

## PEROXO COMPLEXES OF Zr (IV), Th (IV) AND U (VI) CONTAINING TRIDENTATE NEUTRAL AND BI- AND TRIDENTATE NEUTRAL MACROCYCLIC LIGANDS

S. C. PAL AND M. T. H. TARAFDER

*Department of Chemistry, Rajshahi University, Rajshahi-6205, Bangladesh*

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Some new peroxo complexes of zirconium (IV), thorium (IV) and uranium (IV) containing 2, 6-diaminopyridine and two macrocyclic Schiff's bases have been synthesised and characterized by elemental analyses, conductivity measurements and infrared spectral studies. Their reactivities as potential oxygen carriers have also been studied. Complexes containing the bidentate macrocyclic ligand are nonelectrolytes in DMF. The present complexes have the compositions:  $[M(O_2)_2L]$ ,  $[M=Zr$  (IV) and Th (IV);  $L = 2, 6$  - diaminopyridine or Schiff base derived from ethylenediamine and benzil,  $C_{16}H_{16}N_2$  and Schiff base of diethylenetriamine with benzil,  $C_{18}H_{21}N_3$ ];  $[UO(O_2)_2L]$ ,  $[L = 2, 6$ -diaminopyridine or Schiff's base of diethylenetriamine and benzil,  $C_{18}H_{21}N_3$ ]. Infrared spectra of the complexes reveal that for  $M(O_2)_2$  grouping, the  $\nu_1$  (O-O) stretching mode decreases with the increase in the atomic number in a group. The Zr (IV) and Th (IV) complexes containing the bidentate neutral macrocyclic ligand oxidise  $PPH_3$  and  $AsPh_3$  and those containing tridentate acyclic and tridentate macrocyclic ligands are inert towards oxidation reactions.

**Key words:** Peroxo Complexes, Zr (IV), Th (IV), U (VI).

### Introduction

In recent years, peroxo complexes of transition metals have generated wide interest [1-12] because many of them are efficient stoichiometric and catalytic sources of active oxygen atoms for oxidation of inorganic and organic substrates [6]. Metal peroxides incorporated with other co-ligands having different donor sequences exhibit difference in reactivities [5,7]. Total electronic effect of the coligands in the peroxo complexes largely affect the nucleophilicity of olefinic compounds towards metal centres. Tarafder *et al.* [6] reported an easy route to the synthesis of glycerine from allyl alcohol using peroxo complexes. Metal peroxo moiety has been found to be greatly stabilized by multidentate coligands [9-11,13] and the peroxo complexes of these ligands are inert towards oxidation reactions.

Literature survey reveal that peroxo complexes containing tridentate neutral bi- and tridentate neutral macrocyclic ligands of metals of 4A and 6A are yet to be studied. We became interested to extend our studies to peroxo complexes of zirconium (IV), thorium (IV) and uranium (IV) containing the above kinds of ligands with a view to compare the effect of tridentate neutral acyclic and tridentate neutral macrocyclic ligands on  $\nu_1$  (O-O) stretching mode and that of bi and tridentate macrocyclic ligands on the same stretching mode. We report herein the syntheses and characterization of these complexes and their potential for oxygen transfer reactions. We have also studied the effect of size of the metal ions and the electronic effect arising from tridentate ligands on  $\nu_1$  (O-O) stretching modes of the complexes.

### Experimental

Infrared spectra were obtained as KBr discs on a Pye Unicam SP 300 IR spectrophotometer. Molar conductances were obtained using  $10^{-3}$  mol  $dm^{-3}$  solutions of the complexes in dimethyl formamide (DMF) with a digital conductometer Scotte Geratte 857 and a dip type cell with platinized electrodes. Melting points were measured with an electrothermal melting point apparatus.

**Reagents.** All chemicals were reagent grade and were used as supplied by Merck and BDH Ltd. except for ethanol which was purified by refluxing with magnesium turnings and iodine and finally distilled and stored over molecular sieves.

**Analyses.** Carbon, hydrogen and nitrogen analyses were carried out at the Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India. Metals were estimated by converting the complexes to corresponding stable oxides.

