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Hydrothermal Synthesis and Structure of Sodium Tetracopper(II) Triarsenate(V)

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Dedicated to Professor Dr Kurt Komarek (*Vienna*) *on the occasion of his* 60th *birthday*

Abstract. $NaCu_4(AsO_4)_3$, $M_r = 693{\cdot}91$, monoclinic, $C2/c$, $a = 12{\cdot}051$ (1), $b = 12{\cdot}420$ (1), $c = 7{\cdot}290$ (1) Å, $\beta = 118{\cdot}10$ (1)°, $V = 962{\cdot}5$ Å^3, $Z = 4$, $D_x = 4{\cdot}79$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 18{\cdot}6$ mm^{-1}, $F(000) = 1288$, room temperature, $R = 0{\cdot}030$ for 1946 observed reflections up to $\sin\theta/\lambda = 0{\cdot}80$ Å^{-1}. $NaCu_4(AsO_4)_3$ crystallizes in a network structure with no pronounced cleavage. The Na^{I} atom is [8] coordinated by O atoms. The three Cu^{II} atoms are [4] and [4 + 2] coordinated. The two As^{V} atoms have a tetrahedral [4] coordination. Worth mentioning is a common O—O edge of the $Cu(1)O_4$ square and the $As(1)O_4$ tetrahedron of 2·435 Å; O—Cu—O = 78·9° and O—As—O = 89·1°. $NaCu_4(AsO_4)_3$ was synthesized under hydrothermal conditions [490 (5) K, saturated vapour pressure].

Introduction. These investigations on the system CuO–As_2O_3/As_2O_5–H_2O were performed to ascertain the different conditions for the formation of arsenite and arsenate minerals respectively (*cf.* Pertlik, 1977, 1986). The compound $NaCu_4(AsO_4)_3$ crystallizes under the same hydrothermal conditions as $Cu_2(OH)AsO_4$, olivenite (Heritsch, 1938; Walitzi, 1962, 1963; Toman, 1977). Crystals of both compounds were found in the same experiment.

Experimental. Crystals of $NaCu_4(AsO_4)_3$ were synthesized under the following conditions: 2 g of an equimolar mixture of $Na_2HAsO_4.7H_2O$ and $Cu(CH_3COO)_2.H_2O$ were put into a 'Teflon'-coated vessel ($V \simeq 6000$ mm^3) and the vessel was filled to ~80% capacity with water. Crystals of $Cu_2(OH)AsO_4$ and $NaCu_4(AsO_4)_3$ (weight ratio 20:1) were formed after heating at 490 (5) K for 100 days (the liquid phase of the reaction was not investigated in detail). The crystals of both compounds vary up to 0·2 mm in size. $NaCu_4(AsO_4)_3$ is light blue, transparent and the crystals are elongated parallel to [001]. The approximate ratios of the elements Na, Cu and As were determined by XRF analysis; the stoichiometric formula was deduced from the crystal structure analysis.

Data were collected with a Stoe AED 2 four-circle diffractometer, Mo $K\alpha$ radiation. Measurements were taken up to $2\theta = 70°$, $2\theta/\omega$ scan. Minimum step number was 40 [increased to allow for the (α_1, α_2) splitting], step width 0·03°, step time between 0·5 and 1·5 s. Three standard reflections showed no significant variation of intensities during the measurement time.

The crystal size was 0·045 × 0·050 × 0·205 mm. Lattice parameters from 75 reflections up to $2\theta = 50°$ were determined. Empirical absorption corrections were derived from ψ scans of three reflections (transmission factors from 0·13 to 0·29). 4406 measured reflections (h: −19→19, k: −20→0, l: −12→12), $R_{int} = 0{\cdot}040$; 2109 unique reflections of which 263 have $F_o < 3\sigma(F_o)$. $R = 0{\cdot}030$ and $wR = 0{\cdot}026$, $w = 1/[\sigma(F_o)]^2$; number of parameters to refine: 94; max. $\Delta/\sigma < 10^{-3}$; max. and min. height in final difference Fourier map 1·1 and −1·4 e Å^{-3}. The value of g for the isotropic secondary extinction (Zachariasen, 1967) is 2·28 (11) × 10^{-6}.

