Synthesis and characterization of peroxo complexes of dioxomolybdenum(VI) and dioxouranium(VI) ions with tetraaza-macrocyclic ligands

M T H Tarafder & A R Khan*
Department of Chemistry, Rajshahi University, Rajshahi, Bangladesh
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Some peroxo complexes of dioxomolybdenum(VI) and dioxouranium(VI) containing two quadridentate, tetraaza-macrocyclic ligands and an organic molecule of high molecular weight have been synthesized and characterized. The complexes have the general formulae [M(O)₂(L)(O₂)] (M = Mo(VI) and U(VI); L = [15]ane N₄:1, 4, 8, 12-tetraazacyclopentadecane and trans-[14]-diene: (5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene) and [M(O)(O₂)(cyanex-272 -)] (cyanex-272 - = bis(2,4,4-trimethylphenylphosphinate). The peroxo complexes containing macrocyclic ligands are found to be inert towards oxidation, but those containing cyanex-272 are found to oxidize allyl alcohol, trans-stilbene and also PPh₃ and AsPh₃, to their oxides.

Currently there is growing interest in the synthesis and applications of peroxo complexes of transition metals. The coordination chemistry of peroxo complexes has been studied in some detail, but no attempts have been made so far to isolate peroxo complexes containing macrocyclic ligands and ligands of high molecular weights. This was our interest in examining effect of these ligands in stabilizing the metal-peroxo moiety. We have previously demonstrated that labilities of the coordinated peroxo moieties depend both on the metal ions and auxiliary ligands used. To examine this further, we have extended our study to peroxo complexes of molybdenum and uranium containing two macrocyclic ligands and a ligand of high molecular weight. This note deals with the synthetic aspects of these complexes and studies on their oxygen transfer reactions. An attempt has also been made to study the effect of the size of the metal ions on the ν₁(O - O) modes of the complexes in their IR spectra.

Experimental
All the chemicals used were of reagent grade and were used as supplied by Merck. IR spectra (as KBr pellets) were recorded on a pye-Unicam SP3-300 IR spectrophotometer. Conductivities of 10⁻³ M solutions in DMSO were measured at 25°C using a WPA CM35 conductivity meter and dip-type cell with platinized electrodes. Carbon, hydrogen and nitrogen analyses were carried out by Microanalytical Services at the University of St. Andrews, Scotland. The ¹H NMR spectra were obtained on a Bruker AM300 instrument using TMS as an internal standard, and mass spectra on an INCONS 50 spectrophotometer operated at 70 eV.

Preparation of ligands
1, 4, 8, 12-Tetraazacyclopentadecane ([15]ane N₄) and 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradeca-4, 11-diene (trans-[14]-diene) were prepared following the literature procedures. The purity of these compounds were checked by elemental analyses and melting points.

General method for the preparation of complexes [M(O)₂(L)(O₂)] [L = [15]ane N₄ or trans-[14]-diene (1, 2)
A suspension of MoO₃ (0.01 mol) in 30% H₂O₂ (50 cm³) was stirred overnight at 60°C. This was filtered and to the clear filtrate was added a solution of KOH (0.01 mol) in ethanol (75 cm³). The mixture was cooled and the resulting precipitate which separated out was filtered, washed with ether and dried in vacuo over P₂O₅.

Preparation of [Mo(O)(O₅)(cyanex-272 -)] (3)
Cyanaex-272 (0.01 mol, 2.9 g) was added to a solution of KOH (0.01 mol, 0.56 g) in ethanol (80 cm³). To this clear solution was added, with stirring, a solution of MoO₃ (0.005 mol, 0.72 g) in 30% H₂O₂ (60 cm³). The mixture was cooled and the resulting precipitate which separated out was filtered, washed with ether and dried in vacuo over P₂O₅.

To a solution of UO₂(NO₃)₂·6H₂O (0.005 mol) in ethanol (30 cm³) was mixed a solution of the ligand (0.005 mol) in the same solvent (50 cm³) and then 30% H₂O₂ (30 cm³) was added. The product was separated and stored as above.
Preparation of $[\text{U}(\text{O}_2)(\text{cyanex-272}^-)]_2$ (6)

Cyanex-272 (0.004 mol, 1.16 g) was dissolved in a solution of KOH (0.004 mol, 0.22 g) in ethanol (50 cm$^3$). To this solution was added a solution of $\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}$ (0.002 mol, 1.04 g) in the same solvent (25 cm$^3$) and then 30% $\text{H}_2\text{O}_2$ (30 cm$^3$). The product was separated and stored as above.

Results and discussion

The elemental analyses and conductivity data for the complexes are presented in Table 1. The molar conductance data show that all the complexes are non-electrolytes in DMSO indicating that the chelating ligands are covalently bonded in all the cases. The organic moieties of the compounds are shown below.

It also supports that the organic molecule cyanex-272 deprotonates at the $-\text{OH}$ end, providing an oxo coordination, the other coordination site being the oxygen of $>\text{P}=\text{O}$ group. The present data are consistent with eight-fold coordination of complexes containing macrocycles and seven-fold in those containing cyanex-272.

