

PEROXO COMPLEXES OF ZIRCONIUM (IV), THORIUM (IV) AND URANIUM (VI) IONS CONTAINING SOME MONODENTATE, BIDENTATE AND TRIDENTATE ORGANIC LIGANDS

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Some new peroxo complexes of zirconium, thorium and uranium containing monodentate, bidentate, tridentate and quadridentate organic ligands have been synthesized and characterized. The complexes have the general formulae $[M(O_2)_2 L]$ and $[U(O)(O_2)_2 \cdot 2L]$ and $[U(O)_2(O_2)L]$ [$M = Zr^{IV}$ or Th^{IV} ; $L =$ pyridine (py), diethylenetriamine (det), ethylenediamine (en) or aniline]. These complexes were all non-electrolytes in DMSO and those containing monodentate co-ligands were effective oxidants. The ν_1 mode of the $M(O_2)$ grouping decreases with the increase in the atomic number of the metals in a group and also with the increase of σ -donor sites of the multidentate organic moieties causing differences in the reactivities of the peroxides.

Key words: Zirconium, Peroxo, Complexes.

Introduction

The study of the chemistry of peroxo complexes has advanced rapidly in the last two decades due to development in application of such complexes as oxidant in synthetic organic chemistry [1-9]. We have seen earlier that peroxo complexes of lighter metals are thermodynamically unstable but are kinetically stable [7,10]. Kinetic liability towards olefinic compounds increases as the atomic number of metals in a group is increased. Nucleophilicity of olefinic compounds towards metal centres is also greatly affected by the electronic effect of the co-ligands in the complexes. Multidentate organic ligands stabilize the metal-peroxo moiety [10-12] whereas peroxo complexes containing monodentate and bidentate auxiliary ligands have been found to be good stoichiometric and catalytic oxidants for different substrates [1-9]. Question remains hitherto unresolved that with the use of a stronger ligand, the $\nu_1(O-O)$ stretching mode is shifted to lower frequencies and accordingly the peroxo group should be more liable. We have been interested to extend such a study to new peroxo complexes of Zr^{IV} , Th^{IV} and U^{VI} ions containing a variety of organic ligands, monodentate to tridentate. We report here the synthesis of these complexes and compare the liabilities of the complexes on the basis of factors characteristic of metals as well as those of co-ligands.

Experimental

IR spectra (as KBr discs) were recorded with a Pye-Unicam SP3-300 IR spectrophotometer. Conductivities of $10^{-3} M$ solutions of the complexes in dimethylsulphoxide (DMSO) were measured at 25° using a PTI-18 digital conductivity meter and dip-type cell with platinized electrodes.

Reagents. All chemicals used were reagent grade and supplied by Merck.

Analyses. Carbon, hydrogen and nitrogen analyses were carried out at the University of St. Andrews, Scotland.

Preparation of complexes: general method for the preparation of $[M(O_2)_2 \cdot 2py]$ (1 and 2) and $[M(O_2)_2 L]$ (3-5) [$M = Zr^{IV}$ and Th^{IV} ; $L = NH_2CH_2CH_2NHCH_2CH_2NH_2$ (det) and ethylenediamine (en)]. To a solution of metal nitrate hexahydrate (0.0002 mol) in water (20 cm³) was added a stoichiometric amount of the ligand L dissolved in ethanol (25 cm³). The mixture was stirred with 30% H₂O₂ (20 cm³). The precipitate was separated, washed successively with water and ether and dried *in vacuo* over P₄O₁₀.

General method for the preparation of $[U(O)(O_2)_2 \cdot 2L]$ and $[U(O)_2(O_2)L]$ [$L = py$, aniline or det] (6-7). The same procedure was applied to uranyl nitrate hexahydrate (0.0002 mol), stoichiometric amount of ligand L and 25 cm³ of 30% H₂O₂ which yielded the products 6-8.

Reactions of 1, 2 and 6 with triphenylphosphine and triphenylarsine. A solution of triphenylphosphine or arsine (0.004 mol) in THF (30 cm³) was added to a suspension of 1 in the same solvent (70 cm³). Refluxing the mixture for 48 hrs produced phosphine or arsine oxide, the completion of the reaction was monitored by TLC. The same reaction was carried out with 2 and 6 as oxidants and the reactions were found to be complete in 8hrs.

Attempted reaction of 8 with triphenylphosphine. Refluxing 8 with triphenylphosphine in a 1:1 molar ratio in THF medium for 48 hrs failed to produce any reaction; 8 was recovered unchanged.

Results and Discussion

The analytical and conductivity data are given in Table 1. The complexes are non-electrolytes in solution indicating that the oxo and peroxo ligands are undissociated in DMSO

solution. The mono or di-peroxo complexes of Zr^{IV} , Th^{IV} and U^{VI} were all either six or seven coordinated.

