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On the Crystal Chemistry of Three Copper(II)-Arsenates: $Cu_3(AsO_4)_2$-III, $Na_4Cu(AsO_4)_2$, and $KCu_4(AsO_4)_3$

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The three copper(II)-arsenates were synthesized under hydrothermal conditions; their crystal structures were determined by single-crystal X-ray diffraction methods:

$Cu_3(AsO_4)_2$-III: $a = 5.046(2)$ Å, $b = 5.417(2)$ Å, $c = 6.354(2)$ Å, $\alpha = 70.61(2)°$, $\beta = 86.52(2)°$, $\gamma = 68.43(2)°$, $Z = 1$, space group $P\bar{1}$, $R = 0.035$ for 1674 reflections with $\sin\Theta/\lambda \leqslant 0.90$ Å^{-1}.

$Na_4Cu(AsO_4)_2$: $a = 4.882(2)$ Å, $b = 5.870(2)$ Å, $c = 6.958(3)$ Å, $\alpha = 98.51(2)°$, $\beta = 90.76(2)°$, $\gamma = 105.97(2)°$, $Z = 1$, space group $P\bar{1}$, $R = 0.028$ for 2157 reflections with $\sin\Theta/\lambda \leqslant 0.90$ Å^{-1}.

$KCu_4(AsO_4)_3$: $a = 12.234(5)$ Å, $b = 12.438(5)$ Å, $c = 7.307(3)$ Å, $\beta = 118.17(2)°$, $Z = 4$, space group $C2/c$, $R = 0.029$ for 1896 reflections with $\sin\Theta/\lambda \leqslant 0.80$ Å^{-1}.

Within these three compounds the Cu atoms are square planar [4], tetragonal pyramidal [4 + 1], and tetragonal bipyramidal [4 + 2] coordinated by O atoms; an exception is the $Cu(2)^{[4+1]}$ atom in $Cu_3(AsO_4)_2$-III: the coordination polyhedron is a representative for the transition from a tetragonal pyramid towards a trigonal bipyramid. In $KCu_4(AsO_4)_3$ the $Cu(1)^{[4]}O_4$ square and the $As(1)O_4$ tetrahedron share a common O—O edge of 2.428(5) Å, resulting in distortions of both the CuO_4 square and the AsO_4 tetrahedron. The two Na atoms in $Na_4Cu(AsO_4)_2$ are [6] coordinated, the K atom in $KCu_4(AsO_4)_3$ is [8] coordinated by O atoms.

[Keywords: $Cu_3(AsO_4)_2$-III; $Na_4Cu(AsO_4)_2$; $KCu_4(AsO_4)_3$; *Hydrothermal synthesis; Crystal structure; Crystal chemistry]*

Zur Kristallchemie dreier Kupfer(II)-Arsenate: $Cu_3(AsO_4)_2$-III, $Na_4Cu(AsO_4)_2$ *und* $KCu_4(AsO_4)_3$

Die drei Kupfer(II)-Arsenate wurden unter Hydrothermalbedingungen gezüchtet und ihre Kristallstrukturen mittels Einkristall-Röntgenbeugungsmethoden ermittelt:

$Cu_3(AsO_4)_2$-III: $a = 5.046(2)$ Å, $b = 5.417(2)$ Å, $c = 6.354(2)$ Å, $\alpha = 70.61(2)^\circ$, $\beta = 86.52(2)^\circ$, $\gamma = 68.43(2)^\circ$, $Z = 1$, Raumgruppe $P\bar{1}$, $R = 0.035$ für 1674 Reflexe mit $\sin\Theta/\lambda \leq 0.90$ Å^{-1}.

$Na_4Cu(AsO_4)_2$: $a = 4.882(2)$ Å, $b = 5.870(2)$ Å, $c = 6.958(3)$ Å, $\alpha = 98.51(2)^\circ$, $\beta = 90.76(2)^\circ$, $\gamma = 105.97(2)^\circ$, $Z = 1$, Raumgruppe $P\bar{1}$, $R = 0.028$ für 2157 Reflexe mit $\sin\Theta/\lambda \leq 0.90$ Å^{-1}.

$KCu_4(AsO_4)_3$: $a = 12.234(5)$ Å, $b = 12.438(5)$ Å, $c = 7.307(3)$ Å, $\beta = 118.17(2)^\circ$, $Z = 4$, Raumgruppe C2/c, $R = 0.029$ für 1896 Reflexe mit $\sin\Theta/\lambda \leq 0.80$ Å^{-1}.

