Synthesis, characterization and reactivity of some oxoperoxomolybdenum(VI) and oxoperoxo tungsten(VI) complexes of hexamethylenetetramine

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The monooxodiperoxo complexes [MO(O₂)(HMT)] (where M = Mo(I) and W(2)), dioxomonoperoxo complexes [MO₂(O₂)(HMT)] (where M = Mo(Ia) and W(2a)) and dioxosulfato complexes [MO₂(SO₄)(HMT)] (where M = Mo(1b) and W(2b)] of molybdenum and tungsten from hexamethylenetetramine (HMT) have been synthesized and characterized by elemental analyses, magnetic moment data and infrared, Raman and electron spin resonance spectroscopic studies. It is shown that the amine, although a potentially tetradentate ligand coordinates as a bidentate ligand to the metal centres in these complexes retaining its chair conformation. The reactivity of the diperoxo complexes has also been investigated and reported.

Peroxo complexes of molybdenum(VI) have been known for a long time and their catalytic activity has been a topic of considerable interest. Studies of the reactivity of heteroligand molybdenum(VI) peroxy complexes in solutions have shown large differences in the lability of molybdenum(VI) peroxides containing different heteroligands.

Hexamethylenetetramine (HMT) is a potential tetradentate ligand and its complexes have received some attention. However, there is no report on the oxoperoxo complexes of this potentially tetradentate ligand. The present study on the preparation and characterization of oxoperoxomolybdenum and oxoperoxo tungsten complexes of HMT was undertaken to elucidate the nature of bonding of HMT and the peroxo and the stereochemistry of the resulting complexes. Further, in view of the catalytic potential of the peroxo complexes, the reactivity of the diperoxo complexes was also studied and the products were characterized.

Experimental

MoO₃, WO₃, hexamethylenetetramine (HMT), sodium sulphite and triphenyl phosphine were Merck reagents. SO₂ was prepared from reaction of H₂SO₄ on Na₂SO₃, Mo, W and SO₄ were determined by standard literature procedure. The peroxide content was determined iodometrically in the presence of boric acid using a standard solution of sodium thiosulphate. Carbon and hydrogen were determined microanalytically. Magnetic moment data were obtained on powders employing a Faraday balance. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer in the 4000-1800 cm⁻¹ region. Raman spectra of the complexes were recorded on a Raman spectrophotometer (Ramalog 1403) in KBr by employing rotating sample technique to avoid decomposition of the samples. The ESR spectra of the compounds in powdered form at RT and LNT were recorded at X-band frequency on Varian E-112 X/Q band spectrometer. DPPH was used as an internal field marker.

Preparation of the complexes

Preparation of [MO(O₂)(HMT)] (where M = Mo(I) and W(2))

A typical procedure for the preparation of the complexes is given below:

MoO₃ (1.0 g, 6.94 mmol) was suspended in 95% 40 mL ethanol and stirred for about 15 min. To this suspension was added H₂O₂ (10 mL, 30%) accompanied by stirring. This suspension was stirred for about 30-35 min at 60-65°C. Any undissolved material was rejected by filtration and the solution cooled to room temperature. Hexamethylenetetramine (1.0 g, 7.14 mmol) solution in ethanol (40 mL) was added to MoO₃ solution and it was further stirred for 2 h at 30-40°C temperature and then cooled to room temperature. The solution was left standing and after about 4 h, yellow precipitates obtained were filtered off, washed with ethanol and dried in vacuo. Yield : 1.58 g (70%).

The oxoperoxo tungsten complex (2) was also obtained essentially by the above procedure using WO₃ instead of MoO₃. Yield : 1.88 g (65%).

Preparation of [MO₂(O₂)(HMT)] (M = Mo(Ia) and W(2a))

A typical procedure for the preparation of these complexes is given below:

The complex (1) (1.0 g) was taken in a test tube and heated carefully in a hot air oven at 100°C for 2 h.
This yielded the complex \([\text{MoO}_2(\text{O}_2)(\text{HMT})]_2\) (1a). Yield: 0.949 g (100%).

The complexes (2a) was also obtained essentially by the same procedure using complex (2) instead of complex (1). Yield: 0.960 g (100%).

