

Peroxo complexes of molybdenum(VI), uranium(VI), zirconium(IV) and thorium(IV) ions containing some amino acids

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Several new peroxo complexes of molybdenum(VI), uranium(VI), zirconium(IV) and thorium(IV) containing some bidentate amino acids have been synthesized and characterized. The complexes have the general formulae $[M(O)(O_2)L_2]$ and $[M'(O_2)L_2]$, $[Mo(O)(O_2)L^{2-} \cdot H_2O]$ and $[M'(O_2)L^{2-} \cdot H_2O]$ [$M = Mo(VI)$ and $U(VI)$; $M' = Zr(IV)$ and $Th(IV)$; $L^- =$ glycinate, leucinate; $L^{2-} =$ tyrosinate]. The complexes react with trans-stilbene, PPh_3 and $AsPh_3$, giving their oxides. The IR spectra of the complexes indicate that the frequency of the ν_1 -mode of the $M(O_2)$ grouping, which is essentially an O-O stretch decrease with an increase in the atomic number of metal in a group.

There has been a great deal of interest in the peroxo complexes of transition metals because of their intriguing coordination chemistry as well as their role as oxidants in synthetic organic and inorganic chemistry¹⁻¹³. The labilities of the coordinated peroxides depend both on the metal ions and the auxiliary ligands used³⁻¹³. We have previously reported peroxo complexes of metals of groups IVA and VIA containing monodentate- to quadridentate-organic moieties²⁻¹³. No attempt appears to have been made so far to isolate peroxo complexes of transition metals containing amino acids as ancillary ligands. We present here the synthesis of peroxo complexes of molybdenum(VI), uranium(VI), zirconium(IV) and thorium(IV) ions containing glycine, leucine or tyrosine as organic ligands and some of their oxygen transfer reactions. An attempt has also been made to study the effect of the size of the metal ions on the $\nu_1(O-O)$ modes of the complexes in their IR spectra.

Materials and Methods

All chemicals used were of BDH Chemicals of reagent grade and were used as supplied.

General method for the preparation of $[M(O)(O_2)(L^-)_2]$ (1 and 3) and $[Mo(O)(O_2)(L^{2-}) \cdot H_2O]$ [$L =$ glycine or leucine; $L' =$ tyrosine] (4)

The amino acid L (0.02 mol) was dissolved in ethanol (60 cm³) and was treated with potassium hydroxide (0.02 mol). The solution was cooled

and to it was added, a solution of MoO_3 (0.01 mol) in 30% H_2O_2 (75 cm³). The mixture was cooled in an ice-salt bath. The resulting precipitate was separated, washed with ether and dried *in vacuo* over P_4O_{10} . The complex 4 was prepared similarly using equimolar quantities of tyrosine and MoO_3 .

General method for the preparation of $[U(O)(O_2)(L^-)_2]$ [$L =$ glycine and leucine] (2 and 8)

The amino acid L (0.01 mol) was dissolved in a solution of potassium hydroxide (0.01 mol) in 30% H_2O_2 (80 cm³). The solution was cooled and to it was added a solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (0.005 mol) in ethanol (60 cm³). The mixture was cooled in an ice-salt bath. The crystals so obtained were removed by filtration, washed with ether and dried *in vacuo* over P_4O_{10} .

General method for the preparation of $[M(O_2)L^{2-} \cdot H_2O]$ (5 and 7) and $[Th(O_2)L^{2-}]$ (6) [$M = Zr(IV)$ and $Th(IV)$; $L =$ leucine; $L' =$ tyrosine]

The amino acid L or L' (0.01 mol) was added to a solution of potassium hydroxide (0.01 mol) in 30% H_2O_2 (80 cm³). The solution was cooled and to it was added a solution of stoichiometric amount of $M(NO_3)_4 \cdot 4H_2O$ in ethanol (50 cm³). The complexes obtained were removed by filtration, washed with ether and dried *in vacuo* over P_4O_{10} .

