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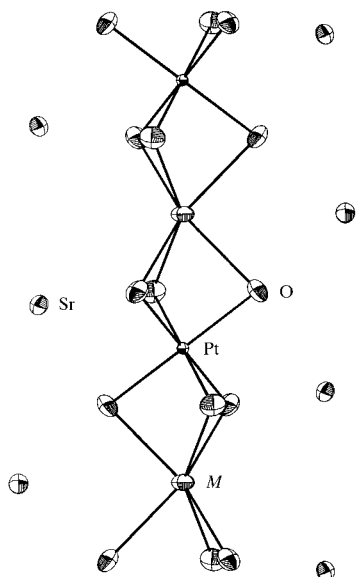
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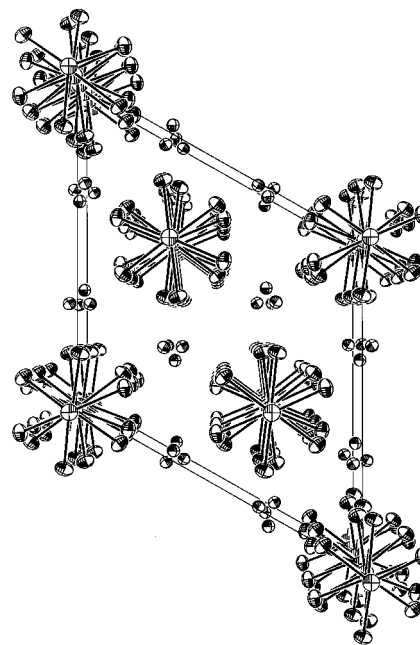
The flux synthesis of single crystals of the isostructural compounds tristrontium zinc platinum hexaoxide, Sr₃ZnPtO₆, and tristrontium cadmium platinum hexaoxide, Sr₃CdPtO₆, is reported. The compounds adopt the pseudo-one-dimensional rhombohedral K₄CdCl₆ structure type, and feature chains of face-shared distorted ZnO₆ or CdO₆ trigonal prisms and PtO₆ octahedra, surrounded by columns of Sr²⁺ ions. All transition metals are located on the threefold axis of symmetry, while the Sr²⁺ cations lie on twofold axes.

Comment

Interest in detailed structural and magnetic measurements on oxides adopting the K₄CdCl₆ 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 platينات of this type have been reported, beginning with Sr₄PtO₆ in 1959 (Randall & Katz, 1959) and

**Figure 1**

A section of the face-shared MPtO₆ (*M* is Zn or Cd) chains in the title compounds. Displacement ellipsoids are drawn (*M* = Cd) at the 80% probability level.

**Figure 2**

A view of Sr₃MPtO₆ (*M* is Zn or Cd) along [001].

including Sr₃CuPtO₆ (Wilkinson *et al.*, 1991), Sr₃NiPtO₆ (Nguyen *et al.*, 1997) and Ca₄PtO₆ (Claridge *et al.*, 1997). During the course of investigations into preparing single crystals of compositions related to Sr₃MPtO₆, we have grown single crystals of Sr₃ZnPtO₆, (I), and Sr₃CdPtO₆, (II), from potassium hydroxide fluxes at high temperatures, employing the Pt⁴⁺-containing precursor (NH₄)₂PtCl₆. 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 ZnO₆ [in (I)] or CdO₆ [in (II)] trigonal prisms which alternate with rhombohedrally elongated PtO₆ 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° for (I) and 13.6° for (II)]. The chains are surrounded by six spiral columns of Sr²⁺ ions, and the Sr²⁺ columns are in turn surrounded by three polyhedral chains (Fig. 2). The Sr²⁺ 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 Sr₃CdIrO₆ (Segal *et al.*, 1996) and 2.338 (4) Å in Sr₃CdRhO₆ (Smith & zur Loye, 2000). The Pt—O distances (Tables 1 and 2) in both compounds are typical of octahedral Pt⁴⁺ in platينات.

Experimental

(NH₄)₂PtCl₆ was prepared according to Kaufman (1967). Subsequently, SrCO₃ (Alfa, 99.95%), ZnO (Alfa, 99.99%) or CdO (Alfa, 99.99%), and (NH₄)₂PtCl₆ (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).

Sr—O ⁱ	2.476 (4) × 2	Zn—O	2.200 (4) × 6
Sr—O ⁱⁱ	2.645 (4) × 2	Zn—Pt	2.8073 (3) × 2
Sr—O ⁱⁱⁱ	2.668 (4) × 2	Pt—O	2.029 (4) × 6
Sr—O ^{iv}	2.718 (4) × 2		

 Symmetry codes: (i) $-x + y, -x, z$; (ii) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$; (iii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (iv) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$.

crucible. The mixture was heated at 1273 K for 2 h and cooled to 1023 K at a rate of 1 K h⁻¹, at which point the furnace was shut off and allowed to cool radiatively to room temperature. The KOH matrix was dissolved with distilled water, leaving numerous blue-green hexagonal prisms and less abundant brown crystals with a rhombohedral habit. Both morphologies were determined to be rhombohedral Sr₃MtPtO₆ by powder X-ray diffraction. However, all of the blue-green hexagonal rods displayed obverse-reverse rhombohedral twinning, and therefore the brown crystals were selected for analysis.

