Oxotetrabromomolybdenum(V) Complex Compounds with s-Triazine Derivatives

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Our current interest is focused on the preparation of novel molybdenum(V) complexes with s-triazine derivatives, 2,4,6-triamine-[1,3,5]-triazine, L1 and 2,4,6-tri(2-pyridyl)-[1,3,5]-triazine, L2. On the basis of elemental chemical analysis, molar electrical conductivities, UV-Vis, IR and RPE spectra we established the formulae (LH2)2[MoOBr4(OH2)]Br3 for monomers 1, 2 and [Mo2O4Br2(OH2)2L2] for dimmers 3 and 4. The structure of (L1H2)2[MoOBr4(H2O)]Br3 was established by X-ray diffraction spectroscopy.

Keywords: molybdenum(V), oxomolybdenum complex compounds, s-triazine derivatives

Molybdenum is a relevant element for the synthesis of coordination compounds, many of these having biological or catalytic activity. The chemical properties of molybdenum make it suitable for preparation of these types of compounds but the most important features are related to the stability and readily attainable oxidation states. The presence of oxo groups lead to the stabilization of high oxidation states (V) and (VI) [1]. Oxomolybdenum complexes are the dominant type especially for the oxidation state (V) and an enormous number of mononuclear and binuclear species are known [2-12]. In our recent work [13] we reported the synthesis and characterization of three novel Mo(V) complex compounds, LH[MoOBr4(H2O)], where L = pyridazone derivatives (6-p-tolyl-2H-pyridazin-3-one, 6-(4-chloro-phenyl)-2H-pyridazin-3-one and 6-(4-bromo-phenyl)-2H-pyridazin-3-one).

The aim of this work is to present some other new molybdenum(V) complexes containing s-triazine derivatives, 2,4,6-triamine-[1,3,5]-triazine, L1 and 2,4,6-tri(2-pyridyl)-[1,3,5]-triazine, L2 (fig. 1).

The new compounds 1-4 have the next general formulae for monomeric 1,2 and dimeric respectively 3, 4 species:

\[ (L'H_2)_2[MoOBr_4(OH_2)]Br_3 \] (1)
\[ (L'H_2)_2[MoOBr_4(OH_2)]Br_3 \] (2)
\[ [Mo_2O_4Br_2(OH_2)2L_2] \] (3)
\[ [Mo_2O_4Br_2(OH_2)2L_2] \] (4)

The complex compounds 1-4 were characterized by elemental analysis, molar electrical conductivities UV-Vis, IR and RPE spectra. The structure of (L1H2)[MoOBr4(H2O)], where L1 = 2,4,6-triamine-[1,3,5]-triazine (melamine) was established by X-ray diffraction.

Experimental part

The organic reagents (2,4,6-triamine-[1,3,5]-triazine, L1 and 2,4,6-tri(2-pyridyl)-triazine, L2) were analytical grade and used as received. MoO3 was obtained by heating of (NH4)6Mo7O24·4H2O at 550°C.

Preparation of (LH2)2[MoOBr4(OH2)]Br3, (L = s-triazine derivatives: 2,4,6-triamine-[1,3,5]-triazine, L1 and 2,4,6-tri(2-pyridyl)-triazine, L2).

The compounds (LH2)2[MoOBr4(OH2)]Br3 (1, 2), where L = 2,4,6-triamine-[1,3,5]-triazine, L1 and 2,4,6-tri(2-pyridyl)-triazine, L2, were obtained from hydrobromic solutions of MoO3 (2.7 mmol dissolved in 1.6 mL of 9M HBr) and L1 or L2 dissolved in HBr 9M under slow heating. By evaporation of these solutions, the dimeric compounds 3-4 have been obtained as brown powders:

\[ [Mo_2O_4Br_2(OH_2)2L_1] \] (3)
\[ [Mo_2O_4Br_2(OH_2)2L_2] \] (4)

The electronic spectra were recorded at the room temperature on a Jasco V560 using the diffuse reflectance technique.

The EPR spectra were registered on the polycrystalline powders of compounds, by using a JEOL JES-FA spectrophotometer of ICF Bucharest.

