

Pb₂Cu(II)₇(AsO₄)₆ and Pb₂Cu(I)₂Cu(II)₆(AsO₄)₆: Two Compounds with Topologically Related Crystal Structures

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Crystals of Pb₂Cu(II)₇(AsO₄)₆ and Pb₂Cu(I)₂Cu(II)₆(AsO₄)₆ have been synthesized under hydrothermal conditions. Their crystal structures were determined from single-crystal X-ray data (space group *P*1̄; *a* = 5.154(1), 5.210(1) Å; *b* = 8.363(2), 8.390(2) Å; *c* = 11.301(3), 11.406(3) Å; α = 90.19(2), 90.16(2)°; β = 90.34(2), 89.88(2)°; γ = 92.83(2), 93.60(2)°; *Z* = 1; *R*_w = 0.039, 0.034). The crystal structures are topologically related: Pb₂Cu(II)₇(AsO₄)₆ contains Cu(II)₃O₁₀ and Cu(II)₄O₁₂ chains formed by edge and corner connections of Cu(II)O₄ squares and remarkably regular CuO₅ polyhedra; they are interconnected by the arsenate tetrahedra. In Pb₂Cu(I)₂Cu(II)₆(AsO₄)₆ one of the former Cu(II)^[4] atoms is substituted by two linearly [2]-coordinated Cu(I) atoms, and the other atomic positions are maintained; the result is a connection of Cu(II)₃O₁₀ chains and Cu(II)₃O₁₂ groups via Cu(I) atoms to corrugated sheets. The Pb atoms are tetragonally antiprismatic coordinated; each two are edge connected to dimers. © 1995

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INTRODUCTION

The coordination figures formed by oxygen atoms around divalent copper atoms are manifold, and as a rule they exhibit four to six ligands. The usual Cu(II)O₅ polyhedron is a tetragonal pyramid with the copper atom in a [4 + 1] coordination; the trigonal dipyrmaid has rarely been found in inorganic compounds (1, 2). Although a limited number of compounds with trigonal dipyrmaid coordinations have been investigated during the past years, only a few of these polyhedra are more or less regular (3-6); one compound with a Cu(II) atom on a threefold rotation axis is known (7). Often distortions of the trigonal dipyrmaid toward the quite common tetragonal pyramid have been observed for CuO₅ polyhedra (8). During structural investigations of Cu(II) compounds two phases with topologically related crystal structures were studied; each structure contains two remarkably regular trigonal dipyrmaid CuO₅ polyhedra. Another special feature of the two title compounds is the substitution of a cation in its divalent oxidation state by two monovalent atoms while the other part of the crystal structure is main-

tained. As a convenience throughout this paper the two compounds Pb₂Cu(II)₇(AsO₄)₆ and Pb₂Cu(I)₂Cu(II)₆(AsO₄)₆ are hereafter denoted **II** and **I-II**.

EXPERIMENTAL

For hydrothermal syntheses Teflon-lined stainless steel autoclaves with an approximate 7-ml capacity were used. Starting materials for investigations in the system PbO-Fe₂O₃-CuO-As₂O₅ included PbCO₃ (for **II**) and PbO (for **I-II**), Fe(NO₃)₃, As₂O₅, and powdered Cu or CuO (all reagent grade). Two grams of the appropriate mixture was ground and heated with 2 ml of H₂O to 503 K for 5 days. Afterward the vessels were cooled to room temperature over 12 hr. During these periods the appearance or even disappearance of compounds was not controlled due to the limits of experimental conditions. Finally, the formation of different amounts of the following compounds could be observed, without considering the time of formation and therefore neither the equilibrium condition: **II**, **I-II**, Cu₂O (cuprite), Cu₃(AsO₄)₂ (lammerite), Cu₂(OH)(AsO₄) (olivenite), PbCu(As₂O₇), PbCu(OH)(AsO₄) (duftite), and PbFe(AsO₄)(AsO₃OH) (to be published elsewhere).

Initially the single crystals used for data collection were investigated by oscillation and Weissenberg-type film methods. Data collection was performed on a STOE four-circle AED2 diffractometer using graphite monochromatized MoK α radiation (for details see Table 1). Data were corrected for Lorentz and polarization effects, complex scattering functions for neutral atoms were used (9), and isotropic extinction was considered.

Both crystal structures were solved by direct and Fourier methods; they were refined by full-matrix least-squares techniques using the programs SHELX-76 and SDP (10, 11). Final structural parameters are given in Table 2. The highest peaks in the final difference Fourier summation are in the area surrounding the Pb atoms. To enable the comparison of the two structures the cell chosen in **I-II** is not the reduced one; a transformation according to $(\bar{1}00/010/00\bar{1})$ gives unit cell parameters with

