

Synthesis and characterization of peroxo complexes of titanium(IV) and zirconium(IV) with some monodentate and multidentate ligands

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A few peroxo complexes of titanium(IV) and zirconium(IV) of the formulae $[Ti(O)(O_2)C_6H_4(NH_2)_2 \cdot H_2O]$, $[M(O)(O_2)L_2]$, $[Ti(O_2)L'_2]$, $[Zr(O)(O_2)2L'' \cdot H_2O]$, $[Ti(O)(O_2)L''']$, $[Zr(O)(O_2)L''' \cdot H_2O]$ and $[Zr(O)(O_2) \cdot tet]$ [where $M = Zr(IV)$ and $Ti(IV)$; $L =$ ethylenediamine, 2-aminopyridine; $L' =$ aminophenoxido, oxoquinolino; $L'' =$ pyridine, triphenylphosphine oxide; $L''' =$ diethylenetriamine; $tet =$ triethylenetetramine] have been synthesized and characterized by elemental analyses, conductivity measurements and IR spectral studies. The complexes containing monodentate and bidentate ligands are found to oxidize both PPh_3 and $AsPh_3$ but those containing tridentate and tetradentate ligands are stable and inert towards oxidation.

The studies on dioxygen complexes of transition metals are of great interest and importance for their ability to catalyze oxygen insertion reactions and oxidize organic substrates¹⁻⁴. In general, peroxo complexes containing multidentate coligands stabilize the metal peroxo moiety which hinders the transfer of active oxygens to organic and inorganic substrates^{1,2,5-10}. Further, the reactivity of peroxo complexes depends greatly on the metal and the nature of the coligands. In this note we report the synthesis of some organoperoxo complexes of $Ti(IV)$ and $Zr(IV)$, and their potential on the oxygen transfer reactions towards PPh_3 and $AsPh_3$. The ligands used in the present study are:

Experimental

All the chemicals used were of reagent grade.

Ethanol was purified by refluxing with iodine and magnesium turnings, and finally distilled and stored over molecular sieves. Titanylacetylacetonate and zirconium oxychloride octahydrate were used for the preparation of $Ti(IV)$ and $Zr(IV)$ solutions in 30% H_2O_2 . The conductivity measurements of the complexes ($10^{-3}M$ solutions) were recorded in DMSO at room temperature using a PTI-18 Digital conductivity meter and a dip-type cell with platinized electrodes. The cell was calibrated with KCl solutions of varying concentrations. The infrared spectra (KBr discs) were recorded on a Pye-Unicam SP3-300 Infrared spectrophotometer in the range 4000-200 cm^{-1} . The recorded spectra were calibrated against the 1601.8 cm^{-1} peak of polystyrene film. The elemental analysis was carried out by Microanalytical services at the University of St. Andrews, Scotland.

General methods of preparation

Complexes 1, 5, 8 and 9 : $[M(O)(O_2)L \cdot nH_2O]$ [where $M = Ti(IV)$ and $Zr(IV)$; $L = C_6H_4(NH_2)_2$, *det* and *tet*; $n = 0$ or 1].

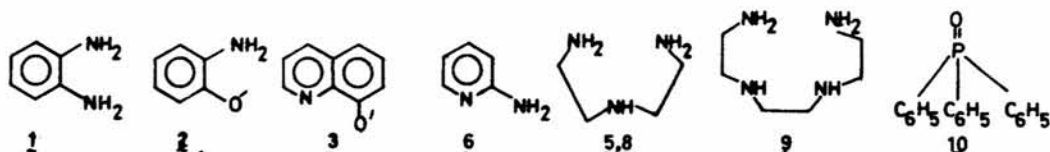
A solution of titanylacetylacetonate (0.002 mol) or $ZrOCl_2 \cdot 8H_2O$ (0.002 mol) in 30% H_2O_2 (25 cm^3) was mixed with solution of the ligand L (0.002 mol) in ethanol (20 cm^3). The precipitate obtained was separated, washed with water and ether, and finally dried *in vacuo* over P_4O_{10} .

Complexes 2 and 3 : $[Ti(O_2)L'_2]$ [$L' = C_6H_4NH_2O$ and C_9H_6NO]

Titanylacetylacetonate (0.002 mol) was dissolved in 30% H_2O_2 (25 cm^3). The solution was filtered and to the filtrate, a solution of L' (0.004 mol) in ethanol (20 cm^3) was added. The precipitate formed was filtered, washed with water and ether, and dried *in vacuo* over P_4O_{10} .

