$Sr_3Cu_3(PO_4)_4$, $Pb_3Cu_3(PO_4)_4$, $BaCu_2(PO_4)_2 \cdot H_2O$, and $Ba_2Cu(PO_4)_2 \cdot H_2O$: Crystal Structures and Topological Relationships

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The four Cu(II)-phosphates(V) $Sr_3Cu_3(PO_4)_4$, $Pb_3Cu_3(PO_4)_4$, $BaCu_2(PO_4)_2 \cdot H_2O$, and $Ba_2Cu(PO_4)_2 \cdot H_2O$ were synthesized under hydrothermal conditions. Their structures were determined from single-crystal X-ray diffraction data. They are related to a group of compounds formed by Cu(II)–PO_4/AsO_4 layers linked by *Me* atoms with large ionic radii like alkali, alkaline earth, Pb(II), or Ag(I), and partly by hydrogen bonds. The layers are formed by Cu_3O_{12} units: one square-planar coordinated Cu atom with $\bar{1}$ symmetry is corner connected to two Cu atoms in a [4 + 1] or [5] coordination. Distinct patterns and links of the Cu_3O_{12} groups by PO_4 tetrahedra were observed, *AA* and *AB* stacking variants of the layers occur. $Ba_2Cu(PO_4)_2 \cdot H_2O$ features isolated CuO_4 squares interconnected by PO_4 tetrahedra to chains which represent a component of the layers found in the other compounds. © 1999 Academic Press

INTRODUCTION

For the three compounds $Na_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ (abbrevation throughout the paper is NAP), its isotypic arsenate analogue $Na_5Cu_3(AsO_4)_2[(AsO_4)H(AsO_4)]$ (NAS), and $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ (AGP) (1–3) an unusual distribution of some of the Cu–O bond lengths and O–Cu–O bond angles were found. Noticable are the hydrogen bonds restricted by symmetry ($\bar{1}$ or 2): $O \cdots H \cdots O$ (2.388 to 2.428 Å) is a common edge between two coordination figures around the *Me*(I) atoms Na or Ag. $K_4Cu_3(AsO_4)_2[AsO_3(OH)]_2$ (KAS) and $Ca_3Cu_3(PO_4)_4$ (CAP) (4, 5) form structurally related Cu-phosphate layers; in addition, a short asymmetric hydrogen bond with $O–H \cdots O = 2.479$ Å was observed in KAS. For details on these hydrogen bonds see (1–4). In connection with investigations of the stereochemistry of divalent copper atoms systematic syntheses in related chemical systems were performed. As a result, the four compounds $Sr_3Cu_3(PO_4)_4$ (SRP), $Pb_3Cu_3(PO_4)_4$ (PBP), $BaCu_2(PO_4)_2 \cdot H_2O$ (BAP), and $Ba_2Cu(PO_4)_2 \cdot H_2O$ (BA1) were obtained. They were structurally characterized for a topological comparison. Structural data on NAP, NAS, AGP, KAS, and CAP used

in this paper refer to (1–5). Boukhari *et al.* (6) and Drillon *et al.* (7) report on cell metrics and magnetic measurements within the "solid solution" $(Ca,Sr)_3Cu_3(PO_4)_4$, based on the structural data given by (5) for $Ca_3Cu_3(PO_4)_4$ (CAP). However, a transformation of the unit cell of the Sr-end member according to ($\bar{1}$ 0 0/0 1 0/1 0 2) gives cell parameters close to that of SRP. It should be mentioned that CAP and SRP are topologically similar, but not isotypic. Isotypy between CAP and a Sr-analogue is not likely due to an exclusive [6] coordination of the Ca(1)-polyhedron.

SYNTHESIS AND X-RAY STRUCTURE INVESTIGATION

Crystals of SRP, PBP, BAP, and BA1 were synthesized under hydrothermal conditions. First, an aqueous Cu-nitrate solution was precipitated with a solution of $(NH_4)_2HPO_4$. The reaction product consists predominantly of $Cu_3(PO_4)_2 \cdot 3H_2O$ and $Cu_2(OH)(PO_4)$ as identified by X-ray powder patterns. The compounds were formed in steel vessels lined with teflon from mixtures of $Sr(OH)_2$, $PbCO_3$, and $Ba(OH)_2$ with the Cu-phosphate precipitate. The vessels were heated to 503 K for 96 h and subsequently cooled to room temperature (cooling rate $1° h^{-1}$).