The analytical data for the complexes are summarised in Table 1.

Table 1 – Analytical and molar conductance data for the complexes

Complex	Found (Calc.) %			Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
	C	H	N	
$[\text{Mo}(\text{O})(\text{O}_2)(\text{NH}_2\text{CH}_2\text{COO}^-)_2](\mathbf{1})$	16.41 (16.45)	2.71 (2.76)	9.48 (9.59)	0
$[\text{U}(\text{O})(\text{O}_2)(\text{NH}_2\text{CH}_2\text{COO}^-)_2](\mathbf{2})$	11.00 (11.01)	1.85 (1.86)	6.41 (6.45)	2
$[\text{Mo}(\text{O})(\text{O}_2)(\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COO}^-)_2](\mathbf{3})$	35.61 (35.65)	5.78 (5.98)	6.89 (6.93)	4
$[\text{Mo}(\text{O})(\text{O}_2)(^-\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^-)\text{H}_2\text{O}](\mathbf{4})$	31.45 (31.69)	3.11 (3.25)	4.10 (4.11)	1
$[\text{Zr}(\text{O}_2)(^-\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^-)\text{H}_2\text{O}](\mathbf{5})$	33.70 (33.74)	3.43 (3.46)	4.34 (4.37)	0
$[\text{Th}(\text{O}_2)(\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COO}^-)_2](\mathbf{6})$	27.45 (27.49)	4.52 (4.61)	5.22 (5.34)	0
$[\text{Th}(\text{O}_2)(^-\text{OC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COO}^-)\text{H}_2\text{O}](\mathbf{7})$	23.23 (23.44)	2.40 (2.40)	3.00 (3.04)	1
$[\text{U}(\text{O})(\text{O}_2)(\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COO}^-)_2](\mathbf{8})$	26.21 (26.38)	4.24 (4.43)	5.11 (5.13)	2

Reaction of 1 with trans-stilbene (Reaction A)

trans-Stilbene (1.8 g, 0.01 mol) was added to a suspension of **1** (2.9 g, 0.01 mol) in CH_2Cl_2 (150 cm^3). The mixture was stirred under reflux and the progress of the reaction was monitored by TLC. After 36 hr of reflux TLC indicated a complete conversion of stilbene to its oxide. The solution was filtered, the filtrate evaporated and the residue extracted with ether. Evaporation of the extract yielded 1.75 g of *trans*-stilbene oxide, m.p. 63-65°C [Found: C, 85.55; H, 6.00; O, 8.12. Calc. for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.71; H, 6.12; O, 8.16%].

Reaction of 2 with trans-stilbene (Reaction B)

trans-Stilbene (1.4 g, 0.005 mol) was added to a suspension of **2** (2.17 g, 0.005 mol) in CH_2Cl_2 (100 cm^3). The mixture was stirred under reflux and the progress of the reaction was monitored by TLC, which after 24 h of reflux indicated a complete conversion of stilbene to its oxide. The solution was filtered, the filtrate evaporated and the residue extracted with ether. The evaporation of the extract yielded 1.35 g of *trans*-stilbene oxide. The product was characterized on the basis of its m.p. and elemental analyses.

Reaction of 6 with triphenylphosphine (Reaction C)

A solution of triphenylphosphine (1.3 g, 0.005 mol) in THF (35 cm^3) was added to a suspension of **6** (2.62 g, 0.005 mol) in the same solvent (80

cm^3). The mixture was refluxed for 24 hr. The progress of the reaction was monitored by TLC which indicated that the reaction was complete. The solution was filtered and the residue collected. A yellowish white powder was recovered from the filtrate which was identified as OPPh_3 [m.p. 155-157°C (lit. 157°C)].

