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Mercury(II) Arsenate, a Graphtonite-Type Structure

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Abstract

$\text{Hg}_3(\text{AsO}_4)_2$ is isostructural with $\text{Hg}_3(\text{PO}_4)_2$. Both compounds crystallize with a graphtonite-type structure. As a result of the tendency of mercury(II) to form two short linear bonds, there are deviations in the coordination polyhedra between the two structures although the arrangements of the tetrahedral anions are very similar.

Comment

Mercury(II) arsenate, $\text{Hg}_3(\text{AsO}_4)_2$, has been investigated as part of a project dealing with the coordination of Hg^{II} in inorganic salts. The arsenate is isostructural with the corresponding phosphate (Aurivillius & Nilsson, 1974). Single crystals of Hg_3 -

$(\text{AsO}_4)_2$ were grown by heating powder from a commercial source to 455 K in 1M HNO_3 for 3 d and slowly decreasing the temperature. Needles with well defined facets were formed.

When coordinated to O atoms, Hg^{II} often forms two short, almost linearly arranged bonds with lengths 2.0–2.2 Å. In addition, three to five O atoms are usually coordinated at distances of 2.4–2.9 Å. This behaviour often causes mercury salts to crystallize in structures different from those of other divalent metal salts. In contrast to this, the arsenate and phosphate salts crystallize in the graphtonite-type structure (Calvo, 1968).

Graphtonite is a mineral with composition $(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ca}^{2+})_3(\text{PO}_4)_2$. Other phosphates and arsenates of divalent metal ions, e.g. $\text{CdZn}_2(\text{PO}_4)_2$, $\text{Cd}_2\text{Zn}(\text{PO}_4)_2$ (Calvo & Stephens, 1968), $\text{Mn}_3(\text{PO}_4)_2$ (Stephens, 1967), $\text{Fe}_3(\text{PO}_4)_2$ (Kostiner & Rea, 1974) and $\text{Cd}_3(\text{AsO}_4)_2$ (Engel & Klee, 1970), crystallize in this type of structure. The anionic arrangement obviously allows the flexibility needed to accommodate different cations. Even the Hg^{2+} ion which normally has a strong influence on the anionic arrangement does not change the basic structure. Small shifts of the oxygen tetrahedra allow mercury to achieve short linear bonds. The anionic arrangements in the structures of $\text{Hg}_3(\text{AsO}_4)_2$ and graphtonite are compared in Fig. 1.

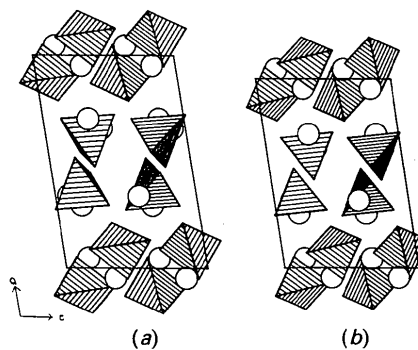


Fig. 1. (a) Mercury(II) arsenate and (b) graphtonite projected along (010). The differences in the cation polyhedra are due to expansion of the *c* axis in mercury(II) arsenate and small tilts of the tetrahedra. [Cell dimensions in graphtonite: *a* = 8.91 (1), *b* = 11.58 (1), *c* = 6.239 (8) Å, β = 98.9 (1)°].

The asymmetric unit of mercury(II) arsenate comprises three Hg^{II} atoms and two AsO_4^{3-} tetrahedra (Table 1). Each Hg^{II} has two short Hg—O bonds [Hg—O = 2.06 (1)–2.14 (1) Å, O—Hg—O = 161.8 (6)–170.6 (5)° (see Table 2)]. The O—As—O bond angles are in the range 99.2 (5)–116.3 (5)° with one short and three long As—O bonds. The three long bonds are to the O atoms that participate in the short Hg—O bonds. This arrangement builds up two

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integrated nets which are related by a centre of symmetry (Aurivillius & Nilsson, 1974). If all O atoms within 2.9 Å of the Hg atom are considered as belonging to the coordination sphere, the Hg atoms occupy three different oxygen polyhedra. Hg1 is seven-coordinated, surrounded by a very distorted pentagonal bipyramid with short axial bonds. The five-coordinated Hg2 and Hg3 are surrounded by distorted square-planar pyramids with the two short bonds at opposite corners of the squares (Fig. 2).

