

partial occupation with lead, adapt to the necessary metal size. Bismuth, however, needs substitution by a smaller cation to reduce its average size. As a result stabilizers, like copper or silver, or substitution by antimony are necessary in the sulfide. In the structure obtained by Macicek the Bi is replaced on half the No. 1 sites by either Ag or one or two Cu atoms at nearby interstitial positions.

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Clinoclase and the Geometry of [5]-Coordinate Cu^{2+} in Minerals

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Abstract. Tricopper arsenate trihydroxide, $\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$, $M_r = 380.58$, monoclinic, $P2_1/c$, $a = 7.257$ (2), $b = 6.457$ (2), $c = 12.378$ (3) Å, $\beta = 99.51$ (2)°, $V = 572.0$ (3) Å³, $Z = 4$, $D_x = 4.42$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 175$ cm⁻¹, $F(000) = 716$, $T = 297$ K, $R = 0.044$ for 1404 observed reflections. The structure is a heteropolyhedral framework of AsO_4 tetrahedra, $\text{CuO}_3(\text{OH})_3$ octahedra and $\text{CuO}_2(\text{OH})_3$ square pyramids. [5]-coordinated Cu^{2+} is common in minerals, and the salient features of square pyramidal and trigonal bipyramidal coordinations are examined in these structures.

Introduction. We have a systematic study of the stereochemistry of Cu^{2+} oxysalt minerals currently

underway (Eby & Hawthorne, 1989a,b; Hawthorne & Eby, 1985; Hawthorne & Groat, 1985, 1986; Hawthorne, 1985a,b, 1986a,b; Groat & Hawthorne, 1987; Hawthorne, Groat & Eby, 1989), focused primarily on the heteropolyhedral connectivity of these structures, and the interaction between local Jahn–Teller distortion, polyhedral connectivity and structural periodicity. As part of this work, a refinement and reconsideration of the structure of clinoclase was initiated.

Experimental. Clinoclase from Roughton Gill, England, National Mineral Collection catalogue number 18291, was obtained from the Geological Survey of Canada. Crystal size: $0.24 \times 0.28 \times 0.32$ mm; unit-cell parameters refined from 25 reflections ($5 < \theta < 15^\circ$) automatically aligned on a Nicolet R3m diffractometer at 297 K. Data collection: 1187 reflections, $3 < 2\theta < 60^\circ$, h 0–13, k 0–14,

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Table 1. Atomic parameters and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$) for clinoclase
$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	U_{eq}
Cu(1)	0.7877 (1)	0.1400 (2)	0.3294 (1)	177 (3)
Cu(2)	0.8153 (1)	0.3813 (2)	0.1274 (1)	169 (3)
Cu(3)	0.3869 (1)	0.3531 (2)	0.4126 (1)	183 (3)
As	0.3087 (1)	0.1499 (1)	0.1796 (1)	142 (2)
O(1)	0.4149 (8)	0.0710 (9)	0.0738 (5)	177 (16)
O(2)	0.8377 (7)	-0.1577 (9)	0.3652 (4)	183 (16)
O(3)	0.1798 (8)	-0.0531 (9)	0.2130 (4)	163 (16)
O(4)	0.4711 (8)	0.2205 (9)	0.2854 (5)	194 (17)
OH(1)	0.7799 (9)	0.2034 (9)	0.4780 (5)	248 (19)
OH(2)	0.8088 (8)	0.0943 (9)	0.1773 (4)	174 (16)
OH(3)	0.1808 (8)	0.1670 (9)	0.4106 (5)	210 (17)

10–8, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan, variable scan speed $4.0\text{--}29.3^\circ \text{ min}^{-1}$, scan range $(K\alpha_1 - 1) \rightarrow (K\alpha_2 + 1)^\circ$, background/scan = 0.5, two standard reflections every 48 reflections, variation 1.3%, absorption correction by ψ -scan method ($T_{\text{min}} = 0.02$, $T_{\text{max}} = 0.04$), Lorentz and polarization corrections, 1404 observed reflections with $I > 3\sigma(I)$.

