INORGANIC COMPOUNDS

Acta Cryst. (1999). C**55**, 271–273

Pentalead tris(vanadate) iodide, a defect vanadinite-type compound

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(Received 14 January 1998; accepted 3 April 1998)

Abstract

A single crystal of $Pb_{9.85}(VO_4)_6I_{1.7}$ was grown at 1073 K from a mixture of lead vanadate and lead iodide. The structure is of the apatite type with a deficiency of lead iodide. The Pb atom is distributed equally in sites I and II of apatite. The Pb^{2+} lone pair induces displacements of the Pb, O and I atoms out of their apatite sites. The apatite structure is preserved by an 'under-stoichiometry' of lead iodide, which allows the distortions to relax.

Comment

Apatites are a large family of compounds of general formula $M_{10}(XO_4)_6Y_2$. The best-known apatite is calcium phosphate hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, because of its use as phosphate ore. The introduction of large ions into the channels has been the subject of numerous investigations (Trombe & Montel, 1980; Suitch *et al.*, 1986; Dykes, 1974). In the case of iodoapatites, the large ionic radius of I^- (1.96 Å; Shannon, 1976) allows particular substitutions in apatitic structures (McConnell, 1974). Several workers have shown that iodoapatites must have tetrahedral groups larger than the phosphate groups, like VO_4 or AsO_4 groups (Vincent, 1960; Klement & Harth, 1961). In this case, the cation *M* can be replaced by Cd (Engel, 1968; Sudarsanan *et al.*, 1977) or by Pb (Merker & Wondratschek, 1959). Iodoapatites bearing rhenium perrhenate have also been synthesized, *e.g.* $Ba_{10}(ReO_5)_6I_2$ (Baud *et al.*, 1979) and $Sr_{10}(ReO_5)_6I_2$ (Schriewer & Jeitschko, 1993). These apatites have stoichiometric deficiencies or smaller anions in the channels. In the study reported here, the structure of a lead iodoapatite of ideal formula $Pb_{10}(VO_4)_6I_2$ was determined. The structure confirms the above observation; a lack of Pb and I is found, with only 98.2 (8)% of Pb1 in site 4*f*, 49.3 (4)% of Pb2 in site 12*i* (corresponding to 98.7% if localized in site 6*h*) and 14.2 (4)% of I in site 12*i* (85.1% if localized in site 2*b*). The resulting formula is $Pb_{9.85}(VO_4)_6I_{1.7}$. A view of the lattice (Fig. 1) shows that the arrangement encountered is that generally observed in apatites.

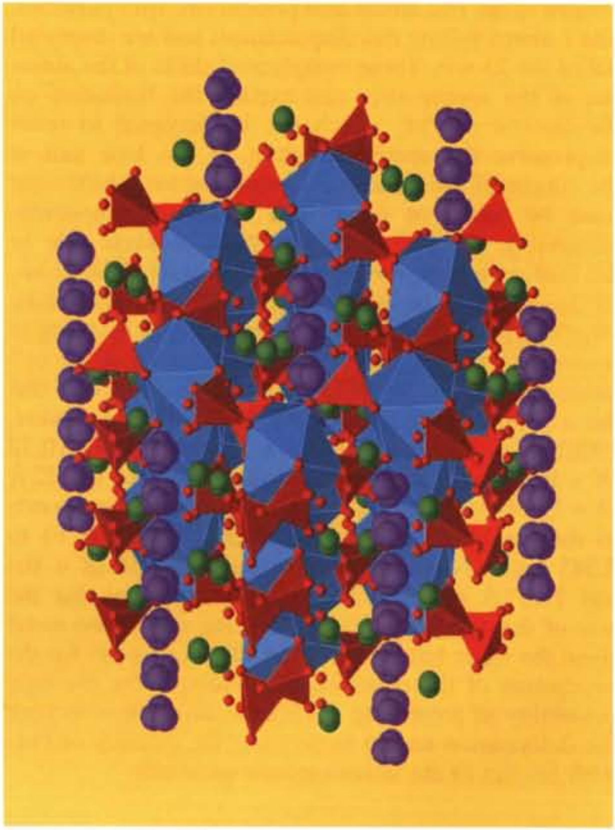

Fig. 1. View of the structure showing V–O and Pb1–O polyhedra; atoms I, O3 and Pb2 are displayed as spheres of arbitrary size in order to show their split positions.

