Xenon(II) Fluoride Fluorosulphate, $FXeSO_3F$, and Xenon(II) Bisfluorosulphate, $Xe(SO_3F)_2$ and Related Compounds

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THERMOCHEMICALLY, the bonds in xenon compounds are weak.[1] This, plus the relative inertness of xenon, generated in oxidative interactions of the type: $XeL^1_2 + nAL^2_x \rightarrow Xe + nAL^1_xL^1_y$, implies effectiveness for such compounds in 'clean oxidative synthesis. However, the variety of established ligands for xenon is small. It appears[1] that only the most electronegative ligands bond effectively with xenon, and the only established compounds available for use at ordinary temperatures and pressure are those in which the ligand atoms are fluorine and unsubstituted oxygen atoms. Hitherto, in the case of xenon(II), the situation had been even more limited, the fluoride being the only available compound,† even the oxide being unknown. Recently, however, Bartlett and Sladky have reported[3] the preparation of xenon(II) fluoride fluorosulphate, $FXeSO_3F$ and the related perchlorate, $FXeClO_4$. An *X*-ray single-crystal analysis of the former has now been completed and the salient molecular dimensions are reported here. Furthermore, the preparative technique of Bartlett and Sladky has been extended to yield the bis-compounds, $Xe(SO_3F)_2$ and $Xe(ClO_4)_2$, in which the xenon(II) atom displays the novel –O–Xe^{II}–O– co-ordination.

Xenon difluoride was prepared and characterized as described in Williamson's modification[4] of the method of Streng and Streng, and Holloway. Fluorosulphate and perchlorate derivatives were obtained by treating it with an appropriate molar amount of acid at temperatures of $-75°$ or below. These interactions are, in considerable measure, driven by the formation of the remarkably stable hydrogen fluoride,[5] which was removed at the lowest possible temperature, before allowing the product to warm up. Some experimental details and physical properties of the compounds are given in the Table.

The fluorosulphates are kinetically more stable than the perchlorates, but all are thermodynamically unstable and decompose at room temperature. Xenon fluoride fluorosulphate decomposes quantitatively, but very slowly at 20° ($t_{\frac{1}{2}}$ *ca.* 1 week), according to the equation: $2\ FXeSO_3F \rightarrow Xe + XeF_2 + S_2O_6F_2$. However, the solid can be completely sublimed *in vacuo* at 20°. Although the solid is colourless the melt is yellow-green. The colour of the melt may derive from either XeF or SO_3F radicals or both. The bisfluorosulphate also decomposes cleanly: $Xe(SO_3F)_2 \rightarrow Xe + S_2O_6F_2$ (the $S_2O_6F_2$ melts sharply at $-51{\cdot}6°$, *ca* 4° higher than the temperature previously given[6]). Unfortunately, efforts to control the decomposition of the perchlorates to generate $(ClO_4)_2$ have failed so far, the products being xenon, oxygen, and Cl_2O_7, with some ClO_2. The preliminary chemical evidence confirms that the fluorosulphates are excellent oxidative fluorosulphonating agents, the behaviour being very like that of peroxydisulphuryl difluoride.[7]

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† Musher has recently described[2] colourless solids, obtained by adding XeF_2 to acetic or trifluoroacetic acids, as xenon acetate and trifluoroacetate, respectively. If this is so, then from the manner of the preparations (employing an excess of acid), the formulations are likely to be $Xe(Ac)_2$ and $Xe(O_2C{\cdot}CF_3)_2$.

The preparation and physical properties of $FXeSO_3F$, $FXeClO_4$, $Xe(SO_3F)_2$, $Xe(ClO_4)_2$, *and* $S_2O_6F_2$

