Supporting Information

Transformations and reductions of γ-octamolybdates with their monomeric and dimeric aminopolycarboxylates

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Figure S1. (a) IR spectra of iminodiacetato molybdates: (NH₄)₄[MoO₃(ida)]₂·3H₂O (4) top; (NH₄)₈{γ-Mo₈O₂₆[MoO₃(ida)]₂}·6H₂O (1) middle, and K₈{γ-Mo₈O₂₄[MoO₃(ida)]₂}·12H₂O (2) bottom; (b) IR spectra of dimeric propanediaminetetraacetato molybdates: (NH₄)₅[Mo₂O₆(1,3-pdta)]Cl·2H₂O (5), K₄[Mo₂O₆(1,3-pdta)]·3H₂O (6); (c) IR spectrum of the complex (NH₄)₆n(Mo₈O₂₇)ₙ·4nH₂O (7). (d) IR spectrum of the complex (NH₄)₄n(Mo₈O₂₀)ₙ (8).

Figure S2. UV spectra of (NH₄)₈{γ-Mo₈O₂₆[MoO₃(ida)]₂}·6H₂O (1) and K₈{γ-Mo₈O₂₄[MoO₃(ida)]₂}·12H₂O (2).

Figure S3. Perspective view of the 3D structure of (NH₄)₄[MoO₃(ida)]₂·3H₂O (4).

Figure S4. Perspective view of the 2D structure of (NH₄)₈{γ-Mo₈O₂₆[MoO₃(ida)]₂}·6H₂O (1).

Figure S5. ¹H NMR spectra of the complexes (NH₄)₅[Mo₂O₆(1,3-pdta)]Cl·2H₂O (5) and K₄[Mo₂O₆(1,3-pdta)]·3H₂O (6); x indicates resonance signals of the coordinated ligand, o for the free ligand.

Table S1. Bond valence calculations of molybdenum complexes.

Table S2. Comparisons of the Mo–O and Mo–N distances (Å) in the iminodiacetato complexes.

Table S3. Comparisons of the Mo–O and Mo–N distances (Å) in the propanediaminetetraacetato molybdenum complexes.
(a) $\nu (\text{cm}^{-1})$

4000 3500 3000 2500 2000 1500 1000 500

$\text{H}_2\text{ida}$

(b) $\nu (\text{cm}^{-1})$

4000 3500 3000 2500 2000 1500 1000 500
Figure S1. (a) IR spectra of iminodiacetato molybdates: \((\text{NH}_4)_4[\text{MoO}_3(\text{ida})]_2\cdot3\text{H}_2\text{O}\) (4) top; \((\text{NH}_4)_8\{\gamma\text{-Mo}_8\text{O}_{26}[\text{MoO}_3(\text{ida})]_2\}\cdot6\text{H}_2\text{O}\) (1) middle, and \(K_8\{\gamma\text{-Mo}_8\text{O}_{24}[\text{MoO}_3(\text{ida})]_2\}\cdot12\text{H}_2\text{O}\) (2) bottom; (b) IR spectra of dimeric propanediaminetetraacetato molybdates: \((\text{NH}_4)_5[\text{Mo}_2\text{O}_6(1,3\text{-pdtal})]\text{Cl}\cdot2\text{H}_2\text{O}\) (5), \(K_4[\text{Mo}_2\text{O}_6(1,3\text{-pdtala})]\cdot3\text{H}_2\text{O}\) (6); (c) IR spectrum of the complex \((\text{NH}_4)_6\text{n}(\text{Mo}_8\text{O}_{27})\text{n}\cdot4\text{nH}_2\text{O}\) (7). (d) IR spectrum of the complex \((\text{NH}_4)_4\text{n}(\text{Mo}_8\text{O}_{26})\text{n}\) (8).
Figure S2. UV spectra of (NH$_4$)$_8$\{γ-Mo$_8$O$_{26}$[MoO$_3$(ida)]$_2$\}·6H$_2$O (1) and K$_8$\{γ-Mo$_8$O$_{26}$[MoO$_2$(ida)]$_2$\}·12H$_2$O (2).
Figure S3. Perspective view of the 3D structure of \((\text{NH}_4)_4[\text{MoO}_3(\text{ida})]_2\cdot 3\text{H}_2\text{O} \ (4)\).

