Structural Characterization of α-Amino Acid Complexes of Molybdates: a Spectroscopic and DFT Study

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SUPPORTING INFORMATION
Synthesis of Mo$_2$O$_4$(OH)$_4$(aaH) complexes: the influence of experimental parameters. Compounds 1-6 were obtained under different experimental conditions as follows. The formation of identical products was checked by comparison of spectroscopic (IR, $^{13}$C CP-MAS NMR) and elemental analysis data (C, H, N, Mo).

A) Formation of Mo$_2$O$_4$(OH)$_4$(GlyH) 1.

at pH = 0. Compound Na$_2$MoO$_4$·2H$_2$O (974 mg, 4.02 mmol) and glycine (153 mg, 2.03 mmol) were dissolved in 1 M HNO$_3$ (35 mL). 65% HNO$_3$ was added up to pH ≈ 0. The resulting pale yellow solution ($c_{Mo} = 0.11$ M) was stirred at room temperature for 19 hours. Thus 1 was isolated (589 mg, 75%).

at pH = 1. Compound (NH$_4$)$_2$MoO$_4$ (100 mg, 0.51 mmol) was dissolved in water (10 mL) and glycine (21 mg, 0.28 mmol) was dissolved in 1 M HCl (3 mL). The two solutions were mixed together and 6 M HCl was added dropwise until pH = 1. The resulting colourless solution ($c_{Mo} = 36$ mM) was stirred at reflux temperature. After ca. 20 minutes 1 precipitated as a colourless solid (102 mg, 91%).

B) Formation of Mo$_2$O$_4$(OH)$_4$(aaH) at different Mo/aaH molar ratios. The following reactions were carried out by a procedure analogous to that described for the Mo/aaH 2:1 synthesis (Experimental Section), unless otherwise specified. Amino acid nitrates, [aaH]$\cdot$NO$_3^-$, were obtained from the filtered solution after complete solvent removal in vacuo.

daH = GlyH, Mo/aaH = 1:2, pH = 1.8. From Na$_2$MoO$_4$·2H$_2$O (271 mg, 1.12 mmol), glycine (169 mg, 2.25 mmol), water (30 mL), 1 M HNO$_3$ (2.8 mL). Mo$_2$O$_4$(OH)$_4$(GlyH), 1 (174 mg, 78%), [GlyH]$\cdot$NO$_3^-$ (218 mg).

daH = GlyH, Mo/aaH = 1:3.7, pH = 1.8. From Na$_2$MoO$_4$·2H$_2$O (279 mg, 1.15 mmol), glycine (1.19 g, 15.8 mmol), water (92 mL), 1 M HNO$_3$ (11.2 mL). Mo$_2$O$_4$(OH)$_4$(GlyH), 1 (161 mg, 70%), [GlyH]$\cdot$NO$_3^-$ (161 mg).

daH = PheH, Mo/aaH = 1:2, pH = 2.0. From Na$_2$MoO$_4$·2H$_2$O (415 mg, 1.71 mmol), L-phenylalanine (566 mg, 3.42 mmol), water (20 mL) and 1 M HNO$_3$ (5.2 mL). Mo$_2$O$_4$(OH)$_4$(PheH), 2 (349 mg, 84%). [PheH]$\cdot$NO$_3^-$ (162 mg). 2 was also obtained by using (NH$_4$)$_2$MoO$_4$ (ca. 1.5 mmol) in the place of Na$_2$MoO$_4$·2H$_2$O, both at room temperature (97%, reaction time 2 hours) and at 70°C (99%, reaction time 1.5 hours).

daH = LeuH, Mo/aaH = 1:1, pH = 1.8. From Na$_2$MoO$_4$·2H$_2$O (358 mg, 1.48 mmol), L-leucine (195 mg, 1.48 mmol), water (20 mL) and 1 M HNO$_3$ (3.5 mL). The mixture was stirred at 50°C for 3.5 hours and then at room temperature for 3 days: no solid formed under these conditions. Then the mixture was concentrated to 14 mL in vacuo, thus allowing the precipitation of 3 (249 mg, 74%).

daH = LeuH, Mo/aaH = 1:2, pH = 1.8. From Na$_2$MoO$_4$·2H$_2$O (358 mg, 1.48 mmol), L-leucine (388 mg, 2.96 mmol), water (20 mL) and 1 M HNO$_3$ (5 mL). The mixture was heated at 50°C and complex 3 formed after 3.5 hours (312 mg, 93%). [LeuH]$\cdot$NO$_3^-$ (312 mg).

