Pak. J. Sci. Ind. Res. 2010 **53** (2) 63-67

Synthesis and Reactivity of Some Peroxo Complexes of Zirconium(IV) Thorium(IV) and Uranium(VI) Ions Containing a Quadridentate, Quadrinegative Ligand and a Pentadentate Dinegative Schiff Base

Md. Tofazzal Hossain Tarafder*, Suvash Chandra Pal and Md. Rabiul Karim
Department of Chemistry, Rajshahi University, Rajshahi - 6205, Bangladesh

(received May 5, 2009; revised January 25, 2010; accepted January 30, 2010)

Abstract. Some new peroxo complexes of zirconium, thorium and uranium containing a quadridentate, quadrinegative organic ligand and a pentadentate dinegative Schiff base ligand have been synthesized and characterized by elemental analyses, magnetic measurements and various spectral studies. Oxygen transfer reactions of some complexes toward different substrates have been investigated. The Schiff base, LH_2, was derived from the condensation of 2,6-diaminopyridine with salicylaldehyde. The present ligands undergo deprotonation during complexation coordinating with $(OOOO)^{4-}$ and $^{-}ONNNO^{-}$ donor sequences, respectively. The complexes have the compositions, $[M(O_2)\ (OOOO)].\ 2H_3O^+$ [M = Zr(IV) and Th(IV), OOOO = DCTA], $[UO(O_2)\ (OOOO)].2H_3O^+$; $[M(O_2)\ (ONNNO)]$ [M = Zr(IV) and Th(IV), $^{-}ONNNO^{-} = L$] and $[U(O)\ (O_2)\ (ONNNO)].H_2O$. The chelate effect of the quadridentate and pentadentate ligands stabilizes the metal peroxide moieties precluding oxygen transfers to organic and inorganic substrates. The mode of coordination is also influenced by the σ-donor electronic nature of the multidentate ligands. The IR spectral data also indicate that the υ_1(O-O) stretching modes decrease with and increase in the atomic number of the metals in a group.

Keywords: peroxo complexes, quadridentate and pentadentate ligands, heavy metal ions

Introduction

The chemistry of peroxo complexes has received considerable attention in recent years. Metal peroxides incorporated with other co-ligands exhibit different reactivities. The metal peroxo complexes are potential sources of active oxygen atoms and can be employed as efficient stoichiometric as well as catalytic reagents for the oxidation of organic and inorganic substrates. Peroxo complexes containing monodentate and bidentate auxiliary ligands have been found to be the sources of active oxygen atoms for oxidation reactions Complexes containing tridentate and quadridentate co-ligands were inert towards such oxidative processes (Sharma *et al*., 2009; Bonchio *et al*., 2001; Justino *et al*., 2000; Tarafder and Khan, 1991a; 1991b; 1987; Tarafder and Islam, 1989; Tarafder, 1987; Tarafder and Ahmed, 1986; Tarafder and Miah, 1986; Westland and Tarafder, 1982; 1981; Westland *et al*., 1980; Mimoun, 1980; Jacobson *et al*., 1978). The crystal structures of many of these complexes have also been reported (Ole *et al*., 2008; Kondo *et al*., 2008; Hou *et al*., 2006; Nica *et al*., 2005; Kaizer *et al*., 2004; Hinnerb *et al*., 2003; Chishiro *et al*., 2003; Deubel *et al*., 2001; Lewis and Wilson, 2001; Meyer and Pritzkow, 2000). However, there seems to be no reports on peroxo complexes containing some multidentate ligands with OOOO and ONNNO donor sequences.

In the present studies, synthesis of some novel peroxo complexes of Zr(IV), Th(IV) and U(VI) containing a quadridentate, quadrinegative and a pentadentate, dinegative ligands and their potential as oxygen transfer reagents have been reported. An attempt is also made to correlate the effect of the size of the metal ions on the υ_1(O-O) stretching modes from the IR spectra of the complexes. The structures of the ligands are shown in Fig. 1 and 2.

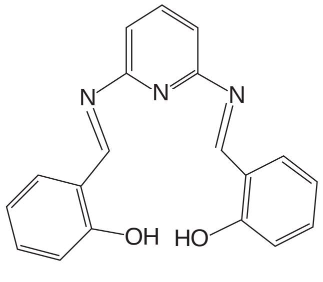

Fig. 1. LH_2: Bis-N,N′-(2-hydroxyphenylmethylene)2,6-diaminopyridine.

