

Synthesis and Structure of Orthorhombic Cadmium Platinum Oxide, CdPt₃O₆

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Abstract. $M_r = 793.7$, orthorhombic, $Cmmm$, $a = 7.2144$ (6), $b = 10.190$ (1), $c = 3.1650$ (2) Å, $V = 232.67$ (6) Å³, $Z = 2$, $D_x = 11.33$ g cm⁻³, $\lambda(\text{Ag K}\alpha) = 0.5609$ Å, $\mu = 513.5$ cm⁻¹, $T = 293$ K, $F(000) = 660$, $R = 0.047$ for 417 unrejected reflections in the range $0.0849 < \sin \theta/\lambda < 0.8914$ Å⁻¹. Crystals of CdPt₃O₆ were grown by a hydrothermal technique. Bulk electrical-resistivity measurements on a pellet of compressed powder yielded values of $\rho(298 \text{ K}) = 0.03$ Ωm and $E_a = 0.04$ e V (1 e V = 1.60×10^{-19} J) in the range 5 to 298 K. This low resistivity is related to metal–metal distances of 3.165 Å in a structure which includes chains of edge-shared PtO₆ octahedra and columnar stacks of planar PtO₄ groups extending along [001].

Introduction. Compounds of the type $M^{2+}\text{Pt}_3\text{O}_6$ are of interest as hydrogenation catalysts (Shannon, 1972) and as fuel cell electrode catalysts (Carcia, Shannon & Staikos, 1981). They are also of interest as one of the few examples of oxide families containing divalent Pt. Other compounds containing Pt²⁺ are PtO (Westwood & Bennowitz, 1974), Na₂PtO₂ (Urland & Hoppe, 1972), Bi_{1.6}Pb_{0.4}PtO₄ (Boivin, Conflant & Thomas, 1976), K₃Pt₂O₄ (Zentgraf, Claes & Hoppe, 1980), and compounds of the type $M_x\text{Pt}_3\text{O}_4$ of which Na_xPt₃O₄ (Waser & McClanahan, 1951; Scheer, van Arkel & Heydig, 1955; Cahen, Ibers & Wagner, 1974; Schwartz, Prewitt, Shannon, Corliss, Hastings & Chamberland, 1982) is the most well known example.

Muller & Roy (1969) prepared polycrystalline CuPt₃O₆ using CuO and Pt black at 1163 K and 20 M Pa of O₂. Hoekstra, Siegel & Gallagher (1971) prepared polycrystalline samples of $M\text{Pt}_3\text{O}_6$ with $M = \text{Ni, Mg, Co, Zn, Cd, and Hg}$ using elevated pressure and temperature. Shannon (1972) prepared $M\text{Pt}_3\text{O}_6$ -type compounds with $M = \text{Ni, Co, Fe, Cu, Mg, Zn, and Cd}$ using elevated pressures and temperatures and in addition was able to prepare crystals of

CdPt₃O₆, CuPt₃O₆, and MnPt₃O₆ using a hydrothermal technique. Cahen, Ibers & Wagner (1974) showed later that CdPt₃O₆ could be prepared under 10⁵ Pa of O₂ at 873 K. In this paper we report the synthesis, crystal structure and electrical-resistivity measurements on CdPt₃O₆.

Experimental. Crystals of CdPt₃O₆ were grown hydrothermally. In a typical experiment 0.674 g PtCl₂, 0.326 g CdO, 0.500 g KClO₃, and 1 ml H₂O were sealed in a Pt tube 0.95 cm in diameter and 12.5 cm long. This tube was heated to 973 K at 300 M Pa for 24 h and cooled slowly to room temperature. The product consisted of Pt crystals and black needles approximately 0.02 × 0.02 × 0.2 mm. X-ray precession photographs indicated the unit-cell dimensions $a = 7.21$, $b = 10.19$, and $c = 3.165$ Å with systematic absences $hkl: h + k \neq 2n$ for possible space groups $Cmmm$, $Cmm2$, or $C222$. X-ray diffraction patterns obtained with a Guinier–Hagg focusing camera ($r = 4$ cm), monochromatic Cu Kα₁ radiation ($\lambda = 1.54051$ Å), KCl ($a = 6.2931$ Å) as internal standard; line positions on the film determined to ± 5 μm with a David Mann film reader; intensities estimated by oscilloscopic comparison of film density with the strongest line of the pattern; cell dimensions (see *Abstract*) found by least-squares refinement. With the exception of c , these values are in good agreement with those of Hoekstra, Siegel & Gallagher (1971). It is probable that some of the weak reflections noted by these authors were caused by an impurity and that the phase prepared by them is identical to CdPt₃O₆ described above. Electron microprobe analyses performed by Micron Inc. of Wilmington, Delaware, using Pt and CdMoO₄ as standards, resulted in Pt 74.4 and Cd 14.9% compared to the theoretical values of 73.74 and 14.16% for CdPt₃O₆.