Corrections were made for Lorentz and polarization effects; complex scattering functions for neutral atoms (*International Tables for X-ray Crystallography*, 1974) were used. All calculations were performed with the program system *STRUCSY* (Fa. Stoe & Cie, Darmstadt). Direct methods yielded the positions of the metal atoms. A subsequent Fourier synthesis revealed the atomic coordinates of the oxygen atoms. Several cycles of full-matrix least-squares calculations on F gave the refined positional and anisotropic temperature parameters of the atoms; structure parameters are listed in Table 1.* Some important interatomic distances are summarized in Table 2.

Discussion. Within a distance of 4·0 Å the Na atom is coordinated with eight O atoms. The individual Na—O distances (2·479 to 2·783 Å) as well as the average

* Lists of structure factors and thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43453 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Na—O distance (2·633 Å) are in good agreement with values known for other compounds. The coordination polyhedron of the Na atom has the site symmetry 2 and can best be described as a combination of a flat and a steep 'tetragonal' disphenoid. The two disphenoids are twisted with respect to each other by 90° and compressed along the '$\bar{4}$ axis', *i.e.* parallel to [010]. The Na coordination polyhedra form chains parallel to [001] sharing edges [O(23)—O(23′) = 3·555 Å, O(23)—Na—O(23′) = 88·5°].

Each of the three crystallographically different Cu atoms has four nearest-neighbour O atoms forming slightly distorted CuO_4 squares. The Cu—O distances in these squares are <2·0 Å. Two of the inequivalent Cu atoms have another two O neighbours at the apices of an octahedron elongated parallel to its fourfold axis (Cu—O between 2·31 and 2·51 Å). Any other O atoms all have Cu—O >3·0 Å. The average Cu—O distances within the CuO_4 squares are 1·964 and 1·980 Å for the [4 + 2] coordinated Cu atoms, but only 1·911 Å for the [4] coordinated Cu atom.

The As atoms are tetrahedrally coordinated with oxygen atoms. The As—O bond lengths are within the range 1·672 to 1·736 Å. The mean values are 1·704 Å for As(1)—O and 1·691 Å for As(2)—O. It is worth mentioning that the As(1)O_4 tetrahedron shares a common O—O edge with the Cu(1)O_4 square. This leads to a significant distortion of these two coordination figures. The O—O distance along the common edge is only 2·435 Å [O(11)—O(11′)]. The O(11)—As(1)—O(11′) angle is only 89·1° and the O(11)—Cu(1)—O(11′) angle is 78·9°. The two As(1)—O(11) bond lengths of 1·736 Å are the longest ones found in $NaCu_4(AsO_4)_3$. In addition the Cu(1)O_4 square shares a common edge with the Cu(2)O_4 square [O(21)—O(21′) = 2·530 Å; O(21)—Cu(1)—O(21′) = 83·2°; O(21)—Cu(2)—O(21′) = 78·8°]. The three atoms, As(1), Cu(1), and Cu(2), whose coordination polyhedra are connected by common O—O edges are located on the twofold axis. The Cu(3)O_4 squares and the As(2)O_4 tetrahedra are connected to these 'linear' Cu(1)Cu(2)As(1)O_8 units by sharing O-atom corners.

