

## Difluoride Dioxides of Molybdenum(VI) and Tungsten(VI)

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*Summary*  $^{19}\text{F}$  N.m.r. and i.r. spectroscopy, mass spectrometry, and chemical analysis show that  $\text{MoO}_2\text{F}_2$  is the main product of reaction of  $\text{MoO}_2\text{Cl}_2$  with anhydrous HF at elevated temperature and pressure or  $\text{XeF}_2$  at low

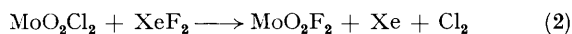
temperature, evidence for  $\text{MoO}_2\text{ClF}$  also being obtained in the  $\text{MoO}_2\text{Cl}_2$ - $\text{XeF}_2$  reactions; controlled hydrolysis of  $\text{WOF}_4$  gives  $\text{WO}_2\text{F}_2$ , and reaction of the difluoride dioxides with  $\text{XeF}_2$  gives  $\text{XeF}_2\cdot\text{MoOF}_4$  and  $\text{XeF}_2\cdot\text{WOF}_4$ .

ALTHOUGH there is spectroscopic evidence for  $\text{MoO}_2\text{F}_2$  the compound has not been prepared in bulk or properly characterized. In 1907 the analysis of a solid resulting from the reaction of  $\text{MoO}_2\text{Cl}_2$  with anhydrous HF suggested that the product was  $\text{MoO}_2\text{F}_2$ .<sup>1</sup> More recently it has been claimed as the product of hydrolysis of  $\text{MoF}_6$  in HF at  $-5^\circ\text{C}$  and the reaction of  $\text{MoO}_3$  with  $\text{IF}_5$ .<sup>3</sup> Evidence for the preparation of bulk  $\text{WO}_2\text{F}_2$  is even more sparse, there being only one paper which claims synthesis by the hydrolysis of  $\text{WF}_6$  in anhydrous HF.<sup>2</sup> We now describe the preparation, isolation, and characterization of  $\text{MoO}_2\text{F}_2$ , together with some of its chemistry, and present good evidence for  $\text{WO}_2\text{F}_2$ .

Stoichiometric quantities of  $\text{MoO}_2\text{Cl}_2$  and anhydrous HF were heated at  $280\text{--}300^\circ\text{C}$  in a nickel reactor [equation (1)].



After 3–4 h volatile material was removed at  $0^\circ\text{C}$  and a pale lilac solid was obtained. A similar product and the expected volume of xenon and chlorine was obtained when stoichiometric quantities of  $\text{MoO}_2\text{Cl}_2$  and  $\text{XeF}_2$  were warmed to  $0^\circ\text{C}$  in anhydrous HF (equation (2)).



The product does not melt or sublime at temperatures up to  $310^\circ\text{C}$  *in vacuo* and is insoluble in  $\text{MeCN}$ ,  $\text{CHCl}_3$ ,  $\text{ClF}_2$ ,  $\text{CCl}_2\text{F}$ , and propylene carbonate. It is soluble in  $\text{SO}_2\text{ClF}$  and slightly soluble in HF. X-Ray powder photography showed that the material is not  $\text{MoO}_3$ ,  $\text{MoO}_2$ ,  $\text{MoO}_2\text{Cl}_2$ , or  $\text{MoOF}_4$  and elemental analyses suggested the empirical formula  $\text{MoO}_2\text{F}_2$ .

The dominant species in the mass spectrum is  $\text{MoO}_2\text{F}_2^+$  and the main fragmentation pathway is *via*  $\text{MoO}_2\text{F}^+$ ,  $\text{MoOF}^+$ , and  $\text{MoO}^+$  to  $\text{Mo}^+$ . The only species observed which were of greater mass than  $\text{MoO}_2\text{F}_2$  were due to traces of  $\text{MoO}_2\text{FCl}^+$  ( $m/e$  178–188) and  $\text{Mo}_2\text{O}_3\text{F}_4^+$  ( $m/e$  309–320), the latter suggesting that  $\text{MoO}_2\text{F}_2$  may be polymeric. This is further supported by the lack of solubility and volatility mentioned earlier.