In order to obtain the conductivity of CdPt₃O₆, a polycrystalline sample was prepared by sealing 0.28 g CdO, 1.31 g PtO₂, and 2 drops of aq. NH₄OH in a gold tube 0.95 cm diameter × 12.5 cm. The tube and contents were heated to 973 K and 200 M Pa for 24 h

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and quenched. The product was heated in *aqua regia* for 12 h, washed and dried. An X-ray diffraction pattern showed only broad lines of CdPt_3O_6 . This sample was placed in a cylindrical gold container, heated at 973 K and 1 GPa for 1 h and cooled at 150 K h^{-1} to room temperature. The resulting dense black pellet was cut into parallelepipeds to be used for conductivity measurements. X-ray examination showed only CdPt_3O_6 . A four-probe measurement of resistivity indicated $\rho(298 \text{ K}) = 0.03 \text{ } \Omega\text{m}$ with an activation energy of resistance of 0.04 eV in the temperature range 5 to 298 K. This compares with values of $0.1 \text{ } \Omega\text{m}$ and 0.04 eV reported by Cahen, Ibers & Wagner (1974) for $\text{Cd}_x\text{Pt}_3\text{O}_6$.

Three-dimensional X-ray diffraction intensities were collected with a Picker computer-controlled diffractometer, graphite-monochromatized $\text{Ag K}\alpha$ radiation. The sample was a single-crystal fiber approximating a cylinder 0.030 mm in diameter and 0.160 mm long. In all, 420 diffraction intensities were recorded, corrected for absorption assuming a cylindrical shape with a linear absorption coefficient of 366 cm^{-1} , and reduced to structure factors. Data were collected in the range $0.0849 < \sin \theta/\lambda < 0.8914 \text{ } \text{Å}^{-1}$.

The program *RFINE* (L. W. Finger, Geophysical Laboratory) was used for least-squares refinement of the structure. This program minimizes the function $w(|F_o| - |F_c|)^2$, where the weight, w , for each reflection is set equal to $1/\sigma_F^2$. Values for σ_F^2 were calculated from counting statistics and modified by an estimate of the fluctuation of the incident X-ray beam. Scattering factors for neutral atoms were taken from Cromer & Waber (1965), and real and imaginary anomalous-dispersion coefficients for Ag X radiation were taken from Cromer (1965).

Although we thought originally that the formula for this material was CdPt_2O_4 , analysis of Patterson maps soon showed that the structure contained both octahedral and square-planar platinum coordination groups with twice as many octahedral groups per cell. This required that the formula be written as $\text{CdPt}^{2+}\text{Pt}^{4+}_2\text{O}_6$, a finding soon confirmed in least-squares refinement. The final cycle of refinement resulted in an R factor of 0.047 for 417 unrejected reflections, a weighted R of 0.058,* and a ratio of maximum least-squares shift to error of < 0.0004 . The final refined parameters are given in Table 1. Three reflections (040, 400, 021) were removed because they were strongly affected by secondary extinction.

Discussion. The crystal structure of CdPt_3O_6 (Fig. 1) consists of planar units with all atoms situated on

Table 1. Positional parameters and isotropic temperature factors for orthorhombic CdPt_3O_6 ($Cmmm$)

Cd	2(b)	$\frac{1}{2}$	0	0	y: O(1)	0.337 (1)*
Pt(1)	2(a)	0	0	0	x: O(2)	0.208 (1)
Pt(2)	4(f)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	y: O(2)	0.129 (1)
O(1)	4(f)	0	y	$\frac{1}{2}$	B: Cd	0.52 (3)†
O(2)	8(p)	x	y	0	B: Pt(1)	0.14 (2)‡
					B: Pt(2)	0.11 (2)‡
					B: O(1)	1.0 (2)‡
					B: O(2)	0.7 (1)‡
					R	0.047
					R_w	0.058

* Errors in parentheses.

† Isotropic temperature factor in Å^2 as calculated from anisotropic temperature factor coefficients ($B = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$).

‡ Isotropic temperature factor (Å^2) as refined.

