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Ca_4PtO_6

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Abstract

Calcium platinum(IV) oxide has been synthesized from a flux and structurally characterized by single-crystal X-ray diffraction. It is isostructural with Sr_4PtO_6 [Randall & Katz (1959). *Acta Cryst.* **12**, 519–521] and Ba_4PtO_6 [Wilkinson & Cheetham (1989). *Acta Cryst.* C**45**, 1672–1674].

Comment

Compounds of the type $A_3A'BO_6$ have received considerable attention in the last few years because of their interesting magnetic properties (Nguyen, Lee & zur Loye, 1996) and their ability to stabilize high oxidation states (Carlson & Stacy, 1992). All structures reported so far have the rhombohedral K_4CdCl_6 structure (Bergerhoff & Schmitz-Dumont, 1956) or, for materials where A' = Cu, a monoclinic distortion (Wilkinson, Cheetham, Kunnman & Kvick, 1991; Hodeau *et al.*, 1992). Although the structures of Sr_4PtO_6 (Randall & Katz, 1959) and Ba_4PtO_6 (Wilkinson & Cheetham, 1989) have been solved, the structure of Ca_4PtO_6 has not been determined previously. However, it has been reported to be either orthorhombic (Cazya, 1970) or rhombohedral (McDaniel, 1972) and to be prone to twinning (Ohasato, Sugimura & Kageyama, 1981).

The structure consists of chains of alternating face-sharing Pt-centered octahedra and Ca-centered distorted trigonal prisms running parallel to the c axis, with the remaining Ca ions arranged between the columns (see Figs. 1 and 2). The PtO_6 octahedra are regular [Pt—O 2.8039 (6) Å and O—Pt—O 89.3 (2)–90.7 (2)°]. The $Ca1O_6$ trigonal prisms are also regular [Ca—O 2.8319 (6)–2.8320 (6) Å] though they exhibit a significant twisting distortion [φ = 18.0 (2)°] from an ideal eclipsed conformation. The Ca2–O square antiprisms are highly distorted [Ca—O 2.8415 (6)–2.8714 (7) Å].

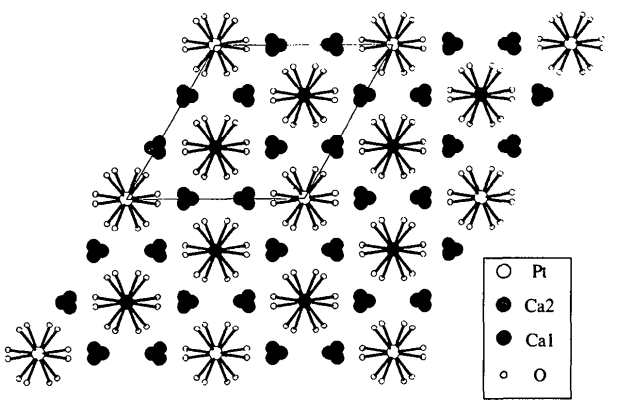

Fig. 1. A view of the structure of Ca_4PtO_6 down [001].

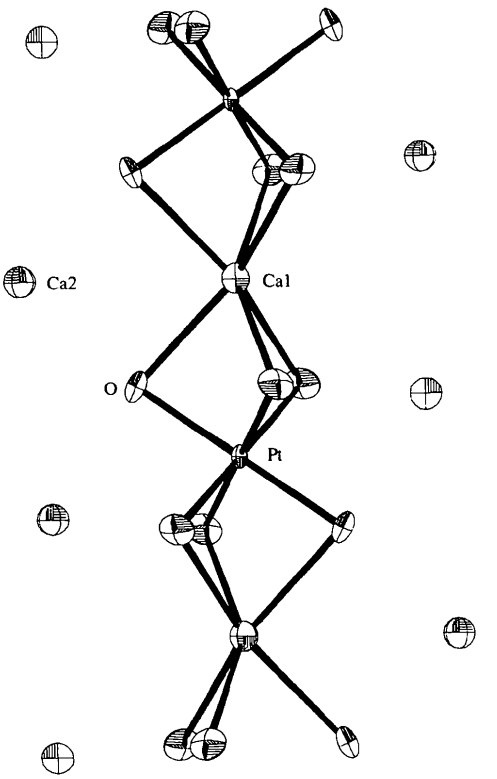

Fig. 2. The structure of a chain in Ca_4PtO_6 showing 50% probability displacement ellipsoids.

