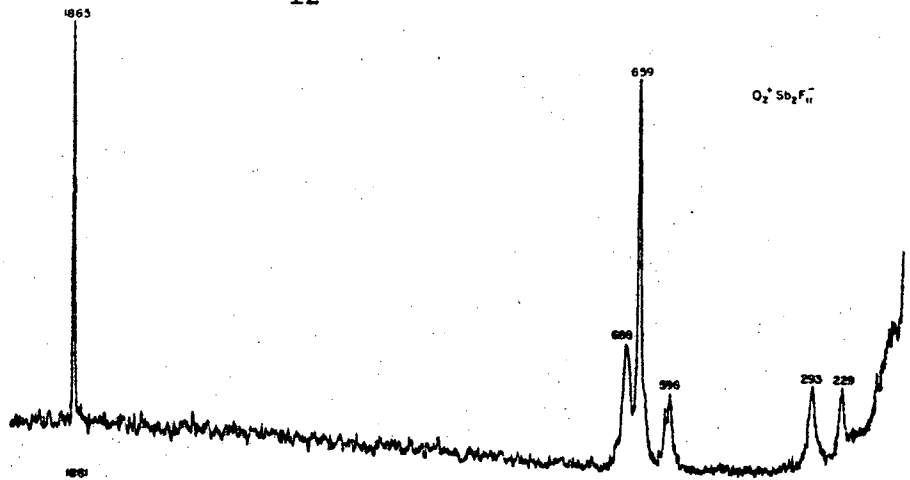
X-Ray Powder Data for $O_2^+ Sb_2 F_{11}^-$
(Cu-K α radiation Ni filter)

<u>d\AA</u>	<u>1/d²</u>	<u>I/I_o</u>
7.809	.0164	1
6.476	.0238	1
5.739	.0304	2
5.354	.0349	6 (broad)
4.941	.0410	2
4.634	.0465	1
4.306	.0539	1
3.951	.0640	10 (broad)
3.767	.0705	1
3.616	.0765	6 (broad)
3.436	.0847	2
3.213	.0969	1 (v. broad)
2.948	.1151	1
2.824	.1253	3
2.721	.1350	3
2.622	.1453	2
2.520	.1575	1
2.454	.1661	3
2.131	.2201	2
2.031	.2423	2
1.949	.2632	1
1.882	.2822	1
1.791	.3117	1

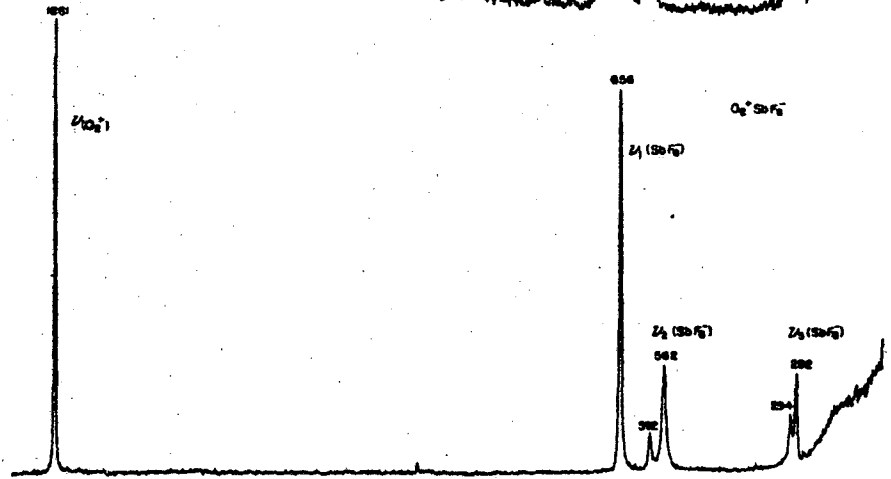
TABLE II Continued

<u>dA</u>	<u>1/d²</u>	<u>I/I_o</u>
1.704	.3442	1
1.651	.3665	1
1.618	.3822	3

A



B



C

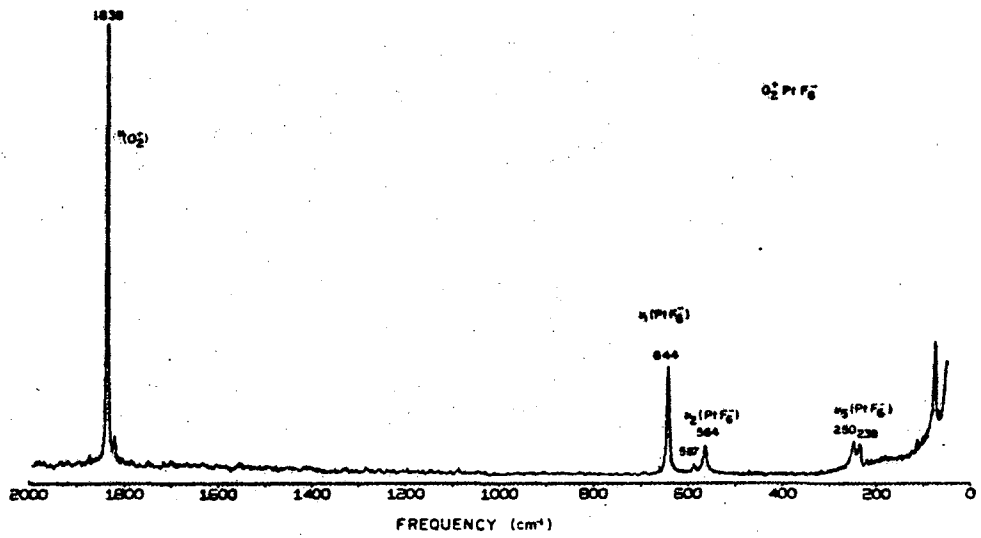


Figure 1

Raman spectra of (a) $O_2^+ Sb_2F_{11}^-$; (b) $O_2^+ SbF_6^-$; (c) $O_2^+ PtF_6^-$

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