IR spectral data are presented in Table 2. The complexes 1, 2 and 6 display $\nu(C=N)$ modes at 1540-1580 cm^{-1} , lower than that of the free ligand value (1610 cm^{-1}) indicating coordination by the ring nitrogen atom [7,13]. This contention is further supported by the presence of $\nu(M-N)$ at 275-350 cm^{-1} in the far IR spectra of the complexes [10,11]. The complexes 3 - 5, 7 and 8 have characteristic $\nu(NH_2)$ and $\nu(NH)$ stretching modes in the regions 3000-3300 and 3060-3180 cm^{-1} , respectively [12,14,15]. The presence of M-N bonding is also evident from the $\nu(M-N)$ modes at 295-350 cm^{-1} in the far

IR spectra of the complexes [7,13]. Uranium peroxo complexes 6 - 8 display $\nu(U=O)$ modes at 900 cm^{-1} . The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman-active vibrational modes (ν_1), the symmetric M-O stretch (ν_2) and the anti-symmetric M-O stretch (ν_3). The characteristic $\nu_1(O-O)$ modes of 1 - 8 appear at 805-840 cm^{-1} (Table 2). In particular, the ν_1 mode decreases upon passing from zirconium complexes (1 and 3) (840 and 830 cm^{-1}) to thorium complexes (2, 4 and 5) (820, 805 and 815 cm^{-1}). The ν_1 mode of the uranium peroxo complexes 6 - 8 occur at lower frequencies than those of chromium, molybdenum and tungsten peroxo complexes reported earlier [9-12]. This is consis-

TABLE 1. ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF THE COMPLEXES^a.

| Compound* | Colour | Carbon (%) | | Hydrogen (%) | | Nitrogen (%) | | Molar conductance $\Omega^{-1} cm^2 mol^{-1}$ |
|---------------------------------------|------------|------------|-------|--------------|-------|--------------|-------|--|
| | | Calc. | Found | Calc. | Found | Calc. | Found | |
| $[Zr(O_2)_2 \cdot 2py]$ (1) | Colourless | 38.3 | 38.1 | 3.2 | 3.1 | 8.9 | 8.8 | 1.5 |
| $[Th(O_2)_2 \cdot 2py]$ (2) | Colourless | 26.4 | 26.2 | 2.2 | 2.2 | 6.2 | 6.2 | 1.0 |
| $[Zr(O_2)_2 (det)]$ (3) | Colourless | 18.6 | 18.4 | 5.0 | 5.0 | 16.3 | 16.2 | 2.5 |
| $[Th(O_2)_2 (det)]$ (4) | Colourless | 12.0 | 12.0 | 2.3 | 3.2 | 10.5 | 10.4 | 3.0 |
| $[Th(O_2)_2 (cn)]$ (5) | Colourless | 6.8 | 6.6 | 3.3 | 2.2 | 7.9 | 7.8 | 1.0 |
| $[U(O)(O_2)_2 \cdot 2py]$ (6) | Yellow | 25.2 | 25.1 | 2.1 | 2.1 | 5.9 | 5.9 | 1.0 |
| $[U(O)(O_2)_2 \cdot 2C_6H_5NH_2]$ (7) | Yellow | 28.6 | 28.3 | 2.8 | 2.8 | 5.6 | 5.5 | 1.0 |
| $[U(O)_2(O_2) (det)]$ (8) | Yellow | 11.9 | 11.7 | 3.2 | 3.2 | 10.4 | 10.3 | 2.0 |

* The organic moiety for the compounds indicated is. * The structures of the compounds are given below.

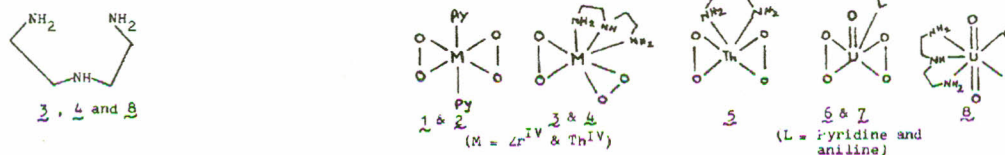


TABLE 2. IR SPECTRAL DATA FOR THE COMPLEXES, BAND MAXIMA (cm^{-1})^a.

