

## The Crystal Structures of Copper Chloroarsenate and Cobalt Chloroarsenate, $\text{Cu}_2(\text{AsO}_4)\text{Cl}$ and $\text{Co}_2(\text{AsO}_4)\text{Cl}$

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Both Cu and Co chloroarsenate,  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  and  $\text{Co}_2(\text{AsO}_4)\text{Cl}$ , crystallize in the space group  $P2_1/m$ . The unit-cell dimensions ( $Z = 2$ ) for  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  are  $a = 6.877(2)$ ,  $b = 6.589(2)$ ,  $c = 4.929(1)$  Å,  $\beta = 91.12(2)^\circ$ ; and  $a = 6.880(1)$ ,  $b = 6.593(2)$ ,  $c = 4.932(1)$  Å,  $\beta = 91.12(1)^\circ$  for  $\text{Co}_2(\text{AsO}_4)\text{Cl}$ . A three-dimensional structural analysis, with automatic diffractometer data, has been completed and refined by full-matrix least-squares procedures to a residual  $R = 0.054$  ( $R_w = 0.074$ ) for the Cu compound and  $R = 0.055$  ( $R_w = 0.073$ ) for the Co compound. The structure is characterized by the same cation-containing face-sharing polyhedra as found in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ ; each of the two crystallographically unique metal atoms is coordinated by four O atoms and by two Cl atoms in the *trans* position. These polyhedra form infinite zigzag chains, the net direction of which is parallel to **b**. The relationship of this structure to that of  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  is discussed.

### Introduction

For the past several years we have been studying the crystal chemistry of compounds having the stoichiometry  $\text{M}_2(\text{PO}_4)\text{Z}$ , where M is a divalent metal ion and Z is a halogen. Recently we have extended our work to the arsenates. Single crystals of both Cu and Co chloroarsenates,  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  and  $\text{Co}_2(\text{AsO}_4)\text{Cl}$ , have been prepared, and complete structural analyses by X-ray diffraction have been carried out. These compounds crystallize in the space group  $P2_1/m$ , and have a structure characterized by the same face-sharing cation-containing polyhedra as were found in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  (Anderson, Rea & Kostiner, 1976). The present structure differs from that of  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  in the linkages between these face-sharing moieties which give infinite two-dimensional chains.

### Experimental

#### $\text{Cu}_2(\text{AsO}_4)\text{Cl}$

Crystals of  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  were grown by standard flux techniques from an excess of  $\text{CuCl}_2$ . A mixture of  $\text{Cu}_3(\text{AsO}_4)_2$  and  $\text{CuCl}_2$  in a mole ratio of 40/60 was packed into a Pt crucible which was then covered with a carefully crimped Pt lid. After heating for several hours at  $850^\circ\text{C}$ , the charge was cooled at  $16^\circ\text{C h}^{-1}$  to  $400^\circ\text{C}$  and then removed from the furnace. Dark blue-

green needles of  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  up to  $0.2 \times 0.3 \times 2.0$  mm were mechanically separated from the mixture.

A sphere was ground to a diameter of  $0.020(1)$  cm. Precession photographs revealed monoclinic symmetry with systematic absences corresponding to space group  $P2_1$  or  $P2_1/m$ . Subsequent analysis showed the space group to be  $P2_1/m$ , and the final refinements were carried out in this space group.

The lattice parameters were determined in a PICK-II least-squares refinement program, with 24 reflections within the angular range  $35^\circ < 2\theta < 47^\circ$ ; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer with  $\text{Mo K}\alpha_1$  radiation ( $\lambda = 0.70930$  Å) and with the crystal bathed in a stream of cold dry air. At  $0^\circ\text{C}$  the lattice parameters are  $a = 6.877(2)$ ,  $b = 6.589(2)$ ,  $c = 4.929(1)$  Å, and  $\beta = 91.12(2)^\circ$ , where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density (with  $Z = 2$ ) is  $4.483$  g  $\text{cm}^{-3}$ .