Reaction of 8 with triphenylarsine (Reaction D)

A solution of triphenylarsine (1.5 g, 0.005 mol) in THF (60 cm^3) was added to a suspension of **8** (2.73 g, 0.005 mol) in the same solvent (70 cm^3). The mixture was refluxed for 24 hr. TLC indicated that arsine was converted completely to its oxide. The solution was filtered and the residue collected. Evaporation of the filtrate yielded the product [m.p. 187-188°C (lit. 189°C)].

IR spectra (as KBr pellets) were recorded on a Pye-Unicam SP3-300 IR spectrophotometer. The ^1H NMR spectra were obtained in CDCl_3 on a Bruker AM 300 instrument using TMS as an internal standard, and mass spectra on an INCOS 50 spectrophotometer operated at 70 eV. Molar conductivities of 10^{-3} M solutions in dimethyl sulphoxide were determined at 25°C using a WPA CM35 conductivity meter fitted with a dip-cell and platinized electrodes.

Results and Discussion

Elemental analyses and conductivity data for the complexes are presented in Table 1. The com-

Table 2 – Infrared spectral data (in cm^{-1}) for the complexes

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}=\text{O})$	$\nu_1(\text{O}-\text{O})$	$\nu_3(\text{M} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix})$	$\nu_2(\text{M} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix})$	$\nu(\text{M}-\text{O}')$	$\nu(\text{M}-\text{N})$
1		3195 m 3105 m	1650 s	920 vs	865 s	630 s	510 m	405 m	360 sh
2		3200 w 3110 m	1665 s	910 vs	840 s	625 m	505 s	400 w	270 s
3		3180 m 3095 w	1655 vs	925 vs	870 vs	635 s	525 m	410 sh	370 m
4	3090 br	3185 m 3075 m	1660 s	920 vs	860 s	635 m	520 m	415 w	375 w
5	3400 br	3180 m 3075 w	1640 vs		830 s	670 m	560 m	430 sh	325 m
6		3195 m 3090 m	1650 s		815 vs	660 m	570 s	395 m	305 w
7	3410 br	3190 m 3095 m	1655 vs		820 s	655 sh	540 s	390 m	310 w
8		3210 w 3115 m	1670 s	915 vs	835 s	635 vs	515 m	405 m	275 m

plexes are all non-electrolytes in solution suggesting that the anions are covalently bonded in all the cases. These data are consistent with seven-fold coordination of molybdenum(VI) and uranium(VI) complexes, and six-fold coordination of zirconium(IV) and thorium(IV).

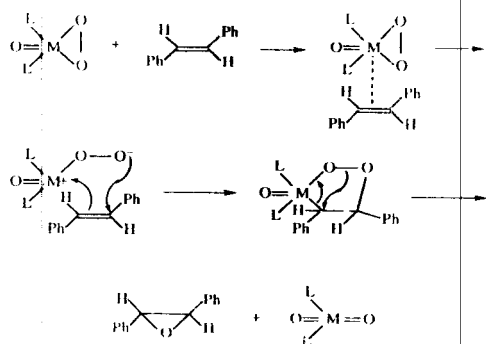
IR spectral data are presented in Table 2. In alkaline medium the amino acids glycine and leucine behave as bidentate ligands coordinating via the amino nitrogen and the carboxylate anions. Tyrosine is, however, potentially tridentate, coordinating via the amino nitrogen, carboxylate anion and the oxo anion generated during complexation. This is also apparent from the non-electrolytic nature of the complexes. In addition, absence of a band in the region $3400\text{--}3600\text{ cm}^{-1}$ in the spectra of the complexes of tyrosine indicates that it undergoes deprotonation at the $-\text{OH}$ end, thus providing an oxo coordination. All the complexes have characteristic $\nu(\text{NH}_2)$ modes in the region $3075\text{--}3195\text{ cm}^{-1}$, indicating coordination by the amino nitrogen. This is also evident from the appearance of bands at $275\text{--}375\text{ cm}^{-1}$ (Table 2) which are tentatively attributed to the $\nu(\text{M}-\text{N})$ mode³⁻¹¹ ($\text{M}=\text{Zr}^{\text{IV}}, \text{Th}^{\text{IV}}, \text{Mo}^{\text{VI}}$ and U_{VI}). Complexes **1-8** display $\nu(\text{C}=\text{O})$ bands at $1640\text{--}1670\text{ cm}^{-1}$, characteristic of carboxylate binding in the complexes^{3,5,10}. This is also evident from the appearance of $\nu(\text{M}-\text{O}')$ ($\text{O}'=\text{oxygen}$ in organic ligands) modes at $390\text{--}430\text{ cm}^{-1}$ in the far-IR spectra of the complexes³⁻¹⁰. Complexes **1-4** and