Crystal data of SRP, PBP, BAP, and BA1 and of the structurally related compounds NAP, NAS, AGP, CAP, and KAS are compiled in Table 1. Some nonstandard space-group settings were chosen to facilitate the topological comparison. For the same reason unit cells used in the previous papers were transformed (*a* and *b* are within the Cu–PO_4 layers, *c* is inclined). Checks by X-ray film methods served for selection of the samples. Details on X-ray data collection and results of structure refinements are given in Table 2. Direct methods (8) and succeeding Fourier and difference Fourier calculations were applied to determine the crystal structures. Refinements were done on F^2 (9). Neutral-atomic complex scattering functions (10) were used. The highest peaks in the final difference-Fourier maps are in the surrounding of the atoms Pb, Ba, and Sr. Structural parameters and interatomic bond distances are given in Tables 3 and 4.

TABLE 1
Cell Parameters of Compounds with $Cu_3(PO_4)_4$ Layers and Related Structures[a]

Compound abbrevation	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	V(Å³) $= n \times V'$ (Å³) Z space group	Reference	Stacking variants	Cu_3O_{12} units
$Na_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$	18.010(6)	5.106(2)	9.052(3)	666.3 = 2 × 333.1	(1)[b]	AA	parallel
NAP	90.09(3)	126.79(3)	91.40(3)	2 $C\bar{1}$			
$Na_5Cu_3(AsO_4)_2[(AsO_4)H(AsO_4)]$	18.388(4)	5.275(1)	9.297(2)	721.7 = 2 × 360.8	(2)[b]	AA	parallel
NAS	89.96(1)	126.75(1)	92.33(1)	2 $C\bar{1}$			
$Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$	17.725(6)	5.162(2)	16.597(6)	1381.5 = 4 × 345.4	(3)[c]	AB	parallel
AGP	90	114.53(2)	90	4 $C2/c$			
$Ca_3Cu_3(PO_4)_4$	17.619(2)	4.8995(4)	8.917(1)	637.6 = 2 × 318.8	(5)	AA	herring-bone pattern
CAP	90	124.08(1)	90	2 $P2_1/a$			
$Sr_3Cu_3(PO_4)_4$	18.035(4)	4.921(2)	17.337(4)	1368.5 = 4 × 342.1	[e]	AB	parallel
SRP	90	117.20(1)	90	4 $C2/c$			
$Pb_3Cu_3(PO_4)_4$	17.895(6)	4.929(2)	17.756(6)	1405.9 = 4 × 351.5	[e]	AA	herring-bone pattern
PBP	90	116.15(2)	90	4 $A2/a$			
$BaCu_2(PO_4)_2 \cdot H_2O$	9.730(2)	5.161(1)	14.565(3)	731.4 = 2 × 365.7	[e]	AB	$Cu_4O_{12}(Ow)_2$ chains
BAP	90	90	90	4 $P2_12_12_1$			
$K_4Cu_3(AsO_4)_2[AsO_3(OH)]_2$	9.992(3)	9.630(3)	9.498(3)	804.9	(4)[d]	AA	parquet
KAS	118.27(2)	90	90	2 $P2_1/b11$			
$Ba_2Cu(PO_4)_2 \cdot H_2O$	12.237(5)	5.125(2)	13.842(5)	833.8	[e]	[f]	isolated CuO_4 squares
BA1	90	106.16(2)	90	2 $I2/a$			

[a] Nonstandard cell settings were chosen for topological comparison.
The unit cells were transformed according to [b] $(\bar{1}2\bar{2}/100/001)$, [c] $(100/0\bar{1}0/\bar{1}0\bar{1})$, and [d] $(010/001/100)$.
[e] This work (cell parameters by least-square refinements of accurate 2ϑ values).
[f] Contains $Cu(PO_4)_2$ chains.

Difficulties arose during the refinement of BA1 in space group $I2/a$. Two of the oxygen sites—O(4) and Ow—showed large anisotropic displacement parameters. No superstructure reflections violating the extinction rules hkl: $h + k + l = 2n$ and $h0l$: $h = 2n$ or indications for a larger cell were observed. Different models were applied based on the assumption of the space groups $I2/a$, Ia, and non-space-group demanded extinctions. In all cases the high anisotropy of the displacement parameters were maintained and the R values were not improved significantly. Retaining the symmetry $I2/a$ and an average position for O(4) and Ow gives final r.m.s. amplitudes for the atoms O(4) and Ow of 0.065, 0.023, 0.013 (elongation parallel to [010]) and 0.221, 0.042, 0.037 Å² (elongation parallel to [001]), respectively. Models with split positions and isotropic displacement parameters for Ow and O(4) did not improve the R values but indicate a plausible hydrogen-bonding scheme (for discussion see the next section).