Structure refinement: atomic scattering factors and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974, Vol. IV), all calculations performed with *SHELXTL* (Sheldrick, 1981) on a Nova 4S computer. Starting parameters from Ghose, Fehlmann & Sundaralingam (1965), refinement by full-matrix least squares (on F) with anisotropic temperature factors converged to $R = 0.044$, $wR = 0.038$, $w = 1/[\sigma^2 F + 0.00070 (F^2)]$, maximum final shift/e.s.d. < 0.05, mean < 0.01, maximum height in final difference Fourier map = $0.70 \text{ e \AA}^{-3}$.

Discussion. Fractional coordinates and equivalent isotropic temperature factors of atoms in the asymmetric unit are listed in Table 1, and interatomic distances and angles are given in Table 2.*

The As atom is tetrahedrally coordinated by O atoms, and the bond lengths and angles fall within the range typically observed in arsenate structures. There are three distinct Cu positions. Cu(1) is coordinated by a fairly distorted but recognizably octahedral arrangement of anions; the sixth bond is Cu(1)—OH(3) at $2.871 \text{ \AA}$, and this coordination is approaching square pyramidal. Cu(2) is coordinated by five anions only; the sixth anion is at a distance of $3.32 \text{ \AA}$, and the *trans* $\phi\text{—Cu(2)—}\phi$ angle ($\phi = \text{unspecified ligand}$) involving this distance is 136.9° , very different from the ideal value of 180° for regular

Table 2. Interatomic distances ($\text{\AA}$) and angles ($^\circ$) in clinoclase

