

[As(V)As(III)O₆]⁴⁻: An Uncommon Anion Group in the Crystal Structure of K₂Cu₃(As₂O₆)₂*

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The crystal structure of K₂Cu₃(As₂O₆)₂ was determined from single-crystal X-ray data by a direct method strategy and Fourier summations [$a = 10.359(4) \text{ \AA}$, $b = 5.388(2) \text{ \AA}$, $c = 11.234(4) \text{ \AA}$, $\beta = 110.48(2)^\circ$; space group $C2/m$; $Z = 2$; $R_w = 0.025$ for 1199 reflections up to $\sin \theta/\lambda = 0.81 \text{ \AA}^{-1}$]. In detail, the structure consists of As(V)O₄ tetrahedra and As(III)O₃ pyramids linked by a common O corner atom to [As(V)As(III)O₆]⁴⁻ groups with symmetry m . The bridging bonds As(V)–O [1.749(3) Å] and As(III)–O [1.838(2) Å] are definitely longer than the other As(V)–O bonds [mean 1.669 Å] and As(III)–O bonds [1.764(2) Å, 2×]. The angle As(V)–O–As(III) is 123.0(1)°. The Cu atoms are [4 + 2]- and [4 + 1]-, and the K atom is [9]-coordinated to oxygen atoms. The As₂O₆ groups and the Cu coordination polyhedra are linked to sheets parallel to (001). These sheets are connected by the K atoms. Single crystals of K₂Cu₃(As₂O₆)₂ suitable for X-ray work were synthesized under hydrothermal conditions. © 1987 Academic Press, Inc.

Introduction

As(V)O₄ (arsenate) tetrahedra and As(III)O₃ (arsenite) pyramids are well-known anion groups in inorganic crystal chemistry. A few compounds simultaneously containing both these groups have been described before now: Mn₉(OH)₉(H₂O)₂(AsO₃)(AsO₄)₂ = synadelphite (1) and CuMn₁₄Fe(OH)₆(AsO₃)₅(SiO₄)₂(AsO₄) = dixenite (2) contain isolated arsenate tetrahedra as well as arsenite pyramids; Fe₂As(AsO₄)₃ (3) has finite groups consisting of three arsenate tetrahedra and one arsenite pyramid; sheets of corner-linked arsenate tetrahedra and arsenite pyramids in the ratio 1 : 1 occur in As₂O₄ (4) and in the ratio 1 : 2 in As₃O₅(OH) (5). The connection of

As(III)O₃ pyramids to rows, to sheets, or even to three-dimensional molecules is well known (6).

Systematic examinations of copper arsenate and copper arsenite bearing systems (7–14) under hydrothermal conditions yielded the new compound K₂Cu₃(As₂O₆)₂. The determination of its crystal structure showed that it consists of novel [As(V)As(III)O₆]⁴⁻ groups. In connection with studies of the crystal chemical behavior of trivalent As atoms (6–13) it seemed appropriate to give a detailed description of its structure.

Synthesis

Crystals of K₂Cu₃(As₂O₆)₂ were prepared in a Teflon-lined vessel of ~6 ml capacity under the following conditions: The vessel

* Dedicated to Dr. H. Nowotny.

TABLE I
SUMMARY OF CRYSTAL DATA, X-RAY DATA COLLECTION, AND CRYSTAL STRUCTURE
REFINEMENT OF $K_2Cu_3(As_2O_6)_2$

$a = 10.359(4) \text{ \AA}$	STOE four-circle diffractometer AED2
$b = 5.388(2) \text{ \AA}$	Program system STRUCSY (STOE & CIE, Darmstadt, FRG)
$c = 11.234(4) \text{ \AA}$	Crystal dimensions: $0.12 \times 0.20 \times 0.03 \text{ mm}$
$\beta = 110.48(2)^\circ$	Graphite monochromatized $MoK\alpha$ radiation
$V = 587.4 \text{ \AA}^3$	Lattice parameters from 72 reflections
Space group $C2/m$	Scan speed ratio $2\theta : \omega = 1 : 1$
$Z = 2\{K_2Cu_3(As_2O_6)_2\}$	0.5 to 1.5 sec per step; step width 0.03°
$\rho_{\text{calc}} = 4.30 \text{ g cm}^{-3}$	65 steps per reflection; 10 steps for background
$\mu(MoK\alpha) = 168 \text{ cm}^{-1}$	3 standard reflections, interval 120 min
Variables = 60	Range of data collection: $2^\circ < 2\theta \leq 70^\circ$
$R = 0.029$	Total number of reflections measured: 2831
$R_w = 0.025, w = [\sigma(F_o)]^{-2}$	Unique data: 1412; 1199 with $F_o > 3\sigma(F_o)$