Table 1. *Fractional atomic coordinates* (×10⁵ *for* Cu *and* As; ×10⁴ *for* O *and* Na) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

$U_{eq} = [(U_{11} + U_{22} + U_{33})/3] \times 10^4$ (Å²).

	x	y	z	U_{eq}
Cu(1)	0	50441 (4)	¼	111
Cu(2)	0	26567 (5)	¼	120
Cu(3)	21999 (3)	15632 (3)	14007 (7)	98
As(1)	0	72320 (4)	¼	80
As(2)	27310 (3)	38249 (3)	37936 (5)	77
O(11)	8968 (2)	6236 (2)	2420 (4)	92
O(12)	9566 (2)	7982 (2)	366 (4)	127
O(21)	1184 (2)	3898 (2)	3249 (4)	140
O(22)	2778 (2)	3064 (2)	1922 (4)	120
O(23)	3331 (2)	5048 (2)	3825 (4)	132
O(24)	3562 (2)	3333 (2)	6225 (4)	112
Na	0	9923 (2)	¼	199

Table 2. *Interatomic distances* (Å) *for the* Cu, As *and* Na *atoms and bond angles* (°) *for the* Cu *and* As *atoms*

The e.s.d.'s are ≤0·003 Å for the interatomic distances and ≤0·1° for the angles.

Cu(1)—O(11)	1·917		2×
O(21)	1·905		2×
O(11)—O(11′)	78·9	2·435	
O(21)	166·9	3·797	2×
O(21′)	100·4	2·936	2×
O(21)—O(21′)	83·2	2·530	
Cu(2)—O(12)	2·509		2×
O(21)	1·994		2×
O(24)	1·965		2×
O(12)—O(12′)	143·2	4·761	
O(21)	94·0	3·311	2×
O(21′)	114·8	3·803	2×
O(24)	73·3	2·707	2×
O(24′)	83·8	3·015	2×
O(21)—O(21′)	78·8	2·530	
O(24)	89·8	2·794	2×
O(24′)	166·2	3·930	2×
O(24)—O(24′)	102·6	3·066	
As(1)—O(11)	1·736		2×
O(12)	1·672		2×
O(11)—O(11′)	89·1	2·435	
O(12)	117·4	2·912	2×
O(12′)	109·5	2·782	2×
O(12)—O(12′)	112·3	2·777	

Cu(3)—O(11)	1·940	
O(12)	1·981	
O(22)	1·964	
O(22′)	2·479	
O(23)	1·970	
O(24)	2·314	
O(11)—O(12)	163·4	3·880
O(22)	84·2	2·618
O(22′)	84·1	2·987
O(23)	95·0	2·882
O(24)	118·4	3·659
O(12)—O(22)	91·7	2·830
O(22′)	79·3	2·872
O(23)	90·6	2·809
O(24)	77·7	2·707
O(22)—O(22′)	81·1	2·915
O(23)	174·3	3·929
O(24)	91·8	3·082
O(22′)—O(23)	104·4	3·529
O(24)	155·7	4·685
O(23)—O(24)	83·6	2·866
As(2)—O(21)	1·716	
O(22)	1·682	
O(23)	1·678	
O(24)	1·687	
O(21)—O(22)	106·9	2·729
O(23)	111·7	2·808
O(24)	107·7	2·748
O(22)—O(23)	109·9	2·751
O(24)	114·8	2·837
O(23)—O(24)	106·0	2·686

Na—O(12)	2·783	2×
O(23)	2·614	2×
O(23′)	2·479	2×
O(24)	2·654	2×

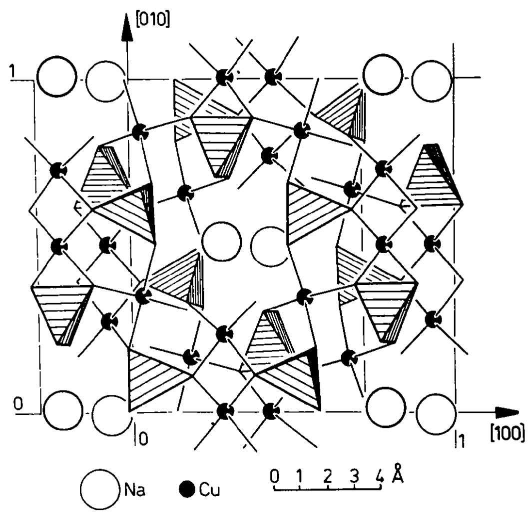

Fig. 1. Orthogonal projection of the crystal structure of $NaCu_4(AsO_4)_3$ onto (001). Within the Cu polyhedra only Cu—O distances <2·0 Å are shown. AsO_4 tetrahedra are shaded.

