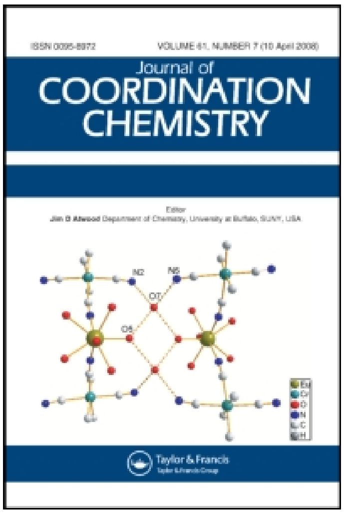

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OXOFLUORO COMPLEXES OF QUINQUEVALENT MOLYBDENUM

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OXOFLUORO COMPLEXES OF QUINQUEVALENT MOLYBDENUM

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A large number of stable salts of the general formulae $M_2[MoOF_5]$ (M = K, Rb and Cs), $(BH)_2[MoOF_5]$ (B = hydroxyl amine, guanidine, 2,6-lutidine, α-naphthyl amine, anthranilic acid, m-amino benzoic acid and quinaldinic acid) and $B'H_2[MoOF_5]$ (B′ = ethylene diamine) have been prepared by crystallising solutions of $MoO(OH)_3$ and the alkali metal fluorides or the bases in 40% HF. The potassium salt has also been prepared by two other methods. The molecular conductances of the salts of the types $M_2[MoOF_5]$ and $(BH)_2[MoOF_5]$ in water indicate that they are unibivalent type of electrolytes. The magnetic moments of the salts fall within the range of 1.51 to 1.76 BM indicating the presence of Mo(V) in them. The i.r. spectra of the salts show strong (Mo = O) bands between 980–900 cm^{-1}. Digestion of the ethylene diamine and 2,6-lutidine salts with ethanol gave the insoluble light pink and yellow brown complexes $MoOF_3(En)$ and $MoOF_3(Lut)$ respectively. Relatively low magnetic moments of these complexes suggest polymerisation through oxide bridge.

INTRODUCTION

Remarkably little work has been done on oxopentafluoromolybdate(V) compared to an extensive volume of work done on its chloride analog. The existence of the salts of the complex ion $[MoOF_5]^{2-}$ has been reported only in recent years[1,2-6]. The detailed method of preparation of any salt is lacking and studies on the properties of the compounds are scanty. Very few salts mostly with inorganic cations have been reported. The potassium salt has been described as anhydrous and monohydrate by two groups of workers[1,5]. It is well known that oxochloro- or oxobromo-molybdates(V) undergo hydrolysis as the acid concentration is decreased and ultimately dimerise to the oxobridged species, $Mo_2O_3^{+4}$ and $Mo_2O_4^{+2}$ containing one and two oxobridges respectively.[7] No report is available on the formation of oxobridged fluoro complexes of Mo(V). The present communication deals with the isolation of a large number of salts of the series $[MoOF_5]^{2-}$ with inorganic and also organic nitrogeneous basic cations from aqueous medium. The potassium salt has been prepared by three different methods. Chemical, i.r. spectral and magnetic properties of the salts have been studied. Isolation of a few complexes of the type $MoOF_3L$ and $MoOF_3L_2$ (where L is an organic base) from the corresponding oxopentafluoromolybdates(V) has also been reported.

EXPERIMENTAL

$MoO(OH)_3$, the starting material for the preparation of the salts, was prepared by standard method.[8] Hydrofluoric acid was E. Merck's G. R. quality (40%). Other chemicals were B. D. H. or E. Merck's extra pure or guaranteed reagents. The organic bases were distilled or crystallized before use. A solution of hydroxyl amine carbonate was prepared by precipitating hydroxyl amine sulphate with barium hydroxide solution and removing excess Ba^{++} from the filtrate by passing carbon dioxide.

The analysis of molybdenum, fluorine, nitrogen and alkali metals, the determination of the oxidation state of molybdenum, recording of i.r. spectra and measurements of magnetic susceptibility and conductivity were made by the methods described earlier.[9,10]

PREPARATION OF THE COMPLEXES

Potassium-rubidium-caesium salts, $M_2[MoOF_5]$, M = K, Rb and Cs.

$MoO(OH)_3$ (2 g) was dissolved in minimum volume of 40% HF and an excess (Mo : alkali fluoride = 1 : 5) of concentrated solutions of the alkali fluorides in 40% HF were then added. Green crystalline precipitates appeared immediately after scratching.

The yields were around 70%.