As—O(1)	1.704 (6)	O(2) ⁱ —O(4)	2.783 (7)
As—O(2) ^j	1.669 (5)	O(3) ⁱ —O(4)	2.788 (8)
As—O(3)	1.701 (6)	(O—O)As	2.754
As—O(4)	1.676 (5)	O(2) ⁱ —O(4)	3.627 (8)
(As—O)	1.688	O(2) ⁱ —OH(1)	2.785 (8)
Cu(2) ⁱ —O(2) ⁱⁱⁱ	2.519 (6)	O(2) ⁱ —OH(2)	2.819 (8)
Cu(2) ⁱ —O(3) ⁱ	2.016 (6)	O(2) ⁱ —OH(3) ⁱⁱ	3.234 (8)
Cu(2) ⁱ —O(4) ⁱ	3.321 (6)	O(3) ⁱ —O(4)	2.923 (8)
Cu(2) ⁱ —OH(1) ^{iv}	1.907 (6)	O(3) ⁱ —OH(1)	2.896 (8)
Cu(2) ⁱ —OH(2)	1.956 (6)	O(3) ⁱ —OH(2)	2.646 (8)
Cu(2) ⁱ —OH(3) ^j	1.905 (6)	O(3) ⁱ —OH(3) ⁱⁱ	3.340 (8)
(Cu(2)—O)[4]	1.946	O(4) ⁱ —OH(1)	2.995 (8)
(Cu(2)—O)[5]	2.061	O(4) ⁱ —OH(2)	3.114 (8)
(Cu(1)—O)[6]	2.271	OH(1)—OH(3) ⁱⁱ	3.165 (8)
Cu(1) ⁱ —O(2)	1.992 (6)	OH(2)—OH(3) ⁱⁱ	3.646 (8)
Cu(1) ⁱ —O(3) ⁱ	2.074 (6)	(O—O)Cu(1)	3.099
Cu(1) ⁱ —O(4)	2.332 (6)	O(2) ⁱⁱⁱ —O(3) ⁱ	3.423 (8)
Cu(1) ⁱ —OH(1)	1.895 (6)	O(2) ⁱⁱⁱ —OH(1) ^{iv}	3.130 (8)
Cu(1) ⁱ —OH(2)	1.938 (6)	O(2) ⁱⁱⁱ —OH(2)	3.143 (9)
Cu(1) ⁱ —OH(3) ⁱⁱ	2.871 (6)	O(2) ⁱⁱⁱ —OH(3) ^j	3.234 (8)
(Cu(1)—O)[4]	1.975	O(3) ⁱ —OH(2)	2.646 (8)
(Cu(1)—O)[6]	2.184	O(3) ⁱ —OH(3) ⁱ	2.829 (8)
Cu(3) ⁱ —O(1) ^j	2.000 (6)	OH(1) ^{iv} —OH(2)	2.770 (8)
Cu(3) ⁱ —O(1) ^y	2.033 (6)	OW(1) ^y —OH(3) ^j	2.751 (8)
Cu(3) ⁱ —O(4)	1.976 (6)	(O—O)Cu(2)[5]	2.991
Cu(3) ⁱ —OH(1)	2.995 (7)	O(1) ^j —O(1) ^y	2.541 (8)
Cu(3) ⁱ —OH(2) ^j	2.272 (5)	O(1) ^j —O(4)	2.894 (8)
Cu(3) ⁱ —OH(3)	1.916 (6)	O(1) ^j —OH(2) ^j	2.939 (8)
(Cu(3)—O)[4]	1.981	O(1) ^y —OH(2) ^j	3.432 (8)
(Cu(3)—O)[5]	2.039	O(1) ^y —OH(3)	2.950 (8)
(Cu(3)—O)[6]	2.199	O(4) ⁱ —OH(2) ^j	3.236 (8)
O(1) ⁱ —O(2) ^j	2.731 (8)	O(4) ⁱ —OH(3)	2.836 (9)
O(1) ⁱ —O(3)	2.738 (8)	OH(2) ^j —OH(3)	2.972 (8)
O(1) ⁱ —O(4)	2.760 (8)	(O—O)Cu(3)[5]	2.975
O(2) ⁱ —O(3)	2.726 (8)		
O(1) ⁱ —As—O(2) ^j	108.1 (3)	OH(1) ^{iv} —Cu(2)—OH(3) ^j	92.4 (2)
O(1) ⁱ —As—O(3)	107.1 (3)	(O—Cu(2)—O)[5]	91.0
O(1) ⁱ —As—O(4)	109.5 (3)	O(4) ⁱ —Cu(2)—OH(2)	118.3 (2)
O(2) ^j —As—O(3)	108.0 (3)	O(4) ⁱ —Cu(2)—O(3) ^j	56.9 (2)
O(2) ^j —As—O(4)	112.6 (3)	O(4) ⁱ —Cu(2)—OH(1) ^{iv}	120.9 (2)
O(3) ⁱ —As—O(4)	111.3 (3)	OH(2)—Cu(2)—OH(3) ^j	175.8 (2)
(O—As—O)	109.4	O(3) ⁱ —Cu(2)—OH(1) ^{iv}	171.9 (3)
O(2) ⁱ —Cu(1)—O(4)	113.8 (2)	O(4) ⁱ —Cu(2)—O(2) ⁱⁱⁱ	136.9 (2)
O(2) ⁱ —Cu(1)—OH(1)	91.5 (2)	O(4) ⁱ —Cu(2)—OH(3) ^j	58.5 (2)
O(2) ⁱ —Cu(1)—OH(2)	91.7 (2)	(O(4) ⁱ —Cu(2)—O)	88.7
O(2) ⁱ —Cu(1)—OH(3) ⁱⁱ	81.2 (2)	O(1) ^j —Cu(3)—O(1) ^y	78.1 (3)
O(3) ^j —Cu(1)—O(4)	82.9 (2)	O(1) ^j —Cu(3)—O(4)	93.4 (2)
O(3) ^j —Cu(1)—OH(1)	93.6 (2)	O(1) ^j —Cu(3)—OH(2) ^j	86.7 (2)
O(3) ^j —Cu(1)—OH(2)	82.5 (2)	O(1) ^y —Cu(3)—OH(2) ^j	105.6 (2)
O(3) ^j —Cu(1)—OH(3) ⁱⁱ	83.3 (2)	O(1) ^j —Cu(3)—OH(3)	96.6 (2)
O(4) ⁱ —Cu(1)—OH(1)	89.6 (3)	O(4) ⁱ —Cu(3)—OH(2) ^j	99.0 (2)
O(4) ⁱ —Cu(1)—OH(2)	92.3 (2)	O(4) ⁱ —Cu(3)—OH(3)	93.5 (3)
OH(1)—Cu(1)—OH(3) ⁱⁱ	80.4 (2)	OH(2) ^j —Cu(3)—OH(3)	90.0 (2)
OH(2)—Cu(1)—OH(3) ⁱⁱ	96.7 (2)	(O—Cu(3)—O)[5]	92.9
(O—Cu(1)—O)	90.0	OH(1)—Cu(3)—O(1) ^j	64.1 (2)
O(2) ⁱⁱⁱ —Cu(2)—O(3) ^j	97.4 (2)	OH(1)—Cu(3)—O(1) ^y	82.9 (2)
O(2) ⁱⁱⁱ —Cu(2)—OH(1) ^{iv}	88.9 (2)	OH(1)—Cu(3)—O(4)	70.7 (2)
O(2) ⁱⁱⁱ —Cu(2)—OH(2)	88.3 (2)	OH(1)—Cu(3)—OH(3)	120.5 (2)
O(2) ⁱⁱⁱ —Cu(2)—OH(3) ^j	92.9 (2)	(OH(1)—Cu(3)—O)	84.6
O(3) ^j —Cu(2)—OH(2)	83.5 (2)	O(1) ^j —Cu(3)—OH(3)	172.7 (3)
O(3) ^j —Cu(2)—OH(3) ^j	92.3 (2)	O(1) ^y —Cu(3)—O(4)	153.3 (2)
OH(1) ^{iv} —Cu(2)—OH(2)	91.6 (2)	OH(1)—Cu(3)—O(2) ^j	147.6 (2)