**Preparation of \([\text{MoO}_3(\text{SO}_4)(\text{HMT})]_2\) [where \(\text{M} = \text{Mo}\) (1b) and \(\text{W}(2\text{b})\)]**

A typical procedure for the preparation of the complexes is given below.

\(\text{MoO}_3\) (1.0 g, 6.94 mmol) was suspended in 40 mL ethanol (95%) and stirred for about 15 min. To this suspension was added \(\text{H}_2\text{O}_2\) (10 mL, 30%) accompanied by stirring. This suspension was stirred for about 30-45 min at 60-65°C. Any undissolved material was rejected by filtration and the solution cooled to room temperature. HMT (1.0 g, 7.14 mmol) in ethanol (40 mL) was added to \(\text{MoO}_3\) solution at room temperature accompanied by slow stirring for 10-15 min. The solution was further stirred for 2 h at ambient temperature. \(\text{SO}_2\) gas was passed through this solution for 30 min. A vigorous reaction occurred accompanied by warming of the solution. This solution was left standing. After about 2 h, an orange yellow precipitate was obtained which was filtered, washed with ethanol, and dried in vacuo. Yield: 1.69 g (65%).

The corresponding tungsten complex (2b) was also obtained essentially by the above procedure using \(\text{WO}_3\) instead of \(\text{MoO}_3\). Yield: 1.937 g (60%).

**Reaction of complexes \([\text{MO}_2(\text{O}_2)(\text{HMT})]_2\) [where \(\text{M} = \text{Mo}\) (1) and \(\text{W}(2)\)] with triphenyl phosphine**

The complex \([\text{MoO}_2(\text{O}_2)(\text{HMT})]_2\) (0.4 g, 1.27 mmol) (1) was suspended in degassed acetonitrile (30 mL). To this, triphenylphosphine (0.4 g, 1.53 mmol) in degassed acetonitrile (20 mL) was added under dinitrogen atmosphere. The reaction mixture was stirred for 1 h at room temperature. After 1 h, the solution was filtered. The filtrate obtained above was evaporated gently to remove the solvent. The yellowish white precipitate of \(\text{OPPh}_3\) so obtained was characterized by IR and its melting point. Yield: 0.10 g (23.6%).

A similar reaction was carried out with complex \([\text{WO}_2(\text{O}_2)(\text{HMT})]_2\) (2) as well. Yield: 0.106 g (25%).

**Reaction of complexes \([\text{MO}_2(\text{O}_2)(\text{HMT})]_2\) [where \(\text{M} = \text{Mo}\) (1) and \(\text{W}(2)\)] with \(\text{SO}_2\)**

The complex \([\text{MoO}_2(\text{O}_2)(\text{HMT})]_2\) (1.0 g, 3.16 mmol) was suspended in 100 mL ethanol which was previously degassed by bubbling \(\text{N}_2\) through it. \(\text{SO}_2\) gas was passed through this reaction mixture under dinitrogen atmosphere for about 30 min. A part of the complex passed into solution accompanied by warming the reaction mixture. Any undissolved material was removed by filtration. The filtrate so obtained was stored overnight which precipitated an orange yellow compound. It was filtered, washed with ethanol and dried in vacuo. Yield: 0.8 g (69.5%).

**Results and discussion**

The compounds \([\text{MO}_2(\text{O}_2)(\text{HMT})]_2\) [where \(\text{M} = \text{Mo}\) (1) and \(\text{W}(2)\)] are obtained when metal oxides dissolved in ethanol by the addition of \(\text{H}_2\text{O}_2\) are allowed to interact with HMT in ethanol. When these compounds are heated carefully at 100°C for 2 h, the di­oxoperoxo compounds \([\text{MoO}_2(\text{O}_2)(\text{HMT})]_2\) [where \(\text{M} = \text{Mo}\) (1a) and \(\text{W}(2a)\)] are obtained. It is to be emphasized that when the complexes (1) and (2) are heated for larger period or heated at temperatures above 120°C, they start losing second molecule of peroxide group also. Both the peroxide groups are lost at temperatures above 150°C. On the other hand, the sulphato complexes \([\text{MoO}_3(\text{SO}_4)(\text{HMT})]_2\) [where \(\text{M} = \text{Mo}\) (1b) and \(\text{W}(2b)\)] are obtained when \(\text{SO}_2\) gas is passed through ethanol solution of metal oxide in \(\text{H}_2\text{O}_2\) and HMT. The same complexes are also obtained as products when the complexes (1) and (2) are treated with \(\text{SO}_2\) in degassed ethanol under dinitrogen.