TABLE I
Crystal Data, X-Ray Data Collection, and Structure Determination

| | Pb ₂ Cu(II) ₇ (AsO ₄) ₆ (II) | Pb ₂ Cu(I) ₂ Cu(II) ₆ (AsO ₄) ₆ (I-II) |
|--|---|--|
| <i>a</i> (Å) | 5.154(1) | 5.210(1) |
| <i>b</i> (Å) | 8.363(2) | 8.390(2) |
| <i>c</i> (Å) | 11.301(3) | 11.406(3) |
| α (°) | 90.19(2) | 90.16(2) |
| β (°) | 90.34(2) | 89.88(2) |
| γ (°) | 92.83(2) | 93.60(2) |
| <i>V</i> (Å ³) | 486.5 | 497.6 |
| <i>Z</i> | 1 | 1 |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Color | Light green | Dark brown to black |
| X-ray density (g cm ⁻³) | 5.78 | 5.86 |
| Reflections for cell parameters | 74; 33.1° ≤ 2 θ ≤ 48.9° | 44; 25.2° ≤ 2 θ ≤ 32.6° |
| Crystal dimensions (mm) | 0.24 × 0.09 × 0.18 | 0.10 × 0.05 × 0.08 |
| Data collection | 3° ≤ 2 θ ≤ 70° | 3° ≤ 2 θ ≤ 60° |
| Scan width (+ α_1 - α_2 dispersion) | 1.14° | 1.05° |
| Scan speed (2 θ/ω scan mode) | 0.9 to 1.8° min ⁻¹ | 0.6 to 1.8° min ⁻¹ |
| Reflections measured | 8472 | 4545 |
| Variation of intensity | ±1.5% (3 standards) | ±3.6% (3 standards) |
| Unique data; <i>R</i> _{int} | 4212; 0.053 | 2744; 0.035 |
| Data with <i>F</i> ₀ > 3 σ (<i>F</i> ₀) | 3699 | 2020 |
| Absorption correction | Crystal shape | ψ scans (6 reflections) |
| Absorption coefficient (cm ⁻¹) | μ (MoK α) = 348 | μ (MoK α) = 352 |
| Transmission factors | 0.017 to 0.106 | 0.029 to 0.115 |
| <i>R</i> | 0.045 | 0.038 |
| <i>R</i> _w ; <i>w</i> | 0.039; <i>w</i> = 1.48/ σ^2 | 0.034; <i>w</i> = 0.84/ σ^2 |
| Variable parameters | 183 | 186 |
| Max Δ/σ | ≤0.002 | ≤0.001 |
| Final difference Fourier (e Å ⁻³) | -5.0 to 3.9 | -1.4 to 0.9 |

α , β , and $\gamma \leq 90^\circ$: $a = 5.210(1)$ Å; $b = 8.390(2)$ Å; $c = 11.406(3)$ Å; $\alpha = 89.84(2)^\circ$; $\beta = 89.88(2)^\circ$; $\gamma = 86.40(2)^\circ$.

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

The two crystal structures are closely related to each other. Their chemical compositions differ by the substitution of one Cu(II) atom in **II** by two Cu(I) atoms at a position with doubled multiplicity in **I-II**. The main part of the structures is maintained. This causes a similar cell metric and similar atomic coordinates for all atoms except Cu(I). The two structures are depicted in Figs. 1 and 2. Selected interatomic distances, bond angles, and bond valences are summarized in Table 3. Bond valence sums of atoms are in accordance with their formal oxidation states. Compounds containing both Cu(I) and Cu(II) atoms on distinct atomic positions have rarely been described before; examples are the oxides LiCu₂O₂ (15), LiCu₃O₃ (16), NaCu₂O₂ (17), TiCu₂O₂ (18), and Cu₃TiO₄ (19); the mineral paramelaconite (20, 21); the high-temperature superconductor YBa₂Cu₃O₆ (22); and the compound Cu_{1.35}Fe₃(PO₄)₃ (23).

PbO₈ polyhedra. The Pb atoms are coordinated to eight oxygen atoms with Pb-O distances from 2.46 to 3.02 Å; further ligands exceed a distance of 3.60 Å. Corresponding individual bond lengths within the two structures show only small differences; the average values are identical within the limits of error. The coordination polyhedra are slightly distorted tetragonal antiprisms with O(12)-O(34)-O(24)-O(21) and O(23)-O(33)-O(31)-O(24) as the basis and the top faces. The distortions chiefly result from the connection with other coordination polyhedra, i.e., with one Cu(2)O₄ square, one Cu(4)O₅ dipyrmaid, and one As(3)O₄ tetrahedron; from these connections result the shortest O-O edges (2.67 to 2.79 Å) and the smallest O-Pb-O angles (54.7(2) to 61.2(2)°) in the PbO₈ polyhedra. Each two PbO₈ polyhedra are connected *via* the O(24)-O(24) edge by $\bar{1}$ symmetry to dimers; O(24)-O(24) and O(24)-Pb-O(24) are 3.117(11) Å and 77.5(2)° in **II** and 3.107(8) Å and 76.8(3)° in **I-II**.