Die Cu-Atome in diesen drei Verbindungen sind durch O-Atome quadratisch planar [4], tetragonal pyramidal [4 + 1] und tetragonal dipyramidal [4 + 2]-koordiniert; eine Ausnahme ist das $Cu(2)^{[4+1]}$-Atom in $Cu_3(AsO_4)_2$-III: Das Koordinationspolyeder stellt einen Vertreter des Übergangs von einer tetragonalen Pyramide zu einer trigonalen Dipyramide dar. In $KCu_4(AsO_4)_3$ haben das $Cu(1)^{[4]}O_4$-Quadrat und das $As(1)O_4$-Tetraeder eine gemeinsame O—O-Kante von 2.428(5) Å, was eine Verzerrung der beiden Koordinationsfiguren CuO_4-Quadrat und AsO_4-Tetraeder bedingt. Die zwei Na-Atome in $Na_4Cu(AsO_4)_3$ sind durch O-Atome [6]-koordiniert, das K-Atom in $KCu_4(AsO_4)_3$ ist [8]-koordiniert.

Introduction

Formally divalent Cu atoms have a d^9 electron configuration. Therefore their stereochemistry is characterized by distortions of the coordination polyhedra known as the *Jahn-Teller* effect. Common coordination figures around Cu atoms in inorganic oxygen bearing compounds are a square ($Cu^{[4]}O_4$), a tetragonal pyramid ($Cu^{[4+1]}O_5$), and a tetragonal bipyramid = "elongated octahedron" ($Cu^{[4+2]}O_6$); transitions between these three ideal coordination polyhedra or minor distortions are well known. Recently various compounds showing definite deviations from this concept were investigated [1–6].

In connection with studies of the stereochemistry of Cu(II) atoms in inorganic compounds the crystal structures of three Cu(II)-arsenates were investigated in detail:

(a) $Cu_3(AsO_4)_2$-III is isotypic to $Cu_3(PO_4)_2$ [7]. Tricopper(II)-diarsenate(V) crystallizes in three different modifications. Two modifications are monoclinic, space group C^5_{2h}; their crystal structures were described for the different cell choices $P2_1/a$ [8] and $P2_1/c$ [9]; the first one is known to occur in nature and it bears the mineral name lammerite [8]. For distinction lammerite is denoted as $Cu_3(AsO_4)$-I, the other monoclinic modification [9] is denoted as $Cu_3(AsO_4)_2$-II, the new triclinc modification is denoted as $Cu_3(AsO_4)_2$-III.

(b) $Na_4Cu(AsO_4)_2$; investigations of phases occuring in the system Na_3PO_4—$Cu_3(PO_4)_2$ including an X-ray powder diffraction diagram of $Na_4Cu(PO_4)_2$ is given among others in [10].

(c) $KCu_4(AsO_4)_3$ is isotypic to $NaCu_4(AsO_4)_3$ [11], but it represents a quite different structure type as compared with $KCu_4(PO_4)_3$ [12].

Experimental

Crystals of $Cu_3(AsO_4)_2$-III, $Na_4Cu(AsO_4)_2$, and $KCu_4(AsO_4)_3$ were synthesized under hydrothermal conditions. To obtain crystals of $Cu_3(AsO_4)_2$-III 2 g of an equimolar mixture of cubic As_2O_3, $Cu(NO_3)_2 \cdot 2H_2O$, and 0.5 g elementary Fe was put into a steel vessel lined with "teflon" and a reaction capacity of ~ 6 ml. H_2O was added to 80% content. Trials to obtain this compound in the system As_2O_3—CuO—H_2O-(± nitrate) failed; these conditions yielded only the modification $Cu_3(AsO_4)_2$-I [8]. The synthesis of $Na_4Cu(AsO_4)_2$ is described in [13], and that of $KCu_4(AsO_4)_3$ is described in [14].