The peroxo complexes are yellow products while sulphato complexes are orange yellow (Table 1). They are all diamagnetic and ESR silent in conformity with the presence of molybdenum(VI) and tungsten(VI) in complexes of the type (1) and (2), respectively. The complexes (1) and (2) are less stable than the complexes (1a) and (2a), respectively. Their stability can be ascertained by chemical estimation of active oxygen contents and recording IR spectra periodically. The peroxide estimation was accompanied by redox titrations involving standard sodium thiosulphate solution. The results of replicate determinations of the peroxide as well as metal contents strongly indicated the ratio of \(\text{M}:\text{O}_2\) as 1:2 in the complexes (1) and (2) while 1:1 in the complexes (1a) and (2a). All the complexes are insoluble in water and common organic solvents. They have poor solubility in the highly coordinating solvents DMF and DMSO. Insolubility of these compounds in suitable organic solvents precluded molecular weight and conductivity measurements.
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Table 1—Analytical data of the complexes

<table>
<thead>
<tr>
<th>Complex (Colour)</th>
<th>Found (Calcd.), %</th>
<th>M</th>
<th>O₂²⁻/SO₄²⁻</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. [MoO(O₂)₂(HMT)] (Yellow)</td>
<td>30.81 (30.38)</td>
<td>19.81</td>
<td>22.29 (20.25)</td>
<td>3.82 (22.75)</td>
<td>3.82</td>
</tr>
<tr>
<td>1a. [MoO₂(O₂)(HMT)] (Yellow)</td>
<td>32.48 (32.00)</td>
<td>10.42</td>
<td>24.42 (10.67)</td>
<td>3.95 (24.00)</td>
<td>4.00</td>
</tr>
<tr>
<td>1b. [MoO₂(SO₄)(HMT)] (Orange yellow)</td>
<td>26.81 (26.37)</td>
<td>26.00</td>
<td>19.42 (19.78)</td>
<td>3.25 (17.83)</td>
<td>3.20</td>
</tr>
<tr>
<td>2. [WO(O₂)₂(HMT)] (Dull yellow)</td>
<td>48.54 (45.85)</td>
<td>16.32</td>
<td>17.43 (15.85)</td>
<td>2.95 (17.83)</td>
<td>2.97</td>
</tr>
<tr>
<td>2a. [WO₂(O₂)(HMT)] (Dull yellow)</td>
<td>47.82 (47.40)</td>
<td>8.00</td>
<td>19.00 (8.25)</td>
<td>3.05 (18.56)</td>
<td>3.09</td>
</tr>
<tr>
<td>2b. [WO₂(SO₄)(HMT)] (Orange yellow)</td>
<td>41.12 (40.69)</td>
<td>20.81</td>
<td>16.39 (21.25)</td>
<td>2.62 (15.94)</td>
<td>2.66</td>
</tr>
</tbody>
</table>