Coordination of the Cu(II) atoms. The Cu atoms (except Cu(I) in **I-II**) have divalent oxidation states, which is proved by crystal chemical experience and by bond valence calculations (see Table 3). Two types of coordina-

TABLE 2
Structural Parameters (Upper Row, Pb₂Cu(II)₇(AsO₄)₆ (II); Lower row, Pb₂Cu(I)₂Cu(II)₆(AsO₄)₆ (I-II))

| Atom | x | y | z | U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ | B _{eq} |
|-------|-------------|-------------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Pb | 0.49654(6) | 0.53917(4) | 0.33142(3) | 0.0157(1) | 0.0209(2) | 0.0140(1) | 0.0013(1) | 0.0020(1) | 0.0004(1) | 1.33 |
| | 0.49700(10) | 0.54223(6) | 0.33052(4) | 0.0171(2) | 0.0161(3) | 0.0191(2) | -0.0005(1) | 0.0021(1) | -0.0004(2) | 1.38 |
| Cu(1) | 0.0 | 0.0 | 0.0 | 0.0191(7) | 0.0139(7) | 0.0165(6) | 0.0005(3) | -0.0052(4) | 0.0012(5) | 1.31 |
| | 0.2668(3) | 0.0541(2) | -0.0249(1) | 0.0283(10) | 0.0347(11) | 0.0186(7) | -0.0031(4) | -0.0007(5) | 0.0091(7) | 2.12 |
| Cu(2) | 0.5 | 0.5 | 0.0 | 0.0114(6) | 0.0181(7) | 0.0125(6) | -0.0004(3) | 0.0016(4) | -0.0005(4) | 1.11 |
| | 0.5 | 0.5 | 0.0 | 0.0119(10) | 0.0151(11) | 0.0161(9) | -0.0018(4) | 0.0012(6) | -0.0010(8) | 1.14 |
| Cu(3) | 0.5 | 0.0 | 0.5 | 0.0125(6) | 0.0220(7) | 0.0106(6) | 0.0016(3) | 0.0007(4) | -0.0023(5) | 1.19 |
| | 0.5 | 0.0 | 0.5 | 0.0129(10) | 0.0158(11) | 0.0141(8) | 0.0005(4) | 0.0003(6) | -0.0026(8) | 1.14 |
| Cu(4) | -0.0175(2) | 0.2830(1) | 0.1646(1) | 0.0131(4) | 0.0217(5) | 0.0107(4) | 0.0006(2) | 0.0012(3) | -0.0006(3) | 1.20 |
| | -0.0176(3) | 0.2918(2) | 0.1682(1) | 0.0151(8) | 0.0188(8) | 0.0140(6) | -0.0003(3) | 0.0005(4) | -0.0019(6) | 1.27 |
| Cu(5) | -0.0341(2) | -0.0818(1) | 0.3214(1) | 0.0137(4) | 0.0172(5) | 0.0147(4) | -0.0005(2) | 0.0010(3) | 0.0015(3) | 1.20 |
| | -0.0348(3) | -0.0810(2) | 0.3200(1) | 0.0149(8) | 0.0133(8) | 0.0180(6) | -0.0015(3) | 0.0013(4) | 0.0004(5) | 1.22 |
| As(1) | 0.4838(2) | 0.0807(1) | 0.2189(1) | 0.0100(3) | 0.0156(4) | 0.0110(3) | 0.0010(1) | 0.0010(2) | 0.0004(2) | 0.96 |
| | 0.4785(2) | 0.0964(2) | 0.2314(1) | 0.0119(6) | 0.0136(6) | 0.0143(5) | 0.0000(2) | 0.0012(3) | 0.0001(4) | 1.05 |
| As(2) | -0.0317(2) | 0.2702(1) | 0.4472(1) | 0.0114(3) | 0.0142(4) | 0.0102(3) | 0.0011(1) | 0.0014(2) | 0.0001(2) | 0.94 |
| | -0.0381(2) | 0.2707(2) | 0.4485(1) | 0.0114(6) | 0.0116(6) | 0.0140(5) | -0.0002(2) | 0.0012(3) | -0.0009(4) | 0.98 |
| As(3) | 0.0263(2) | 0.6592(1) | 0.1165(1) | 0.0114(3) | 0.0140(4) | 0.0101(3) | 0.0010(1) | 0.0015(2) | 0.0002(2) | 0.93 |
| | 0.0423(2) | 0.6602(2) | 0.1108(1) | 0.0114(6) | 0.0121(6) | 0.0143(5) | -0.0004(2) | 0.0010(3) | 0.0000(4) | 1.00 |
| O(11) | 0.3334(11) | 0.0192(8) | 0.3477(5) | 0.014(3) | 0.022(3) | 0.010(2) | 0.002(1) | 0.001(2) | -0.004(2) | 1.23 |