Equivalent positions: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1+x, y, z$; (iii) $2-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53191 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

octahedral coordination. The geometry of the anions around Cu(2) corresponds quite closely to square pyramidal, as noted by Ghose *et al.* (1965). Cu(3) is coordinated by six anions in an octahedral arrangement; however, one apical bond is extremely long

[Cu(3)—OH(1) = 2.995 Å], and so the coordination approaches square pyramidal.

Cu²⁺ is [5]-coordinated in several copper oxysalt minerals; relevant data are summarized in Table 3. There are two possible geometries for [5] coordination: square pyramidal and trigonal bipyramidal. The angular characteristics of these two coordination geometries are quite distinct; they are shown in Fig. 1, where they are compared with the corresponding structural data of the minerals in Table 3. The observed geometries agree closely with those of the ideal polyhedra, and there is no difficulty in assigning either of these geometries to any of the observed [5] coordinations. It is also notable that there seem to

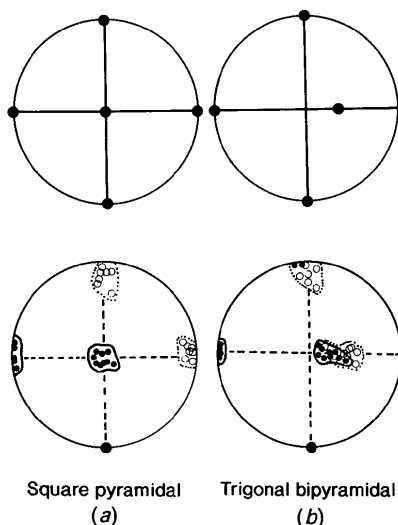


Fig. 1. Stereographic projections for coordinations of Cu²⁺ in minerals: (a) square pyramidal, and (b) trigonal bipyramidal; the upper projections show the ideal angular relationships, and the lower projections show the structural data for copper oxysalt minerals; in (b), the unique axis is oriented north-south.