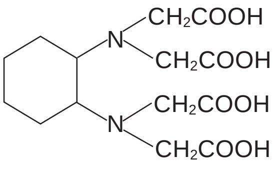

Fig. 2. 1,2-Diaminocyclohexane NNN′N′tetraacetic acid.

---

*Author for correspondence; E-mail: ttofazzal@yahoo.com

Materials and Methods

Physical measurements. The infrared spectra of the complexes were obtained as KBr discs on a Pye Unicam SP3-300 infrared spectrophotometer in the range 4000-200 cm^{-1}. Electronic spectra were obtained on a Schimadzu UV-visible spectrophotometer in nujol mulls spreaded on a filter paper. Carbon, hydrogen and nitrogen analyses were carried out at the Instrumentation Centre, Central Drug Research Institute, Lucknow, India. Metals were determined gravimetrically by standard procedures. Molar masses were determined by the Rast method using camphor as medium.

Reagents and chemicals. All chemicals were of reagent grade and used as supplied by Merck or BDH Ltd. Ethanol was purified by refluxing with iodine and magnesium turnings and finally distilling and storing over molecular sieves.

Preparation of the Schiff base ligand of 2,6-diaminopyridine with salicylaldehyde, $C_{19}H_{13}M_3O_2H_2$ (LH_2). 2,6-Diaminopyridine (50 mmol, 5.4 g) was dissolved in boiling ethanol (150 mL) and filtered to remove the undissolved portion. To the clear, brown filtrate a solution of salicylaldehyde (100 mmol, 12.2 g) in ethanol (20 mL) was added and the mixture was kept under reflux for 8 h when the colour of the solution became orange-yellowish with a distinct turbidity. The mixture was then left overnight at room temperature when a brilliant orange-coloured solid appeared. It was then filtered and washed thoroughly with cold ethanol and dried *in vacuo* over fused $CaC1_2$. Yield 7.5 g, and mp. 230 °C (d). Anal. calc., C, 72.38%; H, 4.13%; and N, 13.3%. Found: C, 72.52%; H, 4.01%; and N, 13.42%. Mass spectra of the Schiff base ligand showed diagnostic peaks at *m/z* 43, 69, 81 and 122.

Preparation of complexes. ***[Zr(O$_2$)(DCTA)]2H$_3$O$^+$ (1).*** $Zr(NO_3)_4.6H_2O$ (2 mmol, 0.89 g) dissolved in hot methanol (40 mL) was added to a solution of the DCTA (2 mmol, 0.73 g) in the same solvent (200 mL). To this mixture was added 30% H_2O_2 (50 mL). The volume of the mixture was reduced to *ca*. 100 mL when a white product appeared. It was then separated, washed successively with methanol and ether and finally dried in *vacuo* over fused $CaC1_2$.Yield, 0.6 g.

[Th(O$_2$)(DCTA)] 2H$_3$O$^+$ (2). $Th(NO_3)_4$. $5H_2O$ (2 mmol, 1.14 g) dissolved in hot methanol (40 mL) was cooled in an ice bath to which a solution of the DCTA (2 mmol, 0.73 g) in hot methanol (160 mL) was added followed by the addition of H_2O_2 (30%, 30 mL). The mixture was then heated at ~60 °C for 0.5 h, when a white product appeared. It was then left overnight at room temperature and the product was separated, washed successively with methanol and finally dried in *vacuo* over fused $CaC1_2$ .Yield 0.4 g.

[U(O)(O$_2$)(DCTA)]2H$_3$O$^+$ (3). $UO_2(NO_3)_2.6H_2O$(2 mmol, 1.04 g) dissolved in water (25 mL) was cooled in an ice bath and the solution of the DCTA (2 mmol, 0.73 g) in hot methanol (160 mL) was added to it followed by the immediate addition of 30% H_2O_2 (30 mL). The mixture was then stirred for 10 min when a yellow solid product appeared. The mixture was then kept in refrigerator for a few hours to allow the precipitate to settle. The product was then separated, washed successively with water and ether and then stored as above. Yield, 0.85 g.

[Zr(O$_2$)L] (4). $Zr(NO_3)_4.6H_2O$ (1 mmol, 0.45 g) was dissolved in methanol (30 mL) and a solution of the Schiff base (1 mmol, 0.3 g) in acetone (100 mL) was added to it followed by the addition of 30% H_2O_2 (40 mL). The volume of the mixture was then reduced to *ca*. 80 mL and kept at room temperature overnight, when a colourless crystalline product appeared. It was filtered, washed successively with water and acetone and finally dried in *vacuo* over fused $CaC1_2$. Yield, 0.61 g.

