Inorganica Chimica Acta, 143 (1988) 247–249

Oxoperoxofluoromolybdate(VI) Complexes. The First Synthesis of Oxodiperoxofluoromolybdate(VI) Complexes

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(Received June 12, 1987)

Abstract

A number of oxoperoxofluoromolybdate(VI) complexes, *viz.* $M_2[MoO(O_2)F_4]$ and $M_2[MoO(O_2)_2F_2]$ where M = K and NH_4 and $K[MoO(O_2)_2F]\cdot 2H_2O$ have been synthesised by various methods. The infrared spectra suggest that the peroxide groups are bonded to the molybdenum centre in a triangular bidentate manner.

Introduction

Peroxo metal compounds are of growing interest in relation to the catalysis of oxidation involving hydrogen peroxide itself, and the storage and transport of oxygen in biological systems. Amongst all elements the peroxo compounds of chromium are probably the best characterised, whereas the chemistry of the peroxo compounds of molybdenum has received only scanty attention. The peroxo molybdenum compounds are quite unstable. They explode when struck or heated. The stability of the peroxo complexes is generally enhanced by introducing a heteroligand. The preparation and the crystal structure of a few peroxofluoromolybdates, *viz.* $K_2[MoO(O_2)F_4]\cdot H_2O$ and $(NH_4)_3[MoO(O_2)F_4]F$ have been described earlier [1–5]. An anhydrous compound, *viz.* $K_2[MoO(O_2)F_4]$ has also been reported [6]. The preparation and the crystal structure of $M[Mo_2O_2(O_2)_2(dipic)_2F_2]$ (where dipic is pyridine-2,6-dicarboxylato) have been reported recently [7, 8]. We have undertaken a detailed study of the peroxofluoromolybdates(VI) and have synthesised for the first time two diperoxofluoromolybdates(VI). The various methods and conditions under which the mono- and diperoxofluoromolybdates(VI) are formed have been critically studied.

Experimental

The chemicals used were A.R. or G.R. quality of reputed manufacturers. $M_2^I[MoO_2F_4]$, where M^I = K and NH_4 were prepared by adding acetone to a solution of $M_2^IMoO_4$ in 40% hydrofluoric acid [9]. The methods of analysis of molybdenum, potassium, fluorine and nitrogen were described in our earlier communications [9, 10]. Peroxide content was determined iodometrically by introducing the samples in potassium iodide solution containing 1 N sulphuric acid.

Infrared spectra were recorded in Nujol mull or in CsI or KBr pellet using a Perkin-Elmer spectrophotometer (No. 598). Magnetic susceptibility was determined by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant.

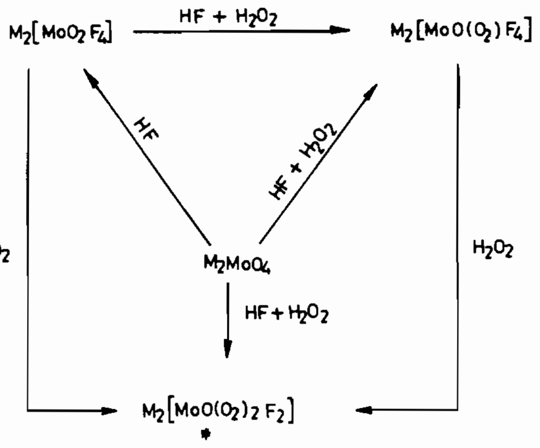

Fig. 1. $Mo:H_2O_2$ = 1:1 for the monoperoxo complexes and $Mo:H_2O_2$ = 1:2 for the diperoxo complexes. $*[MoO(O_2)_2F_2]^{2-}$ was obtained from MoO_4^{2-} only in the case of the K salt.

Preparation of the Compounds

The complexes $M_2[MoO(O_2)F_4]$ and $M_2[MoO(O_2)_2F_2]$, where M = K and NH_4, were prepared by several methods which are shown in Fig. 1. The essential feature of the syntheses is that in the preparation of the monoperoxo complexes $Mo:H_2O_2$ was maintained at about 1:1, while the diperoxo complexes were prepared using $Mo:H_2O_2$ = 1:2. The complexes were precipitated from the solutions by the addition of acetone. In the case of K_2 [MoO-

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0020-1693/88/$3.50

$(O_2)F_4]$, however, the complex crystallised out even without the addition of acetone. Typical procedures for the preparation of $K_2[MoO(O_2)F_4]$ and $K_2[MoO(O_2)_2F_2]$ are given below.

$K_2[MoO(O_2)F_4]$. Potassium molybdate, K_2MoO_4 (2.0 g) was dissolved in 8 ml HF (40%) when the solution got warm. After cooling to room temperature, 1.0 ml hydrogen peroxide (30%) was added. A silky crystalline precipitate appeared within 2 min which was filtered after 30 min and dried by pressing between the folds of filter paper.

$K_2[MoO(O_2)_2F_2]$. Potassium molybdate, K_2MoO_4 (1.0 g) was dissolved in 3.5 ml HF (40%) and then 0.95 ml of hydrogen peroxide (30%) was added. Acetone (25 ml) was added to the yellow solution. The precipitate was filtered and washed with acetone.

$K[MoO(O_2)_2F]\cdot 2H_2O$. A mixture of MoO_3 (2.0 g), KF (0.8 g) and 30% H_2O_2 (20 ml) was digested on a steam bath for 1 h. After cooling, a very small amount of undissolved MoO_3 was removed by filtration. The complex precipitated out on the addition of 50 ml of acetone.

The yields of $K_2[MoO(O_2)F_4]$ and $K_2[MoO(O_2)_2F_2]$ ranged from 60–80%, while the yields of the other compounds were about 30%. All the complexes were dried in a desiccator over sulphuric acid. The analytical data of the complexes are given in Table I.