**Preparation of the ethylenediamine-benzil ( $C_{16}H_{16}N_2$ ) and diethylenetriamine-benzil ( $C_{18}H_{21}N_3$ ) Schiff's bases.** The bases have been prepared by the procedures described earlier [14].

**Preparation of the complexes:**  $[Zr(O_2)_2L_1]$  (1) [ $L_1 = 2, 6$ -diaminopyridine]. To a clear solution of  $Zr(NO_3)_4 \cdot 6H_2O$  (0.002 mol) in distilled water (20  $cm^3$ ), a clear solution of  $L_1$  (0.002 mol) in hot ethanol (50  $cm^3$ ) was added followed by the addition of 30%  $H_2O_2$  (40  $cm^3$ ) at room temperature. The product that appeared was left overnight to settle down and then filtered, washed thoroughly with ethanol and

finally with ether and stored *in vacuo* over fused  $\text{CaCl}_2$ . Yield 0.7 g.

$[\text{Th}(\text{O}_2)_2\text{L}_1]$  (2). To a solution of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  (0.002 mol) in distilled water (20  $\text{cm}^3$ ), a clear solution of  $\text{L}_1$  (2,6-diaminopyridine, 0.002 mol) in hot ethanol (50  $\text{cm}^3$ ) was added followed by addition of 30%  $\text{H}_2\text{O}_2$  (30  $\text{cm}^3$ ) at  $0^\circ\text{C}$  (the temperature was maintained by ice-salt bath). Product that appeared on stirring the mixture for 10 min. was left overnight to settle down. It was then separated, washed thoroughly with cold ethanol and finally with ether and stored *in vacuo* over fused  $\text{CaCl}_2$ . Yield 0.75 g.

$[\text{UO}(\text{O}_2)_2\text{L}_1]$  (3). Ligand  $\text{L}_1$  (0.002 mol) was dissolved in boiling ethanol (50  $\text{m}^3$ ) and a solution of uranyl nitrate hexahydrate,  $\text{UO}_2(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  (0.002 mol) in water (25  $\text{cm}^3$ ) was added to it simultaneously with 30%  $\text{H}_2\text{O}_2$  (50  $\text{cm}^3$ ) at  $0^\circ\text{C}$ . The temperature was maintained by ice-salt bath. The yellowish product that appeared was separated, washed successively with cold water and finally with ether and dried *in vacuo* over fused  $\text{CaCl}_2$ . Yield 0.70 g.

$[\text{Zr}(\text{O}_2)_2\text{L}_{II}]$  (4) [ $\text{L}_{II}$  = Schiff's base of ethylenediamine with benzil,  $\text{C}_{16}\text{H}_{16}\text{N}_2$ ]. To an aqueous solution (20  $\text{cm}^3$ ) of zirconium nitrate, hexahydrate  $\text{Zr}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$  (0.001 mol) an ethanolic solution (20  $\text{cm}^3$ ) of  $\text{L}_{II}$  (0.001 mol) was added at  $0^\circ\text{C}$  followed by addition of 30%  $\text{H}_2\text{O}_2$  (25  $\text{cm}^3$ ). The mixture was stirred at the same temperature for 0.5 hr. when a white solid product appeared. It was then separated, washed thoroughly with ethanol and finally stored *in vacuo* over fused  $\text{CaCl}_2$ . Yield 0.4 g.

$[\text{Th}(\text{O}_2)_2\text{L}]$  (5&6) [ $\text{L} = \text{L}_{II}$  or Schiff's base of diethylenetriamine with benzil ( $\text{L}_{III}$ )]. An ethanolic solution (20  $\text{cm}^3$ ) of  $\text{L}$  (0.001 mol) was added to an aqueous solution (20  $\text{cm}^3$ ) of thorium nitrate, pentahydrate,  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  (0.001 mol) followed by the addition of 30%  $\text{H}_2\text{O}_2$  (20  $\text{m}^3$ ) at  $0^\circ\text{C}$ . The resulting precipitate was filtered, washed thoroughly with cold water and finally with ether and then stored *in vacuo* over fused  $\text{CaCl}_2$ . Yield 0.3 g with  $\text{L}_{II}$  and 0.4 g with  $\text{L}_{III}$ .

