JOURNAL OF SOLID STATE CHEMISTRY 73, 118–126 (1988)

Contribution to the Stereochemistry of Copper. The Transition from a Tetragonal Pyramidal to a Trigonal Bipyramidal Cu(II)O_5 Coordination Figure with a Structure Determination of $PbCu_2(SeO_3)_3$

H. EFFENBERGER

Institut für Mineralogie und Kristallographie der Universität Wien,
Dr. Karl Lueger Ring 1, A-1010 Vienna, Austria

Received January 13, 1986; in revised form May 19, 1986

In inorganic compounds the usual environment of oxygen-coordinated Cu(II) atoms are four nearest atoms at Cu–O ~ 2.0 Å in a more or less square planar arrangement. In some cases distinct deviations from the ideal "CuO_4 square" are found. Obviously the largest distortions occur, if one additional O atom completes the coordination geometry in a "tetragonal pyramidal" $Cu(II)^{[4+1]}O_5$ polyhedron. Now the continuous transition from this "tetragonal pyramidal" polyhedron to a trigonal bipyramidal $Cu(II)^{[5]}O_5$ polyhedron can be verified. In the compound $PbCu_2(SeO_3)_3$ each of the four crystallographically different Cu atoms has four nearest O atoms, which are "square planar" arranged. The "CuO_4 squares" show different kinds of distortion. The crystal structure of $PbCu_2(SeO_3)_3$ was determined by single-crystal X-ray techniques (a = 7.813(1) Å, b = 9.116(1) Å, c = 12.570(1) Å, α = 82.27(1)°, β = 72.90(1)°, γ = 89.69(1)°, space group $P\bar{1}$, $Z = 4$, $R_w = 0.048$ for 5899 reflections up to $\sin \theta/\lambda = 0.81$ Å^{-1}).

Introduction

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 [Cu(II)–O ~ 2.0 Å]. Such a "CuO_4 square" may be completed by one O atom to a tetragonal pyramid or by two O atoms to a distorted octahedron. Usually the Cu–O bond lengths to the additional O atoms are longer than 2.25 Å; transitions between the distinct coordination numbers [4], [4 + 1], and [4 + 2] are well known. In some cases the "CuO_4 square" is definitely distorted. The Cu(II)O_5 coordination figure may also be a trigonal bipyramid; the five Cu–O bond lengths than vary from ~1.90 to ~2.20 Å. It is worth mentioning that other copper–oxygen coordination figures have been described only from a few isolated cases for inorganic crystal structures (see *1–7*). Different kinds of distortion have been found in the compound $PbCu_2(SeO_3)_3$. In connection with studies on Cu(II)–oxygen coordination figures a detailed discussion of its crystal structure seem to be of general interest.

Synthesis of $PbCu_2(SeO_3)_3$

Crystals of $PbCu_2(SeO_3)_3$ were synthesized under hydrothermal conditions in a steel vessel lined with "Teflon." 2 g of an equimolar mixture of PbO, CuO, and SeO_2 were put into the vessel of ~6 ml capacity;

0022-4596/88 $3.00

TABLE I

SUMMARY OF CRYSTAL DATA, X-RAY DATA COLLECTION, AND CRYSTAL STRUCTURE REFINEMENT OF $PbCu_2(SeO_3)_3$

$a = 7.813(1)$ Å
$b = 9.116(1)$ Å
$c = 12.570(1)$ Å
$\alpha = 82.27(1)^\circ$
$\beta = 72.90(1)^\circ$
$\gamma = 89.69(1)^\circ$
Space group $P\bar{1}$
$\rho_{calc} = 5.61$ g cm^{-3}
$\mu(MoK\alpha) = 365$ cm^{-1}
$Z = 4\{PbCu_2(SeO_3)_3\}$
$R = 0.055$
$R_w = 0.048$ ($w = [\sigma(F_o)]^{-2}$)

STOE four-circle diffractometer AED 2
Program system STRUCSY (ECLIPSE S/140)
Crystal dimensions: $0.16 \times 0.18 \times 0.19$ mm^3
Graphite monochromatized Mo$K\alpha$ radiation
Scan speed ratio $2\theta : \omega = 1:1$
Time pro step: 0.5 to 1.5 sec; step width 0.03°
40 steps per reflection; 6 steps for back ground
3 standard reflections measured each 90 min
Range of data collection: $2^\circ \leq 2\theta \leq 70^\circ$
Total measured reflections: 9001
Unique reflections: 7058; 5899 with $F_o > 3\sigma(F_o)$
Number of variables: 272

1 ml H_2O_2 ("perhydrol") was added and the vessel was filled with H_2O to about 80 vol%. After heating for 2 days at 493(5) K and after cooling to room temperature (12 hr) the following compounds were identified: $PbCu_2(SeO_3)_3$; $Cu(SeO_3)$-II, III, and IV (*8*); $Cu_2O(SeO_3)$-I and II (*9*); $Cu_4O(SeO_3)_3$-I and II (*9*). The title compound is triclinic and forms equidimensional crystals. They are light green in color and have a size up to 0.2 mm.

