

Ces deux structures présentent deux différences essentielles:

- remplacement de l'oxygène par du soufre.
- saturation du site cationique, occupé, ici, par le mélange désordonné (Ca,La).

Disposant des deux structures cristallines isotypes: $\text{La}_{3,33}\text{Ga}_6\text{O}_2\text{S}_{12}$ et $\text{Ca}_2\text{La}_2\text{Ga}_6\text{S}_{14}$, il est maintenant possible d'expliquer la variation de paramètres observée dans le système formé entre ces deux corps (qui étaient, alors, considérés comme totalement soufrés). On observe une solution solide restreinte à partir de chacun de ces deux corps et une nette discontinuité entre les deux composés. Il en résulte qu'il n'y a pas de substitution progressive et continue de l'oxygène par le soufre au sein de ce réseau.

Finalement, dans l'état actuel de nos connaissances, en dehors des silicates, la structure type mélilite peut correspondre aux trois formules générales suivantes, sans intermédiaires continus:

- complètement oxygéné: ex.: $\text{Ca}_2\text{La}_2\text{Ga}_6\text{O}_{14}$
- complètement soufré: ex.: $\text{Ca}_2\text{La}_2\text{Ga}_6\text{S}_{14}$
- partiellement oxygéné: ex.: $\text{La}_{3,33}\text{Ga}_6\text{O}_2\text{S}_{12}$

On ne peut actuellement envisager l'existence de l'homologue complètement soufré de ce dernier composé.

Références

- BECKER, P. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
 BUSING, W. R. (1971). *Acta Cryst.* **A27**, 683–684.
International Tables for X-ray Crystallography (1974). Tome IV, pp. 71–78. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)
 ISMATOV, A. A. (1970). *Uzb. Khim. Zh. SSSR Neorg. Khim.* **14**, 17–19.
 ISMATOV, A. A., KOLESOVA, V. A. & PIRJUTKO, M. M. (1970). *Izv. Akad. Nauk SSSR Neorg. Mater.* **6**, 1361–1364.
 LOIREAU-LOZAC'H, A. M., GUITTARD, M. & FLAHAUT, J. (1972). *C. R. Acad. Sci. Sér. C*, **275**, 809–812.
 LOIREAU-LOZAC'H, A. M., GUITTARD, M. & FLAHAUT, J. (1973). *Mater. Res. Bull.* **8**, 75–76.
 MAZURIER, A., GUITTARD, M. & JAULMES, S. (1982). *Acta Cryst.* **B38**, 379–382.
 MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
 SMITH, J. V. (1959). *Am. Mineral.* **38**, 643–646.
 TOROPOV, N. A. & ISMATOV, A. A. (1970). *Izv. Akad. Nauk SSSR Neorg. Mater.* **6**, 590–593.

Acta Cryst. (1987). **C43**, 1861–1863

Structure of Tantalum Cadmium Diphosphate, $\text{Ta}_2\text{Cd}(\text{P}_2\text{O}_7)_3$

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(Received 8 March 1987; accepted 22 May 1987)

Abstract. Cadmium ditantalum tris(diphosphate), $M_r = 996.12$, orthorhombic, $Pnam$ (D_{2h}^{16}), $a = 13.094$ (10), $b = 8.365$ (8), $c = 15.796$ (12) Å, $V = 1730.2$ (3.9) Å³, $Z = 2$, $D_x = 3.823$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5608$ Å, $\mu = 8.06$ mm⁻¹, $F(000) = 1808$, $T = 293$ K, final $R = 0.023$ for 1734 independent observed reflexions. The atomic arrangement, mainly characterized by independent TaO_6 and CdO_6 octahedra interconnected by two kinds of P_2O_7 groups, is related to the orthorhombic $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ diphosphate. One of the P_2O_7 groups has a rather rare mirror configuration.

Introduction. We have previously described some mixed condensed phosphates in the systems P_2O_5 – MO – $\text{M}'\text{O}_5$ ($M' = \text{Nb}$ or Ta): $\text{Nb}_2\text{CaO}(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$ (Averbuch-Pouchot, 1987), $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ and $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$ (Averbuch-Pouchot & Durif, 1987). Chemical preparations of such compounds, generally elaborated by flux methods, are not significantly

different from those used for synthesizing highly condensed phosphoric anions (long-chain polyphosphates for instance) in systems such as P_2O_5 – MO – $\text{M}'_2\text{O}_3$ or P_2O_5 – M_2O – $\text{M}'\text{O}$. In spite of these similarities in the chemical syntheses we have never observed the formation of phosphoric anions with a condensation larger than four. This observation seems to confirm the assumption made by Linde, Gorbunova, Lavrov & Tananaev (1980) who established that the limit of the anion condensation for niobium phosphates is the tetrapoly state. The present work is devoted to the crystal structure determination of $\text{Ta}_2\text{Cd}(\text{P}_2\text{O}_7)_3$.