daH = MetH, Mo/aaH = 1:2, pH = 2.0. From (NH$_4$)$_2$MoO$_4$ (301 mg, 1.53 mmol), L-methionine (458 mg, 3.07 mmol), water (40 mL) and 3 M HNO$_3$ (few drops). Mo$_2$O$_4$(OH)$_4$(MetH), 4: yield 269 mg, 74%. Some unreacted excess methionine was isolated from the liquors.

daH = ProH, Mo/aaH = 1:2. From (NH$_4$)$_2$MoO$_4$ (307 mg, 1.57 mmol), L-proline (361 mg, 3.13 mmol), water (80 mL) and 3 M HNO$_3$ (few drops). Mo$_2$O$_4$(OH)$_4$(MetH), 5 (233 mg, 68%).

C) Influence of pH variations on the formation of 1 and 4. A suspension of 1 (434 mg, 1.09 mmol) in water (20 mL, pH ≈ 3) was treated with 0.194 M NaOH (8.10 mL, 1.57 mmol) up to complete dissolution of the solid (pH = 4.83). Further NaOH (11.1 mL, 2.15 mmol) was added up to pH = 5.31. Afterwards 1.08 M HNO$_3$ (2.05 mL, 2.22 mmol) was added dropwise, thus compound 1 was recovered (yield 411 mg, 95% with respect to the initial amount). A similar behaviour was observed with compound 4.
Table S1. Formation of 1 in variable experimental conditions with pH monitoring.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Mo/GlyH molar ratio</th>
<th>cMo / 10⁻² M</th>
<th>Induction period</th>
<th>pH change interval</th>
<th>Lowest pH</th>
<th>Final pH</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1.0</td>
<td>5.0</td>
<td>15 min</td>
<td>57 min</td>
<td>2.05</td>
<td>2.17</td>
<td>84%</td>
</tr>
<tr>
<td>#2</td>
<td>1.6</td>
<td>1.0</td>
<td>22 min</td>
<td>96 min</td>
<td>2.08</td>
<td>2.48</td>
<td>88%</td>
</tr>
<tr>
<td>#3</td>
<td>2.0</td>
<td>6.7</td>
<td>39 min</td>
<td>93 min</td>
<td>2.08</td>
<td>2.36</td>
<td>87%</td>
</tr>
</tbody>
</table>

a 1.08 M HNO₃ was prepared from 67% HNO₃. Reactions #1-#3 were carried out by mixing appropriate amounts of GlyH (100-150 mg), Na₂MoO₄·2H₂O (600-800 mg) and water (ca. 30 mL), then 1.08 HNO₃ was added until pH = 2 (4-5 mL).
b Initial molar concentration of molybdenum in the reaction mixture.
d period of time during which the pH increased.

Graph S1. Profile of pH vs. time for the reaction reported as entry #2 in Table S1.
Graph S2. Titration of an aqueous mixture of Na$_2$MoO$_4$ and GlyH (2:1 molar ratio) with 1.08 M HNO$_3$. Filled squares refer to pH values measured soon after each HNO$_3$ addition. Empty circles refer to final pH values measured after the formation of I.

pH values did not vary after addition, up to H$^+$/GlyH = 2.70 (in this case, pH = 3.93 did not vary after 15 hours). With H$^+$/GlyH = 3.37, pH quickly reached 2.55 and it began to increase after ca. 30 minutes with the formation of a colourless solid. The final value of pH = 3.93 was reached. When H$^+$/GlyH was raised to 4.05, a small increase in pH was still detected, thus indicating residual formation of I.

**Calculation of $\nu_{H^+}$**: The amount of HNO$_3$ added and the pH of the solution after the second and final reaction are known (the “end of reaction” corresponds to the empty circle for H$^+$/GlyH = 4.05 in Graph S2, when pH stopped increasing). Therefore, the moles of H$^+$ reacted ($\Delta n_{H^+}$) can be calculated by Equation S1. By knowing the amount of product isolated ($m$) and its molar mass ($M$), the molar ratio between $\Delta n_{H^+}$ and Mo$_2$O$_4$(OH)$_4$(GlyH) is given by Equation S2.