The V atoms are located in distorted tetrahedra with two types of surroundings. One tetrahedron is formed by atoms O1, O2, O31 and O31^{iv}, and the second by atoms O1, O2, O32 and O32^{iv} [symmetry code: (iv) $x, y, \frac{1}{2} - z$]. In vanadinite, an axial distortion of the VO_4 tetrahedron has been observed (Dai & Hughes, 1989). In the present case, such a distortion is difficult to reveal, the V—O distances being equal within 2σ [1.68 (4)–1.76 (4) Å]. However, the angular distortions are unexpectedly large [83 (2)–125 (2)°]; this can be attributed to the split model used to describe the spread of the electron density observed around the O3 apatite site.

ISSN 0108-2701

The Pb1 atom lies in a trigonal tricapped prism, the triangular faces of which are formed by O1 atoms for the first and by O2 atoms for the second, with the O31 or O32 atoms capping the side faces. In this cavity, Pb is displaced by 0.17 Å from the centre towards the O1 atoms. Such a displacement is attributed to the Pb^{2+} lone pair, as already mentioned by Galy *et al.* (1975). The Pb2 atom, which also possesses a lone pair, is displaced from the mirror plane. Consequently, a short distance between two Pb2 sites is observed [0.412 (5) Å], which implies that each site is half occupied. The O3 atoms bonded to the Pb2 atoms also present two split positions. The I atoms follow this displacement and are displaced out of the 2*b* site. These complicated shifts of the atoms out of the apatite sites can explain the limitation on the amount of PbI_2 which can be accepted in order to preserve the apatite structure. If the lone pair is the source of the structural distortions, such behaviour must be found in other lead vanadate compounds. Effectively, the Pb^{2+} lone pair plays a steric role in the lead orthophosphovanadate compounds (Kiat *et al.*, 1993). However, no distortion is observed in vanadinite, $Pb_{10}(VO_4)_6Cl_2$, and, moreover, the full stoichiometry is reached (Dai & Hughes, 1989). Observation of the cell parameters of the $Pb_{10}(VO_4)_6X_2$ vanadinites reveal that the *a* parameter increases from 10.113 (X = F; Baker, 1966) to 10.317 (X = Cl; Dai & Hughes, 1989), 10.39 (X = Br; Merker & Wondratschek, 1959) and 10.422 Å (X = I). Meanwhile, the *c* parameter, which corresponds to the tunnel axis, decreases from 7.375 (X = F) to 7.343 Å (X = Cl), and then increases to 7.36 (X = Br) and 7.467 Å (X = I). These variations show that the size of the halogen competes with the size of the metal (here the steric hindrance of the Pb^{2+} lone pair) for the occupation of the main tunnel. Consequently, the only possibility of preserving the apatite structure is to limit the deformation and so to decrease the quantity of PbI_2 with respect to the stoichiometric quantities.

Experimental

The title compound was synthesized from a melt of $Pb_3(VO_4)_2$ and PbI_2 in stoichiometric amounts as described by Merker & Wondratschek (1959). The reaction medium was closed to air; the temperature range was 773–1073 K. IR spectroscopic analysis confirmed the presence of VO_4, with large absorption bands as noted in vanadinite (Von Rahden & Dicks, 1967), and showed that no OH is present. Electron microprobe analysis revealed that the amount of I depends on the synthesis conditions; this was confirmed by X-ray powder diffraction analyses of the products, which resulted in different values for the crystallographic parameters. The crystal studied here was grown at 1073 K.

Crystal data

$Pb_{9.85}(VO_4)_6I_{1.7}$
$M_r = 2946.29$
Hexagonal
$P6_3/m$
$a = 10.422\ (5)$ Å
$c = 7.467\ (3)$ Å
$V = 702.4\ (6)$ Å^3
$Z = 1$
$D_x = 6.965$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–$25°$
$\mu = 62.62$ mm^{-1}
$T = 293\ (2)$ K
Hexagonal prism
0.066 × 0.060 × 0.054 mm
Clear pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: Gaussian (Coppens *et al.*, 1965)
$T_{min} = 0.026$, $T_{max} = 0.135$
1065 measured reflections
525 independent reflections

418 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 39.84°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.071$
$S = 0.834$
525 reflections
47 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 2.57$ e Å^{-3}
$\Delta\rho_{min} = -2.16$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
Pb1	0.982 (8)	1/3	2/3	−0.00970 (14)	0.0190 (2)
Pb2	0.493 (4)	0.00136 (12)	0.26525 (11)	0.2776 (4)	0.0213 (6)
V	1	0.3819 (4)	0.4103 (4)	1/4	0.0114 (7)
O1	1	0.5014 (18)	0.3363 (18)	1/4	0.028 (4)
O2	1	0.479 (2)	0.6016 (19)	1/4	0.042 (5)
O31	0.50	0.243 (4)	0.333 (6)	0.101 (5)	0.044 (10)
O32	0.50	0.294 (4)	0.383 (6)	0.041 (5)	0.044 (10)
I	0.142 (4)	0.027 (2)	0.028 (2)	−0.0210 (12)	0.014 (3)