The crystal data and relevant data concerning the measurement of the X-ray intensities are summarized in Table 1. Corrections were applied for absorption (*Gauss*ian integration according to the crystal shape), and for *Lorentz* and polarization effects. For $Cu_3(AsO_4)_2$-III and $Na_4Cu(AsO_4)_2$ the As and Cu atoms were located by direct methods; subsequent *Fourier* and difference *Fourier* summations yielded the atomic coordinates of the remaining atoms. For $KCu_4(AsO_4)_3$ the atomic parameters of $NaCu_4(AsO_4)_3$ [11] were used in the starting set of refinement. Complex neutral atomic scattering functions [15] were used. Table 2 gives the final obtained structure parameters. Selected interatomic distances and bond angles are compiled in Table 3.

Results and Discussion

The Coordination Polyhedra

The coordination polyhedra of the alkaline earth atoms in $Na_4Cu(AsO_4)_2$ and in $KCu_4(AsO_4)_3$ are clear-cut. The K atom in $KCu_4(AsO_4)_3$ is eight-coordinated, K—O ranges from 2.619 Å to 2.763 Å (average K—O bond length 2.712 Å); next O atom neighbours have K—O $\geqslant$ 3.40 Å. In the isotypic compound $NaCu_4(AsO_4)_3$ [11] the eight Na—O bond lengths vary from 2.479 Å to 2.783 Å (average Na—O bond length 2.633 Å). The two crystallographically different Na atoms in $Na_4Cu(AsO_4)_2$ are six-coordinated and the Na—O bond lengths vary from 2.260 Å to 2.762 Å (average values 2.462 Å and 2.506 Å); next O atom neighbours have Na—O $\geqslant$ 3.10 Å. The lower coordination number of the Na atoms and the shorter Na—O distances in $Na_4Cu(AsO_4)_2$ as compared with $NaCu_4(AsO_4)_3$ are considered to be the reason why a potassium compound isotypic to $Na_4Cu(AsO_4)_2$ has not been observed up to now.

The atoms Cu(1) in $Cu_3(AsO_4)_2$-III, Cu in $Na_4Cu(AsO_4)_2$, and Cu(1) in $KCu_4(AsO_4)_3$ are planar [4]-coordinated. The former two coordination polyhedra are approximately squares, the latter one is strongly distorted: it shares a common O(11)—O(11) edge with the $As(1)O_4$ tetrahedron. This causes a short O(11)—O(11) distance of 2.428(5) Å and a small O(11)—Cu(1)—O(11) angle of 78.6(1)°. The analogous values in the compound $NaCu_4(AsO_4)_3$ are 2.435(3) Å and 78.9(1)° [11]. The coordination polyhedra $Cu(2)^{[4+2]}O_6$ and $Cu(3)^{[4+2]}O_6$ in $KCu_4(AsO_4)_3$

Table 1. *Unit cell, data collection, and structure refinement*

	$Cu_3(AsO_4)_2$-III	$Na_4Cu(AsO_4)_2$	$KCu_4(AsO_4)_3$
a (Å)	5.046(2)	4.882(2)	12.234(5)
b (Å)	5.417(2)	5.870(2)	12.438(5)
c (Å)	6.354(2)	6.958(3)	7.307(3)
α (°)	70.61(2)	98.51(2)	—
β (°)	86.52(2)	90.76(2)	118.17(2)
γ (°)	68.43(2)	105.97(2)	—
V (Å^3)	152.0	189.3	980.2
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
Z	1	1	4
μ(MoKα) (cm^{-1})	206.8	114.7	186.2
ρ_{calc} (g cm^{-3})	5.12	3.80	4.81
Colour	emerald green	light green	bluish violett
Crystal shape	tabular ‖ (001)	needles ‖ [100]	slabs ‖ (010)
Crystal dimensions (mm^3)	$0.05 \times 0.14 \times 0.16$	$0.08 \times 0.08 \times 0.40$	$0.04 \times 0.15 \times 0.24$
Observed crystallographic forms	$\{001\}, \{10\bar{1}\}, \{121\}, \{100\}$	$\{001\}, \{010\}, \{011\}, \{100\}$	$\{010\}, \{10\bar{1}\}, \{100\}, \{001\}, \{101\}, \{201\}$
Max. 2Θ	80	80	70
Measured reflections*	2358	3719	4676
Unique data	1897	2350	2169
Data with $F_o > 3\sigma(F_o)$	1674	2157	1896
Range of transmission factors	0.11–0.41	0.34–0.50	0.07–0.34
Variables	62	71	94
R	0.035	0.028	0.029
R_w, $w = [\sigma(F_o)]^{-2}$	0.032	0.024	0.025
Extinction g according to (17)	$1.67(5) \cdot 10^{-4}$	$6.6(2) \cdot 10^{-3}$	$4.8(2) \cdot 10^{-6}$

