ORGANODIOXYGEN COMPLEXES OF SOME GROUP 4B METAL IONS

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Abstract

Organodioxygen complexes of some group 4B metal ions, viz., zirconium(IV), tin(IV) and lead(II) containing monodentate, bidentate and tridentate ligands were synthesized and characterized. The complexes have the compositions of \([\text{Zr(O)(O}_2\text{)C}_2\text{H}_2\text{N.H}_2\text{O}]\), \([\text{Zr(O(O}_2\text{))}_2\text{.2OPPh}_3]\), \([\text{Sn(O}_2\text{(C}_3\text{H}_6\text{NO})_2}\text{]}\), \([\text{Sn(O}_2\text{(C}_9\text{H}_6\text{NO})_2}\text{.2N\text{H}_2\text{H}_2}]\), \([\text{Pb(O}_2\text{(C}_5\text{H}_5\text{N})_2\text{NO}_3}\text{]}\), \([\text{Pb(O}_2\text{)(C}_8\text{H}_6\text{NOH})]\), \([\text{Pb(O}_2\text{(det)NO}_3]\text{]}\) and \([\text{Pb(O}_2\text{(C}_5\text{H}_4\text{NCOOH})\text{NO}_3\text{.H}_2\text{O}}]\). Because of apparent linearity of M- O\(_2\) grouping, the \(\nu_1(O-O)\) stretching modes were only Raman active, giving bands at 810- 841 cm\(^{-1}\) for the peroxo complexes (1, 3, 4 and 6), while the bands in the superoxo complexes (2, 5, 7 and 8) appeared at 1020- 1100 cm\(^{-1}\). The peroxo complex of Zr(IV) containing monodentate ligands were found to oxidize trans-stilbene to trans-stilbene oxide under stoichiometric conditions. The organoperoxo complexes of tin and lead were insensitive to oxidative processes.

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INTRODUCTION

Studies on dioxygen complexes are of importance not only because they aid in understanding the characteristics of model systems of natural oxygen carriers but also because sometimes these compounds become very efficient sources of active oxygen for stoichiometric and catalytic oxidation [1-18]. Peroxo complexes containing monodentate ligands have been found to exhibit oxidation reactions. But those of non-transition metals were inert towards oxidative processes. Recently, we have reported the syntheses and properties of organoperoxo complexes of tin(IV) [18]. There have been no studies whatsoever on peroxo complexes containing Pb(II), in particular. We report herein the syntheses and reactivity of some peroxo complexes containing zirconium, tin and lead.

EXPERIMENTAL

IR spectra were recorded in KBR with a FT-IR Perkin Elmer 1725X and 1650X instrument. Elemental analyses were carried out by the University of Trieste, Italy. Conductivities of $10^3$ M solutions in dimethylsulfoxide were measured at 28° C by using a 4310 Jenway Digital Conductivity Meter and a dip-cell with plicated electrodes. Laser Raman spectra were recorded in Professor G. Mariotto’s laboratory, Department of Physics, University of Trento, Italy.

Preparation of complexes

Preparation of complex 1, $[\text{Zr(O)(O}_2\text{)}_2\text{C}_4\text{H}_6\text{N}_2\text{H}_2\text{O}]$

$\text{ZrO(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$ (1.015 g, 0.00439 mole) was dissolved in cold 30% H$_2$O$_2$ (20 ml). A solution of pyridine (0.71 ml, 0.00878 mole) in 15 ml of ethanol was then prepared. Both the solutions were mixed together. The resulting mixture was heated to reduce its volume by 50 % and kept in a freezer overnight. The light yellow precipitate was filtered off, washed with ethanol and dried \textit{in vacuo} over silica gel.

Preparation of complex 2, $[\text{Zr(O)(O}_2\text{)}_2\cdot2\text{OPPh}_3]$  

$\text{ZrO(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$ (1.010 g, 0.00437 mole) was dissolved in cold 30% H$_2$O$_2$ (20 ml). A solution of triphenylphosphine oxide (2.435 g, 0.00874 mole) in 20 ml of ethanol was then prepared. Both solutions were mixed together. The white precipitate obtained was separated, washed with ethanol and finally dried \textit{in vacuo} over silica gel.
Preparation of complex 3, \([\text{Sn(O}_2\text{)}(\text{C}_9\text{H}_6\text{NO})_2]\)

\(\text{SnCl}_4.5\text{H}_2\text{O} \ (1.025 \text{ g, 0.00292 mole}) \) was dissolved in cold 30\% \(\text{H}_2\text{O}_2 \ (18 \text{ ml})\). A solution of 8-quinoline (0.425 g, 0.00292 mole) in 15 ml of ethanol was then prepared. Both solutions were mixed together. The yellow precipitate that appeared was filtered and washed with ethanol. Finally, it was dried \textit{in vacuo} over silica gel.

