The compound was prepared by reaction of the elements in the appropriate ratio for SnZrS₃. The mixture of elements was heated for 1 week at a temperature of 1073 K in an evacuated quartz tube. A grey-black powder was obtained. The powder pattern (Guinier-Hägg, Jungner Instruments, Cu $K\alpha_1$ radiation) was indexed using an orthorhombic unit cell with dimensions $a = 9.183\,(2)$, $b = 3.7195\,(5)$ and $c = 13.829\,(3)$ Å, which are close to those of SnHfS₃ (Wiegers *et al.*, 1989). Single crystals were grown by vapour transport using chlorine as the transport agent. Red needle-shaped crystals grew at the low side of the temperature gradient 923–823 K. The needle axis corresponds to the b axis of the orthorhombic unit cell.

Unit-cell parameters were determined from a least-squares treatment of the *SET4* setting angles (de Boer & Duisenberg, 1984) of 20 reflections with $32.90 < i < 34.33$. The unit cell was identified as orthorhombic, space group *Pnma*. Reduced-cell calculations did not indicate any higher metrical lattice symmetry (Spek, 1988).

Scattering factors were those given by Cromer & Mann (1968) and anomalous-dispersion factors taken from Cromer & Liberman (1970) were included in *F*. Calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program package *Xtal* (Hall & Stewart, 1990). Data collection: *CAD-4* (Enraf-Nonius, 1988). Cell refinement: *SET4*. Data reduction: *EUCLID* (Spek, 1982). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Geometric calculations: *PLATON* (Spek, 1990). Molecular graphics: *PLUTO92* (Meetsma, 1992; Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic thermal parameters, complete geometry and powder diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71388 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1082]

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Redetermination of the β-Ca₂P₂O₇ Structure

S. Boudin, A. Grandin, M. M. Borel, A. Leclaire and B. Raveau

Laboratoire CRISMAT/ISMRa, Université de Caen, Boulevard du Maréchal Juin, 14050 Caen CEDEX, France

Abstract

β Dicalcium diphosphate is composed of eclipsed P₂O₇ groups linked through Ca^{2+} cations. The P—O_b bonds involving the bridging O atoms are longer [average 1.620 (5) Å] than the others [average 1.517 (5) Å]. As the 'O₄' tetrahedra are almost regular the displacement of the P atoms involves two sets of O—P—O angles: O—P—O ≃ 112.7 (2) and O—P—O_b ≃ 106.0 (2)°.

Comment

The structure was first studied by Webb (1966) in order to establish the geometry of the P₂O₇ groups and especially to determine accurately the P—O—P angle. During our studies of the Ca–V–P–O system by solid-state chemistry, we obtained single crystals of β-Ca₂P₂O₇. As the structure was established previously using multiple film techniques, we performed a new data collection with an automatic diffractometer in order to obtain the atomic parameters more accurately.

The redetermination of the structure confirms that it is composed of eclipsed P₂O₇ groups linked through Ca^{2+} cations (Fig. 1). The mean interatomic P—O distances are not significantly different from those previously observed within the range of 5σ, but are spread over a range of values narrower than in the first study, *e.g.* 0.01 Å for P—O distances involving the bridging O atoms and 0.05 Å for the other P—O distances instead of 0.05 and 0.08 Å, respectively. The ranges of angles are the same in the two studies. The Ca—O distances are the same as previously found within 3σ except for Ca(1)—O(4)

and Ca(3)—O(5) which differ by 10σ and 6σ, respectively. The Ca(1) atom is linked to eight O atoms which delimit a bicapped trigonal prism. Ca(2) is linked to nine O atoms which form a tricapped trigonal prism. The Ca(3) and Ca(4) atoms are surrounded by seven O atoms which delimit a distorted pentagonal bipyramid.
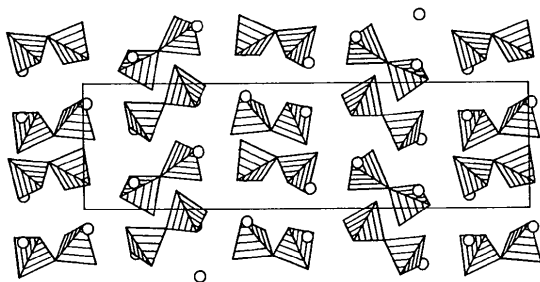