* Four circle diffractometer AED2 and program system STRUCSY (16); 45 steps per reflection increased for α_1–α_2 dispersion, 7 steps each side for background correction, step width 0.03°, measuring time per step 0.5 to 1.5 s, $2\Theta/\omega$ scan mode

Table 2. *Atomic coordinates and thermal parameters*

$$ATF = \exp\left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*\right];\ U_{equ} = \frac{1}{3} \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i a_j a_i^* a_j^*$$

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{equ}
$Cu_3(AsO_4)_2$-III										
Cu(1)	0	0	0	0.0068(2)	0.0081(2)	0.0115(3)	-0.0026(2)	-0.0012(2)	-0.0018(2)	0.0077
Cu(2)	0.26666(9)	0.20595(9)	0.32513(9)	0.0086(2)	0.0141(2)	0.0080(2)	0.0009(1)	-0.0012(1)	-0.0057(2)	0.0091
As	0.36191(6)	0.35468(7)	0.77957(7)	0.0057(1)	0.0073(1)	0.0063(2)	-0.0015(1)	0.0004(1)	-0.0023(1)	0.0056
O(1)	0.1429(5)	0.6794(5)	0.6415(6)	0.0079(8)	0.0085(8)	0.0131(13)	0.0000(6)	0.0001(9)	0.0007(9)	0.0100
O(2)	0.6856(5)	0.3533(5)	0.8349(5)	0.0071(8)	0.0095(8)	0.0143(13)	-0.0030(7)	-0.0016(9)	-0.0021(9)	0.0090
O(3)	0.2208(5)	0.2136(5)	1.0199(5)	0.0102(8)	0.0113(9)	0.0064(10)	-0.0059(7)	0.0024(8)	-0.0036(8)	0.0072
O(4)	0.3803(5)	0.1365(5)	0.6332(5)	0.0110(9)	0.0102(9)	0.0085(11)	0.0005(7)	-0.0024(9)	-0.0052(9)	0.0088
$Na_4Cu(AsO_4)_2$										
Na(1)	0.2898(2)	0.5767(2)	0.1692(1)	0.0172(4)	0.0197(4)	0.0108(4)	0.0033(3)	-0.0004(3)	0.0018(3)	0.0151
Na(2)	0.8394(2)	0.7401(2)	0.4255(2)	0.0185(4)	0.0267(4)	0.0136(5)	0.0083(3)	-0.0013(3)	-0.0034(4)	0.0184
Cu	0	0	0	0.0074(1)	0.0124(1)	0.0071(1)	0.0032(1)	0.0003(1)	-0.0002(1)	0.0084
As	0.60051(4)	0.19540(3)	0.26541(3)	0.0075(1)	0.0113(1)	0.0062(1)	0.0029(1)	-0.0001(1)	-0.0005(1)	0.0078
O(1)	0.6866(3)	0.2751(3)	0.5034(2)	0.0136(6)	0.0227(7)	0.0067(6)	0.0021(5)	-0.0012(5)	-0.0019(5)	0.0141
O(2)	0.6830(3)	-0.0590(2)	0.1691(2)	0.0111(5)	0.0120(5)	0.0123(7)	0.0037(4)	0.0036(5)	-0.0003(5)	0.0111
O(3)	0.2396(3)	0.1440(3)	0.2373(2)	0.0079(5)	0.0296(8)	0.0104(7)	0.0063(5)	-0.0024(5)	-0.0054(6)	0.0153
O(4)	0.7636(3)	0.4271(3)	0.1544(2)	0.0199(7)	0.0135(5)	0.0105(7)	0.0016(5)	-0.0006(5)	0.0028(5)	0.0141
$KCu_4(AsO_4)_3$										
K	0	0.98753(9)	0.25	0.0171(4)	0.0162(4)	0.0177(4)	0	0.0056(3)	0	0.0153
Cu(1)	0	0.50351(4)	0.25	0.0093(2)	0.0068(2)	0.0186(2)	0	0.0071(2)	0	0.0093
Cu(2)	0	0.26307(5)	0.25	0.0083(2)	0.0089(2)	0.0265(3)	0	0.0069(2)	0	0.0124
Cu(3)	0.22379(3)	0.15695(3)	0.14369(6)	0.0079(1)	0.0078(2)	0.0174(2)	0.0001(1)	0.0053(1)	-0.0009(1)	0.0094
As(1)	0	0.72197(4)	0.25	0.0078(2)	0.0077(2)	0.0091(2)	0	0.0030(1)	0	0.0073
As(2)	0.26780(3)	0.38189(2)	0.37532(4)	0.0079(1)	0.0065(1)	0.0101(1)	0.0005(1)	0.0046(1)	0.0001(1)	0.0067
O(11)	-0.1013(2)	0.6228(2)	0.2423(3)	0.0085(8)	0.0074(9)	0.0223(10)	0.0009(7)	0.0076(7)	0.0000(7)	0.0103
O(12)	-0.0466(2)	0.7958(2)	0.0350(3)	0.0089(8)	0.0140(10)	0.0110(8)	0.0009(8)	0.0037(7)	0.0030(7)	0.0101
O(21)	0.1154(2)	0.3869(2)	0.3209(4)	0.0098(9)	0.0094(9)	0.0272(11)	0.0010(8)	0.0104(8)	0.0005(8)	0.0122
O(22)	0.2777(2)	0.3067(2)	0.1931(3)	0.0139(9)	0.0106(9)	0.0121(8)	-0.0014(8)	0.0077(7)	-0.0018(7)	0.0098
O(23)	0.3199(2)	0.5046(2)	0.3676(4)	0.0165(10)	0.0067(9)	0.0225(10)	-0.0005(8)	0.0113(8)	0.0013(8)	0.0117
O(24)	0.3531(2)	0.3329(2)	0.6180(3)	0.0122(9)	0.0114(10)	0.0116(8)	0.0029(8)	0.0055(7)	0.0028(7)	0.0100