Preparation conditions	Stoicheiometry	Compound	m.p.
Initially −110° Completed −60°	0·477 g. XeF_2 (2·82 mmoles) + 0·282 g. $HClO_4$ (2·8 mmoles) → 0·678 g. $FXeClO_4$ (2·72 mmoles) + volatiles (HF + traces of Xe, O_2, ClO_2 and Cl_2O_7)	$FXeClO_4$ Colourless → red melt (+O_2 and Xe)	16·5°
−75°	0·728 g. XeF_2 (4·3 mmoles) + 0·43 g HSO_3F (4·3 mmoles) → 1·04 g. $FXeSO_3F$ (4·2 mmoles) + 0·125 g. volatiles (HF + traces of Xe, $S_2O_5F_2$, and $S_2O_6F_2$)	$FXeSO_3F$ (Colourless)	36·6°
−75°	0·731 g. XeF_2 (4·3 mmoles) + 0·864 g HSO_3F (8·64 mmoles) → 1·371 g. $Xe(SO_3F)_2$ (4·2 mmoles) + 0·212 g. volatiles (HF + traces of Xe, $S_2O_5F_2$, and $S_2O_6F_2$)	$Xe(SO_3F)_2$ (pale yellow)	43—45°
At 20° (< 2 days) more rapidly as a melt	$Xe(SOF_3)_2 \rightarrow Xe + S_2O_6F_2$ (quantitative)	$S_2O_6F_2$	−51°
Initially −110°, completed −60°	XeF_2 + 2 moles $HClO_4$ → yellow solid on removal of HF at −50°. The yellow solid decomposed *ca.* −20°	$Xe(ClO_4)_2$ pale yellow decomposes to red liquid	—

The Raman evidence indicates a structural relationship of the monofluorosulphate to the bis-compound and a relationship of the latter to $S_2O_6F_2$. Both $FXeSO_3F$ and $FXeClO_4$ show a very strong band close to 500 cm.$^{-1}$, in which region the very strong [symmetric ν(Xe–F)] of XeF_2 is located (493 cm.$^{-1}$).[8] Values of ν(Xe–F) > 520 cm.$^{-1}$ imply an Xe–F bond stronger than that in XeF_2, but the bond is clearly weaker than in XeF^+, which occurs[9] in the salts $[XeF]^+[MF_6]^-$ and $[XeF]^+[M_2F_{11}]^-$ [M = noble metal (except Pd) or antimony] where $\nu(Xe–F^+)$ lies in the range 605—621 cm.$^{-1}$. The Raman data also indicate that the xenon(II) bond to oxygen of the acid anion is only slightly weaker than the Xe–bond. The ν(Xe–O) apparently lies in the range 433—507 cm.$^{-1}$ for the monofluoro-compounds. The Xe–O bond is evidently similar in the bisfluorosulphate.

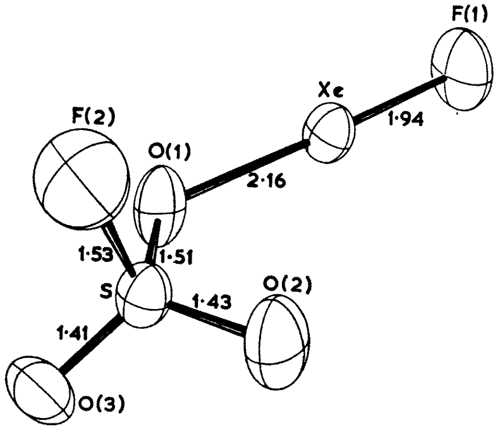

FIGURE. *Molecular structure of* $FXeOSO_2F$. *Precision of bond lengths is* ca. 0·01 Å (*uncorrected for thermal motion*). *The angles* F(1)–Xe–O(1) *and* Xe–O(1)–S *are* 177·5 ± 0·4° *and* 123·4 ± 0·6°·

The bicovalent nature of xenon in $FXeSO_3F$ has been confirmed by a single-crystal *X*-ray analysis. The compound is orthorhombic, with a = 9·88, b = 10·00, c = 10·13 Å (all ±0·01 Å), Z = 8, most probable space group $D_{2h}^{15} = Pbca$. Counter measurements were made at 0° on 1453 unique reflections, of which 849 were observable above background. A straightforward analysis *via* Patterson synthesis, F_{obs}. synthesis, and least-squares refinement has led to a conventional R factor of 0·048 for the observable reflections at the present stage of refinement. The structure of the $FXeSO_3F$ molecule is represented in the Figure.

It is probable that the bonding in $FXeClO_4$ is very similar to that represented by $FXeSO_3F$. Although *X*-ray powder photographs show that they are not isomorphous, some crystallographic relationship is indicated. Single crystals of the bisfluorosulphate have been obtained and a structural analysis will be undertaken.

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