[Th(O$_2$)L] (5). To a solution of $Th(NO_3)_4.5H_2O$ (1 mmol, 0.6 g) in water (20 mL), a solution of the Schiff base (1 mmol, 0.3 g) in acetone (40 mL) was added followed by quick addition of 30% H_2O_2 (30 mL) at 0 °C. After a few minutes the brownish product was separated by filtration, washed with cold acetone and finally stored in *vacuo* over fused $CaC1_2$. Yield, 0.45 g.

[UO(O$_2$)L]. H$_2$O (6). To a solution of UO_2 $(NO_3)_2.6H_2O$ (1 mmol, 0.5 g) in water (20 mL), a solution of the Schiff base (1 mmol, 0. 3 g) in acetone (40 mL) was added followed by the addition of 30% H_2O_2 (50 mL) at 0 °C. A yellow product was produced which was separated, washed thoroughly with acetone and finally with ether and then stored in *vacuo* over fused $CaC1_2$. Yield, 0.3 g.

Attempted reactions of compounds (1) and (3) with allyl alcohol, (4) with triphenylphosphine and (5) with triphenylarsine. Refluxing **1** and **3** separately with allyl alcohol in a 1:1 molar ratio in 50 mL THF (tetrahydrofuran) medium for 48 h at 90 °C failed to produce any reaction. Compounds **1** and **3** were recovered unchanged.

Refluxing **4** or **5** with stoichiometric quantities of triphenylphosphine or triphenylarsine, in 50 mL THF, for 48 h at 90 °C failed to produce any reaction. Compounds **4** and **5** were recovered unchanged.

Results and Discussion

The syntheses of the present peroxo complexes are presented in the following scheme:

$$\begin{gathered}Zr\,(NO_3)_4.\,6H_2O + H_2O_2 + \text{DCTA (protonated)} \rightarrow \\ [Zr\,(O_2)\,(DCTA)].\,2H_3O^+ + 4HNO_3 + 4H_2O\end{gathered}$$

$$\mathrm{Th\,(NO_3)_4.\,5H_2O + DCTA\,(protonated) \rightarrow}$$
$$\mathrm{[Th\,(O_2)\,(DCTA)].\,2H_3O^+ + 4HNO_3 + 3H_2O}$$
$$\mathrm{UO_2\,(NO_3)_2.\,6H_2O + H_2O_2 + DCTA\,(protonated) \rightarrow}$$
$$\mathrm{[U(O)(O_2)(DCTA)].\,2H_3O^+ + 2HNO_3 + 5H_2O}$$
$$\mathrm{Zr\,(NO_3)_4.\,6H_2O + H_2O_2 + LH_2 \rightarrow}$$
$$\mathrm{[Zr\,(O_2)\,L] + 4HNO_3 + 6H_2O}$$
$$\mathrm{Th\,(NO_3)_4.\,5H_2O + H_2O_2 + LH_2 \rightarrow}$$
$$\mathrm{[Th\,(O_2)\,L] + 4HNO_3 + 5H_2O}$$
$$\mathrm{UO_2\,(NO_3)_2.\,6H_2O + H_2O_2 + LH_2 \rightarrow}$$
$$\mathrm{[U\,(O)\,(O_2)\,L] + 2HNO_3 + 7H_2O}$$

The analytical data of the complexes are presented in Table 1. The molar conductance measurements could not be made because the complexes were insoluble in almost all common organic solvents. The analytical and spectral data (Table 2) are consistent with six-fold coordination of Zr(IV) and Th(VI) in **1** and **2**, respectively, seven-fold coordination of U(VI), Zr(IV) and Th(IV) in complexes **3**, **4** and **5**, respectively, and eight-fold coordination of U(VI) in **6**.