are elongated "octahedra" as characteristic for the *Jahn-Teller* distortion caused by the electron configuration of Cu(II) atoms [3, 18–21].

Worthy to note is the coordination polyhedron of the Cu(2) atom in $Cu_3(AsO_4)_2$-III. It forms four "short" Cu—O bonds < 2.0 Å and one "long" bond Cu(2)—O(2) = 2.360 Å. At the one hand this coordination figure can be described as a distorted tetragonal pyramid [one of the two O—Cu(2)—O angles between opposite O atoms within the basal plane is 141.6(2)° instead 180°, whereas the other one is 168.9(2)°]; at the other hand this coordination figure can be described as a distorted trigonal bipyramid [the two axial neighbours O(3) and O(4) build "short" Cu—O bonds, the O—Cu—O angles between the three equatorial O atoms are 141.6(2)°, 117.0(1)°, and 101.3(1)°]. Therefore the coordination figure of $Cu(2)^{[4+1]}O_5$ in $Cu_3(AsO_4)_2$-III is considered as an example for the transition from a tetragonal pyramid to a trigonal bipyramid (cf. [2]).

The average As—O bond lengths within the AsO_4 tetrahedra in $Cu_3(AsO_4)_2$-III, $Na_4Cu(AsO_4)_2$, and within the $As(2)O_4$ tetrahedron in

Table 3. *Selected interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Coordination of the alkaline earth atoms

$Na_4Cu(AsO_4)_2$

Na(1)-O(4) = 2.260(1)
Na(1)-O(1) = 2.304(1)
Na(1)-O(2) = 2.449(1)
Na(1)-O(4) = 2.471(1)
Na(1)-O(3) = 2.598(1)
Na(1)-O(4) = 2.689(1)

Na(2)-O(4) = 2.378(1)
Na(2)-O(1) = 2.389(1)
Na(2)-O(3) = 2.411(1)
Na(2)-O(2) = 2.497(1)
Na(2)-O(1) = 2.601(1)
Na(2)-O(1) = 2.762(2)

$KCu_4(AsO_4)_3$

K-O(23) ≈ 2.619(2) 2x
K-O(23) ≈ 2.725(2) 2x
K-O(24) ≈ 2.740(2) 2x
K-O(12) ≈ 2.763(2) 2x