Figure S4. Perspective view of the 2D structure of \((\text{NH}_4)_8\{\gamma-\text{Mo}_6\text{O}_{26}[\text{MoO}_3(\text{ida})]_2\} \cdot 6\text{H}_2\text{O} \ (1)\).
Figure S5. $^1$H NMR spectra of the complexes $(\text{NH}_4)_5[\text{Mo}_2\text{O}_6(\text{1,3-pdta})]\text{Cl} \cdot 2\text{H}_2\text{O}$ (5) and $K_4[\text{Mo}_2\text{O}_6(\text{1,3-pdta})] \cdot 3\text{H}_2\text{O}$ (6); x indicates resonance signals of the coordinated ligand, o for the free ligand.
Table S1. Bond valence calculations of molybdenum complexes.\textsuperscript{18}

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mo1/Mo6</th>
<th>Mo2/Mo7</th>
<th>Mo3/Mo8</th>
<th>Mo4/Mo9</th>
<th>Mo5/Mo10</th>
</tr>
</thead>
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<tr>
<td>((\text{NH}_4)_8{\gamma\text{-Mo}<em>8\text{O}</em>{26}{\text{MoO}_3\text{(ida)}})_2}\cdot 6\text{H}_2\text{O} (1)</td>
<td>6.142</td>
<td>6.018</td>
<td>5.924</td>
<td>5.865</td>
<td>5.933</td>
</tr>
<tr>
<td>(\text{K}_8{\gamma\text{-Mo}<em>8\text{O}</em>{26}{\text{MoO}_2\text{(ida)}})_2}\cdot 12\text{H}_2\text{O} (2)</td>
<td>5.270</td>
<td>5.205</td>
<td>5.996</td>
<td>6.024</td>
<td>6.052</td>
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<tr>
<td>((\text{NH}_4)_8{\gamma\text{-Mo}<em>8\text{O}</em>{26}{\text{Mo}_2\text{O}_6\text{(1,3-pdta)}}}_n\cdot 30\text{nH}_2\text{O} (3))\textsuperscript{[13]}</td>
<td>6.015</td>
<td>6.112</td>
<td>6.061</td>
<td>6.091</td>
<td>6.117</td>
</tr>
<tr>
<td>((\text{NH}_4)_4{\text{MoO}_3\text{(ida)}}_2\cdot 3\text{H}_2\text{O}(4)</td>
<td>6.117</td>
<td>6.183</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\text{NH}_4)_5[\text{Mo}_2\text{O}_6\text{(1,3-pdta)}]\text{Cl}\cdot 2\text{H}_2\text{O}(5)</td>
<td>6.072</td>
<td>6.062</td>
<td></td>
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<td></td>
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<tr>
<td>(\text{K}_4[\text{Mo}_2\text{O}_6\text{(1,3-pdta)}]\cdot 3\text{H}_2\text{O}(6)</td>
<td>6.087</td>
<td>6.102</td>
<td></td>
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<tr>
<td>((\text{NH}_4)_8\text{Mo}<em>8\text{O}</em>{27}n\cdot 4\text{nH}_2\text{O}(7)</td>
<td>5.955</td>
<td>6.084</td>
<td>6.022</td>
<td>6.095</td>
<td></td>
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<tr>
<td>((\text{NH}_4)_4\text{Mo}<em>8\text{O}</em>{26}n(8)</td>
<td>6.033</td>
<td>5.982</td>
<td>6.004</td>
<td>5.922</td>
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</tr>
</tbody>
</table>
Table S2. Comparisons of the Mo–O and Mo–N distances (Å) in iminodiacetato molybdates.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mo–O&lt;sub&gt;t&lt;/sub&gt;</th>
<th>Mo–O&lt;sub&gt;b&lt;/sub&gt;</th>
<th>Mo–O&lt;sub&gt;c1&lt;/sub&gt;</th>
<th>Mo–O&lt;sub&gt;c2&lt;/sub&gt;</th>
<th>Mo–N</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;[MoO&lt;sub&gt;3&lt;/sub&gt;(ida)]&lt;sub&gt;2&lt;/sub&gt;·3H&lt;sub&gt;2&lt;/sub&gt;O(4)</td>
<td>1.736(2)</td>
<td>2.202(2)</td>
<td>2.226(2)</td>
<td>2.306(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;8&lt;/sub&gt;{γ-Mo&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;[MoO&lt;sub&gt;3&lt;/sub&gt;(ida)]&lt;sub&gt;2&lt;/sub&gt;}·6H&lt;sub&gt;2&lt;/sub&gt;O (1)</td>
<td>1.705(5)</td>
<td>2.089(2)</td>
<td>2.211(5)</td>
<td>2.212(4)</td>
<td>2.285(5)</td>
<td>This work</td>
</tr>
<tr>
<td>K&lt;sub&gt;8&lt;/sub&gt;{γ-Mo&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;[MoO&lt;sub&gt;3&lt;/sub&gt;(ida)]&lt;sub&gt;2&lt;/sub&gt;}·12H&lt;sub&gt;2&lt;/sub&gt;O (2)</td>
<td>1.713(2)</td>
<td>2.067(2)</td>
<td>2.123(2)</td>
<td>2.105(2)</td>
<td>2.342(2)</td>
<td></td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;[MoO&lt;sub&gt;3&lt;/sub&gt;(ida)]·2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.746(2)</td>
<td>2.228(2)</td>
<td>2.228(2)</td>
<td>2.306(4)</td>
<td></td>
<td>[12]</td>
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<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;[UO&lt;sub&gt;2&lt;/sub&gt;(ida)&lt;sub&gt;2&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;]·8H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.781(8)</td>
<td>2.348(8)</td>
<td>2.341(9)</td>
<td>2.585(10)</td>
<td></td>
<td>[a]</td>
</tr>
<tr>
<td>Pd(Hida)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.988(4)</td>
<td>2.061(4)</td>
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<td></td>
<td>[b]</td>
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<td>Pt(Hida)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.014(9)</td>
<td>2.066(10)</td>
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<td></td>
<td>[b]</td>
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<tr>
<td>(pyH)[Fe(ida)&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>1.980(2)</td>
<td>1.984(2)</td>
<td>2.161(3)</td>
<td></td>
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<td>[c]</td>
</tr>
</tbody>
</table>


