

NEW PEROXO COMPLEXES OF TH (IV), U(VI), MO(VI) AND W(VI) IONS CONTAINING TRIEN AND 1, 10 PHENANTHROLINE

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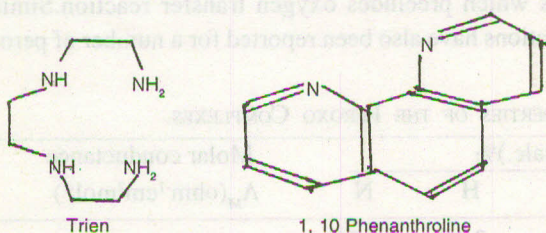
Some novel peroxo complexes of the type $[\text{Th}(\text{O}_2)_2 \text{L}]$, $[\text{U}(\text{O})(\text{O}_2)_2 \text{L}]$ and $[\text{M}(\text{O})(\text{O}_2)_2 \text{L}]$ ($\text{M} = \text{Mo}$ (VI) and W (VI); $\text{L} =$ trien or phenanthroline) have been isolated and characterized by elemental analyses, magnetic measurements and infrared spectral studies and their reactivity has been explored. The experimental data are consistent with octahedral geometry for the thorium complex, nine-fold coordination for the molybdenum and tungsten complexes. None of the complexes oxidised triphenylphosphine or triphenylarsine. The ν_1 (o-o) stretch frequency decreased with increasing metal-ion size.

Key words: Peroxo complexes, Auxiliary ligands, Elemental analysis, Heavy metal ions.

Introduction

The chemistry of peroxo complexes has been reported [1-10]. These complexes are important as they are potential sources of active oxygen atoms and can be utilised as efficient stoichiometric as well as catalytic oxidant for organic and inorganic substrates [1-7]. Their reactivity changes when metal peroxides are incorporated with other coligands. Peroxo complexes containing mono- and bidentate auxiliary ligands have been found to exhibit oxidation reactions [1-5], but those containing tri and tetradentate coligands were inert towards such reactions [5, 9].

We report herein the synthesis and reactivity of some peroxo complexes of heavy metal ions, Th (IV), U(VI), Mo(VI) and W (VI) ions containing trien or 1,10-phenanthroline. The relation between the ν_1 (O-O) stretch and size of the metal ions has also been studied.



Experimental

Reagents and Chemicals. All the metal salts, ligands and solvents were of AR grade and used as supplied by Merck and BDH Ltd excepting ethanol which was used after purification by refluxing with I_2 and Mg turnings and distillation.

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Physical measurements. Infrared spectra were obtained as KBr discs on a Perkin Elmer 883 infrared spectrophotometer in the range of $200 - 4000 \text{ cm}^{-1}$ and electronic spectra on a Shimadzu UV-visible model spectrophotometer. Molar conductivities of $10^{-3} \text{ mol dm}^{-3}$ solutions of these complexes were measured on a digital conductivity meter, Scotte Geratte 857 equipped with dip type cell with platinized electrodes. Magnetic measurements were carried out on a Sherwood Scientific magnetic susceptibility balance at 30°C . Metals were estimated by standard procedure. Melting points were determined by an electrothermal melting point apparatus.

Analyses. Elemental analyses were obtained from the Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India.

Preparation of the Complexes $[\text{Th}(\text{O}_2)_2 \text{trien}]$ (1) and $[\text{U}(\text{O})(\text{O}_2)_2 \text{trien}]$ (2). To an ice-cold solution of thorium nitrate pentahydrate, $\text{Th}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (1.71g, 0.003 mol) or uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.5 g, 0.003 mol) in 30% H_2O_2 (30cm^3) an ethanolic solution (20 cm^3) of trien was added over a few minutes with stirring. The resulting white (thorium complex) or yellow (uranium complex) solid was filtered off, washed successively with ethanol and then with ether and finally dried *in vacuo* over P_4O_{10} . Yield 0.5 g and 0.6 g, respectively, decomp. $>220-230^\circ\text{C}$.

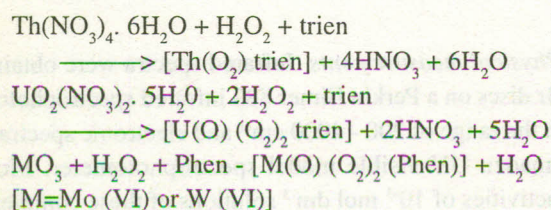
$[\text{M}(\text{O})(\text{O}_2)_2 \text{Phen}]$ ($\text{M} = \text{Mo}$ (VI) or W (VI) and $\text{Phen} = 1, 10 \text{ phenanthroline}$) (3 and 4): General method. Stoichiometric amounts of 1, 10 phenanthroline (0.5g, 0.003 mol) dissolved in ethanol (20cm^3) were added to each of the hot solutions of molybdic acid (0.4g, 0.003 mol) and tungstic acid (0.70g, 0.003 mol) in 30% H_2O_2 (100 cm^3). The yellow molybdenum complex was formed immediately and the pale yellow tungsten complex resulted on boiling the

mixture for 5 min. The products were filtered off, washed successively with water, ethanol and ether and finally dried and stored as above. Yields : 0.6g and 0.83 g respectively; decomp $>220^{\circ}\text{C}$.

Attempted reactions of 1-4 with triphenylphosphine and triphenylarsine: Stoichiometric amounts of 1-4 were allowed to react with triphenylphosphine and triphenylarsine individually in the (tetrahydrofuran) medium by refluxing these reaction mixtures for 12-24 hrs. In each experiment, triphenylphosphine or triphenylarsine was recovered unchanged.