was filled with 2 g of an equimolar mixture of As_2O_3 and KNO_3 , 1 ml H_2O_2 (Perhydrol), and 1 g native copper ("foils"). An aqueous solution of KOH (~20 wt% KOH) was added up to a total content of 80 vol%. After heating to $500(\pm 10) \text{ K}$ during 4 days and after subsequent cooling to room temperature, crystals of the desired compound were obtained, $K_2Cu_3(As_2O_6)_2$ is light green in color. The monoclinic prismatic crystals are ledges elongated parallel to [010] with a tabular habit formed predominantly by {001}. In addition the two crystallographic forms {201} and {010} were indexed. The crystal dimensions range up to $0.20 \times 0.30 \times 0.10 \text{ mm}$.

Experimental

The cell data and relevant information about the measurements of the X-ray data and the structure refinement are given in Table I. The collected intensities were corrected for Lorentz and polarization effects as well as for absorption (Gaussian integration according to the crystal shape).

Parts of the As and Cu atoms were located by a direct method strategy. The coordinates of all the other atoms were found by subsequent Fourier and difference Fourier summations. Complex neutral atomic scattering functions (15) were used. The secondary isotropic extinction was taken into

TABLE II
STRUCTURAL PARAMETERS FOR $K_2Cu_3(As_2O_6)_2$ WITH ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
K	0.63843(9)	0	0.42405(10)	0.0217(4)	0.0147(4)	0.0269(5)	0	0.0094(4)	0	0.0189
Cu(1)	0	0	0	0.0092(2)	0.0072(3)	0.0177(3)	0	0.0002(2)	0	0.0113
Cu(2)	0.23475(4)	0	0.24068(5)	0.0106(2)	0.0084(2)	0.0134(2)	0	0.0008(2)	0	0.0106
As(1)	0.91910(3)	0	0.30660(4)	0.0084(1)	0.0081(2)	0.0130(2)	0	0.0022(1)	0	0.0093
As(2)	0.67330(4)	0	0.04389(4)	0.0102(1)	0.0089(2)	0.0131(2)	0	0.0024(1)	0	0.0102
O(1)	0.8577(3)	0	0.1404(3)	0.010(1)	0.019(1)	0.016(1)	0	0.004(1)	0	0.014
O(2)	1.0894(2)	0	0.3545(3)	0.008(1)	0.021(2)	0.018(1)	0	0.004(1)	0	0.015
O(3)	0.8556(2)	0.2536(5)	0.3529(2)	0.019(1)	0.013(1)	0.015(1)	0.006(1)	0.001(1)	0.000(1)	0.016
O(4)	0.6221(2)	0.2548(4)	0.1156(2)	0.013(1)	0.010(1)	0.014(1)	0.001(1)	0.001(1)	-0.002(1)	0.012

consideration during the final stage of refinement ($g = 8.2(5) \times 10^{-6}$ (16)).

The existence of pentavalent As atoms as well as trivalent As atoms was proved: (a) a final difference Fourier summation showed maximum and minimum peak heights of 1.18 and $-1.74 e \text{ \AA}^{-3}$; (b) coordination polyhedra as well as bond valences are in agreement with crystal chemical experience. The structure parameters are given in Table II, and some interatomic distances and bond angles are given in Table III.

Discussion

The K atom has a clear-cut [9]-coordination with K–O bonds from 2.801 to 3.057 Å as is well known for potassium atoms (18). The next K–O distances of 3.68 Å are longer than K–K, K–Cu, and K–As distances in K₂Cu₃(As₂O₆)₂. The coordination polyhedron itself is conspicuously regular. It consists of a nearly planar six-membered ring [atoms O(2)–O(3′)–O(3′)–O(2)–O(3′)–O(3′)] and a three-membered

TABLE III
INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR K₂Cu₃(As₂O₆)₂ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES [BOND VALENCES s (v.u.) ACCORDING TO (17)]

