Tuning the Structure of Metal Phosphonate Using Uncoordinating Methyl group:
Syntheses, Structures and Properties of a Series of Metal Diphosphonates

Si-Fu Tang, Liang-Jun Li, Xiao-Xia Lv, Chao Wang and Xue-Bo Zhao

Table S1. Selected angles of compounds 1-8.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O(2)#1-Mn(1)-O(2)#2</td>
<td>179.03(10)</td>
<td>O(1)#3-Mn(1)-O(1W)</td>
</tr>
<tr>
<td>2</td>
<td>O(2)#1-Mn(1)-O(1)#3</td>
<td>93.21(7)</td>
<td>O(1)-Mn(1)-O(1W)</td>
</tr>
<tr>
<td>3</td>
<td>O(2)#1-Mn(1)-O(1)</td>
<td>87.43(7)</td>
<td>O(2)#2-Mn(1)-O(1W)#3</td>
</tr>
<tr>
<td>4</td>
<td>O(2)#2-Mn(1)-O(1)</td>
<td>93.21(7)</td>
<td>O(1)#3-Mn(1)-O(1W)#3</td>
</tr>
<tr>
<td>5</td>
<td>O(2)#1-Mn(1)-O(1)</td>
<td>87.43(7)</td>
<td>O(2)#2-Mn(1)-O(1W)#3</td>
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<tr>
<td>6</td>
<td>O(2)#2-Mn(1)-O(1W)</td>
<td>96.67(11)</td>
<td>O(1)-Mn(1)-O(1W)#3</td>
</tr>
<tr>
<td>7</td>
<td>O(2)#1-Mn(1)-O(1W)</td>
<td>87.06(9)</td>
<td>O(2)-Mn(1)-O(1W)#3</td>
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<tr>
<td>8</td>
<td>O(2)#2-Mn(1)-O(1W)</td>
<td>92.24(9)</td>
<td>O(1W)-Mn(1)-O(1W)#3</td>
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</table>

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Symmetry transformations used to generate equivalent atoms: For 1: #1 x, -y, z-1/2; #2 -x+1, -y, -z+2; #3 -x+1, y, -z+3/2; #4 -x+3/2, -y+1/2, -z+2. For 3 and 6: #1 -x+1, -y, -z. For 5: #1 -x+2, -y+2, -z; #2 -x+1, -y+2, -z; #3 x+1, y, z. For 7: #1 x, -y+3/2, z
For 8: #1 -x+1, y, -z+1/2; #2 x, -y,z-1/2; #3 -x+1,-y,-z+1.

Table S2 Some O-H···O interactions found for compounds 1-8.

<table>
<thead>
<tr>
<th>D-H</th>
<th>H···A</th>
<th>D···A</th>
<th>&lt;(DHA)</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.82</td>
<td>1.83</td>
<td>2.638(2)</td>
<td>O3-H3A···O1_$1</td>
</tr>
<tr>
<td>2</td>
<td>0.82</td>
<td>1.89</td>
<td>2.674(3)</td>
<td>O2-H2A···O6_$1</td>
</tr>
<tr>
<td>3</td>
<td>0.85</td>
<td>1.82</td>
<td>2.667(3)</td>
<td>O1W-H2W···O5_$3</td>
</tr>
<tr>
<td>4</td>
<td>0.85</td>
<td>1.99</td>
<td>2.832(3)</td>
<td>O2W-H3W···O3W_$4</td>
</tr>
<tr>
<td>5</td>
<td>0.85</td>
<td>2.00</td>
<td>2.748(3)</td>
<td>O2W-H4W···O4W_$5</td>
</tr>
<tr>
<td>6</td>
<td>0.85</td>
<td>1.94</td>
<td>2.787(3)</td>
<td>O3W-H6W···O8W_$6</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: For 1: #1 x, -y, z-1/2; #2 -x+1, -y, -z+2; #3 -x+1, y, -z+3/2; #4 -x+3/2, -y+1/2, -z+2. For 3 and 6: #1 -x+1,-y+1,-z. For 5: #1 -x+2, -y+2, -z; #2 -x+1, -y+2, -z; #3 x+1, y, z. For 7: #1 x, -y+3/2, z
For 8: #1 -x+1, y, -z+1/2; #2 x, -y,z-1/2; #3 -x+1,-y,-z+1.
<p>| | | | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0.85</td>
<td>1.86</td>
<td>2.704(3)</td>
<td>177.0</td>
<td>O3W-H5W ( \cdots ) O7W</td>
</tr>
<tr>
<td>0.85</td>
<td>1.98</td>
<td>2.681(3)</td>
<td>139.4</td>
<td>O4W-H7W ( \cdots ) O3</td>
</tr>
<tr>
<td>0.85</td>
<td>1.86</td>
<td>2.707(3)</td>
<td>171.6</td>
<td>O6W-H11W ( \cdots ) O3</td>
</tr>
<tr>
<td>0.85</td>
<td>1.96</td>
<td>2.806(3)</td>
<td>174.7</td>
<td>O6W-H12W ( \cdots ) O7W</td>
</tr>
<tr>
<td>0.85</td>
<td>1.96</td>
<td>2.811(3)</td>
<td>175.9</td>
<td>O7W-H14W ( \cdots ) O6</td>
</tr>
<tr>
<td>0.85</td>
<td>1.94</td>
<td>2.787(3)</td>
<td>177.4</td>
<td>O8W-H15W ( \cdots ) O3</td>
</tr>
</tbody>
</table>