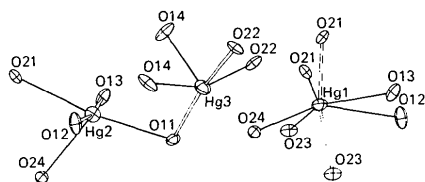


Fig. 2. Oxygen polyhedra around mercury. Hg1O₇ can be described as a pentagonal bipyramid with short axial bonds, Hg2O₅ and Hg3O₅ as square pyramids with two short bonds at opposite corners of the square.

Experimental

Crystal data

Hg₃(AsO₄)₂

M_r = 879.6

Monoclinic

*P*2₁/*c*

a = 10.0049 (11) Å

b = 11.7555 (12) Å

c = 6.5374 (5) Å

β = 99.687 (6)°

V = 757.93 (8) Å³

Z = 4

D_x = 7.71 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 35 reflections

θ = 9.4–27.1°

μ = 71.6 mm⁻¹

T = 298 K

Superellipsoid

(*x*/0.08)⁴ + (*y*/0.09)² +

(*z*/0.09)² ≤ 1

Pale yellow

Data collection

Enraf-Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

by integration from crystal shape

T_{min} = 0.0024, *T_{max}* = 0.0252

5174 measured reflections

4617 independent reflections

2733 observed reflections

[*F_o* > 3σ(*F_o*)]

R_{int} = 0.0132

θ_{max} = 40°

h = 0 → 18

k = 0 → 21

l = -11 → 11

3 standard reflections

frequency: 60 min

intensity variation: 5%

Refinement

Refinement on *F*

Final *R* = 0.0446

wR = 0.0531

S = 1.48

2728 reflections

193 parameters

w = 1/[σ(*F_o*²) + (0.02*F_o*²)^{1/2}]

(Δ/σ)_{max} = 0.1

Δρ_{max} = 5.7 e Å⁻³

Δρ_{min} = -3.8 e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

All atoms are in general position 4(*c*) of space group *P*2₁/*c*. The form of the temperature factor is exp[-2π(*U*₁₁*h*²*a*^{*2} + 2*U*₁₂*hka*^{*}*b*^{*} + ...)].

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Hg1	0.0464 (1)	0.6210 (1)	0.6657 (2)	0.0201 (4)
Hg2	0.7027 (1)	0.3938 (1)	0.8198 (2)	0.0212 (4)
Hg3	0.6589 (1)	0.6704 (1)	0.4063 (2)	0.0226 (5)
As1	0.6045 (1)	0.4044 (1)	0.2951 (2)	0.0132 (3)
As2	0.9037 (1)	0.8682 (1)	0.5930 (2)	0.0119 (3)
O11	0.5472 (11)	0.5383 (9)	0.2289 (19)	0.0228 (28)
O12	0.7232 (11)	0.4156 (12)	0.5145 (18)	0.0261 (31)
O13	0.7050 (11)	0.3504 (10)	0.1291 (16)	0.0205 (27)
O14	0.4785 (14)	0.3146 (11)	0.3172 (19)	0.0290 (34)
O21	0.0499 (11)	0.7937 (9)	0.5836 (19)	0.0215 (28)
O22	0.7871 (11)	0.7702 (9)	0.6303 (16)	0.0195 (26)
O23	0.9137 (12)	0.9427 (8)	0.819 (15)	0.0179 (24)
O24	0.8681 (10)	0.9459 (8)	0.3787 (16)	0.0162 (23)

Table 2. Bond distances (Å) and O—Hg—O angles (°)

Arsenate tetrahedra

As1—O14	1.67 (1)	As2—O24	1.66 (1)
As1—O11	1.71 (1)	As2—O22	1.69 (1)
As1—O12	1.71 (1)	As2—O23	1.71 (1)
As1—O13	1.72 (1)	As2—O21 ⁱ	1.72 (1)