Structure Determination of $PbCu_2(SeO_3)_3$

Lattice parameters were obtained from the accurate 2θ values of 74 reflections. They are listed together with the data concerning the X-ray measurements as well as with the final obtained R values in Table I. The collected intensities were corrected for absorption (empirical ψ scans), and for Lorentz and polarization effects as usual.

The coordinates for the Pb atoms were found by direct methods. Subsequent Fourier summations revealed the positions of the other atoms. Complex atomic scattering functions for neutral atoms (*10*) were employed. Secondary isotropic extinction (*11*) was taken into consideration during the final stage of refinement. Table II gives a list of final obtained structure parameters, Table III some important interatomic distances and bond angles.

Discussion of the Crystal Structure of $PbCu_2(SeO_3)_3$

The coordination geometries of the two Pb atoms in $PbCu_2(SeO_3)_3$ are quite different (see Table III), but are in agreement with common crystal chemical experience (*12*). The Pb(1) atom has an one-sided coordination by five oxygen atoms with Pb–O = 2.45 to 2.61 Å. The distance to the next-nearest neighbor measures 2.92 Å. The Pb(2)–O distances are generally longer than the Pb(1)–O distances; the coordination geometry of the Pb(2) atom is not as clear-cut as that of the Pb(1) atom: There are seven Pb(2)–O distances within the range from 2.61 to 2.79 Å; the eighth Pb–O distance is 2.93 Å. The coordination geometry of the Pb(2) atom is irregular, but not one-sided.

Each of the Cu atoms has four nearest O atom neighbors within the range from 1.92 to 2.03 Å (mean values from 1.96 to 1.99 Å). Considering only these atoms, the coordination may be described as more or less

TABLE II

STRUCTURAL PARAMETERS FOR $PbCu_2(SeO_3)_3$[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	0.12192(5)	0.65409(5)	0.34829(4)	129(2)	120(2)	175(2)	20(1)	−53(2)	−56(1)
Pb(2)	0.05879(6)	0.14271(5)	0.34295(5)	163(2)	179(2)	205(2)	38(1)	−46(2)	−32(2)
Cu(1)	0.4412(2)	0.4338(1)	0.7054(1)	98(5)	115(5)	136(6)	27(4)	−26(5)	−61(5)
Cu(2)	0.2260(2)	0.8323(2)	0.9633(1)	101(5)	158(6)	143(6)	55(4)	−48(5)	−60(5)
Cu(3)	0.1676(2)	0.2424(2)	0.0098(1)	109(5)	135(6)	178(7)	56(4)	−63(5)	−101(5)
Cu(4)	0.3769(2)	0.8321(1)	0.7002(1)	123(5)	123(5)	121(6)	10(4)	−47(5)	−16(5)
Se(1)	0.0839(1)	0.5471(1)	0.8311(1)	92(4)	70(4)	166(5)	27(3)	−39(4)	−60(4)
Se(2)	0.4324(1)	0.8810(1)	0.1309(1)	88(4)	89(4)	121(5)	40(3)	−27(4)	−37(4)
Se(3)	0.3226(1)	0.3713(1)	0.4946(1)	104(4)	78(4)	147(5)	21(3)	−37(4)	−44(4)
Se(4)	0.3594(1)	0.9052(1)	0.4485(1)	93(4)	89(4)	145(5)	19(3)	−47(4)	−42(4)
Se(5)	0.1238(1)	0.1075(1)	0.8020(1)	109(4)	85(4)	129(5)	32(3)	−36(4)	−45(4)
Se(6)	0.4456(1)	0.3716(1)	0.1285(1)	100(4)	97(4)	124(5)	39(3)	−38(4)	−52(4)
O(11)	0.1853(10)	0.6765(8)	0.7172(8)	13(3)	11(3)	22(4)	−1(3)	−9(3)	−3(3)
O(12)	0.0474(10)	0.6432(8)	0.9406(8)	11(3)	12(3)	26(5)	5(3)	−6(3)	−9(3)
O(13)	0.2618(9)	0.4472(8)	0.8489(8)	8(3)	11(3)	25(5)	9(2)	−5(3)	−8(3)
O(21)	0.4373(11)	0.7750(9)	0.2529(8)	21(4)	12(3)	17(4)	4(3)	−10(4)	9(3)
O(22)	0.3463(11)	0.7530(9)	0.0715(7)	20(4)	13(3)	15(4)	4(3)	−10(3)	−6(3)
O(23)	0.6552(9)	0.8989(9)	0.0494(8)	5(3)	17(4)	25(5)	3(2)	−3(3)	−8(4)
O(31)	0.2562(10)	0.3780(9)	0.6362(8)	10(3)	18(4)	16(4)	−2(3)	1(3)	−3(3)
O(32)	0.1187(11)	0.3467(10)	0.4755(9)	12(3)	26(4)	26(5)	−1(3)	−8(4)	−8(4)
O(33)	0.3685(10)	0.5571(8)	0.4396(8)	12(3)	8(3)	19(4)	5(2)	−4(3)	−3(3)
O(41)	0.1470(10)	0.8594(9)	0.4514(9)	10(3)	16(4)	27(5)	1(3)	−6(3)	−8(4)
O(42)	0.3799(10)	1.0750(8)	0.3706(8)	8(3)	10(3)	21(4)	2(2)	−6(3)	−1(3)
O(43)	0.2970(11)	0.9519(9)	0.5837(7)	20(4)	14(4)	8(3)	7(3)	−3(3)	−6(3)
O(51)	0.1348(12)	−0.0775(8)	0.8365(7)	31(4)	8(3)	13(4)	8(3)	−9(4)	−3(3)
O(52)	−0.0428(11)	0.1022(9)	0.7414(8)	20(4)	14(4)	26(5)	10(3)	−17(4)	−8(4)
O(53)	0.0158(10)	0.1615(9)	0.9289(7)	7(3)	24(4)	12(4)	4(3)	3(3)	−13(3)
O(61)	0.3870(10)	0.4335(9)	0.2544(7)	14(3)	19(4)	10(3)	4(3)	−4(3)	−10(3)
O(62)	0.5694(10)	0.2224(8)	0.1603(7)	14(3)	16(4)	8(3)	6(3)	−4(3)	−3(3)
O(63)	0.2476(10)	0.2834(9)	0.1389(8)	6(3)	20(4)	18(4)	−1(3)	−3(3)	−4(3)

