

SOME ORGANOPEROXO COMPLEXES OF ZIRCONIUM (IV), THORIUM (IV) AND URANIUM (VI)

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Some new peroxo complexes of Zr (IV), Th (IV) and U (VI) containing organic ligands, L^I , $[N_4C_8H_{16}(C_6H_4OH)_2]$; L^{II} , $[N_2C_5H_8(C_6H_4OH)_2]$; L^{III} , $[(C_6H_5CNC_2H_4NH_2)_2]$ and L^{IV} , $[C_6H_4NNH=CHC_6H_4OH]$ have been synthesized and characterized. These have compositions, $[Zr(O_2)L^I]$, $[Th(O_2)L^I] \cdot H_2O$, $[U(O)(O_2)L^{II}] \cdot H_2O$, $[U(O)(O_2)L^{II}]$, $Zr(O_2)_2L^{III}$, $[Th(O_2)_2L^{III}] \cdot H_2O$, $[U(O_2)(O_2)L^{III}]$, $[Zr(O_2)(SCN)L^{IV}]$, $Zr(O_2)(SCN)_2L^{III}$, and $[Th(O_2)(SCN)L^{IV}]$. The complexes are found to be inert towards oxidation of triphenylphosphine, triphenylarsine and allyl alcohol. The size of the metals as well as the electronic nature of the organic ligands influence the mode of coordination of the peroxo moiety. IR spectra reveal that ν_1 mode of $Zr(O_2)$, $Th(O_2)$ and $U(O_2)$ groupings (i.e., O-O stretch) decreases with an increase in atomic number of metals in a particular group.

Key words: Organoperoxo complexes, Heavy metals.

Introduction

Recently there has been a growing interest in the field of peroxo complexes of transition metals, in particular, as these are potential sources of active oxygen atoms and can be used as efficient stoichiometric or catalytic oxidants for organic and inorganic substrates (Mimoun 1980; Muccigrosso *et al* 1978; Tarafder and Khan 1987; Tarafder and Islam 1989; Westland *et al* 1980). The reactivity of peroxo complexes depends on the nature of other auxiliary ligands used; the coordinated peroxo moiety being greatly stabilized by co-ligands of multidentate nature (Islam and Uddin 1993; Tarafder and Khan 1987; Tarafder and Islam 1989) Tarafder and Ahmed 1986). Some peroxo complexes of heavier metals have been reported (Pal and Tarafder 1996; Begum *et al* 1997). However, the heavier metals have not been well investigated in this regard. We are, therefore, interested in extending such a study to new peroxo complexes of such metal ions containing different auxiliary organic ligands as well as thiocyanate ligands. We herein report the synthesis of some organoperoxo complexes of Zr (IV), Th (IV) and U (VI), and their characterization along with the preparation of the ligands. Attempts have also been made to study their potential as oxygen transfer reagents and the effect of size of the metal ions on ν_1 (O-O) modes of the complexes in their IR spectra.

Experimental

Physical measurements. The IR spectra (as KBr discs) were obtained using a Perkin Elmer-883 infrared spectrophotometer in the range $4000-200\text{ cm}^{-1}$. Electronic spectra as nujol

mulms, spread on a filter paper, were run on a Shimadzu UV-VIS 160 Recording Spectrophotometer at wavelengths from 200 to 1100 nm. Magnetic susceptibilities (at 299K) were measured with a Sherwood Scientific magnetic balance (Gouy method) using $HgCo(NCS)_4$ as a calibrant. Conductivities of 10^{-3} M solutions of the complexes in dimethylsulfoxide (DMSO) were measured at 298K using a WPA CM 35 conductivity meter and a dip-type cell with platinized electrodes. The cell was calibrate with 0.01N, 0.001N and 0.0001N KCl solutions. Melting points of the complexes were obtained on an Electrothermal melting point apparatus.

Reagents. All Chemicals used were of reagent grade and used as supplied by BDH or Merck.

