Structural Feature of a Hexa-DMSO Cobalt(II) Complex: \textit{Pseudo-S}_6 Symmetry and \textit{Pseudo-C}_2\textsubscript{v} Deformation

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The cobalt(II) complex \([\text{Co(DMSO)}_6](\text{BPh}_4)_2\) (DMSO = dimethylsulfoxide) was prepared, and characterized by single-crystal X-ray method. The compound crystallizes in the triclinic space group \(P\overline{1}\) and \(Z = 2\) with cell parameters \(a = 12.551(2)\,\text{Å},\ b = 13.087(2)\,\text{Å},\ c = 21.491(3)\,\text{Å},\ \alpha = 88.818(4)\,^\circ,\ \beta = 74.243(3)\,^\circ,\ \gamma = 64.296(3)\,^\circ,\ V = 3041.9(9)\,\text{Å}^3\). Six DMSO molecules coordinate to a cobalt(II) center to form a \([\text{Co(DMSO)}_6]^{2+}\) cation, which can be approximated to an \(S_6\) point group. However, the coordination geometry can be best described as a \(\textit{Pseudo-C}_2\textsubscript{v}\) symmetry with elongation along the O-Co-O axis.

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six DMSO molecules coordinate to a cobalt(II) ion to form an octahedral geometry. When we look at the bond distances around the central cobalt(II) ion (Table 3S), we find that the octahedral CoO₆ core seems to be tetragonally elongated along the O(1)-Co(1)-O(4) axis. On the other hand, when we focus on the CoO₆S₆ unit of the cation (see Fig. 3a), we find that the unit can be approximated as an S₆ point group, and the unit is trigonally compressed along the unique pseudo-S₆ axis (see Table 2). i.e. the distance between the O(1)-O(2)-O(3) face and the O(4)-O(5)-O(6) face (2.390 Å) is 1.0% shorter than the average distance (2.415 Å).

The coordination geometry is tetragonally elongated along the O(1)-Co(1)-O(4) axis (+1.5%), while at the same time, it is trigonally compressed along the unique pseudo-S₆ axis. However, the geometry is also tetragonally compressed (–1.1%) along the O(2)-Co(1)-O(5) axis (Table 2), and both trigonal compression and trigonal elongation can be seen in different directions (Table 2). Therefore, the best description for the coordination geometry is to use the C₂v approximation (Fig. 3b).

In conclusion, the present [Co(DMSO)₆]²⁺ complex cation could be approximated to the S₆ point group with a trigonal compression along the unique pseudo-S₆ axis; however, the coordination geometry could be best described by a pseudo-C₂ᵥ symmetry with an elongation along an O-Co-O axis, which was perpendicular to the pseudo-C₂ᵥ axis.

**Table 2** Selected distances between the opposite vertices and between the opposite faces

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atom</th>
<th>Distance (Å)</th>
<th>Deviation (Å)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>O(4)</td>
<td>4.246</td>
<td>+0.062</td>
<td>+1.49</td>
</tr>
<tr>
<td>O(2)</td>
<td>O(5)</td>
<td>4.136</td>
<td>–0.047</td>
<td>–1.13</td>
</tr>
<tr>
<td>O(3)</td>
<td>O(6)</td>
<td>4.168</td>
<td>–0.015</td>
<td>–0.36</td>
</tr>
</tbody>
</table>

Triangular face: Triangular face

<table>
<thead>
<tr>
<th>Distanceᵇ (Å)</th>
<th>Deviationᶜ (Å)</th>
<th>Deviationᶜ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-O(2)-O(3)</td>
<td>O(4)-O(5)-O(6)</td>
<td>2.390</td>
</tr>
<tr>
<td>O(2)-O(3)-O(4)</td>
<td>O(1)-O(5)-O(6)</td>
<td>2.377</td>
</tr>
<tr>
<td>O(1)-O(3)-O(5)</td>
<td>O(2)-O(4)-O(6)</td>
<td>2.440</td>
</tr>
</tbody>
</table>

a. Deviation from the average distance (4.183 Å).
b. Distance between the middle points of the triangular faces at the opposite positions.
c. Deviation from the average distance (2.415 Å).

**Supporting Information**

A CIF format file. This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

**References**