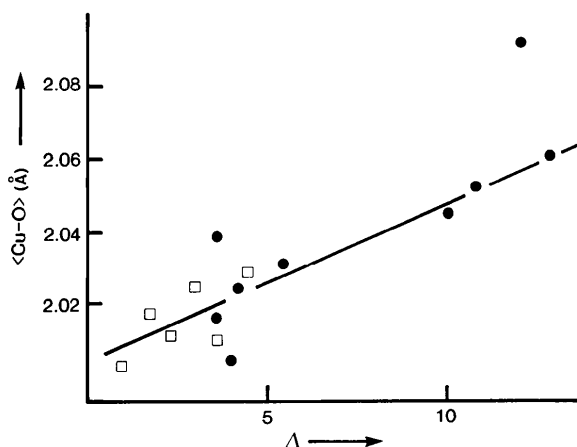


Fig. 2. Variation in $\langle \text{Cu—O} \rangle$ with bond length distortion Δ for [5]-coordinated Cu²⁺ in minerals; ● = square pyramidal; □ = trigonal bipyramidal.

Table 3. Stereochemical details of the [5] coordination of Cu²⁺ in minerals

Mineral	Polyhedron*	$\langle \text{Cu—O} \rangle$ (Å)	Δ ($\times 10^3$)	Bond-valence sum (v.u.)
Clinoclase	SPY	2.061	12.8	2.02
	SPY	2.039	3.6	1.91
Litidionite	SPY	2.092	12.0	1.81
Callaghanite	SPY	2.052	10.8	2.02
Kinoite	SPY	2.016	3.6	2.03
	SPY	2.045	10.0	2.00
Teinite	SPY	2.031	5.4	1.99
Mixite	SPY	2.024	4.1	2.01
Ziesite	SPY	2.004	4.0	2.12
Blossite	SPY	2.058	13.9	2.06
Balyakinite	SPY	2.048	6.7	1.93
Stoiberite	TBY	2.029	4.4	1.99
	TBY	2.010	3.6	2.08
Dolerophanite	TBY	2.025	3.0	1.99
Fingerite	TBY	2.011	2.3	1.90
Olivenite	TBY	2.018	1.7	1.95
Libethenite	TBY	2.003	0.9	2.03

* SPY = square pyramidal; TBY = trigonal bipyramidal.

be no transitional intermediates between the two coordinations; no reaction path is apparent, and presumably there is some sort of energy barrier between the two coordination geometries.

There is a significant range of mean bond lengths in Table 3, and the grand mean bond length for square pyramidal coordination (2.040 Å) is significantly greater than that for trigonal bipyramidal coordination (2.016 Å). However, the bond-valence sums (Brown, 1981) around the central Cu²⁺ cations (Table 3) all cluster about their ideal value of 2.0 v.u. This indicates that the variation in mean bond length occurs as a result of the non-linear relationship between bond valence and bond length, and Fig. 2 shows this to be the case. The variation in $\langle \text{Cu—O} \rangle$ is linearly related to the 'bond length distortion' parameter Δ $\{\Delta = \sum_i [(l_i - l_o)/l_o]^2 / i$, where l_i is the i th bond length and $l_o = \langle l_i \rangle$, both coordination geometries constituting a single population in the relationship. The larger $\langle \text{Cu—O} \rangle$ for square-pyramidal geometry is a result of the larger degree of distortion encountered in this coordination as compared to the more regular trigonal-bipyramidal coordination.