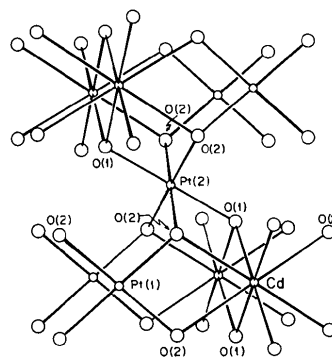


Fig. 1. The crystal structure of CdPt_3O_6 .

mirror planes perpendicular to the c axis. There are distinct coordination polyhedra for each of the three distinct cation species. Pt^{2+} resides in a planar site surrounded by four O(1) atoms with Pt—O(1) distances of $1.99 (1) \text{ Å}$. Octahedrally coordinated Pt^{4+} has four Pt—O(2) bonds of $2.03 (1) \text{ Å}$ and two Pt—O(1) bonds of $2.01 (1) \text{ Å}$. The Cd^{2+} cation resides in an eight-coordinated site made up of interpenetrating O(1) and O(2) rectangular planes. Bond lengths are $2.29 (1) \text{ Å}$ for Cd—O(1) and $2.48 (1) \text{ Å}$ for Cd—O(2).

A most significant feature of the CdPt_3O_6 structure is the short metal—metal distance of 3.165 Å along the [001] direction. This short distance is responsible for the low resistivity and activation energy of semiconducting CdPt_3O_6 . Short metal—metal distances perpendicular to the plane of planar PtO_4 groups are characteristic of a class of one-dimensional conductors which include partially oxidized tetracyanoplatinates, e.g. $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ (see, for example, Williams & Schultz, 1979). The anisotropy of this metal—metal interaction, its relationship with the crystal chemistry and physical properties of CdPt_3O_6 and other compositions with this structure, and further details of the structure will be reported soon (Schwartz, Parise, Prewitt & Shannon, 1983; Schwartz & Parise, 1982).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38209 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Identification of Polytypes of MX_2 -Type Compounds. II. Structures of 20 New Polytypes of Cadmium Iodide*

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Abstract. The identification of polytypes of crystals of MX_2 type using the intensity diagrams of the $10.l$ and $10.\bar{l}$ reflexions is discussed. It is shown that these diagrams enable some standardization of the structures of simple polytypes, classifying them into structural series. The structures of 20 new polytypes of CdI_2 obtained from solutions have been determined: $16H_8$: $(t)_3f1o_1tf5$; $20H_{12}$: $(t)_5f4(t)_3f5$; $22H_6$: $(t)_7f1f1tf5$; $22H_7$: $(t)_5f2(o)_2f2tf4$; $22H_8$: $tf2(o)_2f2f1f2(t)_2f1f1$; $26H_5$: $(t)_7f2(o)_2f2tf4$; $28H_5$: $(t)_9f4(t)_3f5$; $38H_2$: $(t)_{17}f1f2$; $40H_2$: $(t)_{13}f4(t)_5f5$; $40H_3$: $tf1(o)_2f1(t)_{13}f2f2$; $24R_3$: $f1f1f2f2$; $48R_2$: $f1f1tf2f1(t)_2f5$; $48R_3$: $(t)_4f4(t)_2f5$; $54R_3$: $f1f1f2(o)_3f1tf5$; $66R_1$: $f1f1(t)_5f2f1f2f2$; $66R_2$: $f1f1(t)_5f2of1f5$; $84R_3$: $f1f1(tf2f1)_2(t)_4f2f2$; $84R_4$: $f1(o)_6f1(t)_4f2f2$; $96R_1$: $(t)_8f4(t)_6f5$; $120R_1$: $(t)_{10}f4(t)_8f5$; 18 already known polytypes have also been recognized. The uniqueness of the structures of polytypes determined by the standard a -axis oscillation method is discussed.

Introduction. The main source of information on the organization of polytypic crystals is the knowledge of the structures of the periodic modifications. In real polytypic crystals, the number of geometrically possible different modifications for a given material is unlimited; however, only some specific structures do occur.

Recently, we discussed the problem of the identification of MX_2 polytypes, presenting some simple rules of construction for the polytype cells (Pałosz & Przedmojski, 1980; Pałosz, 1980, 1982). The basis for the determination of these rules was the analysis of the stacking of the molecular layers in the identified polytypes of CdI_2 , PbI_2 and $Ti_{1.2}S_2$ (Pałosz, 1983). In this work we present the results of the analysis of the structures of about 300 polytypes of CdI_2 . We identified the stacking of layers in the cells of 20 new polytypes, recognizing also the structures of 18 already known polytypes and determining the period and type of cell (hexagonal or rhombohedral) for 250 polytypes. By means of these data we established some new construction rules for polytype cells of CdI_2 , which enable some standardization in the identification of a number of simple multilayer polytypes. The uniqueness of the structures determined for polytypes by standard X-ray analysis is also discussed.

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