The vibration spectra were recorded with a Bruker Equinox55 spectrophotometer in the wavenumbers range of 400 - 4000 cm⁻¹.

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The molar electrical conductivities were determined (in dimethylformamide 10^{-3} M solutions of compounds 1-4) at 25°C with OK 102/1 Radelkis Conductometer.

**X-ray structure determination**

Data collections were performed at 110 K with a Bruker Smart APEX CCD (Mo-K  text{"\textalpha} radiation, \(\lambda = 0.71073\) Å, graphite monochromator) area detector. The unit cell parameters were obtained by the least-squares refinement of up to 8096 reflections. The structures were solved by direct methods (SHELXS-97) [14] and refined by full matrix least-squares procedures based on \(F^2\) with all measured reflections (SHELXL-97) [15]. The SADABS [16] program was used for absorption correction of the structures. Non-hydrogen atoms were refined anisotropically, and H atoms were introduced in their idealized positions (\(d_{\text{C–H}} = 0.98\) Å, \(d_{\text{N–H}} = 0.95\) Å) and were refined using a riding model. Some H atoms were located in a difference Fourier map and refined freely along with an isotropic displacement parameter.

Crystallographic data (excluding structure factors) for the structures reported in this paper (table 1) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-275223 (LH_2)[MoOBr(OH_2)Br]. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21 EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk; web: www: http://www.ccdc.cam.ac.uk).

**Results and discussions**

According to the literature data, in acidic medium (HBr 9M), MoO_3 is reduced to monomeric Mo(V) species, [MoOBr_3]^{-}, [MoOBr_4]^{2-} and [MoOBr(OH_2)]^{-}. The equilibrium is modified in the presence of small amounts of water and at \(p\text{H} > 7\), the dominant species resulted being the dimers [MoO(OH)_2 Br_2]^{-}, [MoO_2 Br_4]^{4-}, [MoO_2 Br_4 (H_2O)]^{2-} or [MoO_2 Br_2 (H_2O)]^{3-}.

The monomeric species 1-2, (LH_2)[MoOBr(OH_2)Br] have been obtained as yellow-green (1) or green-brown (2) powders from acidic solutions of [MoOBr(OH_2)]^{-} (\(p\text{H} < 1\)) by adding s-triazine derivatives (2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine, L^2). The ligands act as diprotonated bases, as results from X-ray diffraction spectrum of (LH_2)[MoOBr(OH_2)Br where L^1 was 2,4,6-triamine-[1,3,5]-triazine.

The [MoOBr(OH)_2]^{2-}_{\text{L}} dimmers (3, 4), where L = 2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine, L^2 were obtained from the mixture of hydrobromic solutions (9M) of monomers (LH_2)[MoOBr(OH_2)Br and ammonia – water solution (2M) at \(p\text{H} = 8\). By evaporation of these mixed solutions, brown powders of the dimeric compounds 3-4 have been obtained:

\[
\begin{align*}
[\text{MoO}_2 \text{Br}_2 \text{(OH}_2)_2 \text{L}^2]^{-} & \quad 3 \\
[\text{MoO}_2 \text{Br}_4 \text{(OH}_2)_2 \text{L}^2]^{-} & \quad 4
\end{align*}
\]

The general proposed formulae of (LH_2)[MoOBr(OH_2)Br] dimmers (3, 4) were obtained by elemental chemical analysis, molar electrical conductivities, electronic, infrared and RPE spectra. For (LH_2)[MoOBr(OH_2)Br, 1 the structure was established based on the X-ray spectrum.

**Molar electrical conductivity**

The compounds 1 and 2 are electrolytes and the organic groups are located out of coordination sphere as diprotonated species and the protons are bonded at two cyclic nitrogen atoms, perhaps the atoms with the highest electron density as result from X-ray spectrum of (LH_2)[MoOBr(OH_2)]Br. 1 the compounds 3 and 4 are nonelectrolytes, and the organic ligands L^1 and L^2 act as monodentate ligands bonded to molybdenum atoms by nitrogen atoms (table 2).