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Structure of Alkaline-Earth Pentafluoroantimonates(III), $MSbF_5$ ($M = \text{Sr, Ba}$)

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Abstract. Strontium pentafluoroantimonate(III), SrSbF_5 , $M_r = 304.36$, orthorhombic, $Pbcm$, $a = 4.378$ (1), $b = 8.853$ (3), $c = 11.233$ (4) Å, $V = 435.4$ (3) Å³, $Z = 4$, $D_m = 4.60$, $D_x = 4.64$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 18.9$ mm⁻¹, $F(000) = 536$, $T = 298$ K, $R = 0.028$ for 596 independent reflections with $I > 3\sigma(I)$. Barium pentafluoroantimonate(III), BaSbF_5 , $M_r = 354.08$, orthorhombic, $Pbcm$, $a = 4.676$ (1), $b = 9.313$ (2), $c = 11.213$ (3) Å, $V = 488.3$ (2) Å³, $Z = 4$, $D_m = 4.77$, $D_x = 4.82$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 13.6$ mm⁻¹, $F(000) = 608$, $T = 298$ K, $R = 0.015$ for 914 independent reflections with $I > 3\sigma(I)$. SrSbF_5 and BaSbF_5 are isostructural compounds. The three-dimensional network consists of isolated SbF_5^{2-} units which are connected by ten-coordinated alkaline-earth ions Sr^{2+} or Ba^{2+} . The geometry of these pentafluoroantimonate ions is approximately square pyramidal with the Sb atom outside the pyramid, below the four F atoms constituting the basal plane.

Introduction. Most of the previous works devoted to tin(II), antimony(III) or tellurium(IV) compounds have emphasized the prominent role played by the free electron pair, usually leading to original structures (Gillespie & Nyholm, 1957; Fourcade & Masherpa, 1978).

In particular, the reaction of SbF_3 with mono-valent fluorides gives various series of fluoro-complexes: $M_2\text{SbF}_5$ (Byström & Wilhelmi, 1951b; Ryan & Cromer, 1972; Habibi, Ducourant, Fourcade & Masherpa, 1974a), $MSbF_4$ (Byström, Bäcklund & Wilhelmi, 1951; Byström, Bäcklund & Wilhelmi, 1952; Mehrain, Ducourant, Fourcade &

Masherpa, 1974; Habibi, Bonnet & Ducourant, 1978), MSb_2F_7 (Byström & Wilhelmi, 1951a; Ryan, Mastin & Larson, 1971; Mastin & Ryan, 1971; Habibi, Ducourant, Fourcade & Masherpa, 1974b), MSb_4F_{13} (Byström & Wilhelmi, 1950; Ducourant, Fourcade, Philippot & Masherpa, 1975), MSb_3F_{10} (Fourcade, Masherpa & Philippot, 1975; Ducourant, Bonnet, Fourcade & Masherpa, 1975), $M_4Sb_5F_{19}$ and $M_3Sb_4F_{15}$ (Ducourant & Fourcade, 1976). Structural determinations have been carried out on some of them.

SbF_5^{2-} units have so far been found only in the presence of alkali ions (Na^+ , K^+ , Rb^+ , Cs^+) as well as with NH_4^+ and Tl^+ . The possible existence of homologous species in other compounds prompted us to investigate the alkaline-earth fluoride-antimony trifluoride systems. The present paper reports the single-crystal structure determination of SrSbF_5 and BaSbF_5 .

Experimental. The two compounds SrSbF_5 and BaSbF_5 were prepared by solid-state reactions from stoichiometric mixtures of SbF_3 and MF_2 ($M = \text{Sr, Ba}$). The starting materials were mixed in a dry glove box, introduced into gold tubes and heated under vacuum at 393 K. The tubes were then sealed in a dry argon atmosphere and heated over 15 h at 573 K. Single crystals were obtained by heating SrSbF_5 and BaSbF_5 to 783 and 903 K respectively, then by slow cooling (3 K h^{-1}) to 403 K. D_m values were obtained by hydrostatic methods.

Orthorhombic symmetry was deduced from Laue, Weissenberg and precession photographs. Cell parameters were determined from an X-ray powder