

transformation to a solid on the application of pressure. The unit-cell length of CO₂ at 1.0 GPa is 5.4942 (2) Å, compared with 5.624 (2) Å observed by Simon & Peters (1980). However, the C—O bond length appears to be constant under both sets of conditions. Its value, when corrected for simple rigid-bond thermal motion (Downs *et al.*, 1992) is 1.168 (1) Å [1.1486 (9) Å, uncorrected], compared with corrected values of 1.164 (Simon & Peters, 1980) and 1.162 Å (Karle & Karle, 1949, 1950) obtained by electron diffraction in the gas phase.

Experimental

CO₂ was obtained as a commercial product.

Crystal data

CO ₂	Mo K α radiation
$M_r = 44.01$	$\lambda = 0.7107$ Å
Cubic	Cell parameters from 18 reflections
$Pa\bar{3}$	$\theta = 6.4\text{--}14.0^\circ$
$a = 5.4942$ (2) Å	$\mu = 0.172$ mm ⁻¹
$V = 165.85$ (2) Å ³	$T = 293$ K
$Z = 4$	Disc
$D_x = 1.762$ Mg m ⁻³	0.25 mm (radius)
D_m not measured	Colourless

Data collection

Huber four-circle diffractometer	$R_{\text{int}} = 0.034$
Profile data from $\theta/2\theta$ scans	$\theta_{\text{max}} = 30^\circ$
Absorption correction: none	$h = -6 \rightarrow 6$
596 measured reflections	$k = -7 \rightarrow 7$
78 independent reflections	$l = -5 \rightarrow 5$
43 reflections with $I > 2\sigma(I)$	2 standard reflections frequency: 180 min intensity decay: 9%

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.01$
$R = 0.041$	$\Delta\rho_{\text{max}} = 0.063$ e Å ⁻³
$wR = 0.018$	$\Delta\rho_{\text{min}} = -0.082$ e Å ⁻³
$S = 1.28$	Extinction correction: none
43 reflections	Scattering factors from Doyle & Turner (1968)
6 parameters	
$w = 1/[\sigma^2(F) + (0.0055F)^2]$	

Compressed CO₂ liquid was forced into a conventional four-pin Bassett high-pressure diamond anvil cell using a gas-loading apparatus at 8.3 MPa. This was conducted numerous times in order to ensure that the cell was well purged and the confined sample was pure. The cell was constructed with Be seats and 250 μm thick Inconel steel gaskets with a 250 μm diameter hole. The diamond culets were 500 μm in diameter. No pressure medium was included. The pressure in the cell was increased to 1.00 (5) GPa, as measured by the pressure-dependent positions of characteristic fluorescence peaks of small included ruby chips. The sample chamber was visually observed to contain several crystals. A precession photograph demonstrated that although the reflections showed strain broadening, they could be indexed with $Pa\bar{3}$ symmetry. A single crystal was obtained by heating the entire sample assembly in an oven at 473 K overnight. Attempts to obtain

strain-free crystals at higher pressures failed, and most likely will require a pressure medium.

Intensities were measured using a Huber diffractometer and *SINGLE* software (Finger & Angel, 1990), which was also used for cell refinement. The peak profiles were quite sharp, indicating that the strain had been relieved during the heating process. Only peaks belonging to the $Pa\bar{3}$ structure could be found. The structure determination was initiated with the atomic parameters of CO₂ given by Simon & Peters (1980) and refined with a modified version of *RFINE* (Finger & Prince, 1975).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1190). Services for accessing these data are described at the back of the journal.

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A Niobium(V) Arsenate: Nb₉AsO₂₅

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Abstract

Nonaniobium arsenic pentacosaoxide contains 3×3 ReO₃-type NbO₆ octahedral columns extended along *c*. Each column is linked to four crystallographically identical columns through shared edges of NbO₆ octahedra and shared corners of AsO₄ tetrahedra.