Mercury(II) polyhedra

Hg1—O21	2.10 (1)	Hg2—O24 ^{vi}	2.49 (1)
Hg1—O23 ⁱⁱ	2.13 (1)	Hg2—O11 ^v	2.59 (1)
Hg1—O23 ⁱⁱⁱ	2.54 (1)	Hg2—O21 ^{viii}	2.72 (1)
Hg1—O24 ^{iv}	2.56 (1)	Hg3—O22	2.13 (1)
Hg1—O13 ^v	2.65 (1)	Hg3—O11	2.14 (1)
Hg1—O12 ^v	2.79 (1)	Hg3—O14 ^v	2.45 (1)
Hg1—O21 ^{vi}	2.90 (1)	Hg3—O22 ^{ix}	2.48 (1)
Hg2—O12	2.06 (1)	Hg3—O14 ^x	2.49 (1)
Hg2—O13 ^{vii}	2.08 (1)		
O21—Hg1—O23 ⁱⁱ	161.8 (6)	O11—Hg3—O22	166.6 (4)
O12—Hg2—O13 ^{vii}	170.6 (5)		

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 - *x*, *y* - ½, ½ - *z*; (iii) *x* - 1, ½ - *y*, *z* - ½; (iv) *x* - 1, ¾ - *y*, ½ + *z*; (v) 1 - *x*, 1 - *y*, 1 - *z*; (vi) *x*, ¾ - *y*, ½ + *z*; (vii) *x*, *y*, 1 + *z*; (viii) 1 - *x*, *y* - ½, ¾ - *z*; (ix) *x*, ¾ - *y*, *z* - ½; (x) 1 - *x*, ½ - *y*, ½ - *z*.

In a first attempt to refine the structure, intensity data from a cut needle were used. The high linear absorption coefficient together with the sharp edges of the crystal caused the absorption correction to be the limiting factor of the refinement (final *R* = 0.065, *wR* = 0.080). The needles were therefore cut and ground in an attempt to obtain spherical crystals. The final shape of the ground crystals can, however, be better approximated with a superellipsoid. Such shapes of ground crystals are frequently observed. A numerical integration method and software have been developed to correct the intensity data from such crystals for absorption (Lidin, Fogden & Larsson, 1993). The model used for the present crystal is described by (*x*/*p*)⁴ + (*y*/*q*)² + (*z*/*r*)² ≤ 1, where *p* = 0.0080 and *q* = *r* = 0.0090 cm. Five reflections were considered outliers, possibly as a result of multiple diffraction, and were omitted in the last cycles of refinement. The high peaks in the final Δρ map are all ripples around mercury and arsenate. All the programs used are described by Lundgren (1982).

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55713 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU 1008]

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A New One-Dimensional Compound: Synthesis and Structure of $\text{InNb}_3(\text{Se}_2)_6$

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Abstract

The new one-dimensional compound, indium niobium selenide, was synthesized by high-temperature solid-state reactions. The structure is composed of $[\text{Nb}_3(\text{Se}_2)_6]_\infty$ chains running along the *c* axis with In atoms intercalated between these chains. All the Nb atoms have rectangular antiprismatic coordination environments. All the Se atoms in the structure are in the form of Se_2 dimers with Se—Se distances of 2.325 (2) and 2.356 (2) Å.

Comment

Chemical investigations in the field of chalcogen-rich niobium and tantalum chalcogenides have led to the characterization of many new one-dimensional or quasi-one-dimensional compounds. These include, for example, MX_3 ($M = \text{Nb}, \text{Ta}; X = \text{S}, \text{Se}$) (Sambong *et al.*, 1977; Rijnsdorp & Jellinek, 1978; Hodeau, *et al.*, 1978; Bjerkelund, Fermor & Kjerkskus, 1966), $(\text{MX}_4)_n\text{Y}$ ($M = \text{Nb}, \text{Ta}; X = \text{S}, \text{Se}; Y = \text{Br}, \text{I}$) (Gressier, Meerschaut, Guemas, Rouxel & Monceau, 1984), Nb_2Se_9 (Meerschaut, Guemas, Berger & Rouxel, 1979) *etc.* The structures and properties of low-dimensional metal chalcogenides have been reviewed by Rouxel (1986) and Gressier *et al.* (1984). Low-dimensional materials are of great