Table S3. Comparisons of the Mo–O and Mo–N distances (Å) for propanediaminetetraacetato molybdates.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mo–O&lt;sub&gt;t&lt;/sub&gt;</th>
<th>Mo–O&lt;sub&gt;b&lt;/sub&gt;</th>
<th>Mo–O&lt;sub&gt;c1&lt;/sub&gt;</th>
<th>Mo–O&lt;sub&gt;c2&lt;/sub&gt;</th>
<th>Mo–N</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>{Na[M&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;32&lt;/sub&gt;(edta)][H&lt;sub&gt;2&lt;/sub&gt;O]&lt;sub&gt;35&lt;/sub&gt;}&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.700(5)</td>
<td>1.812(4)</td>
<td>2.122(4)</td>
<td>2.173(5)</td>
<td>2.373(4)</td>
<td>[43]</td>
</tr>
<tr>
<td>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;8&lt;/sub&gt;[Mo&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;32&lt;/sub&gt;(1,3-pdta)&lt;sub&gt;2&lt;/sub&gt;·30nH&lt;sub&gt;2&lt;/sub&gt;O]&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.711(7)</td>
<td>1.825(7)</td>
<td>2.118(8)</td>
<td>2.231(7)</td>
<td>2.342(8)</td>
<td>[43]</td>
</tr>
<tr>
<td>(NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;[Mo&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;(1,3-pdta)&lt;sub&gt;2&lt;/sub&gt;Cl·2H&lt;sub&gt;2&lt;/sub&gt;O]&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.739(4)</td>
<td>2.198(4)</td>
<td>2.207(3)</td>
<td>2.347(3)</td>
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<tr>
<td>K&lt;sub&gt;4&lt;/sub&gt;[Mo&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;(1,3-pdta)]·3H&lt;sub&gt;2&lt;/sub&gt;O]&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1.735(4)</td>
<td>2.194(4)</td>
<td>2.221(4)</td>
<td>2.347(5)</td>
<td></td>
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<tr>
<td>Average (Å)</td>
<td>1.713</td>
<td>1.864</td>
<td>2.143</td>
<td>2.187</td>
<td>2.368</td>
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