Infrared spectral studies. The important IR spectral bands of the complexes are presented in Table 2. The ligand 1,2-diaminocyclohexane NNN©N© tetraacetic acid (the DCTA) is potentially quadridentate, quadrinegative coordinating *via* four carboxylato anions (OOOO$^-$) generated during complexation. The υ(OH) band observed of the Hy DCTA at 3557 cm^{-1} disappeared in the complexes indicating deprotonation at the -OH group thus providing carboxylate binding in **1**, **2** and **3**. This is further evident from the appearance of strong υ(C=O) (1635 - 1650 cm^{-1}) and υ(C-O) (1380 -1390 cm^{-1}) modes in the spectra of these complexes. Besides, the far-IR spectra of the complexes display bands (Tarafder, 1987; Tarafder and Khan, 1987; Westland and Tarafder, 1982; 1981) at 320-375 cm^{-1} assignable to υ(M-O©) modes. Complexes **4 - 6** show characteristic strong υ(C=N) modes at 1540-1560 cm^{-1}, suggesting that the ring and imino nitrogen of the Schiff base had been coordinated to the metals (Mimoun *et al*., 1982). This is also apparent from the υ(M-N) modes at ~300 cm^{-1} in the far-IR spectra of these complexes (Tarafder and Khan, 1991a; 1991b). The complexes **3** and **6** showed very strong diagnostic υ(U=O) bands (Tarafder and Islam, 1989; Tarafder *et al*., 1989; Westland and Tarafder,1981) at ~900 cm^{-1}. The metal peroxo moiety

Table 1. Analytical data and some physical properties of the Hy DCTA and LH_2 peroxo complexes

Compound$^{a,\,b}$	Molecular mass; found (calculated)	Melting point (°C)	Found (calculated), x			
			C	H	N	Metal
1. $[Zr(O_2)(DCTA)].2H_3O^+$	490.20	>160	33.09	4.31	5.39	17.82
$(C_{14}H_{24}O_{12}N_2Zr)$	(503.22)		(33.38)	(4.77)	(5.56)	(18.13)
2. $[Th(O_2)(DCTA)].2H_3O^+$	632.50	110-115(d)	26.18	3.27	4.18	35.75
$(C_{14}H_{24}O_{12}N_2Th)$	(644.03)		(26.09)	(3.73)	(4.35)	(36.03)
3. $[U(O)(O_2)(DCTA)].2H_3O^+$	660.40	150-160(d)	25.45	3.29	4.20	35.50
$(C_{14}H_{24}O_{13}N_2U)$	(666.03)		(25.22)	(3.60)	(4.20)	(35.74)
4. $[Zr(O_2)L]$	430.30	80	51.85	2.82	9.51	20.59
$(C_{19}H_{13}O_4N_3Zr)$	(438.22)		(52.03)	(2.97)	(9.58)	(20.82)
5. $[Th(O_2)L]$	570.30	>280	39.10	2.28	7.10	39.72
$(C_{19}H_{13}O_4N_3Th)$	(579.03)		(39.38)	(2.25)	(7.25)	(40.07)
6. $[UO(O_2)L].H_2O$	608.04	240-250(d)	36.62	2.51	6.82	38.20
$(C_{19}H_{15}O_6N_3U)$	(619.03)		(36.83)	(2.42)	(6.78)	(38.45)

^{a} = DCTA = deprotonated 1,2-diaminocyclohexane NNN'N'-tetraacetic acid, $(C_{14}H_{18}O_8N_2)^{4-}$; ^{b} = L = deprotonated Schiff base, $(C_{19}H_{13}O_2N_3)^{2-}$; d = decomposition.

Table 2. Characteristic infrared spectral bands of the complexes (band maxima in cm^{-1})

Compd.	υ(C-O)	υ (C=O)	υ (C=N)	υ_1(O-O)	$\upsilon_3(MO_2)$	$\upsilon_2(MO_2)$	υ(U=O)	υ(M-O')	υ(M-N)
1.				925 m	540 m	500 m			
2.	1390 vs	1650 s		890 m	540 w	500 m			295 m
3.	1380 m	1635 s		840 vs	600 m	500 w	900 vs		295 w
4.			1560 vs	890 vs	618 vs	550 vs		375 vs	300 w
5.			1560 vs	830 m	620 m	540 w		320 w	295 s
6.			1540 s	810 m	600 m	520 w	910 vs	350 vs	295 w

