

08.1-5 THE CONTINUOUS TRANSITION FROM A TETRAGONAL PYRAMIDAL TO A TRIGONAL BIPYRAMIDAL $\text{Cu(II)}\text{O}_5$ COORDINATION FIGURE.

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Cu(II) atoms coordinated by oxygen atoms are in most cases surrounded by four nearest neighbors in a more or less distorted square planar arrangement $[\text{Cu(II)}-\text{O} \sim 2.0 \text{ \AA}]$. Such a " CuO_4 square" may be completed by one O atom to a tetragonal pyramid or by two O atoms to a tetragonal bipyramid. Usually the Cu-O bonds to the additional O atoms are $< 2.25 \text{ \AA}$; but transitions between the distinct coordination numbers [4], [4+1], and [4+2] are well known.

In some cases greater deviations from the ideal " CuO_4 square" are found. Obviously the largest ones occur, if one additional O atom completes the coordination geometry in a "tetragonal pyramidal" polyhedron with [4+1] coordinated Cu(II) atoms. This applies especially for those atoms, whose fifth Cu-O bond length is shorter than 2.25 \AA and the coordination number changes from [4+1] to [5]. The degree of distortion from the tetragonal pyramid (see FIG. 1a) can be expressed by the angles between opposite O atoms within the " CuO_4 square":

$$\alpha_1 = \angle \text{O}^a\text{-Cu-O}^c \quad \text{and} \quad \alpha_2 = \angle \text{O}^b\text{-Cu-O}^d$$

Two principal different kinds of distortion are known: (1) α_1 and α_2 are definitely smaller than 180° (see FIG. 1b). The Cu(II) atom formally is shifted out of the " CuO_4 square" toward the fifth neighbor. (2) The distortion concerns predominantly one of the two angles α (see FIG. 1c). As a limit a trigonal bipyramidal coordination figure with ideal symmetry $\bar{6}2m$ is reached. This coordination figure is known from a few examples only. Recent investigations on the crystal chemistry and stereochemistry of oxygen bearing Cu(II) compounds verified the continuous transition based on some representatives (Effenberger, *Journ. Solid State Chem.*, 1987, **66**, in press).

It is worth mentioning, that the greater amount of compounds containing Cu(II) atoms either with a trigonal bipyramidal coordination or with a transitional coordination mentioned above has $[\text{OCu}_4]$ tetrahedra (Effenberger, *Monatsh. Chem.*, 1985, **116**, 927-931).

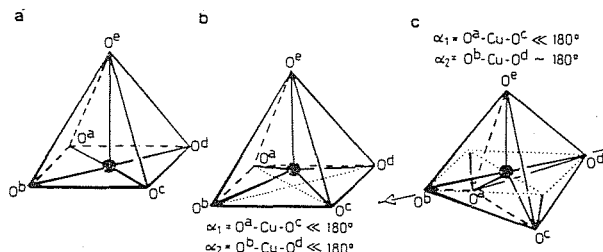


FIG. 1. $\text{Cu(II)}[4+1]\text{O}_5$ and $\text{Cu(II)}[5]\text{O}_5$ coordination polyhedra:

(a) the trigonal pyramidal coordination with Cu(II) in the basal plane; (b) the tetragonal pyramidal coordination figure with the Cu(II) atom shifted toward the fifth nearest neighbor; (c) the transition from the tetragonal pyramidal coordination to a trigonal bipyramidal coordination figure.

08.1-6 ROD-BASED SULPHOSALT STRUCTURES
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From the chemical point of view these compounds represent complex sulphides and selenides with the following cation combinations: Pb-Sb, Pb-Bi, Pb-Sb-Bi-(Cu,Fe), Sn-Sb, Ba-Bi, REE-Sb and REE-Bi. The crystal structures of this group represent packings of lozenge-shaped rods of simple archetypal structures: infinite rods $[\text{O}01]_{\text{Sns}}$, $[\text{O}11]_{\text{Pbs}}$ or, rarely, $[\text{O}10]_{\text{Sns}}$ plus some transitional cases. These rods have both pseudotetragonal surfaces (T), occupied by Pb, Sn, Ba or REE as well as by S, and pseudohexagonal surfaces (H), occupied only by S atoms. In the majority of instances, the two surface types face each other in a non-commensurate match across the rod interface. Interstitial atoms (cations) are rare in these structures whereas combinations of two rod types, even from two archetypes, or of rods with other building elements, are common.

Two large families of rod-based structures exist: those with independent, detached rods and those with rods organized into parallel, periodically constricted layers by means of common atoms or polyhedra. In the first category, cyclically twinned structures occur alongside those with a chess-board pattern of rod distribution. In the second category, five types of layers have been discerned according to the way the lozenge-shaped rods join into layers: (1) by sharing a tightly-bonded double-layer, (2) sharing a common coordination octahedron, (3) sharing a column of S atoms, (4) sharing a column of $[\text{O}10]_{\text{Sns}}$ type, and (5) via an inter-vening sheared $[\text{O}10]_{\text{Sns}}$ pseudo-hexagonal interval. In each layer type, various widths of lozenges in terms of T subcells and various thicknesses in terms of atomic layers can exist. Together with the type of interlayer connection they determine the widths of H and T surfaces. Only the rod layers with pairwise compatible widths of layer surfaces can combine in a single structure. When the H and T surfaces of the same layer can match, structures composed of only one layer type are formed, e.g., jamesonite, boulangerite, cosalite. In other cases structures composed of two distinct, alternating types of layers occur, e.g., dadsonite and robinsonite. The condition of layer match restrains the number of possible phases in this family. Further restrictions are imposed by the requirement of valency balance in these structures in which the exterior positions are preferably occupied by (large) divalent cations and the interior ones (i.e., the lone electron pair micelles that form the rod interiors) are preferably occupied by Sb and Bi.

The geometric and stoichiometric analysis of these structures, their classification scheme and examples of individual categories will be presented.