Compound (I)

Crystal data

Sr ₃ ZnPtO ₆	Mo Kα radiation
<i>M_r</i> = 619.32	Cell parameters from 823 reflections
Trigonal, <i>R</i> 3̄c	<i>a</i> = 9.6267 (7) Å
<i>a</i> = 9.6267 (7) Å	<i>c</i> = 11.2292 (11) Å
<i>c</i> = 11.2292 (11) Å	<i>V</i> = 901.23 (13) Å ³
<i>Z</i> = 6	Fragment, brown
<i>D_x</i> = 6.847 Mg m ⁻³	0.11 × 0.05 × 0.03 mm

Data collection

Bruker SMART APEX CCD diffractometer	493 independent reflections
<i>ω</i> scans	<i>R</i> _{int} = 0.045
Absorption correction: multi-scan (SADABS; Bruker, 1999)	<i>θ</i> _{max} = 36.32°
<i>T</i> _{min} = 0.054, <i>T</i> _{max} = 0.211	<i>h</i> = -13 → 15
2881 measured reflections	<i>k</i> = -13 → 15
	<i>l</i> = -18 → 17

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0272P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	(Δ/σ) _{max} < 0.001
<i>S</i> = 0.981	$\Delta\rho_{\text{max}} = 6.49 \text{ e Å}^{-3}$
493 reflections	$\Delta\rho_{\text{min}} = -4.57 \text{ e Å}^{-3}$
20 parameters	Extinction correction: SHELXL97
	Extinction coefficient: 0.00027 (5)

Compound (II)

Crystal data

Sr ₃ CdPtO ₆	Mo Kα radiation
<i>M_r</i> = 666.35	Cell parameters from 1517 reflections
Trigonal, <i>R</i> 3̄c	<i>a</i> = 9.6413 (4) Å
<i>a</i> = 9.6413 (4) Å	<i>c</i> = 11.5935 (7) Å
<i>c</i> = 11.5935 (7) Å	<i>V</i> = 933.29 (8) Å ³
<i>Z</i> = 6	Chunk, brown
<i>D_x</i> = 7.114 Mg m ⁻³	0.09 × 0.04 × 0.03 mm

Data collection

Bruker SMART APEX CCD diffractometer	505 independent reflections
<i>ω</i> scans	<i>R</i> _{int} = 0.036
Absorption correction: multi-scan (SADABS; Bruker, 1999)	<i>θ</i> _{max} = 36.35°
<i>T</i> _{min} = 0.091, <i>T</i> _{max} = 0.360	<i>h</i> = -15 → 8
2632 measured reflections	<i>k</i> = -16 → 15
	<i>l</i> = -19 → 9

Table 2

Selected geometric parameters (Å) for (II).

Sr—O ⁱ	2.529 (4) × 2	Cd—O	2.328 (4) × 6
Sr—O ⁱⁱ	2.622 (4) × 2	Cd—Pt	2.89837 (18) × 2
Sr—O ⁱⁱⁱ	2.635 (4) × 2	Pt—O	2.039 (4) × 6
Sr—O ^{iv}	2.739 (4) × 2		

 Symmetry codes: (i) $-x + y, -x, z$; (ii) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$; (iii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$; (iv) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	+ 3.1434 <i>P</i>
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.086	(Δ/σ) _{max} < 0.001
505 reflections	$\Delta\rho_{\text{max}} = 5.05 \text{ e Å}^{-3}$
19 parameters	$\Delta\rho_{\text{min}} = -3.56 \text{ e Å}^{-3}$

Systematic absences in the data sets for both compounds confirmed a *c* glide operation, indicating the space groups *R*3̄c and *R*3̄c. Preliminary powder X-ray diffraction showed the compounds to be isostructural with K₄CdCl₆ (space group *R*3̄c); 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^I and Cd^{II} 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: SHELXS97 (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

- Bergerhoff, G. & Schmitz-Dumont, O. (1956). *Z. Anorg. Allg. Chem.* **284**, 10–19.
- Bruker (1999). SMART (Version 5.611), SAINT (Version 6.02a), SHELXTL (Version 5.10) and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Claridge, J. B., Layland, R. C. & zur Loye, H.-C. (1997). *Acta Cryst.* **C53**, 1740–1741.
- Kaufman, G. S. (1967). *Inorganic Syntheses*, Vol. 9, edited by S. Y. Tyree Jr, pp. 182–185. New York: McGraw-Hill.
- Lampe-Önnerud, C. & zur Loye, H.-C. (1996). *Inorg. Chem.* **35**, 2155–2156.
- Nguyen, T. N., Giaquinta, D. M. & zur Loye, H.-C. (1997). *Chem. Mater.* **6**, 1642–1646.
- Randall, J. J. Jr & Katz, L. (1959). *Acta Cryst.* **12**, 519–521.
- Segal, N., Vente, J. F., Bush, T. S. & Battle, P. D. (1996). *J. Mater. Chem.* **6**, 395–401.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Smith, M. D. & zur Loye, H.-C. (2000). Unpublished results.
- Wilkinson, A. P., Cheetham, A. K., Kunnman, W. & Kwick, A. (1991). *Eur. J. Solid State Inorg. Chem.* **28**, 453–459.