Preparation of complex 4, \([\text{Sn(O}_2\text{)}_2(\text{CH}_2\text{)}_2(\text{NH}_3)_2]\)

\(\text{SnCl}_4.5\text{H}_2\text{O} \ (1.100 \text{ g, 0.00314 mole}) \) was dissolved in cold 30\% \(\text{H}_2\text{O}_2 \ (17 \text{ ml})\), which was added to a solution of ethylenediamine (0.2 ml, 0.00314 mole) in ethanol (15 ml). The volume of the mixture was then reduced to 50 \% by heating and kept in a freezer overnight. The product was isolated, washed with ethanol and dried \textit{in vacuo} over silica gel.

Preparation of complex 5, \([\text{Pb(O}_2\text{)}(\text{C}_5\text{H}_5\text{N})_2\text{NO}_3]\)

\(\text{Pb(NO}_3)_2 \ (1.07 \text{ g, 0.00323 mole}) \) was dissolved in cold 30\% \(\text{H}_2\text{O}_2 \ (15 \text{ ml})\) to which a solution of pyridine (0.50 ml, 0.00646 mole) in ethanol (20 ml). The mixture was heated to reduce its volume by 50 \% and kept in a freezer overnight. The product was filtered off, washed with ethanol and dried \textit{in vacuo} over silica gel.

Preparation of complex 6, \([\text{Pb(O}_2\text{)}(\text{C}_8\text{H}_6\text{NO})]\)

\(\text{Pb(NO}_3)_2 \ (1.06 \text{ g, 0.00320 mole}) \) was dissolved in cold 30\% \(\text{H}_2\text{O}_2 \ (18 \text{ ml})\) to which a solution of 8-quinoline (0.465 g, 0.00320 mole) in ethanol (15 ml) was added. The precipitate that appeared was filtered and washed with ethanol. Finally, it was dried \textit{in vacuo} over silica gel.

Preparation of complex 7, \([\text{Pb(O}_2\text{)}(\text{det})\text{NO}_3]\)

\(\text{Pb(NO}_3)_2 \ (1.02 \text{ g, 0.00308 mole}) \) was dissolved in cold 30 \% \(\text{H}_2\text{O}_2 \ (18 \text{ ml})\), which was added to a solution of diethylenetriamine (0.3 ml, 0.00308 mole) in ethanol (15 ml). The precipitate was separated, washed with ethanol and dried \textit{in vacuo} over silica gel.

Preparation of complex 8, \([\text{Pb(O}_2\text{)}(\text{C}_5\text{H}_4\text{NCOOH})\text{NO}_3\cdot\text{H}_2\text{O}]\)

\(\text{Pb(NO}_3)_2 \ (1.04 \text{ g, 0.00314 mole}) \) was dissolved in cold 30 \% \(\text{H}_2\text{O}_2 \ (20 \text{ ml})\) to which a solution of picolinic acid (0.387 g, 0.00314 mole) in ethanol (20 ml) was added. The volume of the mixture was reduced to \textit{ca.} 50 \% by heating and was subsequently cooled in a freezer overnight. The product was isolated, washed and dried as above.

Reaction of complex 6 with \text{PPh}_3
A solution of PPh₃ (0.141 g, 0.00054 mole) in 25 ml of tetrahydrofuran (THF) was added to a suspension of complex 6 (0.2 g, 0.00054 mole) in 25 ml of THF. The mixture was heated under reflux for 72 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was cooled and filtered, and the filtrate was evaporated to dryness using a rotary evaporator. The residue was dried in vacuo over silica gel.

**Reaction of complex 1, [Zr(O)(O₂)₂C₅H₅N.H₂O] with trans-stilbene**

A solution of trans-stilbene (0.057 g, 0.00032 mole) in 25 ml of THF was added to a suspension of complex 1 (0.1 g, 0.00032 mole) in 25 ml of THF. The mixture was heated under reflux for 72 hours. The progress of the reaction was monitored by TLC. After the reaction was complete, the mixture was cooled and filtered, and the filtrate was evaporated to dryness using a rotary evaporator. The residue was dried in vacuo over silica gel.

**Reaction of complex 3, [Sn(O₂)(C₉H₆NO)₂] with trans-stilbene**

A solution of trans-stilbene (0.057 g, 0.00032 mole) in 25 ml of THF was added to a suspension of complex 3 (0.55 g, 0.00125 mole) in 25 ml of THF. The mixture was heated under reflux for 72 hours. The progress of the reaction was monitored using TLC. After the reaction was complete, the mixture was cooled and filtered, and the filtrate was evaporated to dryness using a rotary evaporator. The residue was dried in vacuo over silica gel. Evaporation of the extract from 1 yielded 0.032 g of trans-stilbene oxide [m. p. 110°C (lit. 113°C)].