Experimental. Crystals were obtained by introducing 4.5 g of Ta_2O_5 and 1.8 g of CdCO_3 into 30 cm³ of H_3PO_4 (85%). The mixture was heated to 823 K during three days and slowly cooled to room temperature. The crystals were separated by washing out the excess of phosphoric flux with hot water. They appeared as light-pink elongated octahedra. Density not measured.

0.24 × 0.18 × 0.19 mm crystal fragment. Philips PW 1100 diffractometer, graphite monochromator. Systematic absences: $Ok_l: k+l=2n$; $h0l: h=2n$. 20 reflexions ($9.5 < \theta < 12^\circ$) for refining unit-cell dimensions. ω scan, multiple scan: 3. 2503 reflexions measured ($3 < \theta < 30^\circ$), hkl , $h_{\max}=20$, $k_{\max}=14$, $l_{\max}=22$. Scan width 1.30° , scan speed $0.03^\circ \text{ s}^{-1}$, total background measuring time 16 s. Two intensity and orientation reference reflexions (526 and $\bar{5}\bar{2}\bar{6}$) every 2 h, no variation. Lorentz-polarization correction, no absorption correction. Classical method (Patterson function and Fourier syntheses) used for structure determination. Anisotropic full-matrix least-squares

refinement (on F). Unit weights. Final refinement with 1734 reflexions corresponding to $I > 9\sigma_I$. Final $R = 0.023$ ($wR = 0.025$). For the complete set of 2503 reflexions $R = 0.032$. $S = 3.951$. Max. $\Delta/\sigma = 0$. Max. peak height in final difference Fourier synthesis $3.03 \text{ e } \text{\AA}^{-3}$. Extinction coefficient refined to $g = 2.16 \times 10^{-9}$ (Stout & Jensen, 1968). Scattering factors for neutral atoms and f' , f'' from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1977) SDP used for all calculations. Final atomic coordinates and B_{eq} are reported in Table 1.* Computer used: PDP 11/70.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44087 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and B_{eq} for $\text{Ta}_2\text{Cd}(\text{P}_2\text{O}_7)_3$

$$B_{\text{eq}} = \frac{4}{3} \sum_i \beta_{ij} a_j \cdot a_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
Ta	0.86564 (2)	0.16207 (3)	0.91481 (2)	0.797 (5)
Cd	0.85109 (5)	0.17504 (9)	$\frac{1}{2}$	1.06 (2)
P(1)	0.0283 (1)	0.2051 (2)	0.4172 (1)	0.97 (3)
P(2)	0.1962 (1)	0.4412 (2)	0.4291 (1)	0.95 (4)
P(3)	0.9689 (2)	0.7870 (3)	$\frac{1}{2}$	0.98 (6)
P(4)	0.2879 (2)	0.9201 (3)	$\frac{1}{2}$	0.99 (6)
O(E11)	0.5351 (5)	0.7596 (9)	0.6518 (5)	3.2 (2)
O(E12)	0.4703 (5)	0.3367 (9)	0.0010 (4)	3.2 (2)
O(E13)	0.0994 (4)	0.0647 (6)	0.1024 (3)	1.4 (1)
O(L12)	0.4029 (4)	0.8427 (9)	0.5467 (5)	3.1 (2)
O(E21)	0.2354 (6)	0.3994 (11)	0.3471 (5)	3.8 (2)
O(E22)	0.8368 (5)	0.3849 (6)	0.9390 (4)	2.0 (2)
O(E23)	0.7654 (5)	0.0930 (11)	-0.0044 (5)	3.8 (2)
O(E31)	0.0376 (5)	0.7721 (9)	0.1726 (4)	2.8 (2)
O(E32)	0.4025 (7)	0.5752 (11)	$\frac{1}{2}$	4.4 (4)
O(L34)	0.5940 (5)	0.1268 (8)	$\frac{1}{2}$	1.1 (2)
O(E41)	0.7241 (6)	0.9071 (9)	$\frac{1}{2}$	1.9 (2)
O(E42)	0.2413 (4)	0.8406 (8)	0.1713 (4)	2.4 (2)