Results and Discussion

The preparation of the complexes can be represented as the following.



The elemental analyses and conductance data of the complexes are presented in Table 1. These complexes have been formulated on the basis of these data and the coordination proposed on the basis of the spectral data. Complexes 1 and 2 are insoluble in almost all common organic solvents and their molar conductance could not be measured but molar conductivity measurements on complexes 3 and 4 showed that they are nonelectrolytes in DMSO. The present data are consistent with six - fold coordination for Th(IV) complexes, nine-fold coordination for U(VI) complex and seven-fold coordination for Mo (VI) and W(VI) complexes.

IR studies. Characteristic infrared spectral bands of the complexes are presented in Table 2. In complexes 1 and 2,

the tetramine ligand behaves as a bidentate or quadridentate neutral ligand, respectively coordinating to the metal by the nitrogen sites. This is evident from $\nu(\text{NH}_2/\text{NH})$ stretching modes of the complexes at $3040 - 3280 \text{ cm}^{-1}$ significantly lower than the free ligand values ($3280 - 3360 \text{ cm}^{-1}$). The metal nitrogen coordination is further supported by $\nu(\text{M-N})$ stretch at $350 - 370 \text{ cm}^{-1}$ in the far IR region of the spectra of these complexes. Complexes 3 and 4 exhibit $\nu(\text{C=N})$ stretch at 1620 and 1628 cm^{-1} respectively sufficiently lower than the free 1, 10 phenanthroline value (1650 cm^{-1}) indicating metal nitrogen linkage in these complexes.

The metal peroxo grouping (local C_{2v} symmetry) generally gives rise to three infrared and Raman active vibrational modes. These are predominantly O-O stretch (ν_1), the $\nu(\text{M-O})$ stretch (ν_2) and the antisymmetric $\nu(\text{M-O})$ stretch (ν_3). Complexes 1-4 show ν_1 (O-O) stretching mode at $830-847 \text{ cm}^{-1}$ comparable to the reported values of ν_1 for various peroxo complexes of group 4A and 6A metals [3,4]. In the present complexes the ν_2 and ν_3 modes appear at $536-590 \text{ cm}^{-1}$ and $620-720 \text{ cm}^{-1}$ respectively. The $\nu(\text{M=O})$ mode appears at $910-957 \text{ cm}^{-1}$ for 2 - 4 ($\text{M} = \text{U}, \text{Mo}$ and W). It is interesting to note that ν_1 (O-O) decreased with the increase of atomic size of the metals.

Magnetic measurements and electronic spectra. The magnetic susceptibility measurements on 1 - 4 indicate that all the complexes are diamagnetic. The solid-state reflectance electronic spectra (Table 3) of the complexes display bands in the ultraviolet region ($250-350 \text{ nm}$), which are due to charge transfer as expected for metal ions with d^0 electronic configuration.

Reactivity. Complexes 1 - 4 did not react with triphenylphosphine or triphenylarsine when refluxed together in THF. The negative results show the enhanced stability of the metal peroxo moiety in the presence of multidentate chelating ligands which precludes oxygen transfer reaction. Similar observations have also been reported for a number of peroxo

TABLE 1. ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF THE PEROXO COMPLEXES.

No.	Compound	Colour	Found (calc.)%			Molar conductance $\Lambda_M(\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1})$	
			Metal	C	H		N
1.	$[\text{Th}(\text{O}_2)(\text{C}_6\text{H}_{18}\text{N}_4)]$	Brown	56.12 (56.54)	17.82 (17.56)	3.10 (4.10)	13.21 (13.66)	--
2.	$[\text{U}(\text{O})(\text{O}_2)_2(\text{C}_6\text{H}_{18}\text{N}_4)]$	Yellow	51.10 (51.30)	15.21 (15.52)	4.00 (3.88)	11.82 (12.07)	--
3.	$(\text{MO}(\text{O})(\text{O}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2))$	Yellow	26.59 (26.94)	40.29 (40.46)	1.94 (2.24)	7.50 (7.87)	2.0
4.	$[\text{W}(\text{O})(\text{O}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)]$	Pale Yellow	41.21 (41.42)	32.20 (32.44)	1.62 (1.80)	5.92 (6.31)	1.5

Calculated values are in the parenthesis.

TABLE 2. CHARACTERISTIC INFRARED SPECTRAL BANDS OF THE COMPLEXES (BAND MAXIMA, cm^{-1})

Compound	$\nu(\text{NH}_2/\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}=\text{O})$	$\nu_1(\text{O}-\text{O})$	$\nu_3(\text{M})$	$\nu_2(\text{M})$	$\nu(\text{M}-\text{N})$
1	3220 br 3280 br			830 s	620 s	550w	370 sh
2	3040 br 3280 br		910 vs		720 vs	590 w	350 vs
3		1620m	951 vs	847 vs	662 m	536 s	
4		1628 sv	957 vs	837 vs	654 vs	544 vs	

vs = very strong; s = strong; m = medium; br = broad; w = weak; sh = shoulder

TABLE 3. THE ELECTRONIC SPECTRAL DATA OF THE PEROXO COMPLEXES (BAND MAXIMA, nm).

Compound	Electronic bands (nm)		
1	350	300	250
2	348	298	257
3	350	295	253
4	352	305	252

complexes containing various multidentate organic ligands [11, 12]. Although the tetramine ligand behaves bidentately in 1, the metal chelate ring probably stabilises the metal peroxo moiety and is thus responsible for the negative results in the oxidation reactions.

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