$$\Delta n_{H^+} = V_{HNO_3} \times c_{HNO_3} - V \times 10^{-pH} \quad \text{(Equation S1)}$$

$$\nu_{H^+} = \frac{\Delta n_{H^+} \times M}{m} \quad \text{(Equation S2)}$$

The value obtained for the $\nu_{H^+}$ coefficient is 4.43, which is very close to the stoichiometric coefficient of H$^+$ required for the formation reaction proposed (see Equation 1). The value of $\Delta n_{H^+}$ obtained with equation S2 is inevitably overestimated since it does not consider any possible equilibrium, established after the formation of I, which may involve H$^+$, reducing its concentration. Examples are the protonation of unreacted glycine or molybdate. Nevertheless, since the formation of I was almost quantitative (88% yield) and the reaction was carried out under stoichiometric conditions, the value of $\Delta n_{H^+}$ may be not too biased.
Table S2. Compared $^{13}$C CP-MAS chemical shifts (ppm) of aaH, [aaH$_2$]NO$_3$ and Mo$_2$O$_4$(OH)$_4$(aaH).$^a$

<table>
<thead>
<tr>
<th>α-Amino Acid</th>
<th>Compound</th>
<th>CO</th>
<th>C$_\alpha$</th>
<th>C$_\beta$</th>
<th>C$_\gamma$</th>
<th>C$_\delta$ or Ph</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GlyH</td>
<td>[GlyH$_2$]NO$_3$</td>
<td>171.7</td>
<td>41.1</td>
<td></td>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_4$(OH)$_4$(GlyH), 1</td>
<td>172.0</td>
<td>41.3</td>
<td></td>
<td></td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>βCH$_2$Ph</td>
<td>PheH</td>
<td>175.3</td>
<td>58.3, 56.4</td>
<td>40.4, 37.6</td>
<td></td>
<td>135.4, 130.1, 128.4</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>[PheH$_2$]NO$_3$</td>
<td>173.9, 173.2</td>
<td>56.3, 55.5</td>
<td>37.0, 36.3</td>
<td></td>
<td>135.2, 132.8, 132.3, 129.8, 129.3, 127.6, 127.3</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_4$(OH)$_4$(PheH), 2</td>
<td>172.6</td>
<td>57.3</td>
<td>35.6</td>
<td></td>
<td>134.5, 133.6, 132.5, 129.6</td>
<td>This work</td>
</tr>
<tr>
<td>βCH$_2$CH$_3$</td>
<td>LeuH</td>
<td>176.7, 175.8</td>
<td>53.8, 52.7</td>
<td>42.4, 40.6</td>
<td>24.6</td>
<td>24.6</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>[LeuH$_2$]NO$_3$</td>
<td>173.9, 173.1</td>
<td>52.9</td>
<td>39.2</td>
<td>24.7</td>
<td>23.3, 22.3, 21.7, 20.0</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_4$(OH)$_4$(LeuH), 3</td>
<td>173.2</td>
<td>53.2</td>
<td>39.2</td>
<td>25.1</td>
<td>21.3, 20.1</td>
<td>This work</td>
</tr>
<tr>
<td>H$_2$C=SCH$_3$</td>
<td>MetH</td>
<td>176.7</td>
<td>55.2, 52.1</td>
<td>32.9, 32.0</td>
<td>31.0</td>
<td>17.3, 15.3</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>[MetH$_2$]NO$_3$</td>
<td>173.7, 172.2</td>
<td>54.6, 54.4</td>
<td>32.9</td>
<td>30.2</td>
<td>16.0, 15.5</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_4$(OH)$_4$(MetH), 4</td>
<td>174.4, 171.8</td>
<td>54.7</td>
<td>31.5, 30.4</td>
<td>28.7</td>
<td>15.3, 14.3, 12.4</td>
<td>This work</td>
</tr>
<tr>
<td>βCH$_2$PH</td>
<td>ProH</td>
<td>176.7</td>
<td>60.6</td>
<td>29.6</td>
<td>25.1</td>
<td>47.8</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_4$(OH)$_4$(ProH), 5</td>
<td>176.8, 175.2, 173.5</td>
<td>65.0, 61.0</td>
<td>30.2, 29.4</td>
<td>26.2, 25.8, 23.7</td>
<td>49.7, 47.3, 46.9</td>
<td>This work</td>
</tr>
<tr>
<td>(H$_2$CH)$_2$Ph</td>
<td>dmPheH</td>
<td>172.6</td>
<td>66.5</td>
<td>35.4</td>
<td>39.0 (NCH$_3$)</td>
<td>139.0, 130.6, 129.1, 127.7, 125.1</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Mo$_2$O$_4$(OH)$_4$(dmPheH), 6</td>
<td>171.6</td>
<td>69.9</td>
<td>30.4</td>
<td>42.0, 36.6 (NCH$_3$)</td>
<td>140.9, 130.8, 128.8, 127.8</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ Splitted signals for PheH, [PheH$_2$]NO$_3$, LeuH, [LeuH$_2$]NO$_3$, MetH, [MetH$_2$]NO$_3$ are due to the presence of two crystallographically independent molecules in the asymmetric unit.