The ligands [15] ane $\text{N}_4$ and trans [14]-diene are potentially quadridentate coordinating via the four ring nitrogens. In the IR spectra, the free tetraaza-ligands show $\nu$(N-H) bands (3200-3300, and 3300 cm$^{-1}$) which are shifted to lower frequencies (3050-3150 cm$^{-1}$ in (1, 2, 4 and 5) indicating that the nitrogens are coordinated$^{14}$. Further the free trans-[14]-diene exhibits $\nu$(C=N)$^{15}$ band at 1670 cm$^{-1}$ which is shifted to lower frequencies in (2) and 5). These are also apparent from the $\nu$(M-N) modes at 260-360 cm$^{-1}$ in the far IR spectra of the complexes$^{3,14}$. The complexes are the first reported examples of its kind.

Cyanex-272 is potentially bidentate, coordinating via the $>\text{P}=\text{O}$ oxygen and the oxo anion generated in basic medium. Attempts to prepare complexes from a neutral medium were unsuccessful. This suggests that the nucleophilicity of the ligand is greatly enhanced in alkali medium probably due to creation of an anionic site in situ. The deprotonation and consequent formation of an anionic site in situ is favoured by the basicity of the medium and the $\nu$(OH) band of the free ligand disappears in the spectra of the complexes (3) and 6) thus providing an oxo coordination. That the ligand deprotonates at the $-\text{OH}$ end is also evident from the appearance of $\nu$(M=O)$^{14}$(O'= oxygen in organic ligand) modes at 370-395 cm$^{-1}$ in the far IR spectra of the complexes$^4,10$. The $\nu$(P=O) band observed at 1170 cm$^{-1}$ in the free cyanex is shifted to lower frequencies (1055-1060 cm$^{-1}$) in (3) and 6) indicating coordination via oxygen of $>\text{P}=\text{O}$ group. Complexes (1-6) show diagnostic bands at 885-960 cm$^{-1}$, attributable to $\nu$(M=O) modes$^{3,10}$. Complexes (1, 2, 4 and 5) show two bands due to $\nu$(M=O) modes presumably arising from cis-orientations of two M=O groups. The metal peroxy grouping (local $C_{2v}$ symmetry) gives rise to three IR and Raman-active vibrational modes. These are pre-

| Table 1—Analytical and physical data of the peroxy complexes |
|-------------|------------------|------------------|------------------|
| m.p./ decomp. temp. | Found (Calcd), % | $\Lambda_M$ cm$^{-1}$mol$^{-1}$ |
| [Mo(O)$_2$(O$_2$)15aneN$_4$] | (1) > 350°C | C 35.21 (35.31) H 6.89 (6.95) N 14.85 (14.97) | 0 |
| [Mo(O)$_2$(O$_2$)trans-[14]-diene] | (2) > 300°C | C 43.52 (43.64) H 7.31 (7.27) N 12.58 (12.72) | 2 |
| [Mo(O)$_2$(O$_2$)(cyanex-272$^-$)] | (3) > 250°C | C 53.52 (53.17) H 9.45 (9.48) | 0 |
| [U(O)$_2$(O$_2$)15aneN$_4$] | (4) > 370°C | C 24.46 (25.58) H 5.06 (5.07) N 10.78 (10.85) | 1 |
| [U(O)$_2$(O$_2$)trans-[14]-diene] | (5) > 370°C | C 32.73 (32.99) H 5.48 (5.54) N 9.54 (9.62) | 3 |
| [U(O)$_2$(O$_2$)(cyanex-272$^-$)] | (6) > 260°C | C 44.14 (44.44) H 7.82 (7.93) | 0 |
dominantly $O=O$ stretching ($v_1$), the symmetric $M-O$ stretch ($v_2$) and the antisymmetric $M-O$ stretch ($v_3$). The characteristic $v_1(O=O)$ modes of (1-6) appear at 840-870 cm$^{-1}$. In particular, the $v_1$ mode decreases upon passing from molybdenum complexes (1-3) (860-870 cm$^{-1}$) to the corresponding uranium peroxy complexes (4-6) (840-845 cm$^{-1}$). The present study thus suggests that for the $M(O_2)$ grouping the $v_1(O=O)$ modes decrease with an increase in the atomic number of metals in a particular group. The present peroxy complexes display $v_3$ and $v_2$ modes at 645-660 and 510-570 cm$^{-1}$, respectively. The complexes (1, 2, 4, and 5) are eight-coordinated. Eight-coordinated peroxy complexes are not rare. Griffith et al.$^{11}$ reported a number of eight-coordinated peroxy complexes of various transition metals.

The peroxy complexes (1, 2, 4 and 5) were inert towards oxidation of olefin, phosphine and arsine. These negative results outline the enhanced stability of the metal peroxy moiety in the presence of quadridentate macrocycles which precludes oxygen transfer reactions. We also observed a similar stabilizing effect of the peroxy complexes containing various multidentate organic ligands.$^{3,5,8-10}$ However, (3) and (6) were reactive and oxidations of trans-stilbene, allyl alcohol, phosphine and arsine have been investigated. All these compounds were found to be oxidized by the complexes (3) and (6). A possible reaction path for the oxidation of trans-stilbene with complex (3) is shown in Scheme 1.

So, it can be concluded that although peroxy complexes containing quadridentate ligands are inactive yet complexes containing bidentate ligands are found to transfer their active oxygen to a variety of substrates.

References