[a] 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_{ij} are multiplied by 10^{-4} for the atoms Pb, Cu, and Se, as well as by 10^{-3} for the O atoms.

distorted "square planar." Up to 2.60 Å the atoms Cu(1), Cu(3), and Cu(4) have one further O atom neighbour. For one of the [4 + 1] coordinated Cu atoms in $PbCu_2(SeO_3)_3$ the distance to this fifth neighboring O atom is very short [Cu(1)–O = 2.19 Å]. Similar values have been reported only in a few inorganic compounds (*1, 2, 5, 7*). The Cu(2) atom is [4 + 1 + 1] coordinated: beside the "CuO_4 square" it is coordinated to two further O atoms with Cu(2)–O distances of 2.32 and 2.59 Å. The next nearest Cu–O distances are longer than 2.80 Å and they are excluded from discussion.

In the "CuO_4 squares" the O–Cu–O angles between neighboring O atoms are within the range from 80.0 to 99.6°, and the angles between opposite O atoms are all larger than 150°. In the "$Cu(1)O_4$ square" one of the O–Cu–O angles between opposite O atoms is only 158.0°, whereas the other one is 173.7°. This coordination may

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN $PbCu_3(SeO_3)_3$[a]

Pb(1)–O(32) = 2.447(10)	Pb(2)–O(41) = 2.610(10)		
Pb(1)–O(41) = 2.455(9)	Pb(2)–O(52) = 2.615(8)		
Pb(1)–O(52) = 2.512(8)	Pb(2)–O(42) = 2.690(7)		
Pb(1)–O(21) = 2.581(8)	Pb(2)–O(63) = 2.704(9)		
Pb(1)–O(33) = 2.612(8)	Pb(2)–O(11) = 2.721(7)		
Pb(1)–O(31) = 2.917(7)	Pb(2)–O(43) = 2.762(8)		
Pb(1)–O(61) = 2.980(8)	Pb(2)–O(32) = 2.785(8)		
Pb(1)–O(32) = 3.030(9)	Pb(2)–O(41) = 2.931(8)		
Pb(1)–O(22) = 3.403(8)	Pb(2)–O(51) = 3.174(8)		
Se(1)–O(12) = 1.683(9)	Se(4)–O(42) = 1.698(8)		
Se(1)–O(13) = 1.710(7)	Se(4)–O(41) = 1.702(7)		
Se(1)–O(11) = 1.720(9)	Se(4)–O(43) = 1.736(8)		
Se(2)–O(22) = 1.706(8)	Se(5)–O(51) = 1.692(7)		
Se(2)–O(21) = 1.710(9)	Se(5)–O(52) = 1.694(8)		
Se(2)–O(23) = 1.737(8)	Se(5)–O(53) = 1.707(8)		
Se(3)–O(32) = 1.700(8)	Se(6)–O(61) = 1.686(8)		
Se(3)–O(31) = 1.711(10)	Se(6)–O(63) = 1.710(7)		
Se(3)–O(33) = 1.738(7)	Se(6)–O(62) = 1.736(7)		
Cu(1)–O(13) = 1.950(9)	O(13) O(33)	3.92(1)	173.7(4)
Cu(1)–O(33) = 1.976(9)	O(13) O(31)	2.84(1)	92.2(4)
Cu(1)–O(31) = 1.993(8)	O(13) O(61)	2.82(1)	90.4(3)
Cu(1)–O(61) = 2.025(8)	O(13) O(21)	3.19(1)	100.4(3)
Cu(1)–O(21) = 2.192(8)	O(33) O(31)	2.84(1)	91.5(4)
Cu(1)–O(11) = 2.963(7)	O(33) O(61)	2.69(1)	84.3(3)
	O(33) O(21)	2.79(1)	83.7(3)
	O(31) O(61)	3.94(1)	158.0(4)
	O(31) O(21)	3.32(1)	104.9(3)
	O(61) O(21)	3.14(1)	96.0(3)
Cu(2)–O(22) = 1.933(8)	O(22) O(53)	2.93(1)	97.0(4)
