

Fig. 1. [Ca(H₂O)₇][Cd₂Br₆] viewed down the *a* axis.

Discussion. Crystals of the title compound were formed when a flask containing a saturated solution of CaBr₂·CdBr₂ in equilibrium with the solid was opened to the air. The original crystals which dissolved at the same time have the composition CaCd₂Br₆·6H₂O (Balarew, Duhlev & Panaiotov, 1982). The bonding of

Ca to water and Cd to Br in [Ca(H₂O)₇][Cd₂Br₆] confirms the predictions of Balarew & Duhlev (1984) whose work prompted the present study. The interatomic distances are close to those expected. The Ca(H₂O)₇²⁺ and infinite chain Cd₂Br₆²⁻ ions are linked by hydrogen bonds with O...Br distances ranging from 3.30 to over 3.60 Å.

We wish to thank the Natural Sciences and Engineering Research Council of Canada for an operating grant and Professor Balarew and Dr Duhlev for suggesting the project.

References

- BALAREW, C. & DUHLEV, R. (1984). *J. Solid State Chem.* **55**, 1–6.
 BALAREW, C., DUHLEV, R. & PANAIOTOV, V. (1982). *Bulg. Acad. Sci. Commun. Dep. Chem.* **15**, 187–195.
 HALL, S. R. (1981). *Acta Cryst.* **A37**, 517–525.
International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1986). **C42**, 774–776

Structure of Lead(II) Copper(I) Arsenate(V)

BY F. PERTLIK

Institut für Mineralogie und Kristallographie der Universität Wien, Dr Karl-Lueger-Ring 1, A-1010 Vienna, Austria

(Received 22 July 1985; accepted 21 February 1986)

Abstract. PbCuAsO₄, *M_r* = 409.65, triclinic, *P* $\bar{1}$, *a* = 4.832 (1), *b* = 5.837 (1), *c* = 7.995 (2) Å, α = 78.68 (2), β = 74.95 (1), γ = 84.04 (1)°, *V* = 213.2 Å³, *Z* = 2, *D_x* = 6.382 Mg m⁻³, Mo *K*α, λ = 0.710688 Å, μ = 50.3 mm⁻¹, *F*(000) = 352, room temperature, *R* = 0.030 for 1039 observed reflections up to $\sin\theta/\lambda$ = 0.70 Å⁻¹. PbCuAsO₄ crystallizes in a network structure built up by three characteristic cation coordination polyhedra. The Pb atom is irregularly [4 + 2] coordinated by six O atoms. The monovalent Cu atom has a linear [2] coordination, and the pentavalent As atom has the usual tetrahedral [4] coordination by O atoms. PbCuAsO₄ was synthesized under hydrothermal conditions [490 (5) K, saturation vapour pressure].

Introduction. The oxidation state of arsenic in oxygen compounds indicates in mineralogy the conditions of formation of various ore deposits and their weathering during geologic periods. Therefore investigations within the system PbO, CuO, As₂O₃ and H₂O under hydrothermal conditions were performed to learn the different conditions for the formation of arsenite and arsenate minerals (Pertlik, 1977).

Experimental. PbCuAsO₄ is a product of the following chemical reaction: 2 g of an equimolar mixture of PbO, CuO, and As₂O₃ were placed in a 'Teflon'-coated vessel (*V* ≈ 6000 mm³) and the vessel was filled to ~80% of its volume with 1 *M* acetic acid. After heating for 4 d,

temperature 490 (5) K, crystals of the following compounds were found in the reaction mixture: Cu_2O (cuprite), CuAs_2O_4 (trippkeite), and PbCuAsO_4 (weight ratio $\approx 1:1:5$). Crystal sizes of all three compounds are approximately 0.10 mm^3 . Grains of PbCuAsO_4 are colourless, transparent, with high lustre. The atomic ratio of the elements Pb, As, and Cu was determined by electron-microprobe analysis, the oxidation state of the elements and the chemical formula by the crystal structure analysis. It is worth mentioning that for the formation of PbCuAsO_4 crystals the following reactions took place: Cu^{II} was reduced to Cu^{I} in combination with an oxidation of As^{III} to As^{V} . Under the given conditions, $T \leq 500 \text{ K}$, saturation vapour pressure, the formation of PbCuAsO_4 from a mixture of Cu_2O , PbO and an As^{V} oxide solution was not successful with acetic acid or water as solvent.