Complexes 4, 6, 7 and 10 : $[M(O)(O_2) \cdot 2L'' \cdot nH_2O]$ [where $M = Ti(IV)$ and $Zr(IV)$; $LPP = C_5H_5N$ and $OPPh_3$; $n = 0$ or 1]

Titanylacetylacetonate (0.002 mol) or $ZrOCl_2 \cdot 8H_2O$ (0.002 mol) was dissolved in 30% H_2O_2



(25 cm³) and these were added separately to a solution of the ligand L'' (0.004 mol) in ethanol (25 cm³). The precipitate obtained was separated, washed and stored as above.

Reaction of complex 6 with PPh₃(a)

Triphenylphosphine (0.002 mol) was dissolved in 25 cm³ of THF to which a suspension of complex 6 (0.002 mol) in the same solvent (50 cm³) was added. The mixture was refluxed for 24h. The TLC indicated that phosphine got converted into phosphine oxide. The solution was filtered and the residue collected. A yellowish-white product was recovered from the filtrate which was identified as OPPh₃, m. pt., 156-157° (lit.157°C).

Reaction of 7 with AsPh₃(b)

A solution of triphenylarsine (0.002 mol) in THF (25 cm³) was added to a suspension of complex 7 (0.002 mol) in the same solvent (50 cm³). The mixture was refluxed for 72h. The TLC indicated that the reaction was complete and the arsine got converted

into arsine oxide. The solution was filtered and the residue collected. Evaporation of the filtrate yielded the product (OAsPh₃), m. pt., 186-188°C (lit. 189°C).

Attempted reactions of 8 and 9 with PPh₃ and AsPh₃(c)

The refluxing of complexes 8 and 9 with equimolecular quantities of triphenylphosphine or triphenylarsine in THF for 48h failed to produce any reaction. The complexes 8 and 9 were recovered as such.

Results and discussion

The elemental analyses and conductivity data of the complexes (1-10) are presented in Table 1. The molar conductance values show that all the complexes are non-electrolytes in DMSO indicating that the anions are covalently bonded in all the cases. The analytical, conductivity and IR spectral data of the complexes are consistent with six coordination of Ti(IV) and Zr(IV) in complexes 1, 2, 3, 5, 7 and 10

Table 1—Analytical data of the peroxo complexes (1-10)

Compound	Colour	Found(Calc), %			Molar conduct. ohm ⁻¹ cm ² mol ⁻¹
		C	H	N	
[Ti(O)(O ₂)C ₆ H ₄ (NH ₂) ₂ .H ₂ O] (1)	Ash	32.3 (32.5)	4.3 (4.5)	12.4 (12.6)	0
Ti(O ₂)(C ₆ H ₄ NH ₂ O) ₂ (2)	Ash	48.5 (48.6)	4.1 (4.1)	9.3 (9.5)	1
[Ti(O ₂)(C ₉ H ₆ NO) ₂] (3)	Yellow	58.5 (58.7)	3.3 (3.3)	7.5 (7.6)	3
[Ti(O)(O ₂)(en) ₂] (4)	Yellow	22.1 (22.2)	7.3 (7.5)	25.6 (25.9)	0
[Ti(O)(O ₂).det] (5)	Yellow	24.0 (24.1)	6.5 (6.6)	21.1 (21.1)	1
[Zr(O)(O ₂)(C ₅ H ₄ NNH ₂) ₂] (6)	Yellow	36.5 (36.7)	3.5 (3.7)	17.0 (17.1)	2
[Zr(O)(O ₂) ₂ C ₅ H ₅ NH ₂ O] (7)	White	38.0 (38.1)	3.8 (3.8)	8.7 (8.9)	2
[Zr(O)(O ₂).det.H ₂ O] (8)	Orange	18.3 (18.5)	5.6 (5.8)	16.1 (16.1)	0
[Zr(O)(O ₂).tet] (9)	Brown	25.1 (25.3)	6.3 (6.4)	19.5 (19.6)	0
[Zr(O)(O ₂).20PPh ₃ .H ₂ O] (10)	White	60.2 (60.6)	4.3 (4.5)	—	3

while the complexes **4**, **6**, **8** and **9** are seven-coordinate.