Coordination of the copper atoms

$Cu_3(AsO_4)_2$-III

Cu(1)	O(3)	O(3)	O(2)	O(2)
O(3)	1.913(2)	3.826(5)	2.746(4)	2.759(9)
O(3)	180	1.913(2)	2.759(4)	2.746(4)
O(2)	89.7(1)	90.3(1)	1.979(2)	3.958(6)
O(2)	90.3(1)	89.7(1)	180	1.979(2)

Cu(2)	O(4)	O(1)	O(3)	O(4)	O(2)
O(4)	1.947(3)	2.912(4)	3.881(4)	2.571(6)	3.253(5)
O(1)	96.8(1)	1.947(2)	2.811(4)	3.725(4)	3.341(4)
O(3)	168.9(2)	92.2(2)	1.952(3)	2.732(4)	2.980(4)
O(4)	81.4(2)	141.6(2)	87.6(1)	1.996(2)	3.719(4)
O(2)	97.6(1)	101.3(1)	86.9(1)	117.0(1)	2.360(2)

$Na_4Cu(AsO_4)_2$

Cu	O(2)	O(2)	O(3)	O(3)
O(2)	1.943(1)	3.885(3)	2.654(2)	2.847(2)
O(2)	180	1.943(1)	2.847(2)	2.654(2)
O(3)	86.0(1)	94.0(1)	1.949(1)	3.899(3)
O(3)	94.0(1)	86.0(1)	180	1.949(1)

$KCu_4(AsO_4)_3$

Cu(1)	O(11)	O(11)	O(21)	O(21)
O(11)	1.917(2)	2.428(5)	3.812(3)	2.963(3)
O(11)	78.6(1)	1.917(2)	2.963(3)	3.812(3)
O(21)	167.7(1)	101.2(1)	1.917(2)	2.506(5)
O(21)	101.2(1)	167.7(1)	81.7(2)	1.917(2)

Cu(2)	O(21)	O(21)	O(24)	O(24)	O(2)	O(12)
O(21)	1.986(2)	2.506(5)	2.768(3)	3.934(3)	3.251(3)	3.803(3)
O(21)	78.3(2)	1.986(2)	3.934(3)	2.768(3)	3.803(3)	3.251(3)
O(24)	88.3(1)	164.0(2)	1.987(2)	3.176(5)	2.734(3)	3.092(3)
O(24)	164.0(2)	88.3(1)	106.1(1)	1.987(2)	3.092(3)	2.734(3)
O(12)	91.8(1)	114.9(1)	73.8(1)	85.9(1)	2.513(2)	4.809(4)
O(12)	114.9(1)	91.8(1)	85.9(1)	73.8(1)	146.1(2)	2.513(2)

Cu(3)	O(22)	O(11)	O(23)	O(12)	O(24)	O(22)
O(22)	1.952(2)	2.654(3)	3.904(3)	2.820(3)	3.094(3)	2.933(4)
O(11)	85.6(1)	1.955(2)	2.816(4)	3.930(3)	3.716(3)	3.011(3)
O(23)	172.7(1)	92.0(1)	1.960(2)	2.906(3)	2.877(3)	3.549(3)
O(12)	90.5(1)	162.9(3)	93.8(1)	2.020(2)	2.734(3)	2.884(3)
O(24)	91.8(1)	119.5(1)	83.4(1)	77.3(1)	2.341(2)	4.720(3)
O(22)	81.6(1)	84.3(1)	105.0(1)	78.7(1)	154.9(2)	2.494(2)

Coordination of the arsenic atoms

$Cu_3(AsO_4)_2$-III

As	O(1)	O(2)	O(4)	O(3)
O(1)	1.658(2)	2.746(4)	2.755(4)	2.767(4)
O(2)	110.3(1)	1.689(2)	2.823(4)	2.799(4)
O(4)	110.0(2)	112.5(1)	1.706(2)	2.656(4)
O(3)	110.6(2)	111.0(2)	102.2(1)	1.707(2)

$Na_4Cu(AsO_4)_2$

As	O(1)	O(4)	O(2)	O(3)
O(1)	1.668(1)	2.705(2)	2.808(2)	2.708(2)
O(4)	107.9(1)	1.677(1)	2.789(2)	2.761(2)
O(2)	113.1(1)	111.5(1)	1.698(1)	2.759(2)
O(3)	106.7(1)	109.3(1)	108.2(1)	1.707(1)