Coordination	s		Ligands	Edge	Angle	
Cu(1)–O(4) = 1.970(2)	0.44	4×	O(4) O(4)	3.941(4)	180	2×
Cu(1)–O(1) = 2.507(2)	<u>0.10</u>	2×	O(4) O(4)	2.923(4)	95.8(1)	2×
	1.97		O(4) O(4)	2.643(4)	84.2(1)	2×
			O(4) O(1)	3.237(4)	91.8(1)	4×
			O(4) O(1)	3.140(4)	88.2(1)	4×
			O(1) O(1)	5.014(6)	180	
Cu(2)–O(3) = 1.953(2)	0.46	2×	O(3) O(3) ^a	2.655(5)	85.6(1)	
Cu(2)–O(4) = 1.984(2)	0.42	2×	O(3) O(4)	2.906(3)	95.2(1)	2×
Cu(2)–O(2) = 2.292(2)	<u>0.18</u>		O(3) O(4)	3.932(3)	174.5(1)	2×
	1.95		O(3) O(2) ^a	3.067(3)	92.2(1)	2×
			O(4) O(4)	2.643(4)	83.5(1)	
			O(4) O(2)	3.115(4)	93.3(1)	2×
As(1)–O(1) = 1.749(3)	0.99		O(1) O(2)	2.740(4)	107.2(2)	
As(1)–O(2) = 1.654(2)	1.39		O(1) O(3)	2.757(4)	107.2(1)	2×
As(1)–O(3) = 1.676(2)	<u>1.28</u>	2×	O(2) O(3) ^a	2.775(3)	112.9(1)	2×
	4.94		O(3) O(3) ^a	2.733(5)	109.2(1)	
As(2)–O(1) = 1.838(2)	0.73 ^b		O(1) O(4)	2.728(3)	98.5(1)	2×
As(2)–O(4) = 1.764(2)	<u>0.94^b</u>	2×	O(4) O(4)	2.745(4)	102.2(1)	
	2.61 ^b					
K–O(2) = 2.801(2)	0.15	2×	As(1)–O(1)–As(2) = 123.0(1)			
K–O(3) = 2.818(2)	0.14	2×				
K–O(3′) = 2.971(2)	0.09	2×				
K–O(2′) = 3.038(3)	0.07					
K–O(3′′) = 3.057(2)	<u>0.07</u>	2×				
	0.98					

^a Common O–O edge with the KO₉ polyhedron.

^b Calculated as As(V) because lack of values for As(III).

ring [atoms O(2')–O(3)–O(3)] which are both approximately parallel to (001). The O–K–O angles within the six-membered ring vary from 51.5(1) to 64.1(1)°; the sum of these six angles is 347.0°. The K atom is shifted out of the least-squares plane defined by these six O atoms toward the three other O atoms. The O–K–O angles within the three-membered ring are 56.2(1)° (1×) and 63.0(1)° (2×); the O–K–O angles between O atoms belonging to two different kinds of rings vary from 69.3(1) to 75.4(1)°. This arrangement of the O atoms results in a ditrigonal pyramidal pseudosymmetry of the KO₉ polyhedron.

The Cu atoms are [4 + 2]- and [4 + 1]-coordinated and the four nearest O atom neighbors are in a "square" planar arrangement. Due to their site symmetries *2/m* and *m* the arrangements of the O atoms in both the CuO₄ squares are planar. The O–Cu–O angles between opposite O atoms are restricted by symmetry to 180° at the Cu(1) atom and they are slightly distorted by 5.5° at the Cu(2) atom (19). The O–Cu–O angles between neighboring O atoms vary from 83.5 to 95.8°. The average of the short Cu–O bonds within the CuO₄ squares are equal to each other within limits of error [Cu(1)O₄: 1.970 Å, Cu(2)O₄: 1.969 Å]. The Cu(1) atom has two and the Cu(2) atom has one additional O atom neighbor. These long Cu(1)–O(1) and Cu(2)–O(2) bonds are longer by 27.3 and 16.4% than those within the CuO₄ squares. The angles between the short and long Cu(2)–O bonds are all >90°; the Cu(2) atom is shifted out of the plane defined by its four nearest O atom neighbors toward the O(2) atom, indicating a tetragonal pyramidal coordination figure, as is common for divalent copper atoms in a [4 + 1]-coordination. All the other Cu–O distances are >3.30 Å.

A new structural unit determined in the crystal structure of K₂Cu₃(As₂O₆)₂ is a [As(V)As(III)O₆]⁴⁻ group. The As(1) atom of this group is tetrahedrally coordinated as

characteristic for an As(V) atom (20), whereas the As(2) atom has three one-sided arranged O atom ligands as expected for an As(III) atom (21). These two polyhedra share a common O corner atom labeled O(1). The whole anion group has symmetry *m*. The As(1)–O(1) bond is 1.749 Å and 5.05% longer than the three other As(1)–O bonds. The As(2)–O(1) bond length is 1.838 Å and 4.20% longer than the two other As(2)–O bonds. Similar differences were described in Fe₂As(AsO₄)₃ (3), in As₂O₄ (4), and in As₃O₅(OH) (5).

The average As(1)–O bond of 1.689 Å compares well with common arsenate tetrahedra (20). The average As(2)–O bond of 1.789 Å is within limits of error equal to the mean As(III)–O bond length calculated from 15 well-determined AsO₃ pyramids of 1.785 Å (21). The average angle O–As(1)–O of 109.4° is practically identical to the theoretical value of 109.47°. As compared to that the mean value of the O–As(2)–O angles is 99.7°.