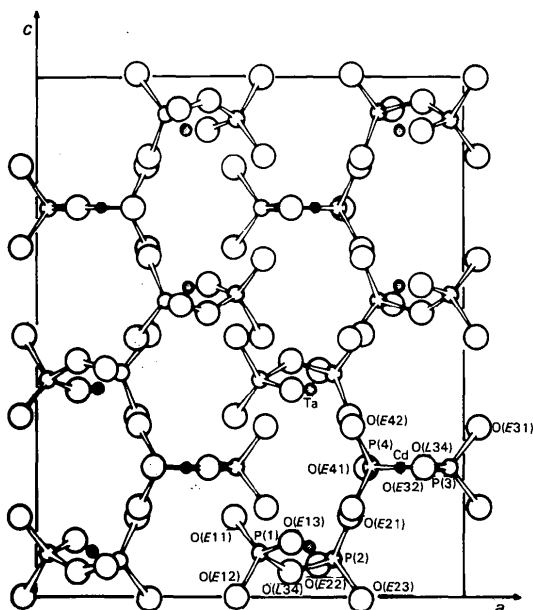


Fig. 1. Projection along the b axis of the atomic arrangement of $\text{Ta}_2\text{Cd}(\text{P}_2\text{O}_7)_3$.

Table 2. Main interatomic distances (\AA) and bond angles ($^\circ$) in $\text{Ta}_2\text{Cd}(\text{P}_2\text{O}_7)_3$

The P(1)P(2)O₇ group

(a) P(1)O₄ tetrahedron

P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.444 (4)	2.515 (6)	2.524 (5)	2.497 (5)
O(E12)	115.0 (2)	1.538 (4)	2.470 (4)	2.351 (5)
O(E13)	116.0 (2)	107.2 (2)	1.531 (3)	2.487 (5)
O(L12)	111.9 (2)	98.3 (2)	106.7 (2)	1.569 (4)

(b) P(2)O₄ tetrahedron

P(2)	O(E21)	O(E22)	O(E23)	O(L12)
O(E21)	1.437 (4)	2.501 (5)	2.516 (6)	2.514 (5)
O(E22)	115.2 (2)	1.525 (3)	2.427 (5)	2.448 (5)
O(E23)	116.5 (2)	105.6 (2)	1.522 (4)	2.408 (5)
O(L12)	112.5 (2)	103.8 (2)	101.6 (2)	1.584 (3)

$$\text{P(1)-P(2)} \quad 2.962 (1) \quad \text{P(1)-O(L12)-P(2)} \quad 139.8 (3)$$

The P(3)P(4)O₇ group

(a) P(3)O₄ tetrahedron

P(3)	O(E31)	O(E31)	O(E32)	O(L34)
O(E31)	1.522 (4)	2.444 (8)	2.500 (6)	2.437 (4)
O(E31)	106.8 (3)	1.522 (4)	2.500 (6)	2.437 (4)
O(E32)	114.9 (2)	114.9 (2)	1.444 (5)	2.493 (6)
O(L34)	103.8 (2)	103.8 (2)	111.4 (3)	1.573 (4)

(b) P(4)O₄ tetrahedron

P(4)	O(E41)	O(E42)	O(E42)	O(L34)
O(E41)	1.454 (4)	2.491 (5)	2.491 (5)	2.505 (5)
O(E42)	112.8 (2)	1.536 (3)	2.487 (5)	2.505 (4)
O(E42)	112.8 (2)	108.0 (2)	1.536 (3)	2.505 (4)
O(L34)	110.4 (2)	106.2 (2)	106.2 (2)	1.596 (4)

$$\text{P(3)-P(4)} \quad 2.936 (2) \quad \text{P(3)-O(L34)-P(4)} \quad 135.8 (3)$$

The TaO₆ octahedron

Ta-O(E12)	1.932 (3)	Ta-O(E23)	1.920 (3)
Ta-O(E13)	1.970 (3)	Ta-O(E31)	1.954 (3)
Ta-O(E22)	1.940 (3)	Ta-O(E42)	1.952 (3)

The CdO₆ octahedron

Cd-O(E11)	2.265 (4) (× 2)	Cd-O(E32)	2.199 (5)
Cd-O(E21)	2.244 (4) (× 2)	Cd-O(E41)	2.176 (4)

Discussion. Fig. 1 gives a projection along the *b* axis of the atomic arrangement.