Comment

There are four known A_9BO_{25} compounds, where cations A are in octahedral sites and B is in a tetrahedral site: Ta_9PO_{25} (Chernorukov *et al.*, 1981; Waring & Roth, 1964), Nb_9PO_{25} (Roth *et al.*, 1965; Benabbas *et al.*, 1991), Ta_9AsO_{25} (Chernorukov *et al.*, 1981) and Nb_9AsO_{25} (Chernorukov *et al.*, 1979). Nb_9PO_{25} is the only compound that has been studied by single-crystal X-ray diffraction. Its structure was first reported by Roth *et al.* (1965) in the space group $I\bar{4}$. Benabbas *et al.* (1991) reported a revised structure in the space group $I4/m$. Nb_9AsO_{25} is a decomposition product of tetragonal $NbAsO_5$ at 1193 K (Chernorukov *et al.*, 1979). It was proposed to be isostructural with Nb_9PO_{25} (Levin & Roth, 1970). The crystal structure of Nb_9AsO_{25} was also solved in space group $I4/m$. The structure contains edge-shared 3×3 ReO_3 -type octahedral columns extending along c (Fig. 1). The neighboring columns are displaced with respect to each other, giving rise to edge-sharing NbO_6 octahedra at the interface.

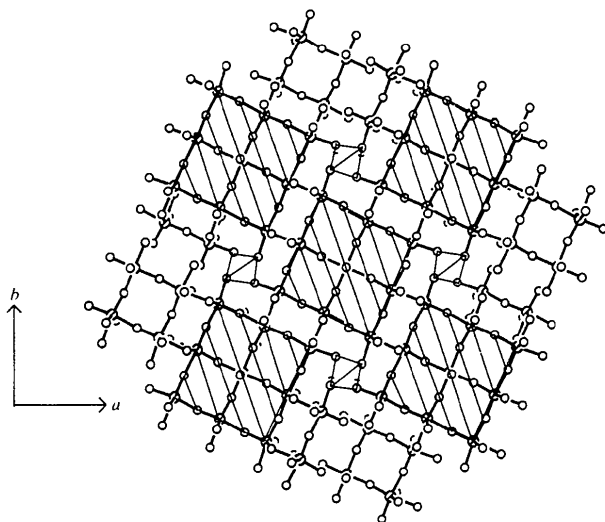


Fig. 1. Projected view of the extended structure of Nb_9AsO_{25} onto the ab plane. Each AsO_4 tetrahedron shares corners with the four neighboring 3×3 NbO_6 columns (indicated by shaded squares).

The Nb(1) atom was refined at half occupancy because it was found to be displaced by approximately 0.2 Å from the origin in the z direction, thus positioning it too close to its symmetry-related partner. The As atom resides on a $\bar{4}$ site; thus the inversion operator generates another As at a distance of 1.92 Å from it (half the length of the c axis). Therefore, its occupancy was also set at 0.5. Data collection on a cell with a doubled c axis showed no indication of a superstructure.

The geometry about Nb(1) represents a disordered octahedron, with O(1) in the axial position. The thermal motion of O(1) is quite anisotropic ($U_{11}/U_{33} = 7$). This could be a result of O(1) being refined in its average

position ($2b$ site). Refinements attempting to model a potential disorder were unsuccessful, perhaps due to the disordered nature of Nb(1) or the relatively small deviation of the atomic position by a small amount of electron density for O(1).

Within the NbO_6 octahedra (Fig. 2) bond distances range from 1.714 (5) to 2.286 (5) Å and *cis* bond angles vary from 74.2 (1) to 98.4 (2)°, while *trans* angles are quite distorted at 143.3 (3) to 180.0 (1)°. These distortions would appear to support the observation that O(1) is probably disordered, since this reported mode imposes crystallographic linearity upon the O(1)—Nb(1)—O(1') angle [symmetry code: (i) $x, y, z - 1$].