$[\text{UO}(\text{O}_2)_2\text{L}_{III}]$  (7). To an aqueous solution (20  $\text{m}^3$ ) of uranyl nitrate hexahydrate  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.001 mol) a solution of  $\text{L}_{III}$  (0.001 mol) in ethanol (25  $\text{cm}^3$ ) was added followed by the addition of 30%  $\text{H}_2\text{O}_2$  (20  $\text{cm}^3$ ). The resulting yellow product was left overnight in a refrigerator and then separated and washed successively with cold ethanol and ether and finally stored *in vacuo* over fused  $\text{CaCl}_2$ . Yield 0.35 g.

*Reaction of complex 4 with  $\text{PPh}_3$  (i).* Triphenylphosphine (0.0001 mol) was dissolved in 20  $\text{cm}^3$  of THF and a suspension of complex 4 (0.00005 mol) in the same solvent (30  $\text{cm}^3$ ) was added to it. The mixture was then kept under reflux for 24 hr. TLC indicated that triphenylphosphine was converted to the corresponding oxide. The contents under reflux were filtered and the residue collected was a yellowish white prod-

uct. This was identified with  $\text{OPPh}_3$ , m.p.  $156\text{-}157^\circ\text{C}$  (lit.  $157^\circ\text{C}$ ).

*Reaction of complex 5 with  $\text{AsPh}_3$  (ii).* A suspension of complex 5 (0.00005 mol) in THF (40  $\text{cm}^3$ ) was added to a solution of triphenylarsine (0.0001 mol) in the solvent (20  $\text{cm}^3$ ) and refluxed for 48 hr. Triphenylarsine was found to be converted to the corresponding oxide on examination with TLC. The contents in the refluxing flask were filtered and the filtrate was evaporated and identified with  $\text{OAsPh}_3$ , m.p.  $186\text{-}188^\circ\text{C}$  (lit.  $189^\circ\text{C}$ ).

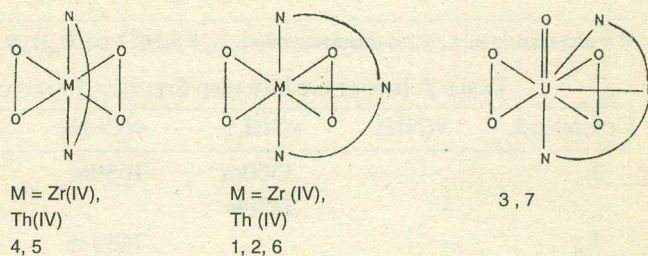
*Attempted reactions with 3 and 7 with ( $\text{PPh}_3$ ) and triphenylarsine ( $\text{AsPh}_3$ ) (iii).* Equimolar quantities of triphenylphosphine or triphenyl arsine were refluxed with 3 and 7 in THF for 48 hr. but failed to produce any reaction product. Complexes 3 and 7 were recovered unchanged.

## Results and Discussion

The analytical data along with some physical properties of the complexes is presented in the Table I. Molar conductivities of complexes 4 and 5 were measured in dimethyl formamide (DMF). All other complexes 1-3, 6 and 7 were insoluble in all common organic solvents. Conductance data shows that 4 and 5 are nonelectrolytes. This indicates that the peroxo ligands do not dissociate in DMF in these complexes.

The analytical data, conductivity measurements and infrared spectral data (Table 2) reveal that Zr (IV) is seven and six-coordinated in 1 and 4 respectively, Th (IV) is seven-coordinated in 2 and 6 while six-coordinated in 5 and U(VI) is eight-coordinated in 3 and 7.

The general skeletal structures of complexes can be proposed as the following.