Diffraction intensities were measured with Zr-filtered  $\text{Mo K}\alpha$  radiation at a take-off angle of  $2.5^\circ$ , with the diffractometer operating in the  $\theta$ - $2\theta$  scan mode. Scans were made at  $1^\circ \text{min}^{-1}$  over  $1.4^\circ$  with allowance for dispersion, and with 20 s background counts taken at both ends of the scan. Of the 710 independent data investigated in the angular range  $2\theta < 60^\circ$ , 673 were considered observable according to the criterion  $|F_o| > 2.0\sigma_{F_s}$ , where  $\sigma_{F_s}$  is defined as  $0.02|F_o| + (C + k^2B)^{1/2}/2|F_o|Lp$ ; the total scan count is  $C$ ,  $k$  is the ratio of scanning time to the total background time, and  $B$  is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than  $\pm 3\%$  over the data-collection period.

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Intensity data were corrected for Lorentz and polarization effects, and absorption corrections (*International Tables for X-ray Crystallography*, 1968) were applied for a spherical crystal with  $\mu R = 1.82$ . The maximum absorption correction was 13% of  $|F_o|$ .

### Co<sub>2</sub>(AsO<sub>4</sub>)Cl

Crystals of Co<sub>2</sub>(AsO<sub>4</sub>)Cl were grown in a like manner from a 40/60 mixture of Co<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> and CoCl<sub>2</sub> slow-cooled from 950°C. Dark burgundy-red crystals were separated from the mixture.

A roughly cubic crystal, 0.015 × 0.014 × 0.018 cm, was chosen for data collection. Precession photographs indicated that the two compounds were isostructural. The *PICK-II* refinement gave lattice parameters at 0°C of  $a = 6.880$  (1),  $b = 6.593$  (2),  $c = 4.932$  (1) Å, and  $\beta = 91.12$  (1)°; the calculated density is 4.339 g cm<sup>-3</sup>.

Diffraction intensities were measured with the diffractometer operating in the  $\omega$  scan mode with 10 s background counts taken at the ends of a 1.4°  $\theta$ -2 $\theta$  scan corrected for dispersion. This technique was used because a splitting in  $\omega$  was observed at high 2 $\theta$  values on the diffractometer which was not observed on precession photographs. We attributed this to minute cracks in the crystal and felt that  $\omega$ -scan data collection would yield more accurate intensities. 688 data were considered observable according to the above criterion.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections ( $\mu = 166$  cm<sup>-1</sup>, Mo  $K\alpha$ ) were made with a program written by N. W. Alcock and B. Lee for a crystal of general shape. The maximum absorption correction was 14% of  $|F_o|$ .

### Solution and refinement of the structure

The structure of Cu<sub>2</sub>(AsO<sub>4</sub>)Cl was solved first. The only systematic extinctions were on  $0k0$  with  $k$  odd, indicating space group  $P2_1$  or  $P2_1/m$ . Since a mirror plane perpendicular to  $\mathbf{b}$  will usually produce a series of peaks on the  $0\nu0$  line in the Patterson map, the map was examined for these peaks. Only one strong peak was found (at  $0, \frac{1}{2}, 0$ ). However, it was realized that for such a small unit cell, all of the heavy atoms might lie on the mirror planes, or half-way between them, and that in such a case no  $0\nu0$  vectors due to the mirror symmetry would be present (other than one at  $0, \frac{1}{2}, 0$ ). Therefore, the presence of the mirror plane was assumed, and the positions of the Cu, As and Cl atoms were determined by a straightforward analysis of the Patterson map. The positions of the O atoms were found by a difference Fourier synthesis.

Full-matrix least-squares refinement (Busing, Martin & Levy, 1962a) with a  $1/\sigma^2$  weighting scheme, zero-valent scattering factors for Cu, As, Cl and O (*International Tables for X-ray Crystallography*, 1974), isotropic temperature factors, and corrections for second-

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and anisotropic thermal parameters for Cu<sub>2</sub>(AsO<sub>4</sub>)Cl