Fig. 1. Projection of the structure along the a axis

Experimental

Crystal data

$Ca_2O_7P_2$	Cell parameters from 25
$M_r = 254.1$	reflections
Tetragonal	$\theta = 18\text{-}22°$
$P4_1$	$\mu = 2.63 \text{ mm}^{-1}$
$a = 6.6858\ (8)$ Å	$T = 294$ K
$c = 24.147\ (3)$ Å	Rectangular
$V = 1079.4\ (4)$ Å^3	$0.129 \times 0.103 \times 0.051$ mm
$Z = 8$	Yellow
$D_x = 3.127$ Mg m^{-3}	Crystal source: solid-state
Mo $K\bar{\alpha}$ radiation	chemistry
$\lambda = 0.71073$ Å	

Data collection

Enraf-Nonius CAD-4	$\theta_{max} = 45°$
diffractometer	$h = 0 \rightarrow 13$
Bisect scans	$k = 0 \rightarrow 13$
Absorption correction:	$l = 0 \rightarrow 48$
none	3 standard reflections
5017 measured reflections	frequency: 50 min
5017 independent reflections	intensity variation: 0.4%
1791 observed reflections	
$[I > 3\sigma(I)]$	

Refinement

Refinement on F	Extinction correction:
$R = 0.031$	Zachariasen
$wR = 0.034$	Extinction coefficient:
$S = 1.001$	4.62×10^{-8}
1791 reflections	Atomic scattering factors
198 parameters	from *International Tables*
$w = F(\sin\sigma/\lambda)$	*for X-ray Crystallography*
$(\Delta/\sigma)_{max} = 0.004$	(1974, Vol. IV)
$\Delta\rho_{max} = 0.7$ e Å^{-3}	
$\Delta\rho_{min} = -0.7$ e Å^{-3}	

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ca(1)	0.1374 (2)	0.2313 (2)	0.0	0.73 (1)
Ca(2)	0.1591 (2)	0.5447 (2)	0.24262 (5)	0.71 (1)
Ca(3)	0.7895 (2)	0.7337 (2)	0.13802 (4)	0.67 (1)
Ca(4)	0.3627 (2)	0.1054 (2)	0.13548 (4)	0.63 (1)
P(1)	0.6213 (2)	0.3078 (2)	0.02345 (6)	0.47 (2)
P(2)	0.8673 (2)	0.2534 (2)	0.12431 (5)	0.42 (2)
P(3)	0.0463 (2)	0.7148 (2)	0.01863 (6)	0.47 (2)
P(4)	0.2873 (2)	0.6462 (2)	0.12074 (5)	0.50 (2)
O(1)	0.4607 (6)	0.1584 (6)	0.0426 (2)	0.83 (6)
O(2)	0.7727 (6)	0.1984 (6)	−0.0133 (2)	0.89 (6)
O(3)	0.5303 (7)	0.4921 (6)	−0.0001 (2)	1.16 (6)
O(4)	0.7395 (6)	0.3776 (6)	0.0789 (2)	0.65 (5)
O(5)	0.7364 (6)	0.0873 (6)	0.1469 (2)	0.77 (6)
O(6)	1.0519 (6)	0.1769 (6)	0.0953 (2)	0.68 (5)
O(7)	0.8994 (6)	0.4088 (6)	0.1695 (2)	0.80 (6)
O(8)	−0.1463 (6)	0.7907 (6)	0.0433 (2)	0.70 (5)
O(9)	0.1855 (6)	0.8795 (6)	−0.0011 (2)	0.90 (6)
O(10)	0.0229 (6)	0.5542 (6)	−0.0249 (2)	0.79 (6)
O(11)	0.1582 (6)	0.5873 (6)	0.0666 (2)	0.83 (6)
O(12)	0.3450 (7)	0.4526 (6)	0.1474 (2)	0.90 (6)
O(13)	0.4622 (6)	0.7756 (6)	0.1015 (2)	0.78 (6)
O(14)	0.1474 (6)	0.7722 (6)	0.1572 (2)	0.71 (6)

Table 2. *Distances* (Å) *and angles* (°) *in the* PO_4 *tetrahedra and main* Ca—O *distances* (Å)