The i.r. spectrum also evidences a possible polymeric formulation. Features at  $993\text{s}$  and  $1007\text{w,sh cm}^{-1}$  are

identical in shape with the band envelope for the symmetric and asymmetric stretching modes of the  $\text{MoO}_2$  unit in gas-phase spectra of  $\text{MoO}_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{or Br}$ )<sup>4</sup> and the frequencies correlate well with data for solid  $\text{CrO}_2\text{F}_2$ ,<sup>5</sup>  $\text{MoO}_2\text{Cl}_2$ , and  $\text{MoO}_2\text{Br}_2$ .<sup>6</sup> The broad absorption at  $835\text{s cm}^{-1}$  can be assigned to bridging  $\text{Mo} \cdots \text{OMo}$  stretching vibrations by comparison with related bands in  $\text{MoO}_3$ <sup>7</sup> and  $\text{MoO}_2\text{Cl}_2$ .<sup>8</sup> Terminal Mo–F stretching modes at  $670\text{s}$  and  $695\text{w,sh cm}^{-1}$  and bridging  $\text{Mo} \cdots \text{F}$  stretches at  $587\text{s}$  and  $522\text{w,sh cm}^{-1}$  are similar in frequency to bands in  $\text{MoOF}_4$ .<sup>9</sup>

<sup>19</sup>F N.m.r. spectra of solutions of  $\text{MoO}_2\text{F}_2$  in HF and  $\text{SO}_2\text{ClF-HF}$  mixtures show a broad singlet, width  $130\text{ Hz}$  at half-height, at  $-131.5\text{ p.p.m.}$  relative to  $\text{CFCl}_3$ . These compare with signals at  $-146$  and  $-140\text{ p.p.m.}$  for  $\text{MoOF}_4$  and  $\text{MoOF}_5^-$  respectively.

Stoichiometric quantities of  $\text{H}_2\text{O}$  in anhydrous HF were distilled on to  $\text{WOF}_4$  at  $-196^\circ\text{C}$  in pre-seasoned FEP tubes. In each case the reactor was warmed slowly by consecutively immersing it in each of a series of low temperature baths at  $-160$ ,  $-139$ ,  $-119$ ,  $-98$ ,  $-78$ ,  $-63$ ,  $-42$ ,  $-23$ , and  $0^\circ\text{C}$  for 30–45 min. Finally, the reactants were brought briefly to room temperature before recooling to  $-78^\circ\text{C}$  and slowly removing the HF under reduced pressure [equation (3)].



Vibrational spectra of the unstable, off-white solid were poor but demonstrated the absence of  $\text{WOF}_4$ . The mass spectrum is similar to that of  $\text{MoO}_2\text{F}_2$ , the main fragmentation pathway being  $\text{WO}_2\text{F}_2^+ \rightarrow \text{WO}_2\text{F}^+ \rightarrow \text{WOF}^+ \rightarrow \text{WO}^+$ . The parent ion of  $\text{WOF}_4$  is totally absent whilst  $\text{WOF}_3^+$  is less abundant than both  $\text{WO}_2\text{F}_2^+$  and  $\text{WO}_2\text{F}^+$ .

Reaction of stoichiometric quantities of solid  $\text{MoO}_2\text{F}_2$  or  $\text{WO}_2\text{F}_2$  with equimolar quantities of  $\text{XeF}_2$  in anhydrous HF gave the tetrafluoride oxides. With excess of  $\text{XeF}_2$  the  $\text{XeF}_2 \cdot \text{MoOF}_4$  and  $\text{XeF}_2 \cdot \text{WOF}_4$  adducts were formed.<sup>10</sup>

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