Some Organoperoxo Complexes of Zr(IV), Th(IV), Mo(VI), W(VI) & U(VI)

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New organoperoxo complexes containing S-benzyldithiocarbazate, NH₂NHCSSCH₂C₆H₅ (L) have been synthesized and characterized. The complexes have the general formulae, M(L⁻ -MO₂) [M = Zr(IV) and Th(IV)], M'(L⁻ -h(0₂h. [M' = Mo(VI), W(VI) and U(VI)] and M(L⁻ )₂(O₂)L⁻. [M = W(VI) and U(VI), L' = OPPh₃ or OAsPh₃ and L⁻ = deprotonated form of S-benzyldithiocarbazate]. The complexes could only be prepared in alkaline medium where L behaves as a uni-negative bidentate ligand. The IR spectra of the complexes reveal that the ν₁ mode of the M(O₂) grouping, which is essentially ν(O–O), shifts to lower wavenumbers with increase in atomic number of metals in a particular group. The IR spectra also indicate that the ν₁ mode varies somewhat with the choice of L'; arsine oxides give rise to generally lower frequencies. The complexes oxidize PPh₃ and AsPh₃ to OPPh₃ and OAsPh₃, respectively.

In recent years, a great deal of interest has been shown in the dioxygen complexes of transition metals as such compounds serve as reagents and catalysts in organic synthesis¹-⁸. No attempt seems to have been made so far to isolate peroxo complexes of transition metals containing nitrogen-sulphur donor ligands, e.g. S-benzyldithiocarbazate. It was, therefore, of interest to synthesize and characterize some new peroxo complexes of different elements of Group 4A and 6A containing such ligands.

We report here the synthesis and properties (in particular, with respect to oxygen transfer to various substrates) of the new Zr(IV), Th(IV), Mo(VI), W(VI) and U(VI) peroxo complexes (1-9). An attempt has also been made to study the effect of the size of the metal ions and the electronic nature of auxiliary ligands (OPPh₃ and OAsPh₃) on ν(O–O) modes of the complexes in their IR spectra.

Materials and Methods
The ligand, S-benzyldithiocarbazate was prepared by the literature method⁹ and its purity checked by elemental analyses, m.p. 125°C.

Physical Measurements and Elemental Analyses
Infrared spectra (nujol mull or as KBr pellets) were recorded on a Pye-Unicam SP3-300 infrared spectrophotometer; spectra between 600 and 200 cm⁻¹ were recorded as nujol mulls sandwiched between caesium iodide plates. Conductivities of solutions in dimethyl sulphoxide (DMSO) were measured at 298K using a conductivity bridge type M.C. 3 (Electronic Switchgear Ltd, London).

Metal⁹,¹⁰,¹¹ and sulphur¹⁰ contents of the complexes were determined gravimetrically. Methanolic solutions of the peroxo complexes were titrated with Ce(IV) to determine the number of active oxygen atoms present⁶. Carbon and hydrogen analyses were obtained from Mikroanalytisches Labor Pascher, Bonn-1, Germany.

Preparation of complexes: General method for the preparation of (a) M(L⁻ )₂(O₂) [M = Zr(IV) and Th(IV)] (complexes 1 and 2)

S-Benzyldithiocarbazate(L) (8 mmol) was added to a solution of KOH (8 mmol) in 30%H₂O₂ (20 ml). The solution was stirred for 5 min, filtered and to the filtrate was added, with stirring, a solution of M(NO₃)₄.4H₂O (4 mmol) in water (20 ml). The resulting orange-yellow precipitate then obtained was filtered off, washed successively with water and ether and dried in vacuo over P₄O₁₀.

(b) M'(L⁻ )₂(O₂) [M' = Mo(VI) and W(VI)] (complexes 3 and 4)

M'O₃ (5 mmol) was stirred and heated in 30%H₂O₂ (20 ml) at 50° for 48 hr. The solution was filtered and the filtrate added to a solution of S-benzyldithiocarbazate (10 mmol, 30 ml). The orange-yellow precipitate then obtained was filtered off, washed successively with water and ether and dried in vacuo over P₄O₁₀.

(c) U(L⁻ )₂(O₂) (complex 5)

A solution of uranyl nitrate hexahydrate (3 mmol) in water (15 ml) was added to a solution of S-benzyldithiocarbazate (6 mmol, 20 ml). The solution was boiled and the yellow precipitate obtained was filtered, washed successively with water and ether and stored.
M'(L -h(OJ2 complexes (0.01 mol) synthesized as above were dissolved in boiling acetone (100 ml) and this solution was added to a solution of L' (0.01 mol) in acetone (15 mI). The resulting mixture was stirred, heated for 24 hr, and kept standing overnight. The yellow precipitate obtained was filtered and stored as above.