<table>
<thead>
<tr>
<th>Compound/</th>
<th>(%\text{Mo}^{\text{calc}})</th>
<th>(%\text{N}^{\text{calc}})</th>
<th>(%\text{Br}^{\text{calc}})</th>
<th>Molar conductivity (\mu\text{S cm}^{-1}\text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (L^1H_2)[MoOBr(OH_2)]Br</td>
<td>10.74</td>
<td>17.76</td>
<td>59.17</td>
<td>&gt; 260</td>
</tr>
<tr>
<td>2 (L^2H_2)[MoOBr(OH_2)]Br</td>
<td>7.25</td>
<td>12.68</td>
<td>42.26</td>
<td>&gt; 260</td>
</tr>
<tr>
<td>3 [MoO_2 Br_3(OH_2)L^2]^{-}</td>
<td>27.26</td>
<td>24.57</td>
<td>22.70</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 2 ELEMENTAL CHEMICAL ANALYSES AND MOLAR ELECTRICAL CONDUCTIVITIES

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The nature of organic groups L1 and L2 is strongly influenced by the pH of synthesis medium: pH < 1 for the compounds 1, 2 and pH > 8 in the case of compounds 3 and 4.

The electronic spectra of all 1-4 compounds exhibit d-d transitions specific for Mo5+(d1);

\[ 2B_2 \rightarrow 2B_1 (\Delta d_{x^2-y^2} \approx 23000 \text{ cm}^{-1}) \]

\[ 2B_2 \rightarrow 2E_1 (\Delta d_{x^2-y^2} \approx 15000 \text{ cm}^{-1}) \]

The position and shape of the absorption bands (Table 3) are specific for Mo(V) coordination species (the absorption bands of BipyH2[MoOBr5] were included) and confirm the distorted octahedral geometry for all the 1–4 complex compounds.

The vibrational infrared spectra of the 1-4 complex compounds were used in order to supply additional data on their stereochemistry, particularly on the coordination manner of the s-triazine derivatives, L1 and L2 (Table 4).

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The EPR spectra of complex compounds 1 and 2 have relatively identical shapes and RPE parameters (Table 5) prove the distorted octahedral geometry, with g|| > g⊥. The absence of RPE signals for the compounds 3 and 4 suggests their dinuclear structure.

The complex compound \((L^1H_2)\_2[MoOBr_4(H_2O)]Br_3\) crystallizes in the centrosymmetric space group P2_1/c. The crystal structure consists in two diprotonated ligands, three

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\gamma)NH (\text{cm}^{-1})</th>
<th>MoO_2Mo (\text{cm}^{-1})</th>
<th>(\nu)Mo=O (\text{cm}^{-1})</th>
<th>(\delta)NH (\text{cm}^{-1})</th>
<th>(\delta)MoN (\text{cm}^{-1})</th>
<th>(\delta)C=N (\text{cm}^{-1})</th>
<th>(\nu)OH (\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>L^1</td>
<td>630</td>
<td>-</td>
<td>1200</td>
<td>1600</td>
<td>3230</td>
<td>1030</td>
<td>-</td>
</tr>
<tr>
<td>((L^1H_2)_2[MoOBr_4(\text{OH}_2)]_Br_3)</td>
<td>640</td>
<td>-</td>
<td>990</td>
<td>1180</td>
<td>1550</td>
<td>3200</td>
<td>1025</td>
</tr>
<tr>
<td>([\text{MoO}_2\text{Br}_5(\text{OH}_2)_2L^1_2])</td>
<td>635</td>
<td>625</td>
<td>760</td>
<td>985</td>
<td>1185</td>
<td>3185</td>
<td>1030</td>
</tr>
<tr>
<td>L^2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1610</td>
<td>33240</td>
<td>1030</td>
</tr>
<tr>
<td>((L^2H_2)_2[MoOBr_4(\text{OH}_2)]_Br_3)</td>
<td>-</td>
<td>-</td>
<td>980</td>
<td>-</td>
<td>1580</td>
<td>3220</td>
<td>1050</td>
</tr>
<tr>
<td>([\text{MoO}_2\text{Br}_5(\text{OH}_2)_2L^2_2])</td>
<td>-</td>
<td>620</td>
<td>760</td>
<td>9980</td>
<td>-</td>
<td>1580</td>
<td>3200</td>
</tr>
</tbody>
</table>

| | \(\nu\)Mo=O \(\text{cm}^{-1}\) | \(\delta\)NH \(\text{cm}^{-1}\) | \(\delta\)C=N \(\text{cm}^{-1}\)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-V</td>
<td>860</td>
<td>550</td>
</tr>
<tr>
<td>Mo-N</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>Mo-Br</td>
<td>230</td>
<td>230</td>
</tr>
</tbody>
</table>