In the IR spectra, it was observed that diethylenetriamine (det) behaves as a tridentate neutral ligand coordinating at three nitrogen sites while triethylenetetramine (tet) behaves as a quadridentate neutral ligand coordinating at four nitrogen sites. All the complexes except **3**, **7** and **10** show two bands, **1** (3340 and 3300 cm^{-1}), **2** (3340 and 3260 cm^{-1}), **4** (3190 and 3120 cm^{-1}), **5** (3300 and 3230 cm^{-1}), **6** (3260 and 3100 cm^{-1}), **8** (3330 and 3240 cm^{-1}) and **9** (3320 and 3260 cm^{-1}) significantly lower than the values for free *o*-phenylenediamine (3400, 3380 cm^{-1} in **1**); 2-aminophenol (3414, 3342 cm^{-1} in **2**); ethylenediamine (3260, 3180 cm^{-1} in **4**); diethylenetriamine (3360, 3290 cm^{-1} in **5** and **8**); 2-aminopyridine (3350, 3200 cm^{-1} in **6**) and triethylenetetramine (3380, 3300 cm^{-1} in **9**), which indicates the coordination by the amino nitrogen. This is also evident from the appearance of bands at 310-350 cm^{-1} which are attributed to the $\nu(\text{M-N})$ mode⁵⁻¹². In complexes **3**, **6** and **7**, the $\nu(\text{C=N})$ modes appear at 1580, 1590 and 1540 cm^{-1} respectively, which are lower than the free ligand value (1610 cm^{-1}), indicating that the ring nitrogen is coordinated to the metal atom⁷⁻¹⁴. The $\nu(\text{O-H})$ band observed in the free 8-hydroxyquinoline and 2-aminophenol disappears in complexes **3** and **2** indicating deprotonation and coordination at oxygen sites. The $\nu(\text{O-H})$ bands observed in complexes **1**, **7**, **8** and **10** at 3410, 3440, 3440 and 3250 cm^{-1} respectively, indicate the presence of coordinated water molecules. In addition, the far IR spectra of **1**, **2**, **3**, **7**, **8** and **10** display bands at 435-500 cm^{-1} which are tentatively attributed to the $\nu(\text{M-O}')$ modes⁵⁻¹⁰ ($\text{O}' = \text{oxygen in co-ligand}$). All the complexes excepting **2** and **3** display $\nu(\text{M=O})$ modes¹⁶ at 880-930 cm^{-1} . The complex **10** shows a decrease in $\nu(\text{P=O})$ mode by 17 cm^{-1} from the free ligand value (1192 cm^{-1})¹⁵ suggesting that OPPh_3 is very weakly coordinated to the metal ion.

The metal peroxo grouping gives rise to three IR- and Raman-active vibrational modes. These are predominantly 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 of **1-10** appear at 820-880 cm^{-1} . There is a decrease in ν_1 upon passing from the titanium complexes (**1-5**, 860-880 cm^{-1}) to the corresponding zirconium complexes (**6-10**, 820-845 cm^{-1}). The present data thus clearly reveal that for the $\text{M}(\text{O}_2)$ grouping, the ν_1 (O-O) modes decrease with the increase in the atomic number of metals in a particular group. In the present

complexes the ν_3 and ν_2 modes appear at 620-685 cm^{-1} and 510-560 cm^{-1} respectively.

Reactivity

The compounds **6** and **7** were allowed to react with PPh_3 and AsPh_3 to explore the possibility of reactivity of the present peroxo complexes. The reactions produced OPPh_3 and OAsPh_3 . The products showed IR bands at 1192 and 880 cm^{-1} , assignable to $\nu(\text{P=O})$ and $\nu(\text{As=O})$ modes respectively. The IR spectra of the metal residues of reactions (a) and (b) showed the disappearance of $\nu_1(\text{O-O})$ bands, thereby indicating the transfer of peroxo oxygens to the substrates. In reaction (c), compounds **8** and **9** were allowed to react with PPh_3 and AsPh_3 , but these compounds failed to oxidize PPh_3 and AsPh_3 even when refluxing at 90°C was continued for 48h. The results outline the enhanced stability of the metal peroxo moiety in the presence of tridentate and quadridentate chelating ligands. Similar results were observed with other peroxo complexes containing tridentate, bidentate-dinegative and quadridentate ligands^{11,12,17}.

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