Reaction of 3t with allyl alcohol (reaction-A)

Compound (3, 3.3 g, 0.006 mol) was dissolved in tetrahydrofuran (30 ml) and a stoichiometric amount of allyl alcohol added to it. Refluxing the mixture at 60°C for 36 hr failed to give any reaction product.

Reaction of 1t with triphenylphosphine (reaction-B)

Triphenylphosphine (0.52 g, 0.002 mol) was added to a solution of 1 (1.03 g, 0.002 mol) in tetrahydrofuran (25 ml). The mixture was heated at 55-60°C for 96 hr after which the solution was filtered and the solvent evaporated. The residue was placed on a column of silica gel (20 g, 35-230 mesh, Merck) and eluted first with benzene (300 ml) and then with methanol (250 ml). Unreacted triphenylphosphine (0.08 g) was recovered from the benzene fraction. Evaporation of the methanol fraction yielded triphenylphosphine oxide (0.42 g), m.p. 155-56° (lit. m.p. 15r).

Results and Discussion

Elemental analyses and conductivity data of the complexes (1-9) are presented in Table 1. Titration of methanolic solution of the peroxo complexes with Ce(IV) indicated that complexes 1, 2 and 3-9 are monoperoxido complexes, respectively. The conductivity data (Table 1) for solutions in DMSO indicate that 1-9 are nonelectrolytes. We have previously9 demonstrated that S-benzylidithiocarbazate forms NS chelated structure

<table>
<thead>
<tr>
<th>Compd.*</th>
<th>Found (Calc.), %</th>
<th>(\Lambda^\circ M^+) ((\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}))</th>
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<tr>
<td>[Zr(L -h(O2)] (1)</td>
<td>17.2 37.3 3.4 24.0 6.2</td>
<td>3</td>
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<tr>
<td>(17.6) (37.1) (3.5) (24.7) (6.2)</td>
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</tr>
<tr>
<td>[Th(L -h(O2)] (2)</td>
<td>35.0 28.9 2.6 19.0 4.8</td>
<td>0</td>
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<td>(35.2) (29.2) (2.7) (19.4) (4.8)</td>
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<tr>
<td>[Mo(L -h(O2)] (3)</td>
<td>17.8 34.5 3.0 22.9 11.5</td>
<td>5</td>
</tr>
<tr>
<td>(17.3) (34.6) (3.2) (23.1) (11.5)</td>
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<td></td>
</tr>
<tr>
<td>[W(L -h(O2)] (4)</td>
<td>28.2 29.5 2.7 19.9 9.9</td>
<td>7</td>
</tr>
<tr>
<td>(28.6) (29.9) (2.8) (19.9) (9.9)</td>
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<td></td>
</tr>
<tr>
<td>[U(L -h(O2)] (5)</td>
<td>34.0 27.3 2.5 17.9 9.2</td>
<td>8</td>
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<tr>
<td>(34.2) (27.6) (2.6) (18.4) (9.2)</td>
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<td></td>
</tr>
<tr>
<td>[W(L -h(O2)] , OPPh 3] (6)</td>
<td>19.6 44.1 3.4 13.8 6.9</td>
<td>8</td>
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<tr>
<td>(19.9) (44.3) (3.6) (13.9) (6.9)</td>
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<td></td>
</tr>
<tr>
<td>[W(L -h(O2)] , OAsPh 3] (7)</td>
<td>19.0 42.2 3.3 12.9 6.6</td>
<td>6</td>
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<td>(19.0) (42.3) (3.4) (13.3) (6.6)</td>
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<tr>
<td>[U(L -h(O2)] , OPPh 3] (8)</td>
<td>24.0 41.6 3.2 13.0 6.5</td>
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<tr>
<td>(24.4) (41.9) (3.4) (13.1) (6.5)</td>
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<tr>
<td>[U(L -h(O2)] , OAsPh 3] (9)</td>
<td>23.1 39.9 3.1 12.1 6.3</td>
<td>3</td>
</tr>
<tr>
<td>(23.3) (40.1) (3.2) (12.5) (6.3)</td>
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(a) Ligand L = NH2 - N = C <S< S< SCH2CH3
(b) Titration of methanolic solutions of the peroxo complexes by aqueous acidified standard ceric sulfate solution.
(c) Values are for \(\approx 10^{-3} M\) solutions of the complexes in DMSO.