| | 0.3260(15) | 0.0261(10) | 0.3549(6) | 0.012(4) | 0.015(4) | 0.013(3) | -0.001(2) | 0.001(2) | 0.004(3) | 1.03 |
| O(12) | 0.6239(11) | 0.2692(7) | 0.2243(5) | 0.011(3) | 0.018(3) | 0.020(3) | 0.002(1) | 0.002(2) | 0.001(2) | 1.28 |
| | 0.6317(14) | 0.2804(10) | 0.2375(7) | 0.004(4) | 0.013(4) | 0.030(4) | -0.001(2) | 0.003(3) | -0.001(3) | 1.24 |
| O(13) | 0.2312(11) | 0.0936(8) | 0.1242(5) | 0.015(3) | 0.021(3) | 0.017(3) | 0.000(1) | -0.002(2) | 0.003(2) | 1.37 |
| | 0.2350(15) | 0.1060(10) | 0.1354(6) | 0.015(4) | 0.016(5) | 0.017(4) | -0.001(2) | -0.004(3) | 0.005(3) | 1.23 |
| O(14) | 0.7126(12) | -0.0456(8) | 0.1820(5) | 0.017(3) | 0.022(3) | 0.014(3) | 0.001(1) | 0.001(2) | 0.004(2) | 1.38 |
| | 0.6962(15) | -0.0356(10) | 0.1900(6) | 0.012(4) | 0.018(5) | 0.019(4) | -0.003(2) | -0.002(3) | 0.005(3) | 1.28 |
| O(21) | 0.1923(11) | 0.2462(8) | 0.5539(5) | 0.017(3) | 0.018(3) | 0.015(3) | 0.002(1) | -0.002(2) | -0.005(2) | 1.34 |
| | 0.1766(16) | 0.2477(10) | 0.5569(6) | 0.022(5) | 0.012(4) | 0.015(4) | 0.000(2) | -0.004(3) | -0.003(3) | 1.29 |
| O(22) | -0.1803(11) | 0.0839(7) | 0.4193(5) | 0.013(3) | 0.014(3) | 0.015(3) | 0.000(1) | 0.003(2) | -0.001(2) | 1.13 |
| | -0.1843(15) | 0.0841(9) | 0.4185(6) | 0.013(4) | 0.006(4) | 0.018(4) | 0.000(2) | 0.005(3) | -0.002(3) | 0.97 |
| O(23) | 0.1090(11) | 0.3415(7) | 0.3216(4) | 0.017(3) | 0.017(3) | 0.008(2) | 0.002(1) | 0.002(2) | -0.006(2) | 1.12 |
| | 0.1157(15) | 0.3410(10) | 0.3259(6) | 0.016(4) | 0.019(5) | 0.012(3) | 0.001(2) | 0.002(3) | 0.000(3) | 1.25 |
| O(24) | -0.2637(11) | 0.3929(8) | 0.4876(5) | 0.016(3) | 0.020(3) | 0.012(2) | 0.000(1) | 0.002(2) | 0.005(2) | 1.26 |
| | -0.2718(16) | 0.3898(10) | 0.4863(6) | 0.020(5) | 0.010(4) | 0.019(4) | -0.003(2) | 0.005(3) | 0.010(3) | 1.25 |
| O(31) | 0.1238(11) | 0.7432(7) | 0.2436(5) | 0.015(3) | 0.015(3) | 0.014(2) | -0.001(1) | -0.001(2) | 0.005(2) | 1.13 |
| | 0.1331(15) | 0.7586(11) | 0.2341(6) | 0.014(5) | 0.023(5) | 0.017(4) | -0.004(2) | -0.003(3) | 0.003(3) | 1.43 |
| O(32) | 0.1153(11) | 0.7788(7) | 0.0001(5) | 0.012(3) | 0.014(3) | 0.015(2) | 0.003(1) | 0.003(2) | 0.001(2) | 1.08 |
| | 0.1384(16) | 0.7604(10) | -0.0109(6) | 0.018(5) | 0.014(4) | 0.015(4) | 0.000(2) | 0.000(3) | 0.002(3) | 1.25 |
| O(33) | 0.1958(11) | 0.4902(7) | 0.1033(5) | 0.017(3) | 0.013(3) | 0.013(2) | 0.002(1) | 0.004(2) | 0.002(2) | 1.11 |
| | 0.2168(15) | 0.4932(10) | 0.1134(6) | 0.014(4) | 0.008(4) | 0.016(4) | 0.000(2) | 0.003(3) | -0.003(3) | 1.03 |
| O(34) | -0.2929(11) | 0.6011(8) | 0.1215(5) | 0.011(2) | 0.022(3) | 0.018(3) | 0.000(1) | 0.004(2) | -0.002(2) | 1.31 |
| | -0.2727(15) | 0.6039(11) | 0.1182(6) | 0.010(4) | 0.024(5) | 0.024(4) | -0.004(2) | 0.001(3) | -0.004(3) | 1.53 |