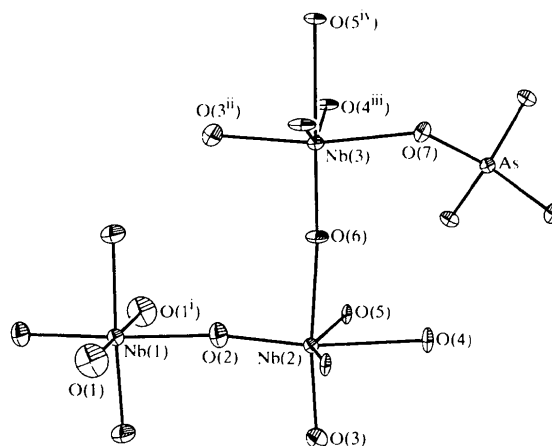


Fig. 2. Unique metal-oxide coordination polyhedra (70% probability ellipsoids) as viewed nearly parallel to the c axis. (Symmetry codes are as given in Table 1.)

Experimental

Nb_9AsO_{25} was synthesized from a stoichiometric mixture of 0.0916 g (0.3446 mmol) of Nb_2O_5 powder (Aesar, 99.9985%) and 0.1584 g (0.6892 mmol) of As_2O_5 powder (Aesar, 99.9%). The mixture was loaded in a fused-silica ampoule inside a dry box. The ampoule was subsequently sealed under vacuum. After initial heating at 473 K for 15 h, the temperature was increased at 20 K h^{-1} to 573 K, and left for 2 d. The reaction was ultimately heated to 1223 K at 20 K h^{-1} with an intermediate soaking for 2 d at 1113 K. After 3 d at 1223 K, the reaction was cooled slowly at 1.2 K h^{-1} to 923 K, then cooled at 15 K h^{-1} to 298 K. Colorless needle crystals of the title compound were obtained from the bottom of the ampoule.

Crystal data

Nb_9AsO_{25}
 $M_r = 1311.1$
 Tetragonal
 $I4/m$
 $a = 15.6684$ (8) Å
 $c = 3.829$ (1) Å
 $V = 940.1$ (3) Å³
 $Z = 2$
 $D_x = 4.632$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 12.2$ – 16.4 °
 $\mu = 7.149$ mm⁻¹
 $T = 298$ K
 Needle
 $0.120 \times 0.072 \times 0.024$ mm
 Colorless

Data collection

Rigaku AFC-7 diffractometer
 ω -2 θ scans
 Absorption correction:
 empirical via ψ scans
 (Sheldrick, 1990)
 $T_{\min} = 0.42$, $T_{\max} = 0.84$
 1152 measured reflections
 620 independent reflections

Refinement

Refinement on F
 $R = 0.026$
 $wR = 0.052$
 $S = 1.69$
 559 reflections
 57 parameters
 $w = 1/[\sigma^2(F) + 0.0005F^2]$
 $(\Delta/\sigma)_{\max} = 0.001$

559 reflections with
 $F > 4\sigma(F)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 27.50^\circ$
 $h = 0 \rightarrow 20$
 $k = 0 \rightarrow 19$
 $l = -4 \rightarrow 4$
 3 standard reflections
 every 100 reflections
 intensity decay: 0.2%