X-ray work: Stoe AED 2 four-circle diffractometer, graphite-monochromatized $\text{Mo K}\alpha$ radiation, $2\theta/\omega$ scan, min. step number 35 increased for (α_1, α_2) splitting, step width 0.03° , step time 0.5 to 1.5 s per step, data collection up to $2\theta = 60^\circ$; three standard reflections, no significant intensity variation. Crystal size: $0.114 \times 0.095 \times 0.019 \text{ mm}$. Lattice parameters from 30 reflections up to $2\theta = 50^\circ$. Numerical absorption correction according to crystal shape (transmission factors from 0.250 to 0.412). 1326 measured reflections ($h: -7 \rightarrow 7, k: -8 \rightarrow 8, l: -1 \rightarrow 11$) were merged; 1142 unique data of which 103 are less than $3\sigma(F_o)$. $R = 0.030$ and $wR = 0.026$, $w = 1/[\sigma(F_o)]^2$; max. $\Delta/\sigma < 10^{-3}$; max. and min. heights in final difference Fourier map 1.79 and -1.86 e \AA^{-3} . g for isotropic secondary extinction (Zachariasen, 1967) is $4.88 (16) \times 10^{-5}$.

Correction for Lorentz and polarization effects; complex scattering functions for neutral atoms (*International Tables for X-ray Crystallography*, 1974). All calculations were performed with the program system *STRUCSY* (Fa. Stoe & Cie, Darmstadt). Structure solved by direct methods, which yielded the positions of the metal atoms. Subsequent Fourier synthesis showed the atomic coordinates of the O atoms. Several cycles of full-matrix least-squares refinements on F with anisotropic temperature parameters. Structure parameters are listed in Table 1.* Some important interatomic distances are summarized in Table 2.

Discussion. The Pb atom is irregularly [4 + 2] coordinated by six O atoms. Such an irregular coordination polyhedron is typical for the crystal-chemical behaviour

* Lists of structure and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42844 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

not only of divalent lead but also of all elements with a 'stereometric activity' of the lone-pair electrons (*cf.* for lead: Sahl, 1970). The next cation neighbour of the Pb atom is a Cu atom. The distance $\text{Pb}-\text{Cu} = 3.325 (1) \text{ \AA}$ is in the same range as the sum of the metallic radii of these two elements and it seems therefore that it should not be considered a chemical bond. Worth mentioning is that two of the O—O edges within the Pb coordination figure are very short [$\text{O}(2)-\text{O}(2) = 2.74 (1)$ and $\text{O}(4)-\text{O}(4) = 2.77 (1) \text{ \AA}$], but both these atom pairs represent further common edges between two Pb coordination figures.

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature parameters (space group $P\bar{1}$, all atoms at general positions)

$$U_{\text{eq}} = (B_{11} + B_{22} + B_{33})/3.$$

	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Pb	0.9387 (1)	0.7103 (1)	0.6760 (1)	0.014
Cu	0.6346 (3)	0.1969 (2)	0.0043 (2)	0.021
As	0.4218 (2)	0.2030 (1)	0.6866 (1)	0.011
O(1)	0.7672 (14)	0.0289 (12)	0.1919 (11)	0.019
O(2)	0.7313 (12)	0.0953 (11)	0.5642 (11)	0.015
O(3)	0.5091 (14)	0.6306 (11)	0.1787 (11)	0.021
O(4)	0.7762 (12)	0.6262 (10)	0.4391 (10)	0.013

Table 2. Some selected bond lengths (\AA) with e.s.d.'s in parentheses for PbCuAsO_4

Pb—O(2)	2.334 (7)	Cu—O(1)	1.848 (8)
Pb—O(4)	2.380 (7)	Cu—O(3)	1.855 (8)
Pb—O(2')	2.462 (6)	As—O(1)	1.699 (7)
Pb—O(4')	2.468 (6)	As—O(2)	1.696 (7)
Pb—O(1)	2.704 (7)	As—O(3)	1.697 (7)
Pb—O(3)	2.945 (7)	As—O(4)	1.681 (6)

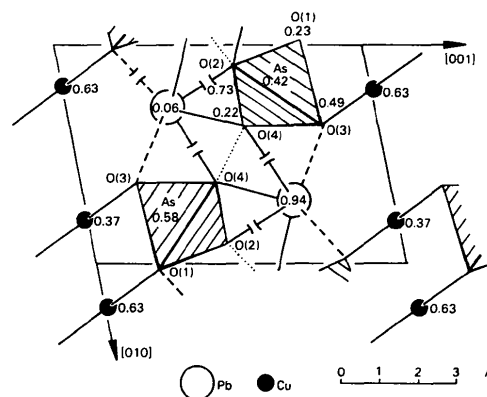


Fig. 1. Projection of the crystal structure of PbCuAsO_4 on to (100). The short O—O edges between the PbO_6 coordination polyhedra are dotted lines ($\text{O}-\text{O} < 2.8 \text{ \AA}$). The Pb—O distances from 2.50 to 3.00 \AA are drawn as broken lines. The atoms are labelled with x .