(local C_{2v} symmetry) gives three infrared and Raman-active vibrational modes *viz*, (i) O-O stretching (υ_1), (ii) the symmetric M-O stretching (υ_2) and (iii) the asymmetric M-O stretching (υ_3). The characteristic υ_1(O-O) stretching bands of compounds **1**-**6** appeared at 810-925 cm^{-1} (Table 2). The υ_1 modes are shifted to lower wave numbers upon passing from zirconium compounds **1** and **4** (925 and 890 cm^{-1}) to the corresponding thorium analogues, **2** and **5** (890 and 830 cm^{-1}), indicating that for the $M(O_2)$ grouping, the υ_1(O-O) stretching band decreases with an increase in the atomic number of the metals in a group. The present complexes exhibit υ_2 and υ_3 modes at 500-550 cm^{-1} and 540-620 cm^{-1}, respectively. It is important, however, that the υ_1 modes of the present zirconium, thorium and uranium complexes appear at lower frequencies than the peroxo complexes of these metals containing mono-, bi- and tridentate ancillary ligands (Tarafder and Islam, 1989; Westland and Tarafder, 1981;). This is presumably due to the greater charge neutralization of the metal centres by the quadridentate, quadrinegative and pentadendate dinegative s-donor ligands causing a weaker coulombic interaction in the M^{n+}- O_2^- moieties (n = 4 or 6). The protonic nature of the complexes **1**-**3** is evident from the positive response of these complexes to litmus solution. These complexes showed conductivity values of the order ~10^{-4} ohm/cm in their saturated aqueous solutions. The alkalimetric titration to determine the number of acidic protons outside the coordination sphere could not be carried out, because the complexes were very poorly soluble in water. Bands at ~3400 cm^{-1} in **1**, **2** and **3** arise from hydronium ions outside the coordination sphere.

Magnetic measurements and electronic spectra. Magnetic measurements were carried out in Nujol mulls spreaded on a filter paper and all the complexes were found to be diamagnetic in nature. The electronic spectra revealed that the complexes showed various bands in the range 245 - 385 nm, presumably arising from metal to ligand charge transfers.

Reactivity. The present peroxo complexes were found to be inert towards olefins and other substrates. Complexes **1** and **3** failed to oxidize allyl alcohol even when refluxing was continued at ~ 90 °C for 48 h. Complexes **4** and **5** also did not react with triphenylphosphine or triphenylarsine. These negative results outline the greater stability of the metal peroxo moiety in the presence of the quadridentate, quadrinegative and the pentadentate, dinegative chelating ligands which hinder oxygen transfers. A similar behaviour was observed for various peroxo complexes containing multidentate ligands (Tarafder and Khan, 1991a; 1991b; Tarafder and Islam, 1989; Tarafder, 1987). According to Mimoun *et al*. (1982) and Mimoun (1980), although the insertion of substrates into the metal peroxo triangle forming a metallocycle is an agreed process, the presence of multidentate ligands stabilize the triangle to such an extent that nucleophiles (Ph_3P or Ph_3As) apparently fail to open up the triangle, thus precluding oxygen transfers.

References

Bonchio, M., Bortolini, O.,Conte, V., Moro, S. 2001. Characterization and reactivity of triperoxo vanadium complexes in protic solvents. *European Journal of Inorganic Chemistry*, 2913-2919.

Chishiro, T., Shimazaki, Y., Tani, F., Tachi, Y., Naruta, Y., Karasawa, S., Hayami, S., Maeda, Y. 2003. Isolation and crystal structure of a peroxo-bridged heme-copper complex. *Angewandte Chemie International Edition*, **115:** 2894-2897.

Deubel, D.V., Sundermeyer, J., Frenking, G. 2001. Olefin epoxidation with transition metal η 2-peroxo complexes: The control of reactivity. *European Journal of Inorganic Chemistry*, 1819-1827.

Hinnerb, M. J., Grosche, M., Herdtweck, E., Thiel, W. R. 2003. A merrifield resin functionalized with molybdenum peroxo complexes: Synthesis and catalytic properties. *Zeitschrift für Anorganische und Allgemeine Chemie*, **629:** 2251-2257.

Hou, S.Y., Zhou, Z.H., Lin, T.R., Wan, H.L.2006. Peroxotungstates and their citrate and tartrate derivatives. *European Journal of Inorganic Chemistry*, 1670-1677.

Jacobson, S.E., Tang, R., Mares, F. 1978. Group 6 transition metal peroxo complexes stabilized by polydentate pyridinecarboxylate ligands. *Inorganic Chemistry*, **7:** 3055-3063.

Justino, L.L.G., Ramos, M.L., Caldeira, M.M., Gil,V.M.S. 2000. Peroxovanadium(V) complexes of L-lactic acid as studied by NMR spectroscopy. *European Journal of Inorganic Chemistry*, 1617-1621.

Kaizer, J., Pap, J., Speier, G., ´Pa´rka´nyi, L. 2004. The Reaction of μ- η2: η2-peroxo- and bis(μ-oxo)dicopper complexes with flavonol. *European Journal of Inorganic Chemistry*, 2253-2259.

Kondo, S., Karuhashi, K., Seki, K., Matsubara, K., Miyaji, K., Kubo, T., Matsumoto, K., Katsuki, T. 2008. A μ- Oxo - μ - η 2: η 2-Peroxo titanium complex as a reservoir of active species in asymmetric epoxidation using hydrogen peroxide. *Angewandte Chemie International Edition*, **47:** 10195-10198.