$KCu_4(AsO_4)_3$

As(1)	O(12)	O(12)	O(11)	O(11)
O(12)	1.671(2)	2.791(4)	2.886(3)	2.788(3)
O(12)	113.3(2)	1.671(2)	2.788(3)	2.886(3)
O(11)	116.1(1)	110.1(1)	1.731(2)	2.428(5)
O(11)	110.1(1)	116.1(1)	89.1(2)	1.731(2)

As(2)	O(23)	O(22)	O(24)	O(21)
O(23)	1.665(2)	2.707(3)	2.714(3)	2.777(4)
O(22)	108.2(1)	1.678(2)	2.809(3)	2.750(3)
O(24)	108.0(1)	113.0(1)	1.690(2)	2.768(3)
O(21)	110.5(1)	108.3(1)	108.8(1)	1.714(2)

$KCu_4(AsO_4)_3$ range from 1.687 Å to 1.690 Å. The $As(1)O_4$ tetrahedron in the latter compound is located at a two-fold axis, it has an average As(1)—O bond length of 1.701 Å probably caused by the common edge O(11)—O(11) shared with the $Cu(1)O_4$ square: the two As(1)—O(11) bond lengths are longer by 3.59% than the two As(1)—O(12) bond lengths, the O(11)—As(1)—O(11) angle is 89.1(2)°. These values compare within limits of error to that in the isotypic sodium compound [11].

Structural Relationships

$Cu_3(AsO_4)_2$-III (Fig. 1): The three modifications of tricopper(II)-diarsenate(V) have distinct type structures, nevertheless $Cu_3(AsO_4)_2$-I and -II both crystallize in space group C_{2h}^5. All these three modifications of $Cu_3(AsO_4)_2$ contain remarkable copper coordination polyhedra. One of the three Cu atoms in $Cu_3(AsO_4)_2$-II [Cu(1)] forms a trigonal bipyramidal CuO_5 coordination polyhedron. Like the Cu(2) atom in $Cu_3(AsO_4)_2$-III the atom Cu(2) in $Cu_3(AsO_4)_2$-I as well as the atoms Cu(2) and Cu(3) in $Cu_3(AsO_4)_2$-II support the transition from a tetragonal pyramidal towards a trigonal bipyramidal coordination polyhedron. Only both the Cu(1) atoms in $Cu_3(AsO_4)_2$-I and $Cu_3(AsO_4)_2$-III show the common square planar [4]-coordination. Obviously these shapes of copper coordination polyhedra cause the possibility to substitute the Cu atoms by atoms of other transition elements: $Co_3(AsO_4)_2$ [22] is isotypic to $Cu_3(AsO_4)_2$-II; the mineral stranskiite [23], $CuZn_2(AsO_4)_2$, is isotypic to $Cu_3(AsO_4)_2$-III [from crystal chemical considerations according to *Keller* et al. [23] it is assumed that the two different atomic positions Cu(1) and Cu(2) in $Cu_3(AsO_4)_2$-III are occupied in stranskiite by Zn and Cu atoms,

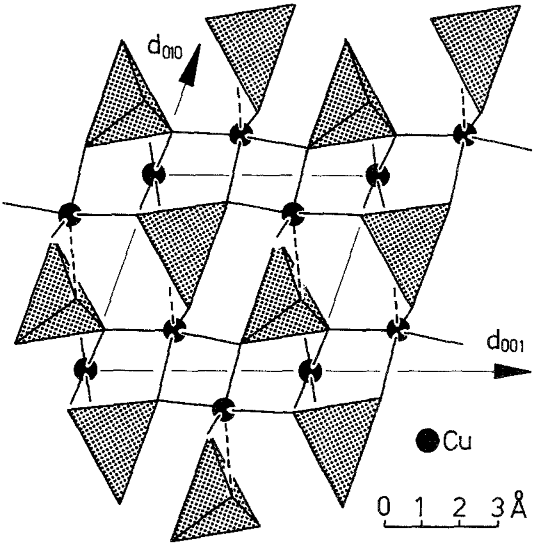

Fig. 1. The crystal structure of $Cu_3(AsO_4)_2$-III in a projection onto (100). The "short" Cu—O bonds are drawn as full lines; the "long" Cu(2)—O(2) bond is drawn as a broken line. The arsenate tetrahedra are hatched

respectively: in stranskiite a quite regular trigonal bipyramid was determined for the ZnO_5 polyhedron, Zn—O from 1.963 Å to 2.153 Å, O—Zn—O angles in the equatorial plane 125.1°, 124.0°, and 110.4°].