The Cd atoms, located on the mirror plane, have their most usual environment: six neighbouring O atoms form an almost regular octahedron with Cd–O distances varying from 2.176 to 2.265 Å (Table 2). The Ta atoms, in general positions, have their usual octahedral coordination with Ta–O distances in the range 1.920–1.970 Å (Table 2). The P₂O₇ groups present two different conformations. The first has mirror symmetry with five atoms of the group [P(3), P(4), O(E41), O(L34) and O(E32)] in the mirror plane. This rare configuration has already been observed in Nb₂CaO(P₂O₇)(P₄O₁₃) (Averbuch-Pouchot, 1987). The mean P–O distance is 1.523 Å for this anion. The second type of P₂O₇ group has no internal symmetry and a mean P–O distance (1.519 Å) that is practically identical. This atomic arrangement is related to that of Nb₂Co(P₂O₇)₃ (Averbuch-Pouchot & Durif, 1987). This last compound is monoclinic (*P*2₁/*m*) with a unit cell (*a* = 15.320, *b* = 7.890, *c* = 6.490 Å, β = 90.76°) quite comparable with that of the title compound after a doubling of *c*. The analogy is not limited to the crystal metrics but extends to the atomic arrangements as can be seen by comparing Figs. 1 and 2. The atomic framework of Ta₂Cd(P₂O₇)₃ can be deduced from that of Nb₂Co(P₂O₇)₃ by a doubling of its unit cell and a translation of about 0.15 along the *y* axis.

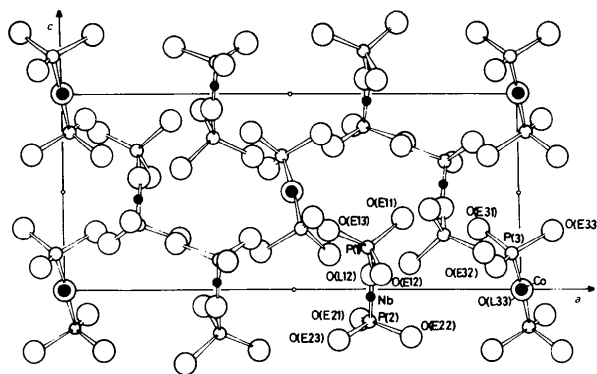


Fig. 2. Projection along the *b* axis of the atomic arrangement of Nb₂Co(P₂O₇)₃.

References

- AVERBUCH-POUCHOT, M. T. (1987). *Z. Anorg. Allg. Chem.* In preparation.
- AVERBUCH-POUCHOT, M. T. & DURIF, A. (1987). *Z. Kristallogr.* In preparation.
- Enraf-Nonius (1977). *Structure Determination Package*, RSX 11M version. Enraf-Nonius, Delft, The Netherlands.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- LINDE, S. A., GORBUNOVA, YU. E., LAVROV, A. V. & TANANAEV, I. (1980). *Sov. Phys. Dokl.* **25**, 4–5.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. London: Macmillan.

Acta Cryst. (1987). **C43**, 1863–1866

Structure Based on a Twinned Crystal of Wolfram's Red Salt, [Pt(C₂H₅NH₂)₄Cl₂][Pt(C₂H₅NH₂)₄]Cl₄·4H₂O

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(Received 10 December 1986; accepted 30 April 1987)

Abstract. Dichlorotetrakis(ethylamine)platinum(IV) tetrakis(ethylamine)platinum(II) tetrachloride tetrahydrate, [Pt(C₂H₅NH₂)₄Cl₂][Pt(C₂H₅NH₂)₄]Cl₄·4H₂O, *M_r* = 1035.6, monoclinic, *Im*, *a* = 13.302 (3), *b* = 13.337 (5), *c* = 5.391 (1) Å, β = 90.98 (3)°, *V* = 956.3 (4) Å³, *Z* = 1, *D_x* = 1.80 Mg m⁻³, λ(Mo *K*α, graphite monochromated) = 0.7107 Å, μ = 7.84 mm⁻¹, *F*(000) = 506, *T* = 298 K, final *R* = 0.036 for 1218 unique significant reflections. The crystals show a twinning with *c* as the twin axis of π/2 rotations; the

twin individuals have a structure similar to that of the bromo analog, Reihlen's green. The structure is pseudo-tetragonal except for the anions and water molecules. The Pt^{IV} coordination octahedron is slightly deformed through non-bonded repulsion of the axial Cl atom and the methylene groups. A three-dimensional network of hydrogen bonds is formed involving anions and water molecules.

Introduction. Dichlorotetrakis(ethylamine)platinum(IV) tetrakis(ethylamine)platinum(II) tetrachloride tetrahydrate, known as Wolfram's red salt, has been extensively studied by means of many

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