RESULTS OF STRUCTURE REFINEMENTS

Parts of the coordination figures around the cations Me = Na, K, Ag, Ca, Sr, Pb, and Ba in the four investigated compounds and within the structurally related compounds NAP, NAS, AGS, KAS, and CAP are irregular. As often observed for these elements some coordinations are not clearcut. A trend toward smaller coordination numbers for the Me(1) atoms and larger ones for Me(2) is maintained. A gap can be seen in the distribution of the Me(1)–O bond lengths often between the sixth and the seventh ligand. Me(1)O$_6$ might be described as related to an octahedron, it is flattened in NAP and CAP, but one-sided distorted in AGP, SRP, and PBP. In SRP the Sr(1) atom is [6] coordinated with an average $\langle$Sr(1)–O$\rangle$ bond distance of 2.500 Å, interactions to three further ligands are evident. The K(1)O$_7$ polyhedron in KAS is formed by 3 and 4 ligands in two coplanar planes.

The Sr(2) atom in SRP has nine ligands in an approximate tricapped trigonal antiprism with uniformly distributed Sr(2)–O distances in the range of 2.488 to 2.985 Å. Caused by the steric active lone-pair electrons, the coordination of the Pb(2) atom in PBP features gaps in the distribution of the Pb–O bonds; the coordination figure formed by the eight nearest neighbors might be described as a monocapped cube with an unoccupied corner. Ca(2)O$_9$ in CAP is related to a tricapped trigonal prism. K(2)O$_8$ in KAS is a bicaped trigonal prism. Na(2)O$_7$ in NAP and NAS are regular pentagonal bipyramids. In AGP the coordination around Ag(2) is irregular.

In NAP, NAS, and AGP an additional Me(3) site occurs, which is vacant in the SRP, PBP, and CAP (Fig. 1): the Na(3) and Ag(3) atoms feature coordination numbers intermediate between those of Me(1) and Me(2). The six nearest ligands form approximate octahedra.

TABLE 2
Single-Crystal X-ray Data Collection and Structure Refinements[a]

Compound abbreviation	$Sr_3Cu_3(PO_4)_4$ SRP	$Pb_3Cu_3(PO_4)_4$ PBP	$BaCu_2(PO_4)_2 \cdot H_2O$ BAP	$Ba_2Cu(PO_4)_2 \cdot H_2O$ BA1
ρ_{calc} [g cm^{-3}]	4.05	5.63	4.29	4.35
Crystal dimensions [mm^3]	$0.04 \times 0.05 \times 0.17$	$0.04 \times 0.06 \times 0.21$	$0.08 \times 0.17 \times 0.18$	$0.05 \times 0.12 \times 0.16$
Color	pale blue	dark green	turquoise	light blue
Scan speed ($2\vartheta/\omega$ scan mode)	0.8 to 1.8°/min	0.9 to 1.8°/min	0.9 to 3.6°/min	0.9 to 1.8°/min
Scan width (+ α_1–α_2 dispersion)	1.11°	1.11°	1.20°	1.35°
Range of data collection [°]	$4 < 2\delta < 70$	$4 < 2\delta < 70$	$4 < 2\delta < 70$	$4 < 2\delta < 70$
$\mu(MoK\alpha)$ [mm^{-1}]	16.8	40.8	11.6	12.3
Absorption correction	ψ-scans	ψ-scans	ψ-scans	ψ-scans
Transmission factors	0.055 to 0.107	0.020 to 0.103	0.048 to 0.113	0.041 to 0.105
Total measured reflection	11,988	7,861	6,783	7,119
Unique reflections	2,999	3,097	3,238	1,837
Observed reflections	1,979	2,058	2,803	1,511
w$R2$ (observed reflections)	0.086	0.097	0.043	0.045
$R1$ (observed reflections)	0.040	0.040	0.020	0.021
s (goodness-of-fit)	0.94	0.93	1.03	1.09
P and Q (weighting scheme)	0.058 and 5.46	0.047 and 0.00	0.018 and 0.00	0.021 and 1.76
Variable parameters	120	121	137	66
Extinction coefficient	not refined	0.00049	0.00215	not refined
Max Δ/σ	≤ 0.001	≤ 0.001	≤ 0.001	≤ 0.001
Difference Fourier map [e Å^{-3}]	− 1.24 to + 1.78	− 5.38 to + 3.86	− 0.75 to + 0.81	− 1.05 to + 1.06

Note. $R1 = \sum ||F_0| - |F_c||/\sum |F_0|$;   w$R2 = \{\sum [w(F_0^2 - F_c^2)^2]/\sum [w(F_c^2)^2]\}^{1/2}$; $w = 1/\{\sigma^2(F_0^2) + [P*([\max(F_0^2, 0)] + 2*F_c^2)/3]^2 + Q*([\max(F_0^2, 0)] + 2*F_c^2)/3\}$; $s = \{\sum [w(F_0^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n, number of reflections; p, number of refined parameters).