Analyses. Carbon, hydrogen and nitrogen analyses were carried out by the Microanalytical Services at the University of Erlangen-Nurnberg, Germany. Zirconium, thorium and uranium were determined by weighing as their oxides (Bagnall *et al* 1968).

Preparation of ligands. Bis(salicylaldehyde)triethylene tetramine, L^I ; Bis(salicylaldehyde) 1, 3-propylenediimine, L^{II} ; Benzil-ethylenediamine, L^{III} and Salicylaldehyde 2-iminopyridine, L^{IV} .

Salicylaldehyde (0.04 mol) or benzyl (0.01 mol) (for L^{III}) in absolute alcohol (30 cm^3) was mixed with a solution of triethylene tetramine, 1,3-diamino propane, ethylene diamine or 2-amino pyridine in the same solvent (30 cm^3). To get L^I , this mixture was heated for 30 min at 313 K and the solution was then kept at room temperature for 72 h; for L^{II} , the mixture was refluxed for 2.5 h following which the solution was kept in a refrigator for 48 h; for L^{III} , the mixture was heated to 343 K,

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stirred for 2 h and then cooled; but for L^{IV} , the mixture was heated to reduce it to about 30 cm³ and the solution was kept in a refrigerator overnight. The yellow precipitate formed (in each case) was collected by filtration, washed with ethanol and dried in *vacuo* over P_4O_{10} [M.P. 102.6 °C (L^I), 69.5 °C (L^{II}), 163 °C (L^{III}), 64.7 °C (L^{IV})].

Preparation of the complexes. General method for the preparation of the complexes 1 and 2: $[Zr(O_2)(SCN)L^{IV}]$ and $[Zr(O_2)(SCN)_2L^{III}]$.

Zirconium nitrate dihydrate (0.005 mol) was dissolved in anhydrous methanol (25 cm³) to which a solution of potassium thiocyanate (0.002 mol) in the same solvent (40 cm³) was added. The precipitated KNO_3 was discarded, and the filtrate added to a methanolic solution (20 cm³) of the ligand L^{IV} or L^{III} (0.005 mol) and 30% H_2O_2 (7 cm³). The precipitate thus obtained was separated, washed with hot ethanol and dried in *vacuo* over P_4O_{10} .

General method for the preparation of the complexes 3, 4 and 6-11. $[Zr(O_2)_2L^{III}]$, $[Zr(O_2)_2L^I]$, $[Th(O_2)_2L^{III}]H_2O$, $[Th(O_2)_2L^{II}]H_2O$, $[Th(O_2)_2L^I]H_2O$, $[U(O)_2(O_2)L^{III}]$, $[U(O)(O_2)L^{II}]$ and $[U(O)(O_2)L^I]$.

$M(NO_3)_4 \cdot 6H_2O$ (0.002 mol) [$M=Zr(IV)$ or $Th(IV)$] was dissolved in distilled water (25 cm³) while $UO_2(NO_3)_2 \cdot 6H_2O$ (0.002 mol) was dissolved in absolute alcohol (25 cm³). These were added separately to a solution of the ligand L^{III} , L^{II} or L^I in ethanol (25-30 cm³) and 30% H_2O_2 (5 cm³). The precipitate was filtered, washed with distilled water and ether, and dried in *vacuo* over P_4O_{10} .

Preparation of the complex 5: $[Th(O_2)(SCN)L^{IV}]$. Thorium nitrate hexahydrate (0.005 mol) in absolute alcohol (25 cm³) was added to a solution of potassium thiocyanate (0.02 mol) in the same solvent (40 cm³). The solution was filtered and the filtrate added to ethanolic solution (20 cm³) of the ligand L^{IV} (0.005 mol) and 30% H_2O_2 (7 cm³). The precipitate thus obtained was filtered, washed with hot ethanol and finally dried in *vacuo* over P_4O_{10} .