The Cu atom has an almost linear [2] coordination by O atoms [O(1)—Cu—O(3) = 178.1 (5)°]. Such a coordination is usual for monovalent Cu (*cf.* Wells, 1984). A comparable example is the structure of Cu₂O with a symmetry-restricted linear [2] coordination and Cu—O distances of 1.84 Å (Eichhorn, Spilker & Fischer, 1984).

The coordination polyhedron of the As atom is a tetrahedron, built up by four crystallographically different O atoms. As shown in Table 2, the four As—O distances are equal within two e.s.d.'s. Also the range of variation of the O—O distances [2.71 (1) to 2.80 (1) Å] within the AsO₄ tetrahedron is small.

The PbO₆ coordination polyhedra and the AsO₄ tetrahedra are connected in two dimensions, resulting in a formal [PbAsO₄] sheet parallel to (001). These sheets are combined *via* strong Cu—O bonds involving the monovalent Cu atom to form a network structure.

The main features of the atomic arrangements are represented in Fig. 1.

This work was supported by the Hochschuljubiläumsstiftung der Stadt Wien.

References

- EICHHORN, K., SPILKER, J. & FISCHER, K. (1984). *Acta Cryst.* **A40**, C160.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 PERTLIK, F. (1977). *Z. Anorg. Allg. Chem.* **436**, 201–206.
 SAHL, K. (1970). In *Handbook of Geochemistry*, Vol. II-5, 82/A. Berlin, Heidelberg, New York: Springer.
 WELLS, A. F. (1984). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.
 ZACHARIASEN, W. A. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1986). **C42**, 776–780

Structure of Deuterated Triammonium Hydrogendisulfate, † (ND₄)₃D(SO₄)₂, Phases (III') and (VI)

BY MASAHIRO TANAKA AND YOICHI SHIOZAKI

Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan

(Received 28 October 1985; accepted 27 January 1986)

Abstract. Phase (III'): $M_r = 260.3$, monoclinic, $P2_1$, $a = 10.087$ (2), $b = 5.835$ (1), $c = 15.542$ (2) Å, $\beta = 101.71$ (2)°, $V = 895.7$ Å³, $Z = 4$, $D_x = 1.930$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.60$ mm⁻¹, $F(000) = 521.84$, $T = 189 \pm 7$ K, $R = 0.028$ for 2156 unique reflections. Phase (VI): triclinic, $P1$, $a = 10.123$ (1), $b = 5.846$ (1), $c = 15.476$ (1) Å, $\alpha = 89.98$ (1), $\beta = 101.78$ (1), $\gamma = 90.01$ (1)°, $V = 896.6$ Å³, $Z = 4$, $D_x = 1.928$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.60$ mm⁻¹, $F(000) = 521.84$, $T = 233 \pm 7$ K, $R = 0.035$ for 4367 unique reflections. The structures in phases (III') and (VI) have pseudo $P2_1/c$ symmetry. It has been found that the ferroelectric polarization observed in phase (VI) is mainly caused by the arrangement of the distorted SO₄²⁻ ions. The polarization along c^* is expected to be easily reversed by slightly changing the SO₄²⁻ geometries.

Introduction. Triammonium hydrogendisulfate, (NH₄)₃H(SO₄)₂, at 0.1 MPa shows successive phase transitions and has six phases (I), (II), (III), (IV), (V),

(VII) (Gossner, 1904; Fischer, 1914; Gesi, 1976*a*; Gesi & Ozawa, 1977; Suzuki, 1979; Suzuki, Oshino, Gesi & Makita, 1979; Gesi, 1980); phase (VII) shows ferroelectricity (Gesi, 1980). Another ferroelectric phase, (VI), exists at a hydrostatic pressure higher than about 500 MPa (Gesi, 1976*b*).

The deuterated crystal also exhibits complicated successive phase transitions; the six isostructural phases at 0.1 MPa are designated (I), (II), (III), (VI), (III') and (VII) with descending temperature (Osaka, Makita & Gesi, 1977; Gesi, Ozawa, Osaka & Makita, 1980). The ferroelectric phase (VI) appears at 0.1 MPa, showing an isotope effect. Recently, phases (IX) and (VIII) were found at hydrostatic pressures higher than about 300 MPa and about 450 MPa (Osaka, Makita & Gesi, 1980).

Gesi (1977) suggested that the modified Mitsui (1958) model was effective for explaining the dielectric behaviour of (NH₄)₃H(SO₄)₂. However, the details of the phase transitions and the origin of the spontaneous polarization are not explained well. The O—H...O hydrogen bonds, which link neighbouring SO₄²⁻ ions, are influenced by deuteration; the O...O bond length is

† Tri(²H₄) ammonium deuteriumbis(sulfate).