$\Delta\rho_{\max} = 0.93 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.06 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 Larson (1970)
 Extinction coefficient:
 0.00028 (5)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Nb(1)—O(1)	1.714 (5)	Nb(3)—O(4 ⁱⁱⁱ)	1.990 (2)
Nb(1)—O(1')	2.115 (5)	Nb(3)—O(5 ^{iv})	2.286 (5)
Nb(1)—O(2)	2.012 (5)	Nb(3)—O(6)	1.770 (5)
Nb(2)—O(2)	1.816 (5)	Nb(3)—O(7)	2.015 (5)
Nb(2)—O(3)	1.843 (5)	Nb(1)—Nb(2)	3.818 (5)
Nb(2)—O(4)	2.253 (5)	Nb(2)—Nb(3')	3.387 (5)
Nb(2)—O(5)	1.987 (1)	Nb(2)—Nb(3'')	3.804 (5)
Nb(2)—O(6)	2.132 (5)	As—O(7)	1.705 (4)
Nb(3)—O(3 ⁱⁱ)	1.970 (5)		
O(1)—Nb(1)—O(1')	180.0 (1)	O(5)—Nb(2)—O(5 ⁱⁱⁱ)	149.0 (3)
O(1)—Nb(1)—O(2)	95.7 (1)	O(6)—Nb(2)—O(5)	84.2 (1)
O(2)—Nb(1)—O(1')	84.3 (1)	O(3 ⁱⁱ)—Nb(3)—O(4 ⁱⁱⁱ)	89.0 (2)
O(2)—Nb(1)—O(2 ⁱⁱ)	89.4 (1)	O(3 ⁱⁱ)—Nb(3)—O(5 ^{iv})	86.0 (2)
O(2 ⁱⁱⁱ)—Nb(1)—O(2 ⁱⁱ)	89.4 (1)	O(4 ⁱⁱⁱ)—Nb(3)—O(4 ⁱⁱⁱ)	148.3 (3)
O(2)—Nb(1)—O(2 ⁱⁱⁱ)	168.5 (3)	O(5 ^{iv})—Nb(3)—O(4 ⁱⁱⁱ)	74.2 (1)
O(2)—Nb(2)—O(3)	98.4 (2)	O(6)—Nb(3)—O(3 ⁱⁱ)	94.8 (2)
O(2)—Nb(2)—O(4)	170.6 (2)	O(6)—Nb(3)—O(4 ⁱⁱⁱ)	105.8 (1)
O(2)—Nb(2)—O(5)	104.2 (1)	O(6)—Nb(3)—O(5 ^{iv})	179.2 (1)
O(2)—Nb(2)—O(6)	88.6 (2)	O(6)—Nb(3)—O(7)	95.3 (2)
O(3)—Nb(2)—O(4)	91.0 (2)	O(7)—Nb(3)—O(3 ⁱⁱ)	169.9 (2)
O(3)—Nb(2)—O(5)	94.0 (1)	O(7)—Nb(3)—O(4 ⁱⁱⁱ)	88.2 (2)
O(3)—Nb(2)—O(6)	173.0 (2)	O(7)—Nb(3)—O(5 ^{iv})	83.9 (2)
O(4)—Nb(2)—O(5)	75.0 (1)	O(7)—As—O(7 ^{iv})	108.4 (1)
O(4)—Nb(2)—O(6)	82.1 (2)	O(7)—As—O(7 ^v)	111.7 (2)

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

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All atoms were refined with anisotropic displacement parameters. The maximum and minimum residual electron-density peaks were located near O(3).

Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*.

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Li₃AsS₃

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Abstract

The structure of lithium trithioarsenate(3–) consists of AsS₃ pyramids in which all S atoms are non-bridging. The Li atoms are involved in LiS₄ tetrahedra and LiS_{3,2} distorted trigonal bipyramids. The tetrahedra are linked together *via* corners. This structure appears to be a new member of the M_3AX_3 group of compounds.

Comment

Sulfide glasses with a high alkali content are studied because of their high ionic conductivities, *e.g.* $10^{-3} \text{ } \Omega^{-1} \text{ cm}^{-1}$ at room temperature for thioborate-based glasses (Ménétrier *et al.*, 1991). Lithium arsenic sulfide based glasses, designated $x\text{Li}_2\text{S} \cdot (1-x)\text{As}_2\text{S}_3$, have been synthesized recently, giving homogeneous glasses for $0.67 < x < 0.75$ (Shastry *et al.*, 1993). The elucidation of the structural evolution occurring on the