Lewis, G.R., Wilson, C. 2001. Mue-Peroxo-bis[trans-chloro (1,4,8,11-tetraazacyclotetradecane)cobalt(III)] bis (tetraphenylborate) diacetone solvate. *Acta Crystallographica C*, **57:** 1159 -1161.

Meyer, F., Pritzkow, H. 2000. μ_4-Peroxo versus bis(μ_2-hydroxo) cores in stucturally analogous tetracopper(II) complexes. *Angewandte Chemie International Edition*, **39:** 2112-2115.

Mimoun, H., Postel, M., Casabianca, F., Fischer, J., Mitschler, A. 1982. Novel unusually stable peroxotitanium(IV) compounds. Molecular and crystal structure of peroxobis (picolinato) (hexamethylphosphoric triamide) titanium(IV). *Inorganic Chemistry*, **21:** 1303-1306.

Mimoun, H. 1980. The role of peroxymetallation in selective oxidative processes. *Journal of Molecular Catalysis*, **7:** 1-29.

Nica, S., Pohlmann, A., Plass, W. 2005. Vanadium (V) oxoperoxo complexes with side chain substituted *N*-salicylidene-hydrazides: modeling supramolecular interactions in vanadium haloperoxidases. *European Journal of Inorganic Chemistry*, 2032-2036.

Ole, S., Anja H., Christian, N., Christian W., Max, C.H., Siegfried, S., Felix, T. 2008. Aromatic hydroxylation in a copper bis (imine) complex mediated by a μ- η 2: η 2 peroxo dicopper core: A mechanistic scenario. *Chemistry-A European Journal*, **14:** 9714-9729.

Sharma, M., Saleem, M., Pathania, M.S., Sheikh, H.N., Kalsotra, B.L. 2009. Peroxo complexes of molybdenum (VI) containing mannich base ligands. *Chinese Journal of Chemistry*, **27:** 311-316.

Tarafder, M.T.H., Khan, A.R. 1991a. Peroxo complexes of zirconium(IV), thorium(IV), molybdenum(VI), tungsten(VI) and uranium(VI) containing a quadridentate SNNS Schiff base. *Polyhedron*, **10:** 973-976.

Tarafder, M.T.H., Khan, A.R. 1991b. Peroxo complexes of zirconium(IV), thorium(IV), molybdenum(VI), tungsten(VI) and uranium(VI) containing two quadridentate ONNO Schiff bases. *Polyhedron*, **10:** 819-822.

Tarafder, M.T.H., Islam, A.A.M.A. 1989. Peroxo complexes of Zr(IV), Th(IV), W(VI) and U(VI) ions stabilized by multidentate organic ligands. *Polyhedron*, **8:** 109-112.

Tarafder, M.T.H., Howlader, M.B.H., Nath, B., Islam, A.A.M.A. 1989. Peroxo complexes of Zr(IV), Th(IV), Mo(VI) and U(VI) ions containing some bidentate organic ligands. *Polyhedron*, **8:** 977-981.

Tarafder, M.T.H. 1987. Adduct type peroxo complexes of thorium. *Indian Journal of Chemistry*, **26A:** 874-876.

Tarafder, M.T.H., Khan, A.R. 1987. Some organoperoxo complexes of molybdenum and tungsten. *Polyhedron*, **6:** 275-279.

Tarafder, M.T.H., Ahmed, A. 1986. Some organoperoxo complexes of Zr(IV), Th(IV), Mo(VI), W(VI) and U(VI). *Indian Journal of Chemistry*, **25A:** 729-732.

Tarafder, M.T.H., Miah, M.A.L. 1986. Novel peroxo complexes of zirconium containing organic ligands. *Inorganic Chemistry*, **25:** 2265-2268.

Westland, A.D., Tarafder, M.T.H. 1982. Novel peroxo complexes of thorium containing organic ligands. *Inorganic Chemistry*, **21:** 3228-3232.

Westland, A.D., Tarafder, M.T.H. 1981. Novel peroxo complexes of uranium containing organic ligands. *Inorganic Chemistry*, **20:** 3992-3995.

Westland, A.D., Haque, F., Bouchard, J.M. 1980. Peroxo complexes of molybdenum and tungsten stabilized by oxides of amines, phosphines, and arsines. Stability studies. *Inorganic Chemistry*, **19:** 2255-2259.