The IR and laser Raman (IR) spectra of the compounds involve bands characteristic of the presence of M=O, cis-MO₂²⁺ groups, coordinated peroxide and sulphate and HMT ligands. A single strong band at ~970 cm⁻¹ in the IR spectra of the complexes (1) and (2) is attributed to arise due to stretching vibration of M=O (M = Mo and W) group. On the other hand, the appearance of two strong bands in the region 945-900 cm⁻¹ in the complexes (1a), (1b), (2a) and (2b) is attributed to arise due to symmetric and asymmetric stretching vibrations of cis-MO₂²⁺ group. A strong band at ~860 cm⁻¹ in the IR spectra of the complexes [MO(O₂)₂(HMT)] [M = Mo(1) and W(2a)] has been assigned to the ν(O-O) mode of η¹-coordinated peroxides. The complementary ν₁(M-O₂) and ν₂(M-O₂) appeared at ca. 610(s) and 570(s) cm⁻¹. The S-O bands arising from the presence of SO₄²⁻ ligand in the complexes [MO₂(SO₄)(HMT)] (where M = Mo(1b) and W(3b)) were observed at ca. 1190, ca. 1115 and ca. 1080 cm⁻¹ assigned to ν₃, at ca. 1000 cm⁻¹ assigned to ν₁, at ca. 660, ca. 600 and ca. 585 cm⁻¹ attributed to n₂ and at ca. 450 cm⁻¹ due to n₁ mode. The SO vibrational pattern, especially the splitting of the ν₂ and ν₃ modes into three bands in the IR spectra, clearly suggests coordination of SO₄²⁻ group to the metal ion as a bidentate chelating ligand.

IR spectrum of the uncoordinated HMT shows two strong absorption bands at 1016 and 1236 cm⁻¹ which are assigned to the fundamentals of the C-N stretching vibrations. Both these bands are split up into doublets and the intensities of some more bands of HMT undergo slight changes in the spectra of the complexes indicating the presence of coordinated HMT. The increase of peak intensity of C = N stretching bands are attributed to the coordination of HMT as a bidentate bridging ligand thus retaining its chair conformation in all the complexes. Although a potentially tetradentate ligand, stereochemically HMT seems to act only as a bidentate bridging ligand thus retaining its chair configuration in these complexes. If chelated, the coordinated HMT must have the cis or boat configuration and IR spectra of such complexes would be anticipated to exhibit multiplicity of bands owing to the increased number of IR active fundamentals. On comparing the IR spectra of the peroxo complexes with those of the sulphato complexes, no additional band in the region 1300-1100 cm⁻¹ could be located assignable to νN=O ruling out the possibility of oxidation of amine nitrogen atom. Considering that peroxo and sulphato groups act as bidentate chelating ligand and HMT acts as a bridging bidentate ligand retaining its chair conformation in all the complexes, they are assigned to have polymeric chain structure. The complexes (1) and (2) are suggested to have pentagonal bipyramidal stereochemistry while the complexes (1a), (1b), (2a) and (2b) are suggested to have distorted octahedral stereochemistry.
Reactivity Study of the Complexes (1) and (2) with triphenyl phosphate and sulphur dioxide

Under dinitrogen, triphenylphosphine dissolved in acetonitrile followed by addition to complexes (1) and (2) underwent facile oxidation at ambient temperature and yellowish white crystalline product was isolated. It took 1 h for the completion of the reaction. The product is highly soluble in organic solvents and free from molybdenum. The distinctive feature of the IR spectrum of the product compared with that of triphenylphosphine is a strong peak at 1192 cm⁻¹ supporting that triphenylphosphine has been oxidized to OPPh₃. The compound melts at 157°C which agrees with the reported value for OPPh₃.

When SO₂ gas was passed through a suspension of the complexes (1) and (2), in degassed ethanol (95%) under dinitrogen at room temperature part of the complexes passed into solution. On storing the filtrate overnight, orange yellow compound precipitated which was insoluble in water, methanol, acetone and other common organic solvents including coordinating solvents like DMF and DMSO. The results of chemical analyses confirmed the presence of sulphate with the stoichiometry Mo₂SO₄:HMT being 1:1:1. Accordingly, these complexes were formulated as [Mo₂(SO₄)(HMT)] and [WO₂(SO₄)(HMT)], respectively. The IR spectra of the newly formed compounds were found to be similar, on comparison to those of the complexes (1b) and (2b), respectively, which were obtained from the reaction of SO₂ gas with a reaction mixture obtained from direct reaction of Mo₃ (M = Mo or W), H₂O₂ and HMT in ethanol. This suggests that the newly formed compounds obtained from reaction of SO₂ with compounds [Mo₂(SO₄)(HMT)](1) and [WO₂(SO₄)(HMT)](2) are same as the complexes (1b) and (2b), respectively. Hence, further discussion on these newly formed compounds in redundant.

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References