The coordination polyhedra of the four O atoms are dissimilar. The O(1) atom is planar (3) coordinated by the atoms As(1), As(2), and Cu(1) (long Cu–O bond). The sum of cation–O(1)–cation angles is 360.0°. The atoms O(2) and O(3) are each bonded to three K atoms, one As(1) atom, and one Cu(2) atom; the O(2) atom is the fifth neighboring ligand of the Cu(2) atom, and the O(3) atom is within the Cu(2)O₄ square. The coordination polyhedron around the O(2) atom is a distorted tetragonal pyramid with the three K atoms and the As(1) atom forming the basal plane and the Cu(2) atom at the apex. The cations around the O(3) atom form a distorted trigonal pyramid with the atoms Cu(2), As(1), and K [O(3)–K = 2.818 Å] as the equatorial plane and the two K atoms with O(3)–K = 2.971 and 3.057 Å as the two apices. The O(4) atom lies simultaneously in the Cu(1)O₄ and Cu(2)O₄ squares and has the As(2) atom as a third neighbor. The coordination figure is ap-

proximately a trigonal pyramid with the O(4) atom at the apex; the sum of angles at the O(4) atom is 342.7°. The sums of bond strengths calculated for the O atoms according to (17) (cf. Table III) are 1.82, 1.94, 2.04, and 1.80 valence units.

It should be mentioned that within the structure of K₂Cu₃(As₂O₆)₂ all atoms [except O(3) and O(4)] are arranged at the mirror planes. In addition some of the atomic coordinates show remarkable similarities [e.g., *x/a* for O(1) and O(3), *y/b* for O(3) and O(4), or *z/c* for O(2) and O(3)]. The result is a high (pseudo)symmetry of the individual coordination polyhedra as well as of the whole atomic arrangement. As shown in Fig. 1 one Cu(1)O₄ square and two Cu(2)O₄ squares are connected to a Cu₃O₈ group sharing two common O(4)–O(4) edges of 2.643 Å. The three CuO₄ squares are approximately parallel to (101). These Cu₃O₈ groups and the As₂O₆ groups are connected to rows parallel to [010]. The longer Cu–O bonds combine these Cu₃(As₂O₆)₂ rows to “7.46-Å sheets” parallel to (001) (see Fig. 2). A three-dimensional structure is formed by the interconnection of the K atoms. The KO₉ polyhedron

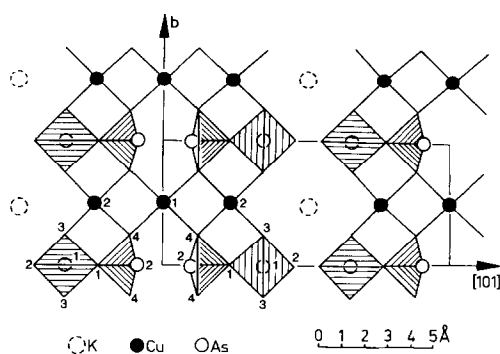


FIG. 1. Detail of the crystal structure of K₂Cu₃(As₂O₆)₂ in a projection onto (101). The Cu₃O₈ groups (edge-sharing CuO₄ “squares”) and their connection with the [As₂O₆]⁴⁻ groups to rows parallel to [010] is shown. The labeling of the atoms is indicated. The AsO₄ and AsO₃ polyhedra are shaded.

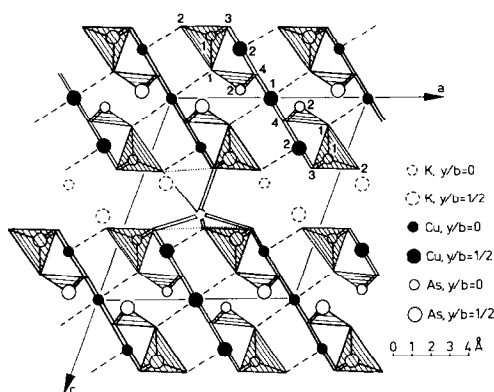


FIG. 2. The crystal structure of K₂Cu₃(As₂O₆)₂ in a projection onto (010). The coordination around the K atoms is given in one case. The planes defining the three- and six-membered rings within the KO₉ polyhedron are dotted. The “short” Cu–O bonds are solid lines; the “long” Cu–O bonds are drawn as broken lines. The labeling of the atoms is indicated. The AsO₄ and AsO₃ polyhedra are shaded.

shares four O–O edges with the Cu(2)O₅ polyhedra [two within the Cu(2)O₄ square] and three O–O edges with the As(2)O₄ tetrahedra. These O–O edges are definitely shorter than the unshared O–O edges.

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