Note. Anisotropic displacement parameters: $\exp[-2 \pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* h_i h_j]$, B_{eq} after (12).

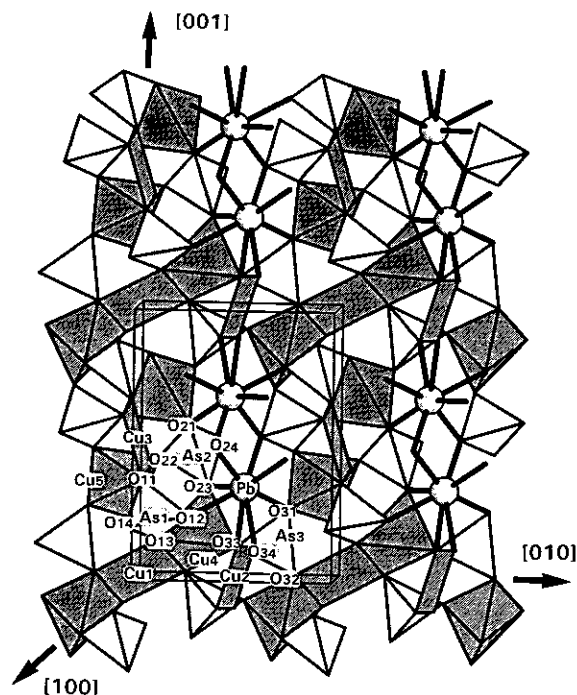


FIG. 1. Projection of the crystal structure of $\text{Pb}_2\text{Cu}(\text{II})_7(\text{AsO}_4)_6$ (II) slightly inclining to $[100]$, using the program ATOMS (13).