The potassium salt was also prepared by 1) reducing a solution of MoO_3 (1 g) in 40% HF with hypophosphorous acid (2 ml 30% solution) in a covered polythene beaker over a water bath and concentrating the solution in presence of potassium bifluoride and 2) concentrating a solution of $K[MoOF_4].KHF_2$ in 20% hydrofluoric acid over a water bath.[10]

Hydroxyl amine, guanidine, 2,6-lutidine, α-naphthyl amine, anthranilic acid, m-aminobenzoic acid, quinaldinic acid salts, $(BH)_2$ $[MoOF_5]$ where B = hydroxyl amine and organic monoacid bases.

These were isolated by adding concentrated solutions of hydroxyl amine carbonate, guanidine carbonate and the organic bases in 40% HF (in the case of 2,6-lutidine the base was just neutralised with HF) to the concentrated solution of $MoO(OH)_3$ (2 g) in the same acid (the amount of the bases and $MoO(OH)_3$ being in the ratio of 5 : 1). The salt with α-naphthyl amine was obtained as fine crystals on stirring the solution during addition, while the other ones were obtained in large crystals after allowing their solutions to concentrate for several days in a dessicator over sulphuric acid and caustic soda. The yields of the salts with α-naphthyl amine and quinaldinic acid were about 80 and 60% respectively, while approximately 45% yields were obtained in the other cases. The anthranilic acid salt was also obtained by concentrating the solutions of $K[MoOF_4].KHF_2$ and anthranilic acid in 20% HF over sulphuric acid and caustic soda.[10]

TABLE I

Analytical data[a] and magnetic moments of the complexes.

Compound with colour	% Mo	% F	% Alkali metal or N	Oxidation number of Mo	μ_{eff}, BM at 30°C
1. $K_2[MoOF_5]$ green	33.9(33.7)	32.8(33.3)	28.8(27.4)	5.1	1.55
2. $Rb_2[MoOF_5]$ green	26.0(25.4)	24.5(25.1)	44.5(45.2)	5.1	1.76
3. $Cs_2[MoOF_5]$ green	20.0(20.3)	20.2(20.1)	56.5(56.2)	4.9	1.54
4. (α-NaphthylH)$_2$$[MoOF_5]$ pale green	19.4(19.4)	18.7(19.2)	6.0(5.65)		1.51
5. (AnthraacidH)$_2$$[MoOF_5]$ green	20.0(19.9)	18.9(19.7)	6.0(5.79)		1.52
6. (QuinaldacidH)$_2$$[MoOF_5]$ greenish yellow	18.0(17.3)	17.6(17.1)			1.58
7. (GuanH)$_2$$[MoOF_5]$ green	28.8(29.3)	28.2(29.1)	25.7(25.7)		1.56
8. $(NH_3OH)_2[MoOF_5]$ light green	35.3(34.9)	33.4(34.6)	10.1(10.2)		
9. (AminobenzH)$_2$$[MoOF_5]$ green	19.9(19.9)	18.9(19.7)	5.9(5.79)		
10. (LutH)$_2$$[MoOF_5]$ pale green	22.9(22.7)	23.0(22.5)			1.64
11. $EnH_2[MoOF_5]$ pale green	35.4(35.7)	34.2(35.4)	10.9(10.4)		1.69
12. $N_2H_6[MoOF_5]$ green	39.8(39.8)	39.8(39.4)	12.0(11.6)	5.1	1.56
13. $MoOF_3$En light pink	40.7(41.9)	24.5(24.9)	11.8(12.2)		1.47
14. $MoOF_3$Lut yellowish brown	33.9(34.8)	20.5(20.7)			1.38

Abbreviations: Naphthyl = Naphthyl amine; Anthraacid = Anthranilic acid; Quinaldacid = Quinaldinic acid; Guan = Guanidine; Aminobenz = m-amino benzoic acid; Lut = 2,6-lutidine; En = Ethylene diamine.

[a] The analytical values in parentheses are the calculated ones.

An ethylene diamine salt of the composition $EnH_2[MoOF_5]$ was prepared by using the same method as that used for the preparation of the salt with 2,6-lutidine.

The hydrazinium salt, $N_2H_6[MoOF_5]$ was prepared by concentrating an aqueous solution of $N_2H_6[Mo(OH)F_6].H_2O$ over a water bath.[10]

In all cases the crystals were pressed between filter papers and dried over sulphuric acid and caustic soda in a dessicator till constant weight. All the compounds were preserved in polythene containers.

