Sr$_3$ZnPtO$_6$ and Sr$_3$CdPtO$_6$

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The flux synthesis of single crystals of the isostructural compounds tristrontium zinc platinum hexaoxide, Sr$_3$ZnPtO$_6$, and tristrontium cadmium platinum hexaoxide, Sr$_3$CdPtO$_6$, is reported. The compounds adopt the pseudo-one-dimensional rhombohedral K$_4$CdCl$_6$ structure type, and feature chains of face-shared distorted ZnO$_6$ or CdO$_6$ trigonal prisms and PtO$_6$ octahedra, surrounded by columns of Sr$^{2+}$ ions. All transition metals are located on the threefold axis of symmetry, while the Sr$^{2+}$ cations lie on twofold axes.

Comment

Interest in detailed structural and magnetic measurements on oxides adopting the K$_4$CdCl$_6$ structure type (Bergerhoff & Schmitz-Dumont, 1956) has been great during recent years, mostly due to the low-dimensional nature and compositional flexibility of this large class of oxides. Though the work to date has involved predominantly powder studies, a few single-crystal studies of platinates of this type have been reported, beginning with Sr$_4$PtO$_6$ in 1959 (Randall & Katz, 1959) and including Sr$_3$CuPtO$_6$ (Wilkinson et al., 1991), Sr$_3$NiPtO$_6$ (Nguyen et al., 1997) and Ca$_4$PtO$_6$ (Claridge et al., 1997). During the course of investigations into preparing single crystals of compositions related to Sr$_3$MPtO$_6$, we have grown single crystals of Sr$_3$ZnPtO$_6$, (I), and Sr$_3$CdPtO$_6$, (II), from potassium hydroxide fluxes at high temperatures, employing the Pt$^{4+}$-containing precursor (NH$_4$)$_2$PtCl$_6$. While (I) has been determined previously by X-ray powder diffraction (Lampe-Önnerud & zur Loye, 1996), (II) has not been reported.

The structures of the title compounds consist of chains of slightly distorted face-shared ZnO$_6$ [in (I)] or CdO$_6$ [in (II)] trigonal prisms which alternate with rhombohedrally elongated PtO$_6$ octahedra along [001] (Fig. 1). The distortion of the trigonal prisms consists of a rotation of the opposite triangular faces away from ideal eclipsed geometry [12.3$^\circ$ for (I) and 13.6$^\circ$ for (II)]. The chains are surrounded by six spiral columns of Sr$^{2+}$ ions, and the Sr$^{2+}$ columns are in turn surrounded by three polyhedral chains (Fig. 2). The Sr$^{2+}$ ions occupy an irregular eight-coordinate position, just off the threefold axis on a position of site symmetry 2.

The Zn—O bond distance in (I) is essentially identical to the value determined previously from powder data [2.199 (4) Å; Lampe-Önnerud & zur Loye, 1996]. The Cd—O distance in (II) also agrees with the few known bond lengths for Cd in a trigonal prismatic coordination, i.e. 2.302 (6) Å in Sr$_3$CdIrO$_6$ (Segal et al., 1996) and 2.338 (4) Å in Sr$_3$CdRhO$_6$ (Smith & zur Loye, 2000). The Pt—O distances (Tables 1 and 2) in both compounds are typical of octahedral Pt$^{4+}$ in platinates.

Experimental

(NH$_4$)$_2$PtCl$_6$ was prepared according to Kaufman (1967). Subsequently, SrCO$_3$ (Alfa, 99.95%), ZnO (Alfa, 99.99%) or CdO (Alfa, 99.99%), and (NH$_4$)$_2$PtCl$_6$ (stoichiometric amounts, ca 1 g total reagent mass) and KOH (Fisher, reagent grade; ~10 times by mass the total reagent amount) were loaded into a covered alumina...
Table 1
Selected geometric parameters (Å) for (I).

<table>
<thead>
<tr>
<th></th>
<th>Sr—O</th>
<th>Zn—O</th>
<th>Pt—O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr—O1</td>
<td>2.476 (4) × 2</td>
<td>2.200 (4) × 6</td>
<td></td>
</tr>
<tr>
<td>Sr—O2</td>
<td>2.645 (4) × 2</td>
<td>2.8073 (3) × 2</td>
<td></td>
</tr>
<tr>
<td>Sr—O3</td>
<td>2.688 (4) × 2</td>
<td>2.029 (4) × 6</td>
<td></td>
</tr>
<tr>
<td>Sr—O4</td>
<td>2.718 (4) × 2</td>
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<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (i) −x + y, −x, z; (ii) 1/2 + x, 1/2 − y, z; (iii) 1/2 + x, 1/2 + y, 1/2 − z; (iv) −1/2 − x, −1/2 + y, −1/2 − z.

Table 2
Selected geometric parameters (Å) for (II).

<table>
<thead>
<tr>
<th></th>
<th>Sr—O</th>
<th>Cd—O</th>
<th>Pt—O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr—O1</td>
<td>2.529 (4) × 2</td>
<td>2.328 (4) × 6</td>
<td></td>
</tr>
<tr>
<td>Sr—O2</td>
<td>2.622 (4) × 2</td>
<td>2.89837 (18) × 2</td>
<td></td>
</tr>
<tr>
<td>Sr—O3</td>
<td>2.635 (4) × 2</td>
<td>2.039 (4) × 6</td>
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<tr>
<td>Sr—O4</td>
<td>2.739 (4) × 2</td>
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</table>

Symmetry codes: (i) −x + y, −x, z; (ii) 1/2 + x, 1/2 − y, z; (iii) 1/2 + x, 1/2 + y, 1/2 − z; (iv) −1/2 − x, −1/2 + y, −1/2 − z.

Refractive
Refinement on $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.072$

$S = 1.086$

505 reflections
19 parameters

Systematic absences in the data sets for both compounds confirmed a $c$ glide operation, indicating the space groups $R3c$ and $R3c$. Preliminary powder X-ray diffraction showed the compounds to be isostructural with $K_xCdCl_3$ (space group $R3c$); therefore, the expected centrosymmetric space group was chosen and confirmed by the solution. The largest difference peaks were both located less than 0.8 Å from the Zn or Cd atoms. The relatively large values of $\Delta \rho_{\text{max}}$ in the vicinity of Zn and Cd suggest a small fraction of these atoms may be located off the threefold axis. However, refinement of the Zn or Cd site-occupancy factors for each structure did not lead to a significant deviation from unity and refinements including off-axis contributions were unstable.

For both compounds, data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELX97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1306). Services for accessing these data are described at the back of the journal.

References


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