P(1)—O(1)	1.537 (5)	O(11)—O(14)	2.514 (6)
P(1)—O(2)	1.533 (5)	O(12)—O(14)	2.524 (6)
P(1)—O(3)	1.487 (5)	O(13)—O(14)	2.498 (6)
P(1)—O(4)	1.625 (4)	Ca(1)—O(1)	2.443 (5)
O(1)—O(2)	2.499 (6)	Ca(1)—O(2^i)	2.469 (5)
O(1)—O(3)	2.501 (6)	Ca(1)—O(5^{ii})	2.522 (4)
O(2)—O(3)	2.566 (6)	Ca(1)—O(6^i)	2.400 (4)
O(1)—O(4)	2.529 (6)	Ca(1)—O(7^{ii})	2.799 (4)
O(2)—O(4)	2.540 (6)	Ca(1)—O(9^{iii})	2.374 (5)
O(3)—O(4)	2.487 (6)	Ca(1)—O(10)	2.368 (5)
P(2)—O(4)	1.619 (4)	Ca(1)—O(11)	2.876 (5)
P(2)—O(5)	1.516 (4)	Ca(2)—O(1^{iv})	2.505 (4)
P(2)—O(6)	1.508 (4)	Ca(2)—O(2^{iv})	2.839 (5)
P(2)—O(7)	1.522 (4)	Ca(2)—O(3^v)	2.340 (5)
O(4)—O(5)	2.541 (6)	Ca(2)—O(7^i)	2.638 (4)
O(4)—O(6)	2.514 (6)	Ca(2)—O(8^{vi})	2.424 (4)
O(5)—O(6)	2.521 (6)	Ca(2)—O(9^v)	2.421 (5)
O(4)—O(7)	2.443 (6)	Ca(2)—O(12)	2.684 (5)
O(5)—O(7)	2.471 (6)	Ca(2)—O(13^v)	2.722 (5)
O(6)—O(7)	2.579 (6)	Ca(2)—O(14)	2.564 (4)
P(3)—O(8)	1.507 (4)	Ca(3)—O(2^v)	2.397 (5)
P(3)—O(9)	1.518 (5)	Ca(3)—O(4)	2.796 (4)
P(3)—O(10)	1.511 (4)	Ca(3)—O(5^{vii})	2.400 (5)
P(3)—O(1)	1.621 (4)	Ca(3)—O(7)	2.416 (4)
O(8)—O(9)	2.534 (6)	Ca(3)—O(8^{viii})	2.358 (4)
O(8)—O(10)	2.548 (6)	Ca(3)—O(13)	2.376 (5)
O(9)—O(10)	2.498 (6)	Ca(3)—O(14^{viii})	2.451 (4)
O(8)—O(11)	2.512 (6)	Ca(4)—O(1)	2.364 (4)
O(9)—O(11)	2.554 (16)	Ca(4)—O(5)	2.516 (4)
O(10)—O(11)	2.398 (6)	Ca(4)—O(6^i)	2.343 (5)
P(4)—O(11)	1.615 (4)	Ca(4)—O(10^v)	2.301 (4)
P(4)—O(12)	1.497 (5)	Ca(4)—O(12)	2.342 (5)
P(4)—O(13)	1.527 (4)	Ca(4)—O(13^{iii})	2.445 (5)
P(4)—O(14)	1.536 (4)	Ca(4)—O(14^{iii})	2.704 (4)
O(11)—O(12)	2.486 (6)	P(1)—P(2)	2.961 (2)
O(11)—O(13)	2.535 (6)	P(3)—P(4)	2.981 (2)
O(12)—O(13)	2.551 (6)		
O(1)—P(1)—O(2)	109.0 (3)	O(8)—P(3)—O(10)	115.2 (3)
O(1)—P(1)—O(3)	111.6 (3)	O(8)—P(3)—O(11)	106.8 (2)
O(1)—P(1)—O(4)	106.2 (2)	O(9)—P(3)—O(10)	111.1 (3)
O(2)—P(1)—O(3)	116.4 (3)	O(9)—P(3)—O(11)	108.8 (2)
O(2)—P(1)—O(4)	107.1 (2)	O(10)—P(3)—O(11)	99.9 (2)
O(3)—P(1)—O(4)	106.0 (2)	O(11)—P(4)—O(12)	106.0 (2)
O(4)—P(2)—O(5)	108.3 (2)	O(11)—P(4)—O(13)	107.6 (2)

O(4)—P(2)—O(6)	107.0 (2)	O(11)—P(4)—O(14)	105.8 (2)
O(4)—P(2)—O(7)	102.1 (2)	O(12)—P(4)—O(13)	115.1 (3)
O(5)—P(2)—O(6)	113.0 (3)	O(12)—P(4)—O(14)	112.6 (2)
O(5)—P(2)—O(7)	108.9 (2)	O(13)—P(4)—O(14)	109.2 (2)
O(6)—P(2)—O(7)	116.7 (2)	P(1)—O(4)—P(2)	131.9 (3)
O(8)—P(3)—O(9)	113.8 (3)	P(3)—O(11)—P(4)	134.2 (3)

Symmetry codes: (i) $x - 1, y, z$; (ii) $y, 1 - x, z - \frac{1}{4}$; (iii) $x, y - 1, z$; (iv) $-y, x, \frac{1}{4} + z$; (v) $1 - y, x, \frac{1}{4} + z$; (vi) $1 - y, 1 + x, \frac{1}{4} + z$; (vii) $x, 1 + y, z$; (viii) $1 + x, y, z$.