*Infrared spectra.* Infrared spectral data of the present peroxo complexes are shown in Table 2. The ligand 2, 6-diaminopyridine exhibits symmetric and asymmetric  $\nu(\text{NH}_2)$  modes at  $3280\text{ cm}^{-1}$  and  $3500\text{ cm}^{-1}$ , respectively and  $\nu(\text{C}=\text{N})$  band at  $1630\text{ m}^{-1}$ . Complexes 1-3 exhibit  $\nu(\text{NH}_2)$  modes at  $3200\text{ m}^{-1}$  and  $3440\text{-}3480\text{ cm}^{-1}$  sufficiently lower than the corresponding ligand values suggesting that amino nitrogens of the ligand are coordinated to the metals [13]. Bands appearing at lower frequencies  $1530\text{-}1560\text{ m}^{-1}$  than the corresponding ligand value ( $1630\text{ cm}^{-1}$ ) reveal that the ring nitrogen is coordinated to the metals in these complexes

[5,7]. These are also apparent from  $\nu(\text{MN})$  modes at 280-320  $\text{cm}^{-1}$  in the far infrared spectra of these complexes [12]. The ethylenediamine-benzil macrocyclic ligand,  $L_{\text{II}}$  displays  $\nu(\text{C}=\text{N})$  stretching band at 1630  $\text{cm}^{-1}$  and diethylenetriamine-benzil macrocyclic ligand,  $L_{\text{III}}$  displays  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{N})$  bands at 3290  $\text{cm}^{-1}$  and 1610  $\text{cm}^{-1}$ , respectively. Complexes 4-7 display  $\nu(\text{C}=\text{N})$  mode at 1570-1590  $\text{cm}^{-1}$  lower than the corresponding ligand value 1610-1630  $\text{cm}^{-1}$  thereby suggesting that amino nitrogens are coordinated to metals. Again  $\nu(\text{NH})$  mode at 3290  $\text{cm}^{-1}$  for the ligand  $L_{\text{III}}$  is shifted to 3160  $\text{cm}^{-1}$  in 6 and 7 suggesting that the secondary amino nitrogen is coordinated to metals. This is also supported by the appearance of  $\nu(\text{MN})$  modes at 275-320  $\text{m}^{-1}$  in far infrared spectra of these complexes [12]. Complexes 3 and 7 show diag-

nostic  $\nu(\text{U}=\text{O})$  bands at 900-920  $\text{cm}^{-1}$ . The metal peroxo moiety (local  $C_{2v}$  symmetry) generally show three infrared and Raman active vibrational modes such as, (i) O-O stretching ( $\nu_1$ ), the symmetric M-O-O stretching ( $\nu_2$ ) and the asymmetric M-O-O stretching ( $\nu_3$ ). The characteristic  $\nu_1$  (O-O) modes of 1-7 appear at 720-860  $\text{cm}^{-1}$  (Table 2). These modes are shifted to lower frequencies on passing from zirconium complexes 1 and 4 (820 and 920  $\text{cm}^{-1}$ ) to corresponding thorium analogues, 2 and 5 respectively (780 and 860  $\text{cm}^{-1}$ ). This indicates that for the  $\text{M}(\text{O}_2)$  moiety, the  $\nu_1$  (O-O) stretching band decrease with an increase in the atomic number of the metals. Complexes 1-7 show  $\nu_2$  and  $\nu_3$  bands at 500-560  $\text{m}^{-1}$  and 590-680  $\text{cm}^{-1}$  respectively. It is noteworthy that  $\nu_1$  (O-O) stretching frequency increases when we

TABLE 1. ANALYTICAL DATA AND SOME PHYSICAL PROPERTIES OF THE COMPLEXES (CALCULATED VALUES ARE IN THE PARENTHESES).