Cu(2)–O(53) = 1.980(8)	O(22) O(62)	2.77(1)	89.8(4)
Cu(2)–O(62) = 1.989(8)	O(22) O(51)	3.93(1)	172.1(4)
Cu(2)–O(51) = 2.008(8)	O(53) O(62)	3.92(1)	162.2(4)
Cu(2)–O(12) = 2.322(7)	O(53) O(51)	2.83(1)	90.5(4)
Cu(2)–O(23) = 2.593(8)	O(62) O(51)	2.66(1)	83.6(4)
Cu(3)–O(23) = 1.940(8)	O(23) O(12)	3.87(1)	167.1(4)
Cu(3)–O(12) = 1.959(8)	O(23) O(53)	2.71(1)	87.6(3)
Cu(3)–O(53) = 1.976(8)	O(23) O(63)	2.99(1)	99.3(4)
Cu(3)–O(63) = 1.981(9)	O(12) O(53)	2.53(1)	80.0(4)
Cu(3)–O(13) = 2.498(9)	O(12) O(63)	2.81(1)	91.1(4)
Cu(3)–O(51) = 2.854(8)	O(53) O(63)	3.89(1)	158.3(4)
Cu(4)–O(62) = 1.922(8)	O(62) O(43)	3.82(1)	159.2(4)
Cu(4)–O(43) = 1.956(8)	O(62) O(42)	2.78(1)	90.9(4)
Cu(4)–O(42) = 1.985(8)	O(62) O(11)	3.01(1)	99.6(4)
Cu(4)–O(11) = 2.013(7)	O(43) O(42)	2.75(1)	88.6(4)
Cu(4)–O(51) = 2.377(8)	O(43) O(11)	2.81(1)	90.2(4)
Cu(4)–O(61) = 3.129(8)	O(42) O(11)	3.89(1)	152.8(4)

[a] Pb–O distances are given up to 3.50 Å, O–Cu–O angles for Cu–O < 2.20 Å.

be considered as an example for the transition from a tetragonal pyramidal [4 + 1] coordination toward a trigonal bipyramidal [5] coordination. The "$Cu(2)O_4$ square" has the smallest distortion as compared with the other "CuO_4 squares" in $PbCu_2(SeO_3)_3$. For the atoms Cu(3) and Cu(4) both the O–Cu–O angles between opposite O atoms in the "CuO_4 square" are smaller than 167°. The "$Cu(3)O_4$ square" is distorted toward a tetragonal pyramid (with the Cu(3) atom at the apex pointing to the fifth nearest oxygen atom). The "$Cu(4)O_4$ square" deviates definitely from the "tetragonal planar" symmetry.

The Se–O bond lengths vary from 1.68 to 1.74 Å and the mean values for the six selenite groups from 1.70 to 1.72 Å. The O–Se–O angles are 94.6 to 104.8° and the O–O edges are 2.53 to 2.72 Å (*13*).

Considering only the "CuO_4 squares," the "$Cu(2)O_4$," "$Cu(3)O_4$," and "$Cu(4)O_4$ squares" are connected by common O atom corners [atoms O(53) and O(62)] to formal Cu_3O_{10} groups. The longer Cu–O bonds [Cu(2)–O(12) and Cu(4)–O(51)] are within these groups resulting in common O–O edges of the Cu polyhedra [O(51)–O(62) = 2.66 Å and O(12)–O(53) = 2.53 Å]. Each of these groups is connected to an "$Cu(1)O_4$ square" by a long Cu(3)–O(13) bond and to a second Cu_3O_{10} group by a long Cu(2)–O(23) bond resulting in a connection of total eight copper coordination polyhedra. A three-dimensional atomic arrangement is built up by the SeO_3 groups and by the coordination polyhedra of the Pb atoms (Fig. 1).