tion polyhedra were found: the square Cu^{4}O_4 and the trigonal dipyramid Cu^{5}O_5 . The former is one of the three common coordination figures known for Cu(II) atoms which include the elongated tetragonal dipyramid ("distorted octahedron," $[4 + 2]$ -coordination) and the tetragonal pyramid ($[4 + 1]$ -coordination) as well as the transitions between them. The $[4]$ -coordinated Cu(II) atoms Cu(1), Cu(2), and Cu(3) have site symmetry $\bar{1}$. The Cu–O bonds vary from 1.90 to 1.98 Å, with average values from 1.93 to 1.97 Å. Each of these Cu atoms has two further neighbors; the Cu–O distances to these additional ligands are over 2.56 Å, and therefore at best weak chemical interactions are expected.

The coordination figures around the Cu(4) and Cu(5) atoms are rather uncommon in two respects. On one hand the trigonal dipyramid is a rarely found coordination figure for divalent copper atoms (1, 2). On the other hand these coordination figures of the title compounds are conspicuously regular regarding Cu–O bond lengths as well as O–Cu–O bond angles. The Cu–O bond lengths vary only 11.5%, from 1.92 to 2.14 Å. As a rule for such coordination figures the axial Cu–O bond lengths are the shortest or at least among the shortest within the relevant coordination polyhedron. The $\text{O}_a\text{--Cu--O}_a$ bond angle (O_a is the apical ligand) is slightly bent. The $\text{O}_e\text{--Cu--O}_e$ bond angles (O_e is a ligand within the equatorial plane) deviate only up to 20° from the ideal value of 120°; it should be mentioned

that the largest one is only 131°. This is remarkable because the CuO_5 coordination polyhedra described as "trigonal dipyramids" often are representatives of the continuous transition between the trigonal dipyramid toward the tetragonal pyramid; examples with the $\text{O}_e\text{--Cu--O}_e$ angle opposite to the largest Cu–O bond of the relevant polyhedron arising from 120° toward 180° (8) are known. Although during the past years a limited number of trigonal dipyramidal CuO_5 polyhedra have been described in inorganic crystal structures, coordination figures like those in the title compounds are rare. Examples are $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ (fingerite) (3), $\text{KCu}_4(\text{PO}_4)_3$ (4), $\text{Cu}_2(\text{OH})(\text{PO}_4)$ (libethenite) (5), and $\text{Cu}_2\text{O}(\text{SeO}_3)$ (6).

Due to edge connections of the $\text{Cu}(1)\text{O}_4$ square and the $\text{Cu}(4)\text{O}_5$ polyhedron in II the $\text{O}(13)\text{--O}(32)$ edge is shortened to 2.54 Å, which is the shortest O–O edge of the copper coordination polyhedra within the two title compounds. The Cu(1)–Cu(4) edge is 3.011(1) Å. In I-II the copper coordination polyhedra do not share common edges.

Coordination of the Cu(I) atom. The principal difference between the two compounds II and I-II concerns the Cu(1) atom: Whereas in II the divalent $\text{Cu}(1)^{4}$ atom occupies the special position (000) with site symmetry $\bar{1}$, in I-II it splits into a general position with doubled multiplicity. As a consequence, the coordination number

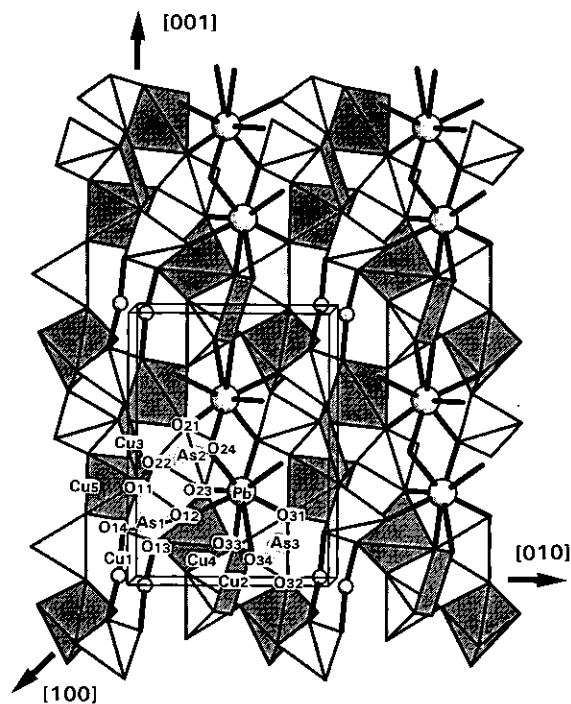


FIG. 2. Projection of the crystal structures of $\text{Pb}_2\text{Cu}(\text{I})_2\text{Cu}(\text{II})_6(\text{AsO}_4)_6$ (I-II) slightly inclining to $[100]$, using the program ATOMS (13).