The compound $Cu_3(PO_4)_2$ [9] is known in a modification isotypic to $Cu_3(AsO_4)_2$-III only. The $Cu(2)O_5$ polyhedron in the phosphate compound is more similar to a trigonal bipyramid than the comparable polyhedron in the arsenate compound [$Cu_3(PO_4)_2$: Cu(2)—O from 1.934 Å to 2.265 Å, O—Cu(2)—O angles in the equatorial plane 135.7°, 122.3°, and 101.8°].

$Na_4Cu(AsO_4)_2$ (Fig. 2): Isolated CuO_4 squares are connected with arsenate tetrahedra to rows parallel [100] sharing common O atom corners. With the coordination polyhedra around the sodium atoms a three-dimensional network is formed. The synthesis of the compound $Na_4Cu(PO_4)_2$ was described by [10] during investigations within the system Na_3PO_4—$Cu_3(PO_4)_2$. From a comparison of the X-ray powder diffraction patterns isotypy is assumed for $Na_4Cu(XO_4)_2$ with $X = P$ and As.

$KCu_4(AsO_4)_3$ [see Fig. 1 given in [11] for the isotypic compound $NaCu_4(AsO_4)_3$]: The Cu—O and As—O bond lengths and the O—Cu—O and O—As—O bond angles in the two phases $MCu_4(AsO_4)_3$, M = Na

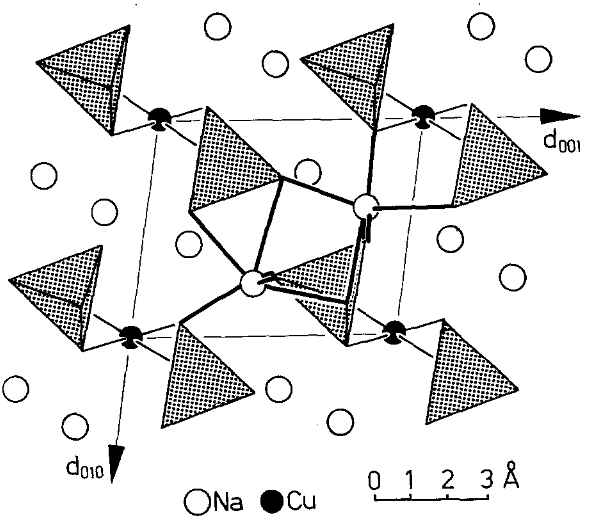

Fig. 2. The crystal structure of $Na_4Cu(AsO_4)_2$ in a projection onto (100). The Cu—O bonds and for each one of the two crystallographically different Na atoms the Na—O bonds are indicated. The arsenate tetrahedra are hatched

and K, correspond to each other within limits of error. In particular, the O—O edges shared between the Cu(1)O_4 square and the As(1)O_4 tetrahedron are for the sodium and potassium compound 2.435(3) Å and 2.428(5) Å, respectively.

Common O—O edges between a tetrahedral XO_4 group and a copper coordination polyhedron occur in the two phosphates α-$NaCuPO_4$ [24] (O—O = 2.435 Å, O—Cu—O = 68.3°, O—P—O = 104.2°) and orthorhombic $KCuPO_4$ [25] (O—O = 2.461 Å, O—Cu—O = 65.2°, O—P—O = 102.9°). In both these cases the common O—O edge occurs in tetragonal pyramidal $Cu^{[4+1]}O_5$ polyhedra, one O atom is within the basal plane and the other one represents the apex. On the contrary, in $MCu_4(AsO_4)_3$ (M = Na, K) the O—O edge is within the CuO_4 square. $KCu_4(PO_4)_3$ [12] crystallizes in a principially different structure type, the reason might be to avoid the common O(11)—O(11) edge. Nevertheless, the latter structure type is of great interest because two of the four different Cu atoms are clear trigonal bipyramidal coordinated to O atoms.

A structural relationship of $MCu_4(AsO_4)_3$ (M = Na, K) to the minerals keyite [26], $(Cu, Zn, Cd)_3(AsO_4)_2$, and johillerite [27], $Na(Mg, Zn)_3Cu(AsO_4)_3$, seems probable from both cell parameters and X-ray powder diffraction diagrams.

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