\(^t\)See Table 1.
(Ia) in neutral medium. In alkaline medium, however, the ligand undergoes deprotonation and behaves as a bidentate uni-negative ligand (Ib). The IR spectrum of S-benzylidithiocarbazate displays strong bands at 3238 and 3180 cm\(^{-1}\), assignable to \(v(N-H)\) and \(\nu(N-H)\) of the NH\(_2\) group. Both the bands are shifted to lower wavenumbers in the metal peroxy complexes (\(\Delta\nu = 35 \text{ cm}^{-1}\) for \(v(N-H)\) and \(70 \text{ cm}^{-1}\) for \(\nu(N-H)\)). This shift of \(v(NH_2)\) bands to lower wavenumbers may be taken as an indication of coordination of metal ion via the amino nitrogen. A band of medium intensity at 3300 cm\(^{-1}\) is assigned to the \(v(N-H)\) of the secondary NH group of the free ligand. As expected, this band disappears in all the complexes (1-9), suggesting deprotonation and possible coordination via structure Ib of the ligand. The NS chelation in 1-9, is also evident from the appearance of \(v(M-N)\) and \(v(M-S)\) modes at 275-368 and 250-265 cm\(^{-1}\), respectively. The IR spectra of the complexes display \(v(C=N)\) in the region of 1510-1580 cm\(^{-1}\). The metal peroxy grouping (local C\(_2v\) symmetry) gives rise to three IR and Raman active vibrational modes. These are predominantly \(v(O-O)\) (\(v_1\)), the \(\nu(M-O)\) (\(v_2\)) and \(\nu_\text{as}(M-O)\) (\(v_3\)). The characteristic \(\nu(M-O)\) band of the present thorium peroxy complex (2) (at 840 cm\(^{-1}\)) occurs at a frequency 30 cm\(^{-1}\) lower than that (at 870 cm\(^{-1}\)) of the zirconium analogue (1). Very recently, Mimoun et al. have reported that in the complex Ti(O\(_2\)C\(_2\)H\(_4\)NCOO)\(_2\)\(\text{HMPT}^+\), the \(\nu(M-O)\) appears at 895 cm\(^{-1}\). Again, in the cases of peroxy complexes of the elements of Group 6A, there is a decrease of \(v_1\) upon passing from molybdenum complex (3) (at 880 cm\(^{-1}\)) to the corresponding tungsten complex (4) (at 845 cm\(^{-1}\)) which is further decreased in the uranium peroxy complex (5) (802 cm\(^{-1}\)). The present data, thus clearly reveal that for M(O\(_2\)) grouping, the \(v_1(M-O)\) modes decrease with the increase in the atomic number of metals in a particular group. In the present examples, \(v_3\) and \(v_2\) modes appear at 662-685 and 600-612 cm\(^{-1}\), respectively. Complexes (6) and (8) show a decrease in \(v(P-O)\) by 142 and 117 cm\(^{-1}\) respectively compared to the free ligand value (1192 cm\(^{-1}\)), suggesting coordination by the oxygen of OPPh\(_3\). Complexes (7) and (9) show a decrease in \(v(As-O)\) of 35 and 32 cm\(^{-1}\), respectively from the free ligand value (880 cm\(^{-1}\)), indicating coordination through the oxygen of OAsPh\(_3\). Further, in the far infrared region, the compounds (6-9) exhibit single bands in the region 400-410 cm\(^{-1}\) assignable to \(\nu(M-O')(O'=oxygen in OPPh\(_3\) or OAsPh\(_3\)). For 6-9, the frequency of the \(v_1\) modes appear at lower wavenumber in the arsenic compounds (7, 840; 9, 810 cm\(^{-1}\)) as compared to that in the phosphorus analogue (6, 858; 8, 832 cm\(^{-1}\)). It is argued that \(v(O-O)\) in peroxy complexes is decreased by replacing a given ligand by one which is a stronger donor. The derived charge separations in the E-O (E=P or As) bonds show that the oxygen in the arsine oxide is more negative, and values of \(2.45 \times 10^{-10}\) and \(1.78 \times 10^{-10}\) e.s.u. were obtained for arsine oxide and phosphine oxides, respectively, using 0.74, 1.10 and 1.21 Å as the covalent radii for oxygen, phosphorus and arsenic, respectively. This points to a greater polarity in the case of arsine oxides and hence \(\equiv As-O\) is a stronger donor than \(\equiv P-O\). This argument seems to account for the lower \(v_1\) values for 7 and 9 compared to those for 6 and 8 respectively.

**Reactivity**

The present peroxy complexes were not found to be explosive. Treatment with aqueous iodide gave a discernible liberation of iodine within 1-2 min. Based on this observation the possible reactivity of the present peroxy complexes toward olefinic compounds could be explored, compound (3) was allowed to react stoichiometrically with allyl alcohol (reaction-A) which failed to produce any reaction. Negative results were also obtained by Mimoun et al. for organoperoxo complexes of Ti(IV). However, reaction-B produced triphenylphosphine oxide as revealed by its m.p. and IR data. Reaction-C produced triphenylarsine oxide, characterized by its m.p. and the IR spectrum which exhibited \(v(As-O)\) at 880 cm\(^{-1}\) (ref. 17).

**References**


\(^{1}\)HMPT = Hexamethylphosphoric triamide.