The structure is a three-dimensional framework with channels parallel to [001] at $x \simeq 0{\cdot}0$ and $y \simeq 0{\cdot}0$ *etc.* The Na atoms are located within these channels. The structure of $NaCu_4(AsO_4)_3$ shown in Fig. 1 is drawn as a projection onto (001).

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Structure of Diammonium Tetrabromodioxouranate(VI) Dihydrate

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Abstract. $[NH_4]_2[UO_2Br_4].2H_2O$, $M_r = 661{\cdot}7$, triclinic, $P\bar{1}$, $a = 6{\cdot}8850\ (9)$, $b = 6{\cdot}887\ (1)$, $c = 7{\cdot}7370\ (7)$ Å, $\alpha = 94{\cdot}44\ (1)$, $\beta = 98{\cdot}78\ (1)$, $\gamma = 116{\cdot}79\ (1)°$, $V = 319\ (1)$ Å^3, $Z = 1$, $D_x = 3{\cdot}44$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 24{\cdot}44$ mm^{-1}, $F(000) = 290$, $T = 295\ (1)$ K, $R = 0{\cdot}030$ for 1027 observed reflections. The structure is composed of $[UO_2Br_4]^{2-}$ and $[NH_4]^+$ ions. U is octahedrally coordinated and the symmetry of $[UO_2Br_4]^{2-}$ is approximately D_{4h} with U—O = 1·766 (6) Å and average U—Br = 2·813 (1) Å.

Introduction. A large number of uranyl tetrahalide complexes of the type $M_2UO_2X_4$ (M = univalent cation, X = Cl, Br) are known; among them the structures of $Cs_2UO_2Cl_4$ (Hall, Rae & Waters, 1966), $Cs_2UO_2Br_4$ (Mikhailov & Kuznetsov, 1971), $[N(CH_3)_4]_2[UO_2Cl_4]$ and $[N(CH_3)_4]_2[UO_2Br_4]$ (Di Sipio, Tondello, Pelizzi, Ingletto & Montenero, 1974*a*; Jensen & Dickerson, 1974), $[NH(C_2H_5)_3]_2[UO_2Cl_4]$ (Bois, Nguyen Quy Dao & Rodier, 1976), $[N(C_3H_7)_4][UO_2Cl_4]$ (Di Sipio *et al.*, 1974*d*), $[N(C_3H_7)_4][UO_2Br_4]$ (Di Sipio *et al.*, 1974*b*), $[N(C_4H_9)_4][UO_2Cl_4]$ (Di Sipio *et al.*, 1974*c*), $[N(C_4H_9)_4][UO_2Br_4]$ (Di Sipio *et al.*, 1977) have been determined.

Experimental. Crystals of the title compound obtained by slow cooling of a boiling solution of UBr_4 in methyl nitrite. Single crystal (0·2 × 0·3 × 0·2 mm) suitable for X-ray analysis sealed in a thin-walled glass capillary under an inert atmosphere. Enraf CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections. Space group $P1$ or $P\bar{1}$ with $P\bar{1}$ consistent with statistics. 2247 reflections collected (θ–2θ scan mode) in range $4 \leq 2\theta \leq 50°$, 2142 considered observed [$I \geq \sigma(I)$, $\pm h$, $\pm k$, $\pm l$; index range h −8/8, k −8/8, l −9/9], averaged to 1118 unique reflections ($R_{\text{int}} = 0{\cdot}008$).

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