Operators for generating equivalent atoms:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$.

3 and 6:

1: $-x+2, -y+2, -z$;
$2x-1, y-1/2, -z+1/2$;
$3x-1, -y+1/2, -z+1/2$;
$4x-1, -y+1, -z$;
$5x-1, -y+2, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

4:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

6:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

7:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

8:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

Operators for generating equivalent atoms:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

3 and 6:

1: $-x+2, -y+2, -z$;
$2x-1, y-1/2, -z+1/2$;
$3x-1, -y+1/2, -z+1/2$;
$4x-1, -y+1, -z$;
$5x-1, -y+2, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

Operators for generating equivalent atoms:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

3 and 6:

1: $-x+2, -y+2, -z$;
$2x-1, y-1/2, -z+1/2$;
$3x-1, -y+1/2, -z+1/2$;
$4x-1, -y+1, -z$;
$5x-1, -y+2, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

Operators for generating equivalent atoms:

1: $1x, -y+1, z+1/2$;
2 and 4: $1x, y-1, z$;
$2x-1, y, z$;
$3x+1, y, z$;
$4x-2, -y+1, -z$;
$5x-1, -y+1, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

3 and 6:

1: $-x+2, -y+2, -z$;
$2x-1, y-1/2, -z+1/2$;
$3x-1, -y+1/2, -z+1/2$;
$4x-1, -y+1, -z$;
$5x-1, -y+2, -z$;
$6x-1, -y+2, -z$;
$7x, y+1, z$. 

Operators for generating equivalent atoms:
$4 \ -x+1, \ y-1/2, \ -z-1/2; \ \$5\ -x+2, \ -y+1, \ -z; \ \$3\ x+1,\ y-1,\ z.$

$5: \ \$1 \ x-1, \ y, \ z; \ \$2 \ -x+2, \ -y+1, \ -z; \ \$3 \ x+1, \ y-1, \ z.$

$7: \ \$1 \ x, \ -y, \ z-1/2; \ \$2 \ -x+1, \ y, \ -z+1/2; \ \$3 \ x+1/2, \ y, \ -z-1/2.$

$8: \ \$1 \ x, \ -y, \ z-1/2; \ \$2 \ -x+1, \ y, \ -z+1/2; \ \$3 \ x, \ -y+1, \ z-1/2.$

Figure S1. Three-dimensional packing diagram of compound 1 viewing along \(b\)-direction. The CPO\(_3\) tetrahedrons and MnO\(_6\) octahedrons are shaded in pink and green respectively. O-H···O interactions are shown as dash lines.

Figure S2. Three-dimensional packing diagram of compound 2 viewing along \(b\)-direction. The CPO\(_3\) tetrahedrons and CoO\(_6\) octahedrons are shaded in pink and green respectively. O-H···O interactions are shown as dash lines.
Figure S3. Three-dimensional packing diagram of compound 7 viewing along $c$-direction. The CPO$_3$ tetrahedrons and CdO$_6$ octahedrons are shaded in pink and green respectively.

Table S3. Comparison of the structures reported in this paper and those from literature synthesis condition used for 1,4-phenylenediphosphonic acid.