The "Tetragonal Pyramidal" $Cu(II)O_5$ Polyhedron

The ideal tetragonal pyramidal $Cu(II)O_5$ polyhedron can be described as follows: the Cu(II) atom is in the middle of a basal plane defined by the atoms O^a, O^b, O^c, and O^d (Fig. 2a). Under the recent topic slight deviations of the "CuO_4 square" from the symmetry 4/*mmm* are neglected. Strong distortions have been found especially for those Cu(II) atoms, whose fifth Cu–O bond length is shorter than 2.30 Å. The degree of

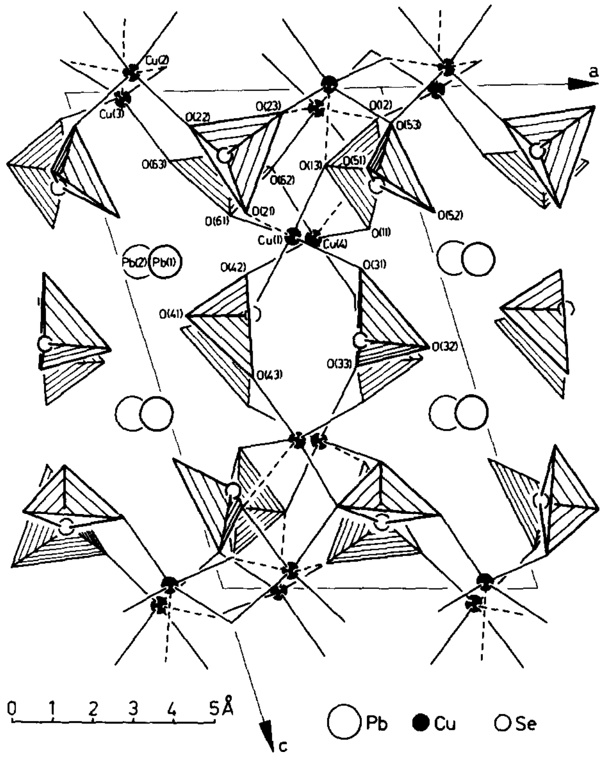

FIG. 1. Projection of the crystal structure of $PbCu_2(SeO_3)_3$ parallel [010] onto (010).

distortion can be expressed by the angles between opposite O atoms within the "CuO_4 square": $\alpha_1 = O^a$–Cu–O^c and $\alpha_2 = O^b$–Cu–O^d. Two principal different kinds of distortion are known:

(a) α_1 and α_2 are definitely smaller than

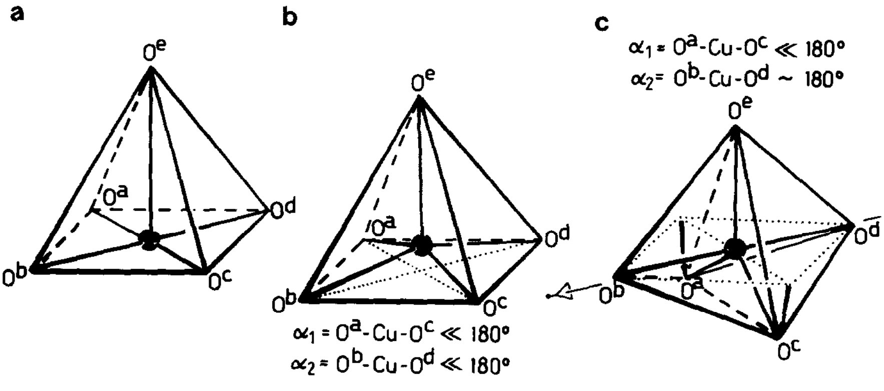

FIG. 2. $Cu(II)^{[4+1]}O_5$ and $Cu(II)^{[5]}O_5$ coordination polyhedra: (a) the tetragonal pyramidal coordination with the Cu(II) atom in the basal plane; (b) the tetragonal pyramidal coordination figure with the Cu(II) atom shifted toward the fifth nearest neighbor; (c) the transition from a tetragonal pyramidal coordination to a trigonal bipyramidal one.

TABLE IV

$Cu(II)^{[4+1]}O_5$ COORDINATION POLYHEDRA IN INORGANIC CRYSTAL STRUCTURES WITH A STRONGLY DISTORTED "CuO_4 SQUARE"[a]