TABLE 3
Interatomic Distances (Å), Bond Angles (°), and Bond Strengths ν (νu)

| | $\text{Pb}_2\text{Cu}(\text{II})_7(\text{AsO}_4)_6$ (II) | | $\text{PbCu}(\text{I})\text{Cu}(\text{II})_3(\text{AsO}_4)_6$ (I-II) | | | | | |
|---|--|------|--|------|------|-------|------|------|
| Pb-O(12), ν | 2.670(6) | 0.22 | 2.573(8) | 0.29 | | | | |
| Pb-O(21), ν | 2.674(6) | 0.22 | 2.696(8) | 0.21 | | | | |
| Pb-O(23), ν | 2.531(6) | 0.32 | 2.526(8) | 0.33 | | | | |
| Pb-O(24), ν | 2.456(5) | 0.39 | 2.477(7) | 0.37 | | | | |
| Pb-O(24), ν | 2.505(6) | 0.35 | 2.541(8) | 0.31 | | | | |
| Pb-O(31), ν | 2.811(6) | 0.15 | 2.924(8) | 0.11 | | | | |
| Pb-O(33), ν | 3.016(5) | 0.09 | 2.893(7) | 0.12 | | | | |
| Pb-O(34), ν | 2.657(6) | 0.23 | 2.737(7) | 0.18 | | | | |
| $\langle \text{Pb}-\text{O} \rangle$, $\Sigma \nu$ | 2.665 | 1.97 | 2.671 | 1.92 | | | | |
| Cu(I)-O(13), ν | 1.971(6) 2 × | 0.45 | 1.888(7) | 0.45 | | | | |
| Cu(I)-O(32), ν | 1.971(6) 2 × | 0.45 | 2.517(9) | 0.08 | | | | |
| Cu(I)-O(14), ν | 2.561(6) 2 × | 0.09 | 1.899(7) | 0.43 | | | | |
| $\langle \text{Cu}^{\text{I}}-\text{O} \rangle$, $\Sigma \nu$ | 1.971 | 1.98 | 1.894 | 0.96 | | | | |
| O-Cu-O (cis-arranged) | 80.4(2) and 99.6(2) | | 171.4(4) (short bonds) | | | | | |
| Cu(2)-O(33), ν | 1.959(5) 2 × | 0.47 | 1.958(7) 2 × | 0.47 | | | | |
| Cu(2)-O(34), ν | 1.904(6) 2 × | 0.54 | 1.962(8) 2 × | 0.47 | | | | |
| Cu(2)-O(32), ν | 3.134(6) 2 × | 0.02 | 2.976(8) 2 × | 0.03 | | | | |
| $\langle \text{Cu}^{\text{II}}-\text{O} \rangle$, $\Sigma \nu$ | 1.932 | 2.06 | 1.960 | 1.94 | | | | |
| O-Cu-O (cis-arranged) | 89.0(2) and 91.0(2) | | 89.6(3) and 90.4(3) | | | | | |
| Cu(3)-O(11), ν | 1.929(5) 2 × | 0.51 | 1.908(7) 2 × | 0.54 | | | | |
| Cu(3)-O(22), ν | 1.987(5) 2 × | 0.43 | 1.980(7) 2 × | 0.44 | | | | |
| Cu(3)-O(21), ν | 2.730(6) 2 × | 0.06 | 2.830(8) 2 × | 0.06 | | | | |
| $\langle \text{Cu}^{\text{II}}-\text{O} \rangle$, $\Sigma \nu$ | 1.958 | 2.00 | 1.944 | 1.96 | | | | |
| O-Cu-O (cis-arranged) | 85.5(2) and 94.5(2) | | 86.7(3) and 93.3(3) | | | | | |
| Cu(4)-O(12) _e , ν | 1.969(5) | 0.46 | 1.986(7) | 0.44 | | | | |
| Cu(4)-O(13) _e , ν | 2.136(6) | 0.29 | 2.134(8) | 0.29 | | | | |
| Cu(4)-O(23) _a , ν | 1.939(5) | 0.50 | 1.962(7) | 0.47 | | | | |
| Cu(4)-O(32) _a , ν | 1.985(5) | 0.44 | 1.943(7) | 0.49 | | | | |
| Cu(4)-O(33) _e , ν | 2.126(6) | 0.30 | 2.117(8) | 0.31 | | | | |
| $\langle \text{Cu}^{\text{II}}-\text{O} \rangle$, $\Sigma \nu$ | 2.031 | 1.99 | 2.028 | 2.00 | | | | |
| O _e -Cu-O _e | 103.2(2), 127.5(2), 128.9(3) | | 100.4(3), 129.7(3), 129.8(3) | | | | | |
| O _e -Cu-O _a | 76.1(2) to 100.2(2) | | 83.2(3) to 94.9(3) | | | | | |
| O _a -Cu-O _a | 175.1(2) | | 178.0(3) | | | | | |
| Cu(5)-O(11) _e , ν | 2.055(6) | 0.36 | 2.071(8) | 0.35 | | | | |
| Cu(5)-O(14) _e , ν | 2.072(6) | 0.34 | 2.095(7) | 0.32 | | | | |
| Cu(5)-O(21) _e , ν | 2.111(6) | 0.31 | 2.086(8) | 0.33 | | | | |
| Cu(5)-O(22) _a , ν | 1.954(6) | 0.48 | 1.977(7) | 0.45 | | | | |
| Cu(5)-O(31) _a , ν | 1.922(6) | 0.52 | 1.916(8) | 0.54 | | | | |
| $\langle \text{Cu}^{\text{II}}-\text{O} \rangle$, $\Sigma \nu$ | 2.023 | 2.01 | 2.029 | 1.99 | | | | |
| O _e -Cu-O _e | 112.2(2), 119.6(2), 128.2(2) | | 112.8(3), 115.8(3), 131.1(3) | | | | | |
| O _e -Cu-O _a | 86.1(2) to 93.4(2) | | 87.1(3) to 96.1(3) | | | | | |
| O _a -Cu-O _a | 172.7(2) | | 175.2(3) | | | | | |
| As(1)-O(11), ν | 1.721(5) | 1.13 | 1.704(7) | 1.19 | | | | |
| As(1)-O(12), ν | 1.702(6) | 1.19 | 1.694(8) | 1.22 | | | | |
| As(1)-O(13), ν | 1.688(6) | 1.24 | 1.683(7) | 1.25 | | | | |
| As(1)-O(14), ν | 1.675(6) | 1.28 | 1.700(8) | 1.20 | | | | |
| $\langle \text{As}-\text{O} \rangle$, $\Sigma \nu$ | 1.697 | 4.84 | 1.695 | 4.86 | | | | |
| O-As-O | 102.5(3) to 116.8(3) | | 102.7(4) to 117.8(4) | | | | | |
| As(2)-O(21), ν | 1.684(6) | 1.25 | 1.688(7) | 1.24 | | | | |
| As(2)-O(22), ν | 1.729(6) | 1.11 | 1.731(8) | 1.10 | | | | |
| As(2)-O(23), ν | 1.694(5) | 1.22 | 1.699(7) | 1.20 | | | | |
| As(2)-O(24), ν | 1.679(6) | 1.27 | 1.678(8) | 1.27 | | | | |
| $\langle \text{As}-\text{O} \rangle$, $\Sigma \nu$ | 1.697 | 4.85 | 1.699 | 4.81 | | | | |
| O-As-O | 107.1(3) to 113.0(3) | | 107.1(4) to 113.1(4) | | | | | |
| As(3)-O(31), ν | 1.661(5) | 1.33 | 1.683(8) | 1.25 | | | | |
| As(3)-O(32), ν | 1.706(6) | 1.18 | 1.684(7) | 1.25 | | | | |
| As(3)-O(33), ν | 1.704(6) | 1.19 | 1.717(8) | 1.14 | | | | |
| As(3)-O(34), ν | 1.694(5) | 1.22 | 1.681(8) | 1.26 | | | | |
| $\langle \text{As}-\text{O} \rangle$, $\Sigma \nu$ | 1.691 | 4.92 | 1.691 | 4.90 | | | | |
| O-As-O | 105.6(3) to 115.4(3) | | 103.7(4) to 115.8(4) | | | | | |
| Sums of the bond valences at the O atoms in II and I-II | | | | | | | | |
| O(11) | 2.00 | 2.08 | O(21) | 1.84 | 1.84 | O(31) | 2.00 | 1.90 |
| O(12) | 1.87 | 1.95 | O(22) | 2.02 | 1.99 | O(32) | 2.09 | 1.85 |
| O(13) | 1.98 | 1.99 | O(23) | 2.04 | 2.00 | O(33) | 2.05 | 2.04 |
| O(14) | 1.71 | 1.95 | O(24) | 2.01 | 1.95 | O(34) | 1.99 | 1.91 |