<table>
<thead>
<tr>
<th></th>
<th>Synthesis conditions</th>
<th>product</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Literature method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This paper</td>
<td>Co(en)$_3$Cl$_3$ (0.3 mmol, 0.12 g), H$_4$L (0.3 mmol, 0.0798 g), 8 ml H$_2$O, pH=3-4, 140 °C, 54 h</td>
<td>Blue green powder and pink plate crystals</td>
<td>Unknown phases (see Figure S11)</td>
</tr>
<tr>
<td></td>
<td>H$_4$L (0.0665 g), Co(ac)$_2$·4H$_2$O (0.0623 g), 3 mL H$_2$O, 160 °C, 3 days</td>
<td>Pink block crystals</td>
<td>Compound 2</td>
</tr>
<tr>
<td></td>
<td>H$_4$L (0.0665 g), CoCl$_2$·6H$_2$O (0.0595 g), 3 mL H$_2$O, 160 °C, 3 days</td>
<td>Pink block crystals</td>
<td>Compound 3</td>
</tr>
<tr>
<td>Ni</td>
<td>Literature method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This paper</td>
<td>NiSO$_4$·6H$_2$O (0.2 mmol, 0.0525 g), H$_4$L (0.2 mmol, 0.0532 g), 8 ml H$_2$O, pH=3-4, 140 °C, 54 h</td>
<td>Clear solution</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>NiSO$_4$·6H$_2$O (0.2 mmol, 0.0525 g), H$_4$L (0.2 mmol, 0.0532 g), 2 ml H$_2$O, pH=3-4, 140 °C, 54 h</td>
<td>Small green block crystals</td>
<td>Same to that of compound 4 (see Figure S12)</td>
</tr>
<tr>
<td></td>
<td>H$_4$L (0.0665 g, 0.25 mmol), NiSO$_4$·H$_2$O (0.1586 g, 0.25 mmol), 10 mL H$_2$O, 160 °C, 3 days</td>
<td>Green block crystals</td>
<td>Compound 4</td>
</tr>
<tr>
<td>Zn</td>
<td>Literature method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This paper</td>
<td>ZnCl$_2$ (1 mmol, 0.136 g), H$_4$L (0.5 mmol, 0.1331 g), 60 °C, 7 days</td>
<td>Small colorless crystals</td>
<td>Compound 7</td>
</tr>
<tr>
<td></td>
<td>H$_4$L (0.0665 g), ZnCl$_2$ (0.0623 g), 3 mL H$_2$O, 160 °C, 3 days</td>
<td></td>
<td>Compound 6</td>
</tr>
<tr>
<td>Cu</td>
<td>Literature method</td>
<td>CuSO₄·5H₂O (1 mmol, 0.2497 g), H₄L (0.25 mmol, 0.0665 g), 60 °C 1 day</td>
<td>Blue plate crystals</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------------------------</td>
<td>---------------------------------------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>This paper</td>
<td>H₄L (0.0887 g, 0.3333 mmol), CuSO₄·5H₂O (0.1665 g, 0.6666 mmol), and 10 mL H₂O, 160 °C, 3 days</td>
<td>Blue plate crystals</td>
<td>Compound 5</td>
</tr>
</tbody>
</table>

Figure S4. Comparison of simulated and experimental XRD pattern of compound 1.

Figure S5. Comparison of simulated and experimental XRD pattern of compound 2.
Figure S6. Comparison of simulated and experimental XRD pattern of compound 3.

Figure S7. Comparison of simulated and experimental XRD pattern of compound 4.
Figure S8. Comparison of simulated and experimental XRD pattern of compound 5.

Figure S9. Comparison of simulated and experimental XRD pattern of compound 6.
Figure S10. Comparison of simulated and experimental XRD pattern of compound 7.

Figure S10. Comparison of simulated and experimental XRD pattern of compound 8.
Figure S11. Comparison of the XRD pattern of the products synthesized from 
\( \text{Co(en)}_3\text{Cl}_3 \) and \( \text{H}_4\text{L} \) and those from simulated compounds 2 and 3 and simulated 
from \( \text{Co}_2(\text{O}_3\text{PC}_6\text{H}_4\text{PO}_3)(\text{H}_2\text{O})_2 \) reported in the literature (D.-K. Cao, S. Gao, L.-M. 

Figure S12. Comparison of the simulated and experimental XRD pattern of the 
product synthesized from \( \text{NiSO}_4\cdot6\text{H}_2\text{O} \) and \( \text{H}_4\text{L} \) using literature method.
Figure S13. Comparison of the simulated and experimental XRD pattern of the product synthesized from CuSO₄·5H₂O and H4L using literature method.