No pure compound could be isolated with NH_4^+, Zn^{+2}, Cu^{+2} and Cd^{+2} and the bases like α-picoline, pyridine, oxine, quinoline, meta nitro aniline, aniline, 2,2′-dipyridyl and 1,10-phenanthroline.

$MoOF_3En/MoOF_3Lut$ (where En = ethylene diamine and Lut = 2,6-lutidine)

A suspension of very finely powdered $EnH_2[MoOF_5]$ or $(LutH)_2[MoOF_5]$ in ethanol was boiled for a long time (20–30 hours) in a partly covered polythene beaker over a water bath till there was no further change in colour of the residue. The colourless mother liquor was occasionally drained up and the residue was ground and again boiled with ethanol. Ultimately the residue was separated by filtration and washed with ethanol.

The analytical data of the compounds are given in Table I.

RESULTS AND DISCUSSIONS

The formulation of the complexes is based on elemental analysis, oxidation state of molybdenum, magnetic moment values, i.r. spectral and conductivity studies. Oxidation number of molybdenum in the potassium, rubidium and caesium salts determined by oxidation with hot acid dichromate was about +5 (vide Table I). The effective magnetic moments of all the salts (vide Table I) which fall within the range 1.51 to 1.76 BM at 30°C also indicate the quinquevalency of molybdenum. The magnetic moment of the potassium salt remains unchanged even after heating it at 110°.

The molecular conductances of aqueous solutions of the alkali metal salts and organic basic salts of the type $(BH)_2[MOOF_5]$ indicate that they are uni-bivalent type of electrolytes and that the ion $[MoOF_5]^{2-}$ does not undergo dissociation to any appreciable extent (vide Table II).

The i.r. spectral band positions in the salts with potassium, rubidium, caesium, guanidine, ethylene diamine, anthranilic acid and 2,6-lutidine are given in Table III. The spectra show ν(Mo = O) at about 970 cm^{-1} as a strong or very strong band with an additional band of weak, medium or strong intensity at about 900 cm^{-1}. The position of the latter band appears to be too high to be assigned as Mo–F band. In view of the almost normal magnetic moment of the complexes the assignment of this band as δ(Mo–O–Mo) arising due to dimerisation of the complexes (if any) is not favoured. It is possible that an axial fluoride (trans to oxygen) is more tightly bound and gives rise to two Mo = O bands because of what may be considered symmetric and antisymmetric motions of the oxygen and fluorine atoms. Similar complexes, viz., $[CrOF_5]^{2-}$ and $[UOX_5]^{2-}$ (X = F, Cl, Br) have been reported[11–13] to give two M = O bands. The position of Mo = O vibration in the spectrum of the lutidine salt (vide Table III) is difficult to locate since

TABLE II
Molecular conductances of the complexes in aqueous solution at 30°C.

	Molecular conductances (ohm^{-1}) at different concentration					
Compound	M/32	M/64	M/128	M/256	M/512	M/1024
$K_2[MoOF_5]$	160	173	182	256	262	289
$Rb_2[MoOF_5]$	182	214	220	231	240	266
$Cs_2[MoOF_5]$	151	182	209	243	263	296
$(\alpha\text{-NaphthylH})_2[MoOF_5]$	70	95	120	133	153	178
$(\text{AnthraacidH})_2[MoOF_5]$	75	92	122	149	190	240
$(\text{QuinaldacidH})_2[MoOF_5]$	107	115	125	161	194	265
$(\text{GuanH})_2[MoOF_5]$	121	125	134	182	199	255
$(\text{LutH})_2[MoOF_5]$	130	156	182	220	266	281

Abbreviations are the same as in Table I.

TABLE III
Band positions in the i.r. spectra (in nujol) of the compounds.

