Osmium Tetrafluoride Dioxide, OsF_4O_2: a New Osmium(VIII) Oxide Fluoride

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The reaction of OsO_4 with KrF_2 in anhydrous HF produces *cis*-OsF_4O_2 and not OsF_6O as previously reported.

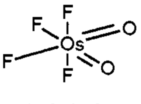
Of the three possible mononuclear oxide fluorides of osmium in its +VIII oxidation state, OsF_6O, OsF_4O_2 and OsF_2O_3, only the latter had been well known and characterized.[1–3] Attempts to prepare the other two oxide fluorides had not only failed, but also suggested that such compounds will disproportionate readily.[2,4,5] Very recently, a new osmium(VIII) oxide fluoride was prepared at Saclay and identified as OsF_6O by elemental analysis, X-ray powder data and vibrational spectroscopy.[6]

During an ongoing effort at Rocketdyne on highly coordinated, high oxidation state compounds, including several XF_6O type ions,[7] a poor agreement between the vibrational spectra of the alleged OsF_6O and the other XF_6O ions was noticed, and the Saclay experiments were repeated at Rocketdyne. The following results establish that the new osmium(VIII) oxide fluoride, discovered at Saclay, is not OsF_6O but *cis*-OsF_4O_2. Further characterization of the material carried out independently at Saclay also led to this conclusion.

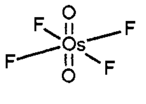
The synthesis of the new osmium(VIII) oxide fluoride was carried out from OsO_4 and an excess of KrF_2 in anhydrous HF solution, as previously described.[6] A careful separation, measurement and identification of all reactants and reaction products by both pressure–volume–temperature measurements for the volatile species and weights for all of them established the following quantitative 1:2 reaction (1). The excess of KrF_2 used was recovered unchanged.

$$OsO_4 + 2KrF_2 \rightarrow OsF_4O_2 + 2Kr + O_2 \qquad (1)$$

The physical properties of the osmium oxide fluoride prepared in this manner (burgundy-red solid, m.p. 90 °C, vapour pressure ~ 1 Torr at room temperature), its X-ray powder diffraction pattern and vibrational spectra were within experimental error identical to those previously reported[6] and leave no doubt that the two compounds are the same.†



cis-OsF_4O_2



trans-OsF_4O_2

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† Vibrational spectra: The IR and Raman spectra of the solid and the Raman spectrum of an HF solution were recorded. The general pattern of these spectra resembles that[8] of *cis*-$IF_4O_2^-$ more closely than those[7] of IF_6O^- and TeF_6O^{2-}. Furthermore, two Raman bands at 942 and 932 cm^{-1} are observed for the solid in the Os=O stretching region that had previously been interpreted[6] as being due to a crystal field splitting of an Os=O group containing a single oxygen atom. The present study, however, shows that in HF solution this splitting is retained and suggests the presence of more than one oxygen atom in the molecule.

^{19}F NMR spectrum: The ^{19}F NMR spectrum of the new osmium oxide fluoride in HF solution was recorded and exhibits an A_2B_2 pattern, *i.e.* two almost identical 1:2:1 triplets at δ 61.3 and 14.7 downfield from external $CFCl_3$ with J_{FF} 136 Hz. No other signals were observed. This clearly establishes that the new osmium oxide fluoride contains only four and not five fluorine atoms and must be OsF_4O_2 and not OsF_6O. Furthermore, the observation of two nonequivalent sets of two fluorine atoms each shows that the OsF_4O_2 is present exclusively as the *cis*- and not as the *trans*-isomer. For *trans*-OsF_4O_2, only a single resonance should be observed with no signs of splittings due to F–F coupling.