| Compound | $\nu(NH)$ | $\nu(C=N)$ | $\nu(M=O)$ | $\nu_1(O-O)$ | $\nu_3(M \begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix})$ | $\nu_2(M \begin{smallmatrix} O \\ \diagdown \\ O \end{smallmatrix})$ | $\nu(M-N)$ |
|----------|-----------|------------|------------|--------------|--|--|------------|
| 1 | — | 1580 m | — | 840 s | 645 m | 520 w | 300 m |
| 2 | — | 1540 vs | — | 820 m | 660 m | 540 m | 350 m |
| 3 | 3300 w | — | — | — | — | — | — |
| | 3250 m | — | — | 830 s | 660 m | 550 m | 350 s |
| | 3180 m | — | — | — | — | — | — |
| 4 | 3270 w | — | — | — | — | — | — |
| | 3200 m | — | — | 805 m | 670 vs | 540 vs | 310 m |
| | 3060 w | — | — | — | — | — | — |
| 5 | 3180 w | — | — | — | — | — | — |
| | 3000 w | — | — | 815 w | 615 vs | 545 vs | 305 m |
| 6 | — | 1560 m | 900 s | 840 m | 625 w | 560 m | 275 vs |
| 7 | 3160 m | — | 900 s | 830 vs | 640 m | 560 m | 300 s |
| | 3055 m | — | — | — | — | — | — |
| 8 | 3280 w | — | — | — | — | — | — |
| | 3245 m | — | 900 vs | 820 s | 650 m | 530 m | 295 m |
| | 3180 w | — | — | — | — | — | — |

^a Relative band intensities are denoted by vs, s, m, w, br and sh, representing very strong, strong, medium, weak, broad and shoulder, respectively.

tent with the connotation that the ν_1 modes decrease with an increase in the atomic number of metals in a group [7-12]. More importantly, the ν_1 mode of the peroxo complexes containing bidentate and tridentate occurs at lower frequencies than those containing monodentate co-ligands. This is presumably due to greater charge neutralization of the metal centres by the multidentate σ -donor ligands, causing a weaker coulombic interaction in the $M^{n+} - O_2^{2-}$ moiety ($n = 4$ or 6).

Reactivity. Complexes 1, 2 and 6 were found to oxidize phosphines and arsines to their oxides. It is interesting however, that the thorium and uranium peroxo complexes were more reactive than the lighter zirconium analogue. This is perhaps expected that with the increase of size, the kinetic instability of metals increases, thereby enhancing the nucleophilicity of substrates for an attack [10]. The insertion of phosphines and arsines into the metal-peroxide bond forming a peroxy-metallocycle is a concerted process [2,10,13] which is very facile for heavier metals. The products $OPPh_3$ and $OAsPh_3$ were characterized from the melting points and IR spectra. The uranium peroxo complex 8 containing a tridentate co-ligand was, however, inert toward triphenyl-phosphine. This finding contradicts the information that the total electronic effect of the multidentate ligand on the metal centre weakens the bonding $M \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$ [10,11] (Table 2) which should render stronger oxidizing character to 8 than those containing monodentate ligands. We believe that the positive gain in entropy while using multidentate ligands [16] predominates the electronic effect thereby giving a huge kinetic stability to the metal peroxo moiety in 8.

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References

1. H. Mimoun, I.S. de Roch and L. Sajas, *Tetrahedron*, **26**, 37 (1970).
2. H. Minoun, *J. Mol. Catal.*, **7**, 1 (1980).
3. S.E. Jacobson, R. Tang and F. Mares, *Inorg. Chem.*, **17**, 3055 (1978).
4. A.D. Westland, F. Haque and J.M. Bouchard, *Inorg. Chem.*, **19**, 225 (1980).
5. A.D. Westland and M.T.H. Tarafder, *Inorg. Chem.*, **20**, 3992 (1981).
6. A.D. Westland and M.T.H. Tarafder, *Inorg. Chem.*, **21**, 3228 (1982).
7. M.T.H. Tarafder and M.A.L. Miah, *Inorg. Chem.*, **25**, 2265 (1986).
8. M.T.H. Tarafder and A. Ahmed, *Ind. J. Chem.*, **25A**, 729 (1986).
9. M.T.H. Tarafder and A.R. Khan, *Polyhedron*, **6**, 275 (1987).
10. M.T.H. Tarafder and A.R. Khan, *Polyhedron*, **10**, 973 (1991).
11. M.T.H. Tarafder and A.R. Khan, *Polyhedron*, **10**, 819 (1991).
12. M.T.H. Tarafder, P. Bhattacharjee and A.R. Sarkar, *Polyhedron*, **11**, 795 (1992).
13. H. Mimoun, M. Postel, F. Casabianca, J. Fischer and A. Mitschles, *Inorg. Chem.*, **21**, 1303 (1982).
14. D.A. House, R.W. Hay and M.A. Ali, *Inorg. Chim. Acta.*, **72**, 239 (1983).
15. R.W. Hay and M.T.H. Tarafder, *J. Chem. Soc., Dalton Trans.*, 823 (1991).
16. F.A. Cotton and G. Wilkinson, *Basic Inorganic Chemistry* (Wiley Eastern Ltd., New Delhi, 1989), pp. 142.