Table S3. Main solid state IR absorptions (cm\(^{-1}\)) and vibrational assignments for compounds 1-6 and the related α-amino acids.

<table>
<thead>
<tr>
<th>α-Amino Acid</th>
<th>Compound</th>
<th>Carboxylate group</th>
<th>Ammonium group</th>
<th>Mo-O backbone</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GlyH</td>
<td></td>
<td>ν(_{\text{asym}})(CO(_2))</td>
<td>ν(_{\text{sym}})(CO(_2))</td>
<td>Δν(_{\text{asym}})(NH(_3^+))</td>
<td>δ(_{\text{asym}})(NH(_3^+))</td>
</tr>
<tr>
<td>H(_3)N(\text{H}2)C=O</td>
<td>Mo(_2)O(_4)(GlyH), 1</td>
<td>1610</td>
<td>1407</td>
<td>203</td>
<td>1580</td>
</tr>
<tr>
<td>H(_3)N(\text{CH}2)Ph</td>
<td>PheH</td>
<td>1556</td>
<td>1408</td>
<td>148</td>
<td>1622</td>
</tr>
<tr>
<td>H(_3)N(\text{CHMe}2)CH(_2)</td>
<td>LeuH</td>
<td>1578</td>
<td>1406</td>
<td>172</td>
<td>1608</td>
</tr>
<tr>
<td>H(_3)N(\text{CH}2)S(\text{CH}3)</td>
<td>MetH</td>
<td>1582, 1560</td>
<td>1406</td>
<td>165 (av.)</td>
<td>1608</td>
</tr>
<tr>
<td>H(_3)N(\text{CH}2)C(\text{SCH}3)</td>
<td>Mo(_2)O(_4)(MetH), 4</td>
<td>1575</td>
<td>1427</td>
<td>148 (~17)</td>
<td>1603</td>
</tr>
<tr>
<td>H(_3)N(\text{H}2)C=O</td>
<td>ProH</td>
<td>1613</td>
<td>1404</td>
<td>209</td>
<td>δ(NH(_2^+)): 1553</td>
</tr>
<tr>
<td>H(_3)N(\text{H}2)C=O</td>
<td>Mo(_2)O(_4)(ProH), 5</td>
<td>1603</td>
<td>1432</td>
<td>171 (~38)</td>
<td>δ(NH(_2^+)): 1558</td>
</tr>
<tr>
<td>(H(_3)C)(_2)HN(\text{CH}2)Ph</td>
<td>dmPheH</td>
<td>1610</td>
<td>1416</td>
<td>194</td>
<td>ν(N–CH(_3)): 1485</td>
</tr>
<tr>
<td>(H(_3)C)(_2)HN(\text{CH}2)Ph</td>
<td>Mo(_2)O(_4)(dmPheH), 6</td>
<td>1626</td>
<td>1412</td>
<td>214 (+20)</td>
<td>ν(N–CH(_3)): 1495</td>
</tr>
</tbody>
</table>

Figure S1. Solid state IR spectrum of Mo$_2$O$_4$(OH)$_4$(GlyH), 1.

Figure S2. Solid state IR spectrum of Mo$_2$O$_4$(OH)$_4$(PheH), 2.
**Figure S3.** Solid state IR spectrum of Mo$_2$O$_4$(OH)$_4$(LeuH), 3.

**Figure S4.** Solid state IR spectrum of Mo$_2$O$_4$(OH)$_4$(MetH), 4.
**Figure S5.** Solid state IR spectrum of Mo$_2$O$_4$(OH)$_4$(ProH), 5.

**Figure S6.** Solid state IR spectrum of Mo$_2$O$_4$(OH)$_4$(dmPheH), 6.
Figure. S7. Comparison of Mo$_2$O$_4$(OH)$_4$(aaH) (straight line) and [aaH$_2$]NO$_3$ (dashed line) IR spectra in the 2300-3400 cm$^{-1}$ interval for glycine (a), L-phenylalanine (b), L-leucine (c) and L-methionine (d).