**RESULTS AND DISCUSSION**

The molar conductance data indicated that all of the complexes were undissociated. The analytical and conductance data are presented in Table 1. The IR spectral data are presented in Table 2. Complexes 1 and 8 showed ν(O-H) modes at 3430 cm⁻¹ and 3479 cm⁻¹, respectively, arising from the coordinated water molecules. 4 (3250 cm⁻¹ and 3122 cm⁻¹) showed the ν(NH₂) bands significantly lower than the free ligand values, ethylenediamine (3260 cm⁻¹ and 3180 cm⁻¹), indicating coordination by the amino nitrogen. 7 displayed ν(NH₂) bands in the range of 3100-3450 cm⁻¹. All the complexes except 2, 4 and 7 exhibited ν(C=N) bands; 1 (1542 cm⁻¹), 3 (1578 cm⁻¹), 5 (1600 cm⁻¹), 6 (1568 cm⁻¹) and 8 (1587 cm⁻¹), which appeared at lower frequencies relative to the free ligand value (1610 cm⁻¹), indicating that the ring nitrogen was coordinated to the metal atom [12]. This is further supported by the appearance of ν(M-N) bands in the range, 402-460 cm⁻¹, in the far IR spectra of the complexes. In addition, complex 2 showed a decrease in ν(P=O) compared to the free ligand values (1188 cm⁻¹). The metal peroxy grouping gives rise to three IR and Raman-active vibrational modes. These are predominantly O-O stretching (ν₁), the
symmetric M-O stretch ($\nu_2$) and the antisymmetric M-O stretch ($\nu_3$). The $\nu_1$(O-O), $\nu_2$(M<O$_2$) and $\nu_3$(M<O$_2$) modes of 1, 3, 4 and 6 appeared at 818-841, 500-565 and 600-672 cm$^{-1}$, respectively. Dengel and Griffith [2] have established that the $\nu_1$(O-O) modes in compounds of niobium and tantalum appear at 800-900 cm$^{-1}$, and bands at 500-700 cm$^{-1}$ are likely to arise from the $\nu_2$ and $\nu_3$ modes. Complexes 3 and 4 showed $\nu_1$(O-O) at 828 and 820 cm$^{-1}$ while 6 showed $\nu_1$(O-O) at 818 cm$^{-1}$, respectively. These indicated that the $\nu_1$(O-O) stretching modes decreased with the increase in atomic number of metals in a particular group. For the metal–superoxo grouping, the $\nu_1$(O-O) stretching modes appeared at 1020-1145 cm$^{-1}$ in the Raman spectra of 2, 5, 7 and 8. None of these bands were IR active, because of apparent linearity of the metal-O$_2$ grouping; however, the bands were all Raman active.

Reactivity

Complex 6 was allowed to react with triphenylphosphine. But it failed to produce any reaction even when the process was continued for 72 hours as monitored by TLC. Complexes 1 and 3 were allowed to react with trans-stilbene. 3 failed to produce any reaction even when the process was continued for 72 hours. 1 produced trans-stilbene oxide. The infrared spectrum of the product showed band a diagnostic band at 1030 cm$^{-1}$, assigned to the C-O-C stretching mode. The organoperoxo complexes of tin were stable thermodynamically as well as kinetically. The kinetic stability is attributed to the presence of extensive p$\pi$-d$\pi$ bonding giving some double-bond character to the metal ligand bonding, thus making the complexes coordinatively saturated. This hinders nucleophilic substrates from becoming coordinated to tin before formation of peroxy metallocycles to facilitate the oxygen transfer. We have found a similar behavior with organoperoxo complexes of lead. The inertness of organoperoxo complexes of non-transition metals toward oxidation reactions is attributed to their ineffectiveness to expand the coordination shell as would be necessary prior to oxygen transfer to both organic and inorganic substrates.