A diffractometer with graphite monochromator was used to collect data; the θ scan width was $(1.00 + 0.35\tan\theta)°$ with a ω-$4/3\theta$ scan. Calculations were performed using a MicroVAX II computer with the *SDP* system (B. A. Frenz & Associates, Inc., 1982). The figure was prepared using *STRUPLO*84 (Fischer, 1985).

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Chlorure de Triamminetrichloroplatine(IV) Chlorure d'Ammonium Monohydrate

L. Balde, P. Khodadad et N. Rodier

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, 5 Rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France

R. Julien

Laboratoire de Chimie Bioorganique et Bioinorganique, Faculté de Pharmacie, 1 Rue des Louvels, 80000 Amiens CEDEX, France

Abstract

The structure of ammonium triamminetrichloroplatinum dichloride monohydrate consists of Cl^- anions, NH_4^+ and $[Pt(NH_3)_3Cl_3]^+$ cations and water molecules. The Pt atom displays slightly distorted octahedral coordination. The bond lengths Pt—Cl and Pt—N are in the ranges 2.304 (5)–2.315 (4) Å

and 2.03 (2)–2.05 (2) Å, respectively. Numerous hydrogen bonds, O—H⋯Cl, N—H⋯O and N—H⋯Cl, take part in the cohesion of the structure.

Commentaire

Le produit étudié a été obtenu en ajoutant un excès d'acide chlorhydrique 5 *M* à un mélange équimolaire de $[Pt(NH_3)_4]Cl_2$ et de *cis*-$Pt(NH_3)_2Cl_2$. On chauffe à l'ébullition à reflux pendant 24 h. Après refroidissement, l'excès de HCl s'évapore dans une atmosphère limitée et est absorbé par une solution de KOH. Le cristal utilisé est issu de la préparation. La détermination de sa structure a été entreprise dans le cadre de la synthèse et de l'étude des dérivés du platine(II) et du platine(IV).

Le cation $[Pt(NH_3)_3Cl_3]^+$ a la forme d'un octaèdre légèrement déformé. Les distances Pt—Cl vont de 2,304 (5) à 2,315 (4) Å et les distances Pt—N de 2,03 (2) à 2,05 (2) Å. Elles sont partiquement identiques à leurs homologues respectives dans le *cis-cis-trans*-$PtCl_2(NH_3)_2(OH)_2.H_2O_2$ (Vollano, Blatter & Dabrowiak, 1984) ou dans le tétrachloroplatinate(II) de *trans*-dichlorobis(propanediamine-1,3)platine(IV) (Delafontaine, Toffoli, Khodadad & Rodier, 1988). Les angles formés par deux droites joignant l'atome métallique à deux atomes présents sur les sommets de l'octaèdre sont compris entre 87,6 (5) et 92.8 (5)° lorsque ces atomes sont contigus et entre 178,5 (2) et 179,8 (2)° lorsqu'ils sont opposés.

Les ions chlorure Cl(4) et Cl(5) ont chacun pour proches voisins six entités chimiques. Cl(4) est entouré d'une molécule d'eau, de quatre coordinats NH_3 et d'un cation NH_4^+. Autour de Cl(5), on trouve trois NH_3 et trois NH_4^+. Les atomes d'azote et d'oxygène dans le premier cas, d'azote dans le second réalisent des octaèdres très déformés. La distance Cl(4)—O est égale à 3,31 (2) Å et les distances Cl(4)—N et Cl(5)—N sont comprises entre 3,19 (2) et 3,39 (2) Å. Les voisins immédiats de H_2O sont quatre atomes de chlore, deux groupements NH_3 et un cation NH_4^+ et ceux de NH_4^+ sept atomes de
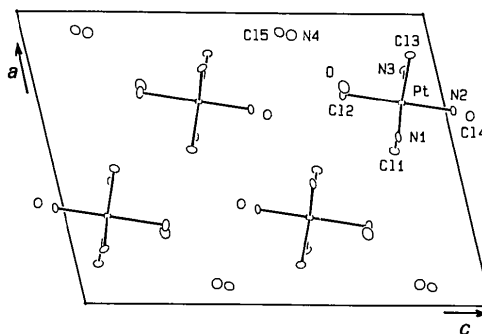

Fig. 1. Projection de la structure sur la face (010) et noms des atomes de l'unité asymétrique.