interest, because they exhibit some remarkable properties such as the Peierls transition, charge-density wave (CDW) *etc.* Studies of the collective dynamics of charge-density waves and other low-dimensional phenomena have promoted the need for the new materials to support experimentally the growing development of theories. During the investigations of ternary Nb and Ta selenides, we have recently synthesized a new pseudo-one-dimensional compound, $\text{InNb}_3(\text{Se}_2)_6$.

Crystals of $\text{InNb}_3(\text{Se}_2)_6$ were obtained initially from a reaction mixture of Nb_2Se_9 and In in approximately stoichiometric proportions at 773–873 K. Better-quality single crystals used in the structure determination were obtained by a vapour transport method at 923 K with a small amount of selenium as the transport agent.

The title compound is isostructural with $\text{I}_{0.33}\text{NbSe}_4$ (Meerschaut, Palvadeau & Rouxel, 1977). The atomic coordinates and selected distances and angles are given in Tables 1 and 2, respectively. As shown in Fig. 1, the structure is composed of $[\text{Nb}_3(\text{Se}_2)_6]_\infty$ chains with the In atoms intercalated between them. There exists a periodic sequence of distances (in Å) $\cdots\text{Nb}(1^{\text{ii}})—3.037—\text{Nb}(1^{\text{i}})—3.248—\text{Nb}(2)—3.248—\text{Nb}(1)\cdots$ in a $[\text{Nb}_3(\text{Se}_2)_6]_\infty$ chain (see Fig. 2). The bonding between the chains is very weak and is of typical van der Waals type. The $\text{Nb}(1^{\text{i}})—\text{Nb}(1^{\text{ii}})$ bonding distance of 3.037 Å is somewhat longer than the values found in NbS_2Cl_2 (2.871 Å), NbSe_2Cl_2 (2.973 Å) (Rijnsdorp, de Lange & Wiegers, 1979) and $\text{Nb}_3\text{Se}_5\text{Cl}_7$ (2.94 Å) (Rijnsdorp & Jellinek, 1979), but a Nb—Nb bond of similar length (3.029 Å) has been found in NbCl_4 (Taylor, Calabrese & Larsen, 1977) and even longer Nb—Nb bonds (3.12–3.16 Å) in the oxide halides NbOX_2 ($X = \text{Cl}, \text{Br}, \text{I}$; Schafer & Schnering, 1964). In comparison with the much longer Nb—Nb bonds (3.308 Å) in $\alpha\text{-NbI}_4$ (Dahl & Wampler, 1962), the $\text{Nb}(1)—\text{Nb}(2)$ distance of 3.248 Å should also involve chemical bonding. According to the periodic sequence of Nb—Nb distances along the *c* axis, the $\text{Nb}_3(\text{Se}_2)_6$ unit can be viewed formally as the building block of a chain. The reason for our not choosing the NbSe_4 unit as the building block is that there are two crystallographically independent Nb atoms in each chain and the coordination polyhedra $[\text{Nb}(1)(\text{Se}_2)_4]$ and $[\text{Nb}(2)(\text{Se}_2)_4]$ have crystallographic C_2 and D_2 symmetry, respectively; a simple NbSe_4 unit cannot therefore represent the basic unit from which the chain is constructed. The $\text{Nb}_3(\text{Se}_2)_6$ units are linked together through bridging $(\text{Se}_2)^{2-}$ ligands as well as through Nb—Nb bonding to form infinite $[\text{Nb}_3(\text{Se}_2)_6]_\infty$ chains parallel to the *c* axis. Considering the long distance (6.69 Å) between the centre lines of different chains, the metal–metal interaction is very anisotropic and typical of the one-dimensional character.