Attempted reactions of 3, 4 and 6-11 with triphenylphosphine and triphenylarsine. Refluxing of each of the complexes **3**, **4** and **6-11** (0.002 mol) triphenylphosphine or triphenylarsine in THF for 48 h failed to produce any reaction; the complexes were recovered unchanged.

Attempted reactions of 3, 4 and 6-11 with allyl alcohol. Each of the complexes **3**, **4** and **6-11** (0.002 mol) was suspended in 25 cm³ THF and a stoichiometric amount of allyl alcohol was added. The mixture was stirred under reflux at 75-78 °C for 72 h, but failed to produce any product.

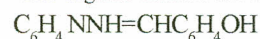
Results and Discussion

The analytical and conductivity data of the complexes are presented in Table 1. Complexes **1** and **5** are soluble in DMSO and behave as 1:1 electrolytes, but the rest are insoluble. The analytical data are consistent with six-fold coordination of Zr (IV) and Th (IV) in **1**, **5** and **7**; seven-fold coordination of U(VI) in **10**; eight-fold coordination of Zr (IV), Th (IV) and U(VI) in **2-4**, **6,8** and **9**; and nine-fold coordination of U(VI) in

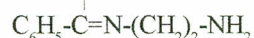
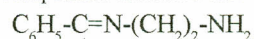
Table 1
Analytical data and other physical properties of the complexes ^a

Compound (No.)	Colour	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)		Molar conductance, $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
$[Zr(O_2)(SCN)L^{IV}]$ (1)	Colourless	23.87	23.00	41.25	41.10	2.38	2.21	11.10	10.96	37
$[Zr(O_2)(SCN)_2L^{III}]$ (2)	Redish brown	16.85	16.30	45.01	44.87	4.13	4.00	15.75	15.66	-
$[Zr(O_2)_2L^{III}]$ (3)	Brown	20.30	20.80	48.08	47.97	4.90	4.88	12.47	12.23	-
$[Zr(O_2)_2L^I]$ (4)	Brown	19.19	19.76	50.50	50.32	5.05	5.00	11.78	11.65	-
$[Th(O_2)(SCN)L^{IV}]$ (5)	Colourless	44.35	44.70	31.64	31.55	1.69	1.67	7.91	7.73	41
$[Th(O_2)(SCN)L^{IV}]$ (6)	Colourless	41.58	41.95	35.53	35.32	3.95	3.78	9.21	9.20	-
$[Th(O_2)L^{II}]H_2O$ (7)	Black	42.64	42.90	36.20	36.00	3.20	3.12	4.98	4.77	-
$[Th(O_2)L^I]H_2O$ (8)	Colourless	37.66	37.24	37.85	37.73	4.42	4.32	8.83	8.75	-
$[U(O_2)_2(O_2)L^{III}]$ (9)	Yellow	39.93	39.30	36.24	36.00	3.69	3.58	9.39	9.05	-
$[U(O)(O_2)L^{II}]$ (10)	Black	42.05	42.90	36.04	36.00	2.83	2.76	4.95	4.80	-
$[U(O)(O_2)L^I]$ (11)	Yellow	37.30	37.30	37.62	37.53	3.76	3.44	8.78	8.67	-

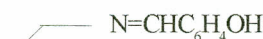
^aThe organic moieties for the compounds indicated are:



1 and 5



2, 3, 6 and 9



7 and 10



4, 8 and 11

Table 2
IR spectral data for the complexes band maxima (cm⁻¹)^a

Compound	$\nu(\text{NH}_2/\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}=\text{O})$	$\nu_1(\text{O}-\text{O})$	$\nu_3(\text{M} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array})$	$\nu_2(\text{M} \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	Others
(1)	-	1600s	-	830s	630s	535s	405m	320w	$\nu_{(\text{CN})}$ 2085vs
(2)	3220w 3060w	1580s	-	800s	610s	505w	-	330w	$\nu_{(\text{CN})}$ 2080vs
(3)	3300 3080w	1550	-	850m	615w	505w	-	310w	-
(4)	3255sh	1540w	-	840w	620w	520w	410w	300w	-
(5)	-	1555w	-	825w	610vs	500m	-	330w	$\nu_{(\text{CN})}$ 2080m
(6)	3200 3250	1540	-	820M	615W	510W	-	310W	$\nu_{(\text{OH})}$ 3400br
(7)	-	1520w	-	820s	650w	510w	425w	325m	$\nu_{(\text{OH})}$ 3400br
(8)	3220w	1510w	-	820vs	635w	520w	420w	310w	$\nu_{(\text{OH})}$ 3430br
(9)	3280 3195	1530s	920vs	817m	640w	510w	-	345w	-
(10)	-	1530w	900vs	790m	630w	520w	450m	340w	-
(11)	3170w	1520w	900vs	830m	640w	520w	430w	310w	-

Relative band intensities are denoted by vs, s, m, w, br and sh, representing very strong, strong, medium, weak, broad and shoulder, respectively.

11. The schiff bases L^I, L^{II} and L^{IV} are potentially hexadentate-dinegative, tetradentate-dinegative and tridentate uninegative ligands respectively. However, L^{III} behaves as a tetradentate neutral ligand. Based on analytical data, L^I has a donor sequence of ONNNNO while L^{II} and L^{IV} have donor sequences of ONNO and NNO respectively. L^{III}, however, has a donor sequence of NNNN. The M.P. of all the complexes **1-11** is found to be above 200°C.

IR spectral data are shown in Table 2. The spectra of the complexes **3**, **6** and **9** show bands (**3**, 3300 and 3080 cm⁻¹), (**6**, 3300 and 3250 cm⁻¹) and (**9**, 3280 and 3195 cm⁻¹) at frequencies significantly lower than that of ligand L^{III} (3410 and 3350 cm⁻¹) which indicate coordination by primary amino nitrogen (Tarafder and Miah 1986); complexes **4**, **8** and **11** show one band (**4**, 3255 cm⁻¹), (**8**, 3220 cm⁻¹) and (**11**, 3170 cm⁻¹) significantly lower than the values for free ligand L^I (3435 cm⁻¹) indicating coordination by secondary amino nitrogen, and complexes **6**, **7** and **8** show broad band at 3430-3400 cm⁻¹ arising from coordinated water molecules.

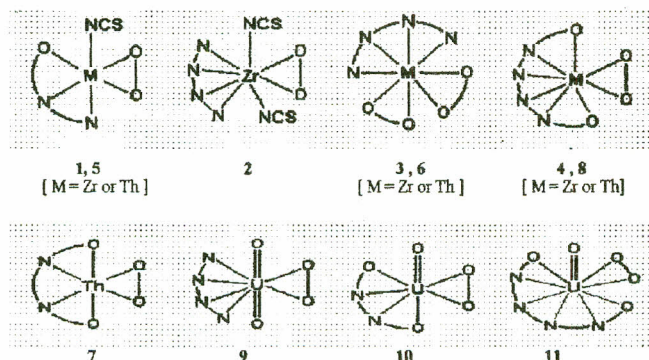
In the complexes **3**, **4** and **6-11**, the (C=N) modes appear at 1550-1510 cm⁻¹ which is lower than the free ligand values L^I, 1625 cm⁻¹ and L^{III}, 1610 cm⁻¹ suggesting coordination by imino nitrogen of (C=N). These are also evident from the appear-