The presence of Mo=O vibrations was assigned to stretching frequencies \(\nu\)Mo=O. For the 3 and 4 dimmers the shifting of the N-H or C=N specific bands \(\nu\)NH, \(\rho\)NH, \(\delta\)NH, \(\delta\)C=N cycle) is associated with the formation of coordinative bonds Mo-N, supported also by the presence of new band, \(\nu\)MoN in the 450 cm\(^{-1}\) range.

The presence of the strong absorption bands in 990-1010 cm\(^{-1}\) range was assigned to stretching frequencies \(\nu\)Mo=O specific for molybdenum-oxygen terminal group which exist in all the compounds 1-4.

The vibrational infrared spectra of the 1-4 complex compounds were used in order to supply additional data on their stereochemistry, particularly on the coordination manner of the s-triazine derivatives, L1 and L2 (Table 4).

The presence of coordination H2O is supported by some additional bands in 1600 cm\(^{-1}\) and 3000-3500 cm\(^{-1}\) ranges (\(\delta\)H\_O and \(\nu\)OH) but these are superposed with \(\delta\)NH, \(\nu\)NH specific vibrational bands for 1 and 3 [18].

The EPR spectra of complex compounds 1 and 2 have relatively identical shapes and RPE parameters (Table 5) prove the distorted octahedral geometry, with g|| > g⊥. The absence of RPE signals for the compounds 3 and 4 suggests their dinuclear structure.

The complex compound \((L^1H_2)\_2[MoOBr_4(H_2O)]\_Br_3\)

<table>
<thead>
<tr>
<th>Complex compound</th>
<th>(g_|)</th>
<th>(g_\perp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((L^1H_2)_2[MoOBr_4(H_2O)]_Br_3)</td>
<td>1.94</td>
<td>1.92</td>
</tr>
<tr>
<td>((L^2H_2)_2[MoOBr_4(H_2O)]_Br_3)</td>
<td>2.09</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Br anions and a [MoBr₄(OH₂)]⁻ unit (fig. 2). Weak H bonds form an infinite three-dimensional framework around the neighbouring molecules. Selected bonds and angles around Mo atom are presented in table 6.

Conclusions

Four new complex compounds of Mo(V) with s-triazine derivatives (2,4,6-triamine-[1,3,5]-triazine, L¹ and 2,4,6-tri(2-pyridyl)-triazine L²) as organic ligands have been obtained. The general proposed formula, (LH₂)₂[MoOBr₄(OH₂)]Br₃ for 1 and 2 monomers and [Mo₂O₄Br₂(OH₂)L₂] for 3 and 4 dimmers were supported by elemental chemical analysis, molar electrical conductivities, UV-Vis, IR and EPR spectra. The structure of (L₁H₂)₂[MoOBr₄(H₂O)]Br₃ was established by X-ray diffraction spectroscopy. In monomers 1 and 2 the organic groups are located out of coordination sphere as diprotonated species and the protons are bonded at two cyclic nitrogen atoms, as result from X-ray spectrum of (L₁H₂)₂[MoOBr₄(H₂O)]Br₃, 1.

The compounds 3 and 4 have dimeric nature and the organic groups L₁ and L₂ act as neutral monodentate ligands, bonded to molybdenum atoms by nitrogen atoms. The EPR spectra of complex compounds 1-4 confirm their monomeric (for 1, 2) and dimeric (for 3 and 4) nature. The spectral data (UV-Vis, IR and EPR) prove the distorted octahedral geometry for all compounds. The s-triazine derivatives, L¹ and L² act as protonated species in the compounds 1 and 2 and as neutral ligand for 3 and 4 and the nature of the organic groups L¹ and L² is strongly influenced by the pH of synthesis medium: pH < 1 for 1, 2 and pH > 8 in the case of 3 and 4.

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