Numbers in parentheses are estimated standard deviations in the last significant figure. The  $B$ 's are defined by the general temperature factor  $\exp[-\frac{1}{3}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Cu(1)	0	0	0	1.01 (5)	0.44 (5)	1.30 (6)	0	0.08 (4)	0
Cu(2)	2735 (2)	$\frac{1}{2}$	3538 (3)	1.01 (5)	0.47 (5)	1.39 (6)	0	0.12 (4)	0
As	2471 (1)	$\frac{1}{2}$	5085 (2)	0.34 (4)	0.05 (4)	0.75 (4)	0	0.18 (3)	0
Cl	2426 (3)	$\frac{1}{2}$	8376 (5)	0.91 (8)	0.62 (8)	0.68 (8)	0	0.30 (6)	0
O(1)	4496 (10)	$\frac{1}{2}$	6697 (17)	0.40 (24)	1.39 (31)	1.57 (31)	0	-0.27 (21)	0
O(2)	636 (10)	$\frac{1}{2}$	7582 (15)	0.52 (22)	0.04 (22)	1.02 (26)	0	0.18 (19)	0
O(3)	1990 (7)	5454 (8)	3062 (10)	0.87 (17)	0.05 (15)	0.96 (18)	0.08 (13)	0.15 (13)	-0.11 (14)

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and anisotropic thermal parameters for Co<sub>2</sub>(AsO<sub>4</sub>)Cl

Numbers in parentheses are estimated standard deviations in the last significant figure. The  $B$ 's are defined by the general temperature factor  $\exp[-\frac{1}{3}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Co(1)	0	0	0	1.53 (6)	0.64 (5)	0.69 (5)	0	-0.14 (4)	0
Co(2)	2736 (2)	$\frac{1}{2}$	3535 (3)	1.42 (6)	0.62 (5)	0.84 (5)	0	-0.16 (4)	0
As	2373 (1)	$\frac{1}{2}$	5088 (2)	1.14 (5)	0.51 (4)	0.64 (4)	0	-0.10 (3)	0
Cl	2414 (3)	$\frac{1}{2}$	8378 (5)	1.63 (9)	1.04 (8)	0.75 (8)	0	0.00 (6)	0
O(1)	4494 (11)	$\frac{1}{2}$	6683 (16)	1.77 (29)	1.84 (29)	1.19 (29)	0	0.05 (22)	0
O(2)	641 (11)	$\frac{1}{2}$	7567 (15)	1.71 (26)	0.61 (21)	0.85 (25)	0	0.12 (20)	0
O(3)	1987 (7)	5448 (8)	3086 (10)	1.52 (18)	0.84 (15)	0.99 (18)	0.03 (14)	-0.22 (14)	0.01 (15)

dary extinction and anomalous dispersion, yielded a residual  $R = 0.076$  and a weighted residual  $R_w = 0.116$ . The final anisotropic refinement, based on a data:parameter ratio of 16, with 45 independently varied parameters, yielded  $R = 0.054$  and  $R_w = 0.074$  for the observed data. The maximum extinction correction (Zachariasen, 1968) was 20% of  $|F_o|$  for the 040 reflection. Table 1 lists the final positional and anisotropic thermal parameters for  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$ .

With the positional parameters for  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  as a trial structure and isotropic temperature factors, the

data for  $\text{Co}_2(\text{AsO}_4)\text{Cl}$  converged to a residual  $R = 0.075$  ( $R_w = 0.093$ ). The final anisotropic refinement yielded  $R = 0.055$  ( $R_w = 0.073$ ). The maximum extinction correction was 30% of  $|F_o|$ . Table 2 lists the final positional and anisotropic thermal parameters for  $\text{Co}_2(\text{AsO}_4)\text{Cl}$ .\*

\* A list of structure factors for both compounds has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32125 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond distances, polyhedral edge lengths, and bond angles for the metal polyhedra*

Numbers in parentheses are e.s.d.'s in the last significant figure.