Experimental

Crystals of Ca_4PtO_6 were obtained by the reaction of platinum metal and CaO (molar ratio 1:2) in Na_2CO_3–H_2O for 24 h at 1198 K in an open ceramic crucible. The crystals were recovered mechanically.

Crystal data

Ca_4PtO_6
M_r = 451.41
Trigonal
$R\bar{3}c$
a = 9.332 (3) Å
c = 11.264 (2) Å
V = 849.5 (2) Å^3
Z = 6
D_x = 5.294 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 27.65–34.05°
μ = 28.248 mm^{-1}
T = 296.2 K
Irregular
0.08 × 0.06 × 0.05 mm
Black

Data collection

AFC-6*S* diffractometer	352 reflections with $F > 3\sigma(F)$
ω–2θ scans	$R_{int} = 0.047$
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)	$\theta_{max} = 34.97°$
	$h = 0 \rightarrow 13$
	$k = 0 \rightarrow 12$
$T_{min} = 0.717$, $T_{max} = 0.981$	$l = 0 \rightarrow 18$
496 measured reflections	3 standard reflections
481 independent reflections	every 150 reflections
	intensity decay: 9.14%

Refinement

Refinement on F	$\Delta\rho_{max} = 5.55$ e Å^{-3}
$R = 0.042$	$\Delta\rho_{min} = -4.85$ e Å^{-3}
$wR = 0.049$	Extinction correction: Zachariasen (1968)
$S = 3.282$	Extinction coefficient: 10.48
338 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
20 parameters	
$w = 1/\sigma^2(F)$	
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters (Å)*

Pt—O	2.8039 (6)	Ca2—O^{ii}	2.8415 (6)
Ca1—O	2.8320 (6)	Ca2—O^{iii}	2.8511 (6)
Ca1—O^{i}	2.8319 (6)	Ca2—O^{iv}	2.8714 (7)
Ca2—O	2.8475 (6)		

Symmetry codes: (i) $\frac{1}{3} + y, x - \frac{1}{3}, \frac{1}{6} - z$; (ii) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iii) $\frac{1}{3} + x - y, x - \frac{1}{3}, \frac{2}{3} - z$; (iv) $1 - y, x - y, z$.

The remaining residual electron density is concentrated around the Pt ion at a distance of 0.65 Å. Structure solution and refinement were performed on a Silicon Graphics INDIGO^2 computer using the *TEXSAN* (Molecular Structure Corporation, 1993) structure solution program library.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1172). Services for accessing these data are described at the back of the journal.

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Dibarium Magnesium Phosphate

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Abstract

$Ba_2Mg(PO_4)_2$ is found to be isostructural with $Ba_2Ni(PO_4)_2$. The structure can be described as a three-dimensional framework of MgO_6 octahedra and PO_4 tetrahedra generating tunnels which accommodate Ba atoms.

Comment

Compounds with the general formula $A_2Ni(PO_4)_2$, A = Sr, Ba, have been investigated recently because of their potential magnetic properties (Elbali, Boukhari, Holt & Aride, 1993; Elbali *et al.*, 1994). Most of the structural features of analogous diamagnetic compounds where Ni is replaced by Zn or Mg are still unknown, although the existence of such compounds was reported some time ago (Hoffman, 1965).

A powder pattern of $Ba_2Mg(PO_4)_2$, indexed from the approximate parameters measured from single-crystal diffraction photographs, showed it to be isostructural with $Ba_2Ni(PO_4)_2$. The systematic absences are consistent with space group $P2_1/n$. As in the case of $Ba_2Ni(PO_4)_2$, $Ba_2Mg(PO_4)_2$ has as a non-compact structure (23.6 Å^3 per O atom). The framework is based on bipolyhedral $MgP(1)O_8$ entities: the MgO_6 octahedron shares an edge with the $P(1)O_4$ tetrahedron (Fig. 1).

$P(1)O_4$ appears to be a fairly regular tetrahedron. The MgO_6 octahedron is slightly distorted because one of the two O atoms, O(12), forming the common edge is only weakly bound to the Mg atom: 0.19 valence units (v.u.) for O(12), compared to 0.36±0.02 v.u. for the other five. Inclusion of the sixth O atom in the coordination polyhedron of Mg is the result of a choice between two possible descriptions: distorted octahedron or square-based pyramid. The short distance