Compound	Atom	Cu–O distances within the "CuO_4 squares"				$Cu–O^e$ distance	α_1	α_2
$Cu_4O(PO_4)_2$ (*15*), see also (*16*)	Cu(3)	1.895	1.942	2.029	2.053	2.226	132.8	170.9
	Cu(4)	1.907	1.949	1.957	2.093	2.302	129.0	176.4
$Cu_5O_2(PO_4)_2$ (*17*)	Cu(3)	1.931	1.932	1.943	2.167	2.254	136.0	177.2
$Ca_3Cu_3(PO_4)_4$ (*18*)	Cu(2)	1.906	1.941	2.038	2.090	2.169	132.6	171.0
$Cu_4O(SeO_3)_3$–I (*9*)	Cu(5)	1.932	1.962	1.963	1.981	2.265	150.0	175.3
	Cu(9)	1.897	1.942	1.964	2.035	2.312	149.2	171.2
	Cu(11)	1.906	1.980	1.981	2.053	2.205	142.4	169.2
	Cu(12)	1.910	1.939	1.983	2.017	2.348	143.7	165.1
	Cu(13)	1.919	1.950	1.974	2.132	2.170	140.5	171.1
	Cu(14)	1.889	1.957	1.987	2.031	2.252	141.9	170.4
	Cu(15)	1.918	1.960	1.972	2.029	2.242	148.8	170.0
	Cu(16)	1.895	1.962	1.994	2.048	2.240	136.1	168.7
$Cu_4O(SeO_3)_3$–II (*9*)	Cu(2)	1.917	1.947	2.004	2.032	2.229	144.7	168.2
	Cu(4)	1.920	1.962	1.964	1.999	2.343	145.6	167.5

[a] Interatomic distances in Å, bond angles in °.

180° (see Fig. 2b). It might be that the Cu(II) atom formally is shifted out of the "CuO_4 square" toward the fifth neighbor. Examples are the Cu(3) atom in $PbCu_2(SeO_3)_3$ or the Cu(1) atom in the monoclinic modification of $KCuPO_4$ (*14*) (in monoclinic $KCuPO_4$ α_1 and α_2 are 165.9° and 147.5°, $Cu–O^e = 2.154$ Å).

(b) The distortion may concern predominantly one of the two O–Cu–O angles α (see Fig. 2c), Table IV lists some examples with the angle α_1 smaller than 150° and the angle α_2 larger than 165°. Their stereographic projections are given in Fig. 3: The angle α_1 is drawn counterclockwise from the southern point at the ground circle; the atoms O^b and O^d lie near the middle point (one at the upper and one at the bottom side). Comparing Fig. 3 and Table IV it can be seen, that distorted tetragonal pyramidal $Cu(II)O_5$ coordination polyhedra are known, for which

(1) the $Cu–O^e$ bond length is "short" as compared with $Cu(II)^{[4+1]}O_5$ coordination polyhedra containing undistorted or even less distorted "CuO_4 squares,"
(2) one of the two O–Cu–O angles between opposite O atoms within the "CuO_4 square" is definitely smaller than 180° (α_1),
(3) the angle α_2 deviates only slightly from 180°, and
(4) the direction of the longest Cu–O bond within the coordination polyhedron (i.e., $Cu–O^e$) lies off the angle α_1.

The "Trigonal Bipyramidal" $Cu(II)O_5$ Polyhedron

The trigonal bipyramidal coordination polyhedron with its ideal symmetry $\bar{6}2m$ is shown in Fig. 4. The highest known point symmetry for a Cu(II) atom is 3 [atom Cu(1) in $Cu_2O(SeO_3)$–I (*9*)]. Usually the Cu–O bond lengths to the equatorial atoms O^a, O^b, and O^c are somewhat longer than to the axial atoms O^d and O^e; a distortion predominantly concerns the arrangement of the equatorial O atoms. Table V lists the $Cu(II)O_5$ polyhedra in inorganic crystal

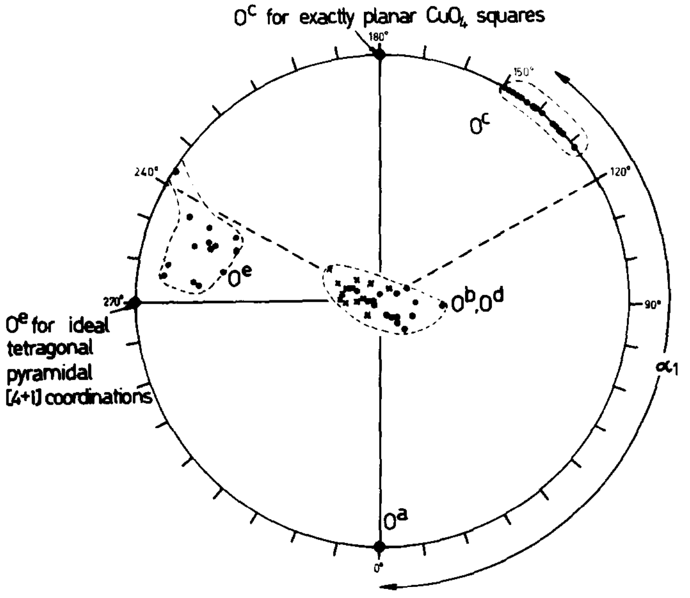

FIG. 3. $Cu(II)^{[4+1]}O_5$ coordination polyhedra with strongly distorted "CuO_4 squares." ○, At the upper side, ×, at the bottom side of the stereographic projection. The polyhedra mentioned in Table IV are shown.

structures described as trigonal bipyramids.