Compound	ν, cm^{-1}
$K_2[MoOF_5]$	3660 m, 3580 w, 3250 w, 1620 m, 980 s, 943 w, 910 m, 740 m, 545 s, 480 w, 440 m
$Rb_2[MoOF_5]$	(3600–3100) w br, 980 s, 943 w, 900 m, 730 m, 530 s, 480 w, 440 m
$Cs_2[MoOF_5]$	(3600–3100) w br, 975 s, 950 w, 908 w, 730 m, 525 s, 475 w, 425 m
$EnH_2[MoOF_5]$	3200 br, 2600 br, 1900 br, 1610 s, 1340 w, 1200 w, 1115 m, 1080 s, 1050 s, 1030 s, 980 m, 950 m, 910 m, 810 s, 725 s, 580 sh, 530 m, 460 s
$(GuanH)_2[MoOF_5]$	3200 v br, 1630 vs, 1140 m, 935 vs, 910 s, 735 vs, 570 br, 450 s
$(LutH)_2[MoOF_5]$	1950 br, 1650 m, 1620 m, 1270 m, 1175 m, 1050 m, 930 s, 890 vs, 830 s, 720 s, 540 vs, 455 w, 430 m
$(AnthraacidH)_2[MoOF_5]$	3100 br, 1830 w, 1670 m, 1590 w, 1550 w, 1310 sh, 1270 m, 1140 vw, 1090 m, 1000 vw, 965 vs, 945 sh, 910 vs, 830 m, 805 w, 750 vs, 720 w, 690 w, 650 m, 580 m, 560 m, 490 w
$MoOF_3En$	3100 br, 2150 br, 2000 w, 1870 v br, 1610 s, 1550 sh, 1515 sh, 1190 sh, 1120 w, 1045 s, 1025 sh, 980 w, 950 s, 910 s, 825 w, 805 sh, 790 s, 720 s, 570 sh, 530 br, 460 s
$MoOF_3Lut$	3320 m, 1600 br, 1170 w, 1145 w, 1065 w, 1045 w, 1025 w, 970 m, 925 w, 880 w, 720 s, 480 s
AnthraacidHF	3100 br, 2650 br, 1690 m, 1530 m, 1240 s, 1170 w, 1085 m, 1030 w, 970 w, 935 vw, 925 vw, 755 sh, 720 vs, 630 s, 560 w, 520 w, 500 sh, 470 s, 440 w
$(GuanH)_2CO_3$	3400 s br, 2700 s br, 2420 w, 2200 w, 1660 s, 1560 s, 1170 m, 810 m, 540 m (excluding the bands due to CO_3)

Abbreviations are the same as in Table I.

the cation $(LutH)^+$ gives strong bands[14] between 900–1000 cm^{-1}. Anthranilic acid fluoride and guanidine carbonate give only weak or very weak bands in this region (vide Table III). The spectrum of the potassium salt shows medium intensity bands at 1620 cm^{-1} and around 3500 cm^{-1} which may be caused due to some absorption of water by the salt. The spectra of the rubidium and caesium salts also show very weak broad bands in the region of 3400 cm^{-1}. The bands in the low frequency region (750–500 cm^{-1}) may be assigned as ν(Mo–F) bands.[15]

The compounds are generally crystalline and green in colour. They are stable when dry, but the moist samples turn blue. All the salts except that with α-naphthyl amine are highly soluble in water, while *the α-naphthyl* amine salt is moderately soluble. The aqueous solutions gradually change from green to orange on standing. The α-naphthyl amine is slightly soluble in dilute hydrofluoric acid, while the other salts are fairly soluble. The anthracilic acid salt can be recrystallised unchanged from 20% hydrofluoric acid while the recrystallisation of the other salts did not give pure product. The salts with 2,6-lutidine, guanidine and ethylene diamine are deliquescent. All the salts are insoluble in common organic solvents.

The complexes $MoOF_3En$ and $MoOF_3Lut$ are light pink and yellowish brown respectively. Both are practically insoluble in water and common organic solvents and hence conductivity or molecular weight could not be determined. They are paramagnetic, but the magnetic moment (vide Table I) is rather low for mononuclear Mo(V) complexes. It is likely that they are to some extent polymerised with Mo–O–Mo grouping.

The i.r. spectrum of the ethylene diamine complex in the Mo = O region (vide Table III) is practically identical with that of the parent complex, viz., $EnH_2[MoOF_5]$. Between 1000–900 cm^{-1} three bands (980 w, 950 s, 910 s, cm^{-1}) are observed. The assignment of the first band is difficult since ethylene diamine complexes give strong bands[16] around 1000 cm^{-1}. In the same region the spectrum of the lutidine complex (vide Table III) shows two bands (970 m, 925 w, cm^{-1}) compared to those at 930 s and 890 vs, cm^{-1} in the parent complex. The presence or absence of δ(Mo–O–Mo) in the spectra of these complexes is difficult to ascertain in view of the presence of absorption bands due to the organic part and ν(Mo–F) in the expected region. Various complexes of the type $MoOCl_3L_2$ and $MoOCl_3L'$ (where L is a unidentate base, e.g., pyridine and L′ is a bidentate base, e.g., 2,2′-dipyridyl) are well known.[17–19] Analogous fluoro complexes have not received much attention. Only two complexes, viz., $MoOF_3 \cdot 2NH_3$ (dark brown) and $MoOF_3 \cdot NH_3$ (black) have been reported very recently.[20]

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