Table 2. *Selected geometric parameters (Å, °)*

Pb1—O1^{i}	2.498 (11)	Pb2—I^{v}	3.27 (3)
Pb1—O2	2.751 (12)	Pb2—I^{i}	3.128 (10)
Pb1—O31	3.23 (3)	Pb2—I^{vi}	3.20 (3)
Pb1—O32	2.80 (3)	Pb2—I^{vii}	3.28 (3)
Pb2—O32^{ii}	2.26 (4)	Pb2—I	3.44 (3)
Pb2—O2^{iii}	2.316 (18)	Pb2—I^{viii}	3.45 (3)
Pb2—O31^{iv}	2.43 (3)	Pb2—I^{ix}	3.48 (3)
Pb2—O31^{ii}	2.56 (4)	Pb2—I^{x}	3.49 (3)
Pb2—O31	2.61 (3)	V—O31	1.68 (4)
Pb2—O31^{i}	2.95 (4)	V—O31^{iv}	1.68 (4)
Pb2—O32	3.18 (3)	V—O2	1.727 (17)
Pb2—O32^{i}	2.63 (4)	V—O32	1.76 (4)
Pb2—O32^{iv}	2.98 (3)	V—O32^{iv}	1.76 (4)
Pb2—I^{ii}	2.894 (10)	V—O1	1.762 (15)
Pb2—I^{iv}	3.19 (3)		
O2—V—O1	111.6 (9)	O2—V—O32	98.3 (17)
O31—V—O1	114.7 (18)	O2—V—O32^{iv}	98.3 (17)
O31^{iv}—V—O1	114.7 (18)	O32—V—O1	110.7 (15)

O31—V—O2	114.9 (19)	O32—V—O32^{iv}	125.2 (19)
O31^{iv}—V—O2	114.9 (19)	O32^{iv}—V—O1	110.7 (15)
O31—V—O31^{iv}	83 (2)		

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

The heavy-atom positions were obtained from Patterson analysis and the O atoms were obtained from Fourier syntheses. It appeared that, compared with the apatite structure, the Pb atom situated in site II (6*h*) must be shifted out of the site. According to this shift, the O3 atoms had to be split into two positions. Meanwhile, a difference Fourier synthesis revealed that I must be displaced from the 2*b* site occupied by Cl in chlorapatite (Hendricks *et al.*, 1932). Optimization of the Pb and I occupation factors was undertaken considering a PbI_2 deficit. All atoms, except the disordered I atoms, were refined with anisotropic displacement parameters. Although an absorption correction was performed using a numerical method (Coppens *et al.*, 1965), the high absorption of the material leads to large $\Delta\rho$ residues. The highest value is situated 1.40 Å from Pb2, and the lowest one at 1.40 Å from O31 and 1.39 Å from V.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *MOLVIEW* (Cense, 1989). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1208). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 273–276

$Cs_2Mo_3O_{10}$

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(Received 3 July 1998; accepted 7 October 1998)

Abstract

Single crystals of dicaesium trimolybdate have been grown by solid-state reaction. The structure is built up of infinite molybdate chains interleaved by Cs atoms. The Mo atoms exhibit two coordination modes towards O atoms, namely, CN6 and CN5 as distorted octahedral and trigonal bipyramidal polyhedra, respectively, while Cs atoms, responsible for the cohesion of the network, sit in bicapped dodecahedra.

Comment

Within extended solid-state chemistry devoted to the system Cs–Nb–Mo–O, we grew single crystals of $Cs_2Mo_3O_{10}$. Such a compound has been synthesized as a microcrystalline powder, and rough cell dimensions have been reported by both Gatehouse & Leverett (1968) (a = 14.55, b = 8.43, c = 9.52 Å and β = 99°) and Foerster *et al.* (1985) (a = 14.47, b = 8.35, c = 9.31 Å and β = 99.1°). It was decided to carry out the present structure determination in order to examine, in particular, the coordination of molybdenum and its evolution in comparison with the potassium and rubidium homologous structures of this phase. To this end, we prepared single crystals of $Cs_2Mo_3O_{10}$ using caesium carbonate and molybdenum trioxide.

The projection of the title compound onto the (010) plane (Fig. 1) shows the infinite $[Mo_3O_{10}]_n$ molybdate chains running along the [001] direction associated by Cs atoms. Within the chain, the Mo atoms occupy two