8 show diagnostic bands at $910\text{--}925\text{ cm}^{-1}$, attributable to $\nu(\text{M}=\text{O})$ modes^{3,6,7,9,10,12}. The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman-active vibrational modes. These are predominantly O–O stretching (ν_1), the symmetry M–O stretch (ν_2) and the antisymmetric M–O stretch (ν_3). The characteristic $\nu_1(\text{O}-\text{O})$ modes of **1-8** appear at $815\text{--}870\text{ cm}^{-1}$ (Table 2). In particular, the ν_1 mode decreases upon passing from molybdenum complexes (**1**, **3** and **4**) (865 , 870 and 860 cm^{-1}) to the corresponding uranium complexes (**2** and **8**) (840 and 835 cm^{-1}). Again, in the case of the peroxo complexes of the elements of group IIA, there is a decrease in ν_1 upon passing from the zirconium complex (**5**) (830 cm^{-1}) to the thorium complexes (**6** and **7**) (815 and 820 cm^{-1}). The present study thus clearly reveals that for the $\text{M}(\text{O}_2)$ grouping, the $\nu_1(\text{O}-\text{O})$ mode decreases with an increase in the atomic number of metal in a particular group. The present peroxo complexes display ν_3 and ν_2 modes at $625\text{--}670$ and $505\text{--}570\text{ cm}^{-1}$, respectively (Table 2).

Reactivity

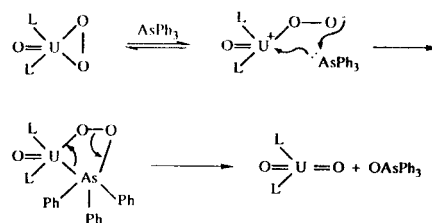
To explore the reactivity of the present peroxo complexes, **1** and **2** were allowed to react with *trans*-stilbene while **6** and **8** were used to oxidize triphenylphosphine and triphenylarsine, respectively.

Reactions A and B produced *trans*-stilbene oxide as indicated by a strong IR band near 1060



M = Mo^{VI} and U^{VI}; L = NH₂CH₂COO

Scheme 1



Scheme 2

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cm⁻¹ assigned to the C-O-C stretching mode and the methine absorption at 3.8 ppm in the ¹H NMR spectra as required for *trans*-stilbene oxide. The mass spectra indicated molecular ion peak at *m/z* + 196. Experimental details indicated that Reaction B was faster than Reaction A, which means that the uranium peroxo complex was kinetically more labile than its molybdenum analogue. A possible reaction path is shown in Scheme 1.

Reaction C produced triphenylphosphine oxide. The IR spectrum of the product showed $\nu(\text{P}=\text{O})$ at 1190 cm⁻¹ (ref. 14). Reaction D, with triphenylarsine, produced triphenylarsine oxide, as was evident from the IR band at 880 cm⁻¹, assigned to $\nu(\text{As}=\text{O})$ ¹⁵. The IR spectra of the metal residues of Reactions C and D showed the disappearance of $\nu_1(\text{O}-\text{O})$ bands. A possible reaction path is shown in Scheme 2. In order to obtain additional evidence for transfer of peroxo oxygen to PPh₃ or AsPh₃, a blank experiment was performed in the absence of the complex under identical conditions, which failed to give the product.