ACKNOWLEDGEMENTS

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REFERENCES


Table 1: Analytical data and other physical properties of the complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Complex</th>
<th>% C (found)</th>
<th>% C (calc.)</th>
<th>% H (found)</th>
<th>% H (calc.)</th>
<th>% N (found)</th>
<th>% N (calc.)</th>
<th>Molar conductance [Ω cm² mole⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Zr(O)(O₂)₂C₅H₅N.H₂O] (1)</td>
<td>38.12</td>
<td>38.07</td>
<td>2.75</td>
<td>3.81</td>
<td>8.97</td>
<td>8.88</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>[Zr(O)(O₂)₂.2OPPh₃] (2)</td>
<td>59.23</td>
<td>59.41</td>
<td>3.98</td>
<td>4.13</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>[Sn(O₂)(C₉H₆NO)₂] (3)</td>
<td>49.11</td>
<td>49.2</td>
<td>2.53</td>
<td>2.73</td>
<td>6.42</td>
<td>6.39</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>[Sn(O₂)₂.(CH₂)₂(NH₂)₂] (4)</td>
<td>9.56</td>
<td>9.88</td>
<td>3.12</td>
<td>3.29</td>
<td>11.46</td>
<td>11.52</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>[Pb(O₂)₂(C₅H₅N)₂NO₃] (5)</td>
<td>25.92</td>
<td>26.14</td>
<td>2.1</td>
<td>2.18</td>
<td>8.97</td>
<td>9.15</td>
<td>3.36</td>
</tr>
<tr>
<td>6</td>
<td>[Pb(O₂)(C₄H₆NOH)] (6)</td>
<td>25.76</td>
<td>25.81</td>
<td>1.87</td>
<td>1.88</td>
<td>3.38</td>
<td>3.76</td>
<td>5.0</td>
</tr>
<tr>
<td>7</td>
<td>[Pb(O₂)₂(det)NO₃] (7)</td>
<td>11.68</td>
<td>11.88</td>
<td>3.21</td>
<td>3.22</td>
<td>13.64</td>
<td>13.86</td>
<td>3.7</td>
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<td>8</td>
<td>[Pb(O₂)₂(C₅H₄NCOOH)NO₃.H₂O] (8)</td>
<td>15.67</td>
<td>16.29</td>
<td>1.47</td>
<td>1.58</td>
<td>6.38</td>
<td>6.33</td>
<td>1.57</td>
</tr>
</tbody>
</table>

M stands for Zr (1 and 2), Sn (3 and 4) and Pb (5-8).

Table 2. Infrared spectral data for complexes 1-8 (band maxima, cm⁻¹)

<table>
<thead>
<tr>
<th>No.</th>
<th>Complex</th>
<th>ν(OH)</th>
<th>ν(NH₂)</th>
<th>ν(C̈N)</th>
<th>ν(P=O)</th>
<th>ν₁(O-O)</th>
<th>ν₂(M&lt;O)</th>
<th>ν₃(M&lt;O)</th>
<th>ν(M-N)/ν(M-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Zr(O)(O₂)₂C₅H₅N.H₂O]</td>
<td>3430 br</td>
<td>-</td>
<td>1542 w</td>
<td>-</td>
<td>841 m</td>
<td>672 m</td>
<td>500 w</td>
<td>402 m</td>
</tr>
<tr>
<td>2</td>
<td>[Zr(O)(O₂)₂.2OPPh₃]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1179 m</td>
<td>1030 s</td>
<td>-</td>
<td>-</td>
<td>420 s</td>
</tr>
<tr>
<td>3</td>
<td>[Sn(O₂)(C₉H₆NO)₂]</td>
<td>-</td>
<td>-</td>
<td>1578 s</td>
<td>-</td>
<td>828 m</td>
<td>600 sh</td>
<td>538 s</td>
<td>419 s</td>
</tr>
<tr>
<td>4</td>
<td>[Sn(O₂)₂.(CH₂)₂(NH₂)₂]</td>
<td>3250</td>
<td>-</td>
<td>3122 w</td>
<td>-</td>
<td>820 br</td>
<td>672 br</td>
<td>565 m</td>
<td>431 s</td>
</tr>
<tr>
<td>5</td>
<td>[Pb(O₂)₂(C₅H₅N)₂NO₃]</td>
<td>-</td>
<td>-</td>
<td>1600 s</td>
<td>-</td>
<td>1040 m</td>
<td>-</td>
<td>-</td>
<td>405 w</td>
</tr>
<tr>
<td>6</td>
<td>[Pb(O₂)(C₄H₆NOH)]</td>
<td>-</td>
<td>-</td>
<td>1568 w</td>
<td>-</td>
<td>818 w</td>
<td>600 m</td>
<td>560 w</td>
<td>405 w</td>
</tr>
<tr>
<td>7</td>
<td>[Pb(O₂)(det)NO₃]</td>
<td>-</td>
<td>-</td>
<td>3450</td>
<td>-</td>
<td>3100 br</td>
<td>-</td>
<td>-</td>
<td>460 w</td>
</tr>
<tr>
<td>8</td>
<td>[Pb(O₂)₂(C₅H₄NCOOH)NO₃.H₂O]</td>
<td>3479m</td>
<td>-</td>
<td>1587 s</td>
<td>-</td>
<td>1100 br</td>
<td>-</td>
<td>-</td>
<td>460 w</td>
</tr>
</tbody>
</table>

Relative band intensities are denoted by: s, strong; m, medium; w, weak and sh, shoulder.