Note. Subscripts *e* and *a* indicate equatorial and apical oxygen atoms within the trigonal bipyramidal CuO_5 coordination figure. Bond valences (including the contribution of the additional ligands at the Cu atoms) are given according to (14).

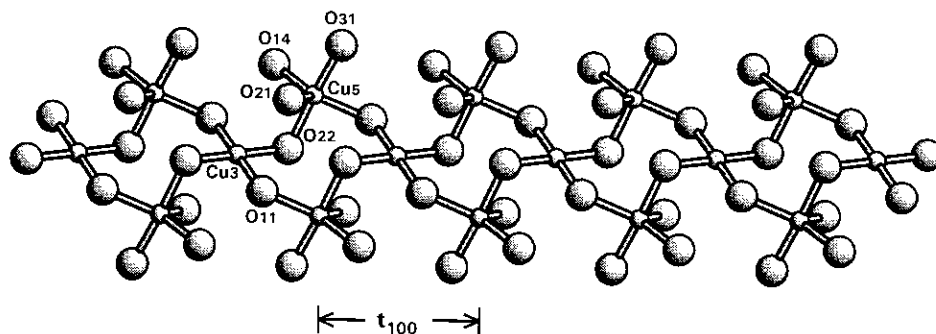


FIG. 3. The $\text{Cu}^{4+}\text{Cu}_2^{5+}\text{O}_{10}$ chain occurring in **II** and **I-II**, using the program ATOMS (13).

is changed to [2], as is characteristic for monovalent copper atoms (24, 25). This approximately linear [2]-coordination is formed between one O atom of the former $\text{Cu}(\text{I})\text{O}_4$ square and the additional ligand of the Cu(I) atom in **II**; i.e., two edges in the $\text{Cu}(\text{I})^{4+2+}\text{O}_6$ polyhedron (but not in the $\text{Cu}(\text{I})^{4+}\text{O}_4$ square) in **II** represent a $\text{O}-\text{Cu}(\text{I})^{2+}-\text{O}$ configuration in **I-II**. Weak chemical interactions between the Cu(I) atom and a third ligand at 2.517 Å are assumed; this O atom is a ligand of the $\text{Cu}(\text{I})\text{O}_4$ square in **II**. The Cu(1)–Cu(1) distance in **I-II** is 2.709(2) Å. These changes give rise to a reorganization of the coordination of the oxygen atoms O(13), O(14), and O(32).

Arsenate tetrahedra and oxygen atoms. The AsO_4 tetrahedra are regular, and average (As–O) bond lengths are in accordance with common crystal chemical experience. Neglecting the additional Cu–O bonds, the greater part of the oxygen atoms in both title compounds show approximate planar [3]-coordination. The O(33) atom is [4]-coordinated, and the atoms O(14) in **II** and O(32) in **I-II** are [2]-coordinated. Stronger distortions were observed for the atoms representing the additional ligands at the Cu^{4+} atoms and for the O atoms involved in the coordination around the Cu(I) atoms. The unbalanced bond valences

predominantly observed for the latter ones enable the formation of both of these structure types.

Connection. In **II** the CuO_4 squares and CuO_5 coordination polyhedra are linked to two different chains: the $\text{Cu}(\text{I})\text{O}_4$ square shares its corners with four different $\text{Cu}(\text{II})\text{O}_5$ polyhedra forming Cu_3O_{10} chains parallel to [100] (Fig. 3). Cu_4O_{12} chains which parallel [110] arise by the connection of the $\text{Cu}(\text{I})\text{O}_4$ and $\text{Cu}(\text{II})\text{O}_4$ squares and the $\text{Cu}(\text{II})\text{O}_5$ polyhedra (Fig. 4): the $\text{Cu}(\text{I})\text{O}_4$ square shares two O(13)–O(32) edges with two $\text{Cu}(\text{II})\text{O}_4$ squares; further connection is verified by O(33) corners to the $\text{Cu}(\text{II})\text{O}_4$ squares. Whereas the former chain is maintained in **I-II**, the latter is interrupted by the substitution of the $\text{Cu}(\text{I})\text{O}_4$ square by the two linear [2]-coordinated monovalent copper atoms. From this bonding result $\text{Cu}(\text{II})_3\text{O}_{12}$ groups with branched Cu(I) atoms. O–Cu(I)–O bonds connect the Cu_3O_{12} groups and the Cu_4O_{12} chains to the corrugated layers parallel (01 $\bar{1}$).

In both compounds the structural units formed by the connection of the copper atoms are three-dimensionally interconnected by the arsenate tetrahedra. The Pb atoms are located in channels formed by this network parallel to [100].

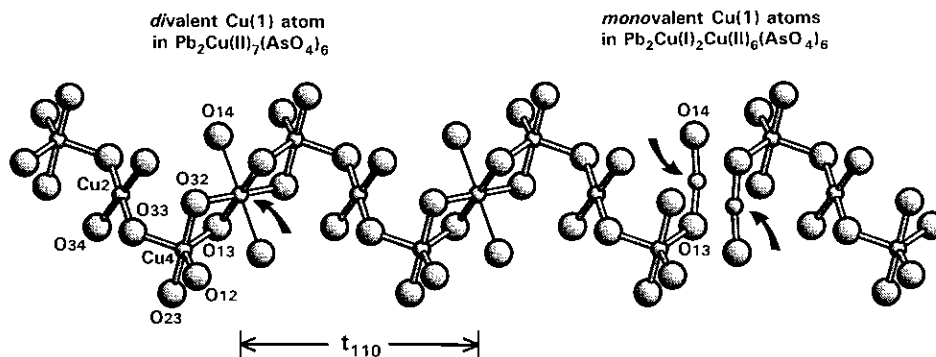


FIG. 4. The $\text{Cu}^{4+}\text{Cu}_2^{5+}\text{O}_{12}$ chain in **II**. The Cu(1)–O(14) distances to the additional ligands are indicated by thin lines. On the right is shown the substitution of the divalent Cu^{4+2+} atom by two monovalent Cu^{2+} atoms as was found in **I-II**, using the program ATOMS (13).

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