TABLE I. Analytical Data of the Complexes

Compounds	Found (calc.) (%)			
	Mo	O_2^{2-}	F	Alkali metal or N
$K_2[MoO(O_2)F_4]$	31.9	10.5	25.6	26.4
	(32.2)	(10.7)	(25.5)	(26.1)
$(NH_4)_2[MoO(O_2)F_4]$	37.2	12.2	29.8	10.8
	(37.5)	(12.5)	(29.6)	(10.9)
$K_2[MoO(O_2)_2F_2]$	32.9	22.0	13.2	26.5
	(32.8)	(21.9)	(13.0)	(26.7)
$(NH_4)_2[MoO(O_2)_2F_2]$	38.2	25.2	14.9	11.3
	(38.4)	(25.6)	(15.2)	(11.2)
$K[MoO(O_2)_2F]\cdot 2H_2O$	35.7	23.9	7.2	14.5
	(35.5)	(23.7)	(7.0)	(14.4)

Results and Discussion

All the complexes are light yellow in colour. The dried samples are quite stable in air, except $(NH_4)_2[MoO(O_2)_2F_2]$ which decomposes rather slowly. All the complexes are highly soluble in water from which only $K_2[MoO(O_2)F_4]$ can be recrystallised. Permanganate titration of the complexes in 1 N sulphuric acid medium gives a little low peroxo content indicating that they are slowly decomposed in acid solution. All the complexes are very weakly paramagnetic ($\mu_{eff} = 0.1$ to 0.3 BM), which is consistent with the presence of Mo(VI).

The potassium salt $K_2[MoO(O_2)F_4]$ is stable and does not lose weight up to 130 °C. At the same temperature the ammonium salt, $(NH_4)_2[MoO(O_2)F_4]$, however, loses weight corresponding to the removal of one atom of oxygen and one molecule of NH_4F and the residue analysed as $NH_4[MoO_2F_3]$. The two diperoxo complexes, $K_2[MoO(O_2)_2F_2]$ and $K[MoO(O_2)_2F]\cdot 2H_2O$ readily decompose at 100 °C giving $K_2[MoO_3F_2]$ and $K[MoO_3F]$ respectively.

TABLE II. Infrared Spectral Band Positions in the Complexes (cm^{-1})

Compounds	ν(Mo=O)	ν(O–O)	$\nu(Mo-O_2)$ and ν(Mo–F)
$K_2[MoO(O_2)F_4]$	955vs	920vs	590s, 550s, 490s
$(NH_4)_2[MoO(O_2)F_4]$	955vs	915vs	590vs, 555vs, 490vs
$K_2[MoO(O_2)_2F_2]$	945sh, 935vs	865s, 850vs	645s, 570s, 515s
$(NH_4)_2[MoO(O_2)_2F_2]$	970vs, 935vs	890vs, 860vs	650vs, 580vs, 500vs
$K[MoO(O_2)_2F]\cdot 2H_2O$	970vs, 950vs	860vs	670vs, 610vs, 580vs, 510vs

The infrared spectral band positions of the complexes are given in Table II. The spectra of all the complexes show a very strong terminal Mo=O band at 970 to 935 cm^{-1}. The position of ν(O–O) suggests that the peroxide groups (O_2^{2-}) are bonded to the molybdenum centre in a triangular bidentate manner [11]. A distinct shift of ν(O–O) (ν_1) mode of the coordinated peroxide from *ca.* 920 to *ca.* 860 cm^{-1} in going from the monoperoxo to the diperoxo complexes is a clear indication of a decrease in O–O bond order with increase in the number of coordinated peroxide group. The spectra of all the complexes show three to four strong intensity bands between *ca.* 650 and *ca.* 500 cm^{-1}. The assignment of $\nu(Mo-O_2)$ (ν_2) and $\nu(Mo-O_2)$ (ν_3) which are likely to appear around 530 and 600 cm^{-1} respectively could not be made since Mo–F bands are also likely to appear in the same region.

French and Russian workers have determined the structure of a hydrated compound $K_2[MoO(O_2)F_4]\cdot H_2O$ by X-ray crystallography [2, 4]. The IR spectra of an anhydrous compound $K_2[MoO(O_2)F_4]$ were studied earlier [6]. It appears that both the two hydrated and anhydrous complexes were prepared by the same method. Our method of preparation of the compound is also essentially the same. As noted earlier, our compound $K_2[MoO(O_2)F_4]$ does not lose practically any weight on heating even at

130 ℃ indicating it to be anhydrous. The IR spectra of the freshly prepared samples do not show any band attributable to water. Samples stored for several days showed weak absorptions near 3500 and 1600 cm^{-1} indicating that some water is absorbed on storing. Two earlier reports [11, 12] on the IR spectra of $K_2[MoO(O_2)F_4]$ are in disagreement. In one publication [12] the peroxo stretching frequency was assigned at 933 cm^{-1}, while in the latter publication [11] this frequency was reported at 876 and 856 cm^{-1}. Nakamoto and coworkers [6] have made extensive studies of the IR spectra of $K_2[MoO(O_2)F_4]$ and $(NH_4)_3[MoO(O_2)F_4]F$. Their results agree with ours. These authors have noted that the IR spectra of these two complexes change with exposure to air causing absorption to occur in the 800–900 cm^{-1} region.

All our attempts to prepare the triperoxofluoro complex of molybdenum under varying experimental conditions have been unsuccessful.

Acknowledgements

The authors gratefully acknowledge financial support from the Council of Scientific and Industrial Research, India. Thanks are also due to C.D.R.I., Lucknow and to Prof. A. Paul of this Institute for recording the IR spectra.

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