(i) Interatomic distances (Å)

		$\text{Cu}_2(\text{AsO}_4)\text{Cl}$	$\text{Co}_2(\text{AsO}_4)\text{Cl}$		$\text{Cu}_2(\text{AsO}_4)\text{Cl}$	$\text{Co}_2(\text{AsO}_4)\text{Cl}$
M(1)—O(3)	2 ×	2.040 (5)	2.048 (5)	M(2)—O(1)		1.911 (7)
M(1)—O(2)	2 ×	2.085 (5)	2.091 (5)	M(2)—O(3)	2 ×	2.025 (5)
M(1)—Cl	2 ×	2.488 (2)	2.484 (2)	M(2)—O(2)		2.373 (7)
				M(2)—Cl		2.399 (3)
				M(2)—Cl'		2.550 (3)
M(1) octahedron				M(2) octahedron		
O(3)—O(2)	2 ×	2.671 (7)	2.670 (7)	O(1)—O(3)	2 ×	3.103 (7)
O(3)—O(2)	2 ×	3.144 (8)	3.162 (8)	O(1)—Cl		3.309 (9)
O(3)—Cl	2 ×	3.386 (5)	3.382 (5)	O(1)—Cl'		3.190 (8)
O(3)—Cl	2 ×	3.040 (5)	3.047 (6)	O(3)—O(2)	2 ×	2.671 (7)
O(2)—Cl	2 ×	3.536 (3)	3.535 (3)	O(3)—Cl	2 ×	3.272 (5)
O(2)—Cl	2 ×	2.928 (7)	2.930 (8)	O(3)—Cl'	2 ×	3.040 (5)
				O(2)—Cl		3.581 (8)
				O(2)—Cl'		2.928 (7)
						2.930 (8)

(ii) Angles (°)

O(3)—M(1)—O(2)	2 ×	80.7 (2)	80.3 (2)	O(1)—M(2)—O(3)	2 ×	104.0 (1)	104.2 (1)
O(3)—M(1)—O(2)	2 ×	99.3 (2)	99.7 (2)	O(1)—M(2)—Cl		99.7 (3)	99.6 (3)
O(3)—M(1)—Cl	2 ×	96.3 (1)	96.1 (1)	O(1)—M(2)—Cl'		90.1 (3)	90.6 (3)
O(3)—M(1)—Cl	2 ×	83.7 (1)	83.9 (1)	O(3)—M(2)—O(2)	2 ×	74.3 (1)	74.3 (1)
O(2)—M(1)—Cl	2 ×	100.9 (2)	100.9 (2)	O(3)—M(2)—Cl	2 ×	95.1 (2)	94.6 (2)
O(2)—M(1)—Cl	2 ×	79.1 (2)	79.1 (2)	O(3)—M(2)—Cl'	2 ×	82.4 (2)	82.8 (1)
				O(2)—M(2)—Cl		97.3 (2)	96.8 (2)
				O(2)—M(2)—Cl'		72.9 (2)	72.9 (2)
				O(1)—M(2)—O(2)		163.0 (3)	163.6 (3)
				O(3)—M(2)—O(3)		148.0 (3)	148.0 (3)
				Cl—M(2)—Cl'		170.2 (1)	169.7 (1)

Table 4. *Bond distances, polyhedral edge lengths, and bond angles for the arsenate tetrahedron*

Numbers in parentheses are e.s.d.'s in the last significant figure.

(i) Interatomic distances (Å)

		$\text{Cu}_2(\text{AsO}_4)\text{Cl}$	$\text{Co}_2(\text{AsO}_4)\text{Cl}$		$\text{Cu}_2(\text{AsO}_4)\text{Cl}$	$\text{Co}_2(\text{AsO}_4)\text{Cl}$
As—O(1)		1.649 (7)	1.644 (8)	O(1)—O(3)	2 ×	2.807 (8)
As—O(2)	2 ×	1.694 (5)	1.693 (5)	O(1)—O(2)		2.697 (9)
As—O(3)		1.731 (7)	1.724 (8)	O(3)—O(3)		2.697 (9)
				O(2)—O(3)	2 ×	2.781 (8)

(ii) Angles (°)

O(1)—As—O(3)	2 ×	114.1 (2)	114.0 (2)	O(3)—As—O(2)		105.5 (3)
O(1)—As—O(2)		105.8 (4)	106.2 (4)	O(2)—As—O(3)	2 ×	108.6 (2)