The stereographic projections of these coordination polyhedra are given in Fig. 5. The largest angle within the equatorial plane β_1 = O^a–Cu–O^b is drawn counterclockwise from the southern point at the ground circle. The third atom within the equatorial plane is signed as O^c and lies off the angle β_1. Both the axial atoms O^d and O^e lie near the center of the projection (one at the upper side and one at the bottom side). The angle β_2 = O^d–Cu–O^e deviates up to ~10° from the ideal value of 180°. From Fig. 5 and Table V follows:

(1) for some of the coordination figures one of the three O–Cu–O angles (= β_1) within the equatorial plane is definitely larger than 120° and the two others are smaller than 120°,

(2) in most cases one of the five Cu–O distances is large as compared with the others, and

(3) with a few exceptions Cu–O^c is the longest one of the five Cu–O bond lengths.

Conclusion

Comparing the CuO_5 coordination figures mentioned above (see Figs. 3 and 5 and

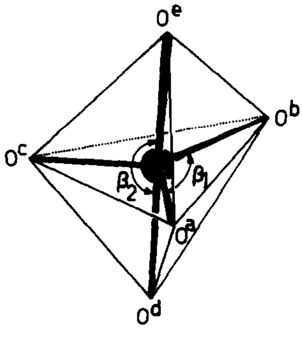

FIG. 4. The $Cu(II)O_5$ polyhedron forming a trigonal bipyramid.

TABLE V

COORDINATION FIGURES OF Cu(II) ATOMS IN INORGANIC CRYSTAL STRUCTURES CITED IN LITERATURE AS TRIGONAL "BIPYRAMIDAL" [5] COORDINATED[a]

Compound and mineral name	Atom	Cu–$O^{d,e}$	Cu–$O^{a,b}$	Cu–O^c	β_2 = O^d–Cu–O^e	$O^{a,b}$–Cu–O^c	β_1 = O^a–Cu–O^b
$Cu_2(OH)(PO_4)$, libethenite (*19*)	Cu(2)	1.934 1.938	2.046 2.057	2.057	172.5	111.6 124.2	124.2
$KCu_4(PO_4)_3$ (*20*)	Cu(3)	1.882 1.957	2.048 2.179	2.028	169.2	101.5 119.4	137.8
	Cu(4)	1.921 1.924	1.971 2.199	2.113	167.5	111.6 122.3	125.5
$Cu_2O(SO_4)$, dolerophanite (*21*)	Cu(2)	1.906 1.907	2.155 2.155	2.000	179.5	112.1 112.1	130.2
$Cu_5V_2O_{10}$ (*3*)	Cu(3)	1.932 1.969	1.924 2.034	2.287	177.0	94.7 127.2	138.2
	Cu(5)	1.890 1.930	1.965 2.034	2.230	170.2	100.3 117.2	139.9
$Cu_{11}O_2(VO_4)_6$, fingerite (*22*)	Cu(6)	1.929 1.971	1.907 2.102	2.147	179.6	93.2 133.2	133.5
$Cu_3(AsO_4)_2$ (*23*)	Cu(1)	1.931 1.933	1.993 2.010	2.157	173.8	102.1 125.7	132.1
$Cu_2(OH)(AsO_4)$, olivenite (*24*)	Cu(1)	1.917 1.984	1.988 2.048	2.163	172.0	103.5 108.4	148.0
$Cu_2O(SeO_3)$–I (*9*)	Cu(1)	1.916 1.924	2.081 2.081	2.081	180.0	115.7 115.7	115.7
$Cu_5Se_2O_8Cl_2$ (*25*)	Cu(1)	1.964 2.286[a]	1.927 2.050	2.572[b]	171.0	96.2 113.7	150.1
Cu_3WO_6 (*26*)	Cu	1.921 1.953	2.002 2.060	2.243	170.8	85.1 135.8	136.3

[a] Interatomic distances in Å, bond angles in °.

[b] Cu–Cl distance within a "trigonal bipyramidal" $Cu^{[3O+2Cl]}$ polyhedron.