ance of bands at 345-300 cm⁻¹ which are tentatively attributed to the $\nu(\text{M}-\text{N})$ modes [M=Zr (IV), Th (IV) and U(VI)]. The presence of metal-oxygen bands in **4** and **7-11** are evident from the appearance of $\nu(\text{M}-\text{O})$ at 450-400 cm⁻¹ in the far IR spectra of the complexes (O in organic ligand). Again in the IR spectra of **1**, **2** and **5**, the $\nu(\text{C}=\text{N})$ modes appear at 1600-1555 cm⁻¹ which is lower than the free ligand L^{III} (1610 cm⁻¹) and L^{IV} (1620 cm⁻¹) values suggesting coordination by imino nitrogen. The $\nu(\text{NH}_2)$ mode is shifted to lower wave number and appear at around 3220-2940 cm⁻¹ in **2**; this shifting is indicative of coordination of the ligand via the primary amino nitrogen (Tarafder and Miah 1986). Further, complexes **1**, **2** and **5** show bands at around 330-320 cm⁻¹ (Burnstein *et al* 1964; Liang *et al* 1979; Tarafder and Miah 1986) indicating the presence of M-N bonding in the complexes. The IR spectra of the free ligand, L^{IV} show a band at 3500 cm⁻¹ which disappears upon coordination indicating the presence of M-O bonding in **1** and **5**. These are also evident from the appearance of $\nu(\text{M}-\text{O})$ at 410-405 cm⁻¹ in the complexes **1** and **5** (O= oxygen in organic ligand) (Tarafder 1987; Westland and Tarafder 1981; Westland and Tarafder 1982).

The metal peroxo grouping gives rise to three IR active vibrational modes, viz., the O-O stretching (ν_1), the symmetric M-O

stretch (ν_2) and the antisymmetric M-O stretch (ν_3). The characteristic ν_1 (O-O) modes in **1**, **2** and **5** appear at 830-760 cm^{-1} while that for the rest complexes appear at 830-790 cm^{-1} . The ν_1 mode shifts to lower frequencies upon passing from zirconium complexes **1** and **2** (830 and 800 cm^{-1}), **3**, and **4** (850-830 cm^{-1}) to Thorium complexes **5** (825-760 cm^{-1}) and **6-8** (820 cm^{-1}). Again in the cases of peroxy complexes of the elements of group 6A, the ν_1 mode of the uranium peroxy complexes **9-11** appear at 830-790 cm^{-1} is lower than that of the molybdenum peroxy complex $[\text{Mo}(\text{O})(\text{O}_2)(\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2]$ ($\nu_1=870 \text{ cm}^{-1}$) (Tarafder *et al* 1989). From this study, it is evident that for $\text{M}(\text{O}_2)$ grouping, the ν_1 (O-O) modes decrease with an increase in the atomic number of metals in a particular group. The organoperoxo complexes **1**, **2** and **5** display ν_3 and ν_2 modes at 650-600 cm^{-1} and 535-505 cm^{-1} respectively and all other complexes show ν_3 and ν_2 modes at 640-615 cm^{-1} and 520-505 cm^{-1} respectively (Table 2).

Magnetic measurements of all the complexes ($\mu_{\text{eff}} = -0.2$ to $+0.3$ B.M.) and electronic spectral data (bands at 250-350 nm) reveal that they are diamagnetic in nature and exhibit only charge transfer bands.



In the light of the above discussion, the proposed skeleton structures of the prepared complexes are picturized as follows:

In complex **9**, the oxo groups may be assumed to be in trans positions.

Reactivity. The present organoperoxo complexes **3**, **4** and **6-11** were found to be inert towards triphenylphosphine, triphenylarsine and allyl alcohol. These negative results outline the enhanced stability of the metal peroxy moiety in the presence of multidentate ligands which precludes oxygen transfer reactions. Similar behaviour was observed for other peroxy complexes containing multidentate ligands (Tarafder 1987; Tarafder and Khan 1991; Tarafder and Khan 1991). Mimoun *et al* (Mimoun 1980; Mimoun *et al* 1982) argued that insertion of substrates like phosphines or arsines into the metal peroxide bond forming a peroxy metalocycle is a concerted process, but perhaps the multidentate co-ligands

greatly stabilize the peroxy ligand and that the nucleophiles (PPh_3 or AsPh_3) can not cause opening of the metal peroxy triangle, thus explaining the inertness of these complexes.

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