## Discussion

Although  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  and  $\text{Co}_2(\text{AsO}_4)\text{Cl}$  are not isostructural with  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  (Anderson, Rea & Kostiner, 1976), the structures of these two compounds have many features in common with that structure, including the coordination of the ions and the manner in which the cation-containing polyhedra face-share to form the basic structural unit. It is only in the extended face-sharing chains of polyhedra that the structures differ. Like the three Fe atoms in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ , each of the two metal atoms in this structure is coordinated by four O atoms and two Cl atoms in *trans* positions. Table 3 lists the bond angles and distances in these distorted octahedra for both the Cu and Co compounds. The standard deviations for all bond lengths and bond angles were computed by the function-and-error program (*ORFFE*) of Busing, Martin & Levy (1962*b*). M(1) is at the origin (symmetry  $\bar{1}$ ) and M(2) is on a mirror plane (symmetry *m*).

The arsenate tetrahedron, like the phosphate tetrahedron in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ , is quite distorted despite its mirror symmetry (Table 4). The average As—O distance in the Cu compound is 1.692 (+0.039, -0.042 Å); and 1.689 (+0.035, -0.045 Å) in the Co compound; the average angle in both compounds is 109.4° (+4.7, -3.9° for the Cu compound; +4.7, -3.3° for the Co compound).

As in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ , the coordination about the O atoms is unbalanced, with O(1) being bonded only to an M(2) and the As; O(2) to two M(1)'s, one M(2), and

the As; and O(3) to an M(1), an M(2), and the As. As expected, the bonds involving O(1) are quite short, whereas those involving O(2) are longer than average. The Cl in both structures is bonded to four metal atoms. The bond distances and angles for the anion environments are given in Table 5.

The basic structural unit in  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  [and  $\text{Co}_2(\text{AsO}_4)\text{Cl}$ ] is the same as that in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ . Each Cu(2)-containing octahedron shares adjacent faces with two Cu(1) octahedra, shown in dark outline in Fig. 1. The distortions in this unit are essentially the same as those in the corresponding unit in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  except that there is more symmetry since the two Cu(1) octahedra are related by a mirror operation; the corresponding octahedra in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  are not crystallographically similar. These triplets are bridged across the O(3) atoms by arsenate tetrahedra; the O(3)—O(3) distance is 2.70, as compared to 2.35 Å for the corresponding phosphate bridge in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ .

The triplets of Fig. 1 are linked together by further face-sharing to give infinite zigzag chains of face-sharing Cu-containing octahedra, the net direction of which is parallel to **b**. The chain can also be described as being composed of condensed linear segments of successive Cu(2)—Cu(1)—Cu(2) octahedra.

The infinite face-sharing chains of Fe-containing octahedra in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  differ from the chains in  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  in the way in which the linear segments are joined. A succession of any three linear segments in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  is identical to a section of three segments of the chain in  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$ . In the latter structure a

Table 5. Bond distances (Å) and bond angles (°) for the anion polyhedra

Numbers in parentheses are e.s.d.'s in the last significant figure.

	$\text{Cu}_2(\text{AsO}_4)\text{Cl}$	$\text{Co}_2(\text{AsO}_4)\text{Cl}$		$\text{Cu}_2(\text{AsO}_4)\text{Cl}$	$\text{Co}_2(\text{AsO}_4)\text{Cl}$
(i) Cl polyhedron					
Cl—M(2)	2.399 (3)	2.403 (3)	M(1)—Cl—M(2)	2×	113.1 (1)
Cl—M(1)	2.488 (2)	2.484 (2)	M(2)—Cl—M(2)		170.2 (1)
Cl—M(2)	2.550 (3)	2.549 (3)	M(1)—Cl—M(1)		82.3 (1)
			M(2)—Cl—M(1)	2×	73.4 (1)
					74.0 (1)
(ii) O(1) polyhedron					
O(1)—As	1.650 (7)	1.644 (8)	As—O(1)—M(2)		147.6 (5)
O(1)—M(2)	1.911 (7)	1.911 (8)			148.2 (5)
(iii) O(2) polyhedron					
O(2)—As	1.730 (7)	1.724 (8)	As—O(2)—M(1)	2×	124.2 (2)
O(2)—M(1)	2.085 (5)	2.091 (5)	As—O(2)—M(2)		121.2 (4)
O(2)—M(2)	2.373 (7)	2.376 (8)	M(1)—O(2)—M(1)		104.4 (3)
			M(1)—O(2)—M(2)	2×	85.3 (2)
					85.1 (2)
(iv) O(3) polyhedron					
O(3)—As	1.694 (5)	1.693 (5)	As—O(3)—M(2)		131.4 (3)
O(3)—M(1)	2.040 (5)	2.022 (5)	As—O(3)—M(1)		130.2 (3)
O(3)—M(2)	2.025 (5)	2.048 (5)	M(2)—O(3)—M(1)		96.3 (2)
					96.2 (2)