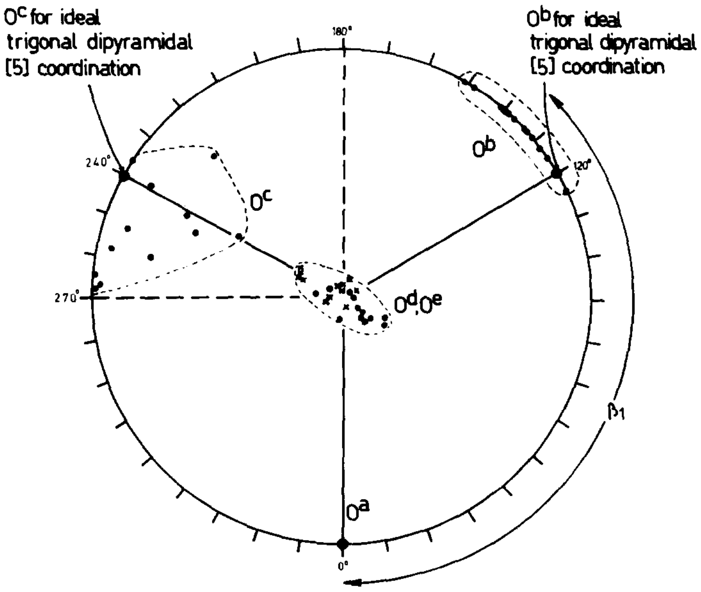

FIG. 5. Coordination figures of Cu(II) atoms cited in literature as trigonal bipyramidal [5] coordinated. O, at the upper side, ×, at the bottom side of the stereographic projection. The polyhedra mentioned in Table V are shown.

Tables IV and V, resp.) it can be deducted, that there is a continuous transition between the two ideal coordination polyhedra (a) [4 + 1] coordination with "square planar" arrangement of the four nearest neighbors and (b) trigonal bipyramidal [5] coordination. These two different types of coordination figures of formal divalent copper atoms towards oxygen atoms in inorganic crystal structures have been described in the literature (cf. *1–7*), but the transition has never been taken into consideration for Cu(II)O_5 polyhedra.

It should be mentioned that many of the compounds listed in Tables IV and V contain an oxo-oxygen atom which is approximately tetrahedrally coordinated by four Cu(II) atoms (*21*). It should be taken into consideration that these OCu_4 tetrahedra might cause a stronger distortion of the "CuO_4 squares" or might favor a trigonal bipyramidal coordination geometry (steric aspects).

Acknowledgments

The author thanks Prof. Dr. J. Zemann for many discussions and expresses sincere thanks to Prof. Dr. F. Pertlik for his continuous encouragement and helpful suggestions. The synthesis was supported by the "Hochschuljubiläumsstiftung der Stadt Wien."

References

1. J. Zemann, *Fortschr. Mineral.* **39,** 59 (1961).
2. J. Zemann, "Handbook of Geochemistry," Vol. II-3, p. 29-A, Springer-Verlag, Berlin, 1972.
3. R. D. Shannon and C. Calvo, *Acta Crystallogr. Sect. B* **29,** 1339 (1973).
4. W. Eysel, K.-H. Breuer, and U. Lambert, *Acta Crystallogr. Sect. A* **40** (Suppl.), C-209 (1984).
5. B. J. Hathaway, *Structure and Bonding* **57,** 55 (1984).
6. M. Trömel, *Acta Crystallogr. Sect. B* **40,** 338 (1984).
7. A. F. Wells, "Structural Inorganic Chemistry," Oxford Univ. Press (Clarendon), London, 1984.
8. H. Effenberger, *Z. Kristallogr.* **175,** 61 (1986).
9. H. Effenberger and F. Pertlik, *Monatsh. Chem.* **117,** 887 (1986).
10. "International Tables for X-ray Crystallography," Vol. IV, The Kynoch Press, Birmingham, England, 1974.
11. W. H. Zachariasen, *Acta Crystallogr.* **23,** 558 (1967).
12. K. Sahl, "Handbook of Geochemistry," Vol. II-5, p. 82-A, Springer-Verlag, Berlin, 1970.
13. R. Fischer and J. Zemann, "Handbook of Geochemistry," Vol. II-3, p. 34-A, Springer-Verlag, Berlin, 1974.
14. G. L. Shoemaker, E. Kostiner, and J. B. Anderson, *Z. Kristallogr.* **152,** 317 (1980).
15. J. B. Anderson, G. L. Shoemaker, and E. Kostiner, *J. Solid State Chem.* **25,** 49 (1978).
16. M. Brunel-Laügt, A. Durif, and J. C. Guitel, *J. Solid State Chem.* **25,** 39 (1978).
17. M. Brunel-Laügt and J.-C. Guitel, *Acta Crystallogr. Sect. B* **33,** 3465 (1977).
18. J. B. Anderson, E. Kostiner, and F. A. Ruszala, *J. Solid State Chem.* **39,** 29 (1981).
19. P. H. Keller, H. Hess, and F. Zettler, *N. Jb. Miner. Abh.* **134,** 147 (1979).
20. H. Effenberger, *Z. Kristallogr.*, in press.
21. H. Effenberger, *Monatsh. Chem.* **116,** 927 (1985).
22. L. W. Finger, *Am. Mineral.* **70,** 197 (1985).
23. S. J. Poulsen and C. Calvo, *Can. J. Chem.* **46,** 917 (1968).
24. K. Tomann, *Acta Crystallogr. Sect. B* **33,** 2628 (1977).
25. J. Galy, J. J. Bonnet, and S. Andersson, *Acta Chem. Scand. A* **33,** 383 (1979).
26. E. Gebert and L. Kihlborg, *Acta Chem. Scand.* **23,** 221 (1969).