Compound	Colour	Melting point ( $^{\circ}\text{C}$ )	Analysis (%)			Metal %	Molar Conductivity, $A_M(\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1})$
			C	H	N		
$[\text{Zr}(\text{O}_2)_2L_1]$ (1)	Black	>320	22.52 (22.71)	2.41 (2.65)	15.46 (15.90)	34.20 (34.52)	-
$[\text{Th}(\text{O}_2)_2L_1]$ (2)	Black	>320	14.65 (14.81)	1.65 (1.73)	10.27 (10.37)	56.85 (57.29)	-
$[\text{UO}(\text{O}_2)_2L_1]$ (3)	Yellowish	>340 (d)	13.82 (14.05)	1.61 (1.64)	9.80 (9.84)	54.80 (54.34)	-
$[\text{Zr}(\text{O}_2)_2L_{\text{II}}]$ (4)	White	120	48.75 (49.08)	4.07 (4.09)	7.20 (7.16)	23.42 (23.31)	8.0
$[\text{Th}(\text{O}_2)_2L_{\text{II}}]$ (5)	White	80	36.00 (36.09)	3.12 (3.01)	5.06 (5.26)	43.70 (43.61)	9.0
$[\text{Th}(\text{O}_2)_2L_{\text{III}}]$ (6)	White	>250 (d)	37.42 (37.56)	3.61 (3.65)	7.41 (7.30)	40.12 (40.35)	-
$[\text{UO}(\text{O}_2)_2L_{\text{III}}]$ (7)	Yellow	240-260 (d)	35.10 (35.18)	3.62 (3.52)	7.09 (7.03)	39.18 (39.87)	-

d = decomposition.  $L_1$  = 2,6-diaminopyridine.  $L_{\text{II}}$  = Schiff base,  $\text{C}_{16}\text{H}_{16}\text{N}_2$ .  $L_{\text{III}}$  = Schiff base,  $\text{C}_{18}\text{H}_{21}\text{N}_3$ .

TABLE 2. IMPORTANT INFRARED SPECTRAL BANDS OF THE LIGANDS AND THE COMPLEXES (BAND MAXIMA,  $\text{CM}^{-1}$ ).

Compound	$\nu(\text{NH})$	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{N})$	$\nu_1$ (O-O)	$\nu_3(\text{M} \langle \text{O} \rangle)$	$\nu_3(\text{M} \langle \text{O} \rangle)$	$\nu(\text{M}=\text{O})$	$\nu(\text{MN})$
$L_1$	-	3500m 3280w	1630m	-	-	-	-	-
$L_{\text{II}}$	-	-	1630 m	-	-	-	-	-
$L_{\text{III}}$	3290 w	-	1610 m	-	-	-	-	-
1	-	3440 m 3280 w	1540 m	820 Sh	640 m	500 m	-	280 s
2	-	3400 m 3200 w	1530 m	780 m	680 m	500 m	-	280 s
3	-	3480 m 3200 w	1560 Sh	720 vs	590 M	-	900vs	325 s
4	-	-	1590 vs	920 vs	630 vs	560 m	-	320 m
5	-	-	1585 s	860 vs	620 vs	560 m	-	320 m
6	3160 w	-	1580 vs	795 vs	630 s	510 m	-	320 m
7	3160 br	-	1570 vs	820 s	650 br	500 m	920 vs	275 s

pass from acyclic tridentate neutral (2 and 3) to tridentate neutral macrocyclic coligands (6 and 7). This is presumably due to the greater charge neutralisation of the metal centres by the tridentate neutral  $\sigma$  donor coligands which weakens the coulombic interaction in  $M^{n+} - O_2^{2-}$ . Moreover, complexes 4 and 5 containing bidentate neutral macrocyclic ligand show  $\nu_1$  (O-O) stretching band at high frequency than the complexes 6 and 7 containing tridentate neutral macrocyclic ligands.

**Reactivity.** In order to explore the re-activity of the present peroxo complexes, compound 4 and 5 were allowed to react with  $PPh_3$  and  $AsPh_3$ . The reaction products exhibited infra-red bands at 1190 and 885  $cm^{-1}$  assignable to  $\nu(P=O)$  and  $\nu(As=O)$  modes respectively indicating that reactions produced  $OPPh_3$  and  $OAsPh_3$ . The IR spectra of metal residues of reactions (i) and (ii) did not show  $\nu_1$  (O-O) band. This indicates the transfer of peroxo oxygens to the substrates. In reaction (iii), the compounds 3 and 7 were allowed to react with  $PPh_3$  and  $AsPh_3$  but failed to oxidise  $PPh_3$  and  $AsPh_3$ . These results suggest the increased stability of the metal peroxo moiety in the presence of tridentate chelating ligands. Similar results were reported with other peroxo complexes containing multidentate ligands [11, 15].

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