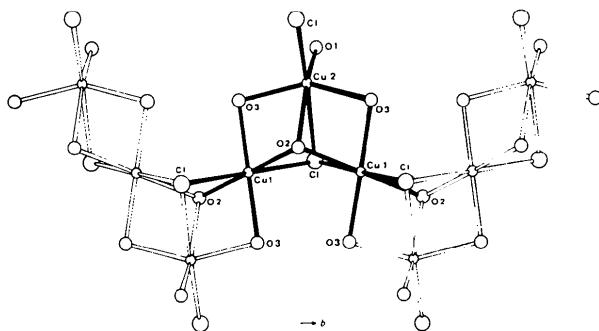


Fig. 1. The structural unit of  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  is shown in dark outline. The distorted octahedron with Cu(2) at the center shares adjacent faces with Cu(1)-containing octahedra. These octahedra then face-share to other Cu(2)-containing octahedra to form zigzag chains in the  $b$  direction. The two free vertices [O(3)] are bridged by an As atom.

fourth segment is added in the same orientation as the second, giving the flat zigzag structure of Fig. 1. In  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ , however, a fourth segment is added in a different direction, giving a chain made up of twisted, square, U-shaped units, as shown in Fig. 3 of Anderson, Rea & Kostiner (1976).

As in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$ , the adjacent chains of face-sharing octahedra in  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  are linked directly only by corner-sharing through the Cl atoms, and indirectly through corner-sharing with arsenate tetrahedra. Both types of linkage can be seen in Fig. 2, which is a polyhedral representation of the Cu-containing octahedra viewed from the  $(0\bar{1}0)$  direction. Since the holes in the structure as seen in Fig. 2 are located on screw axes, and because the  $b$  metric is so short, the screw axes generate zigzag tunnels parallel to  $b$ , at  $\frac{1}{2}, \nu, 0$ .

The Cu ion does not impose its unique micro-symmetry of four short and two longer bonds on the cation polyhedra in  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$ , as we have observed in the structure of  $\text{Cu}_2(\text{PO}_4)\text{F}$  (Rea & Kostiner, 1976). Rather, pairs of metal-anion distances are within one standard deviation of each other in these two structures. We attribute this to the extreme constraints placed on the polyhedra by the extensive face-sharing which occurs in the structures of  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  and  $\text{Co}_2(\text{AsO}_4)\text{Cl}$ .

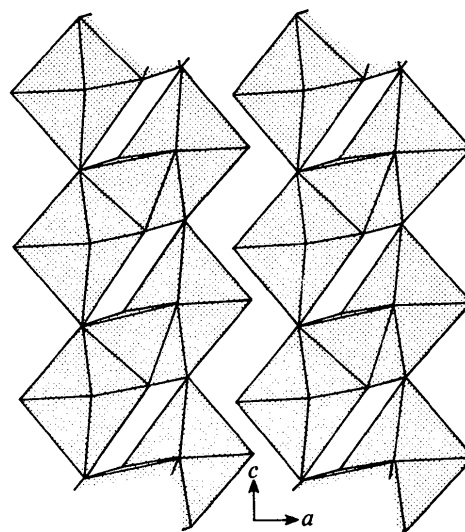


Fig. 2. A polyhedral representation of the  $\text{Cu}_2(\text{AsO}_4)\text{Cl}$  structure projected onto the  $ac$  plane (see text).

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