[a] A STOE AED 2 four-circle diffractometer was used for data collection (Mo tube, graphite monochromator), corrections for Lorentz and polarization effects were applied.

Obviously, the $Me(1)O_6$ coordination figure is too small for Ba and K atoms; BAP and BA1 form modified structure types, both have one [11] and [10] coordinated Ba site, respectively. The coordination figures are a tricapped cube and a bicapped tetragonal antiprism. The average ⟨Ba–O⟩ distances are 2.943 and 2.874 Å. The longest of the Ba–O bond distances in BA1 is to the Ow atom.

The Cu(1) atoms in SRP and PBP and the Cu atom in BA1 are square planar coordinated by four O atoms with average ⟨Cu–O⟩ bond distances between 1.944 and 1.950 Å; additional ligands are not within bonding distance. The Cu(2) atoms in SRP and PBP feature a [5] coordination: in SRP the coordination figure is a tetragonal pyramid with the four nearest neighbors in an approximate square (diagonal O–Cu(2)–O angles > 160°). In PBP, Cu$^{[5]}$O$_5$ forms the rare and here relatively regular trigonal bipyramid: the two shortest of the Cu–O bonds represent the axis, equatorial O–Cu(2)–O angles are 104.9(2), 122.1(9), and 133.0(2)°. In BAP the two crystallographically different Cu atoms feature a [4 + 1] coordination: the CuO$_4$ squares have average ⟨Cu–O⟩ bond distances of 1.959 and 1.966 Å, an additional water–oxygen atom Ow completes the coordination to the usual tetragonal pyramid.

The phosphate tetrahedra are fairly regular. The average ⟨P–O⟩ bond distances vary from 1.539 to 1.547 Å. The

distortions are moderate, O–P–O bond angles scatter from 103.9(3)° to 119.3(2)° and O–O edges are 2.446(8) to 2.666(5) Å. Extreme values were observed in BA1 for the split phosphate group.

In BAP, the H atoms were found in a difference Fourier summation at crystal-chemically probable positions and their atomic coordinates were refined successfully: Ow–H(1)/H(2) = 0.77(5)/0.75(5),   Ow···O(12)/O(23) = 2.740(3)/2.839(3) Å, H(1)–Ow–H(2) = 110(4)°, and O(12)···Ow···O(23) = 99.7(1)°.

The Ow atom in BA1 is weakly bound to barium. The hydrogen bonding scheme is not quite clear due to the impossibility of locating the atoms Ow and O(4) with certainty. Similar effects have been widely described for water molecules, e.g., in zeolites. Refinements in space group $I2/a$ with average positions of O(4) and Ow gave very long hydrogen bonds to two O(4) atoms, Ow···O(4) = 2.948(6) Å 2 ×, O(4)···Ow···O(4) is only 61.0(1)°. In addition, four distances of similar lengths occur, which are edges within the coordination polyhedron around Ba: Ow···O(3) = 2.902(2), 2 ×, and Ow···O(4) = 2.987(6) Å, 2 ×. It is assumed that the local site disorder enables the formation of suitable hydrogen bonds. Refinements with split positions –O(4a), O(4b), Ow(a), Ow(b)–allow multiple hydrogen bond lengths due to the splitting of both atoms O(4) and Ow.

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Parameters in Å² (11) (ESDs Shown in Parentheses)

Atom	x	y	z	U_{equiv}
		Sr$_3$Cu$_3$(PO$_4$)$_4$ (abbrevation SRP)		
Sr(1)	0.0	0.27466(16)	0.25	0.01716(14)
Sr(2)	0.34689(3)	0.19923(10)	0.86078(3)	0.01372(10)
Cu(1)	0.25	0.25	0.0	0.01174(16)
Cu(2)	0.39948(4)	0.23306(13)	0.52924(4)	0.01282(12)
P(1)	0.21933(7)	0.2552(2)	0.38092(8)	0.0097(2)
P(2)	0.51691(8)	0.2981(3)	0.10217(8)	0.0124(2)
O(11)	0.2848(2)	0.0675(7)	0.4543(2)	0.0126(6)
O(12)	0.1346(2)	0.2129(9)	0.3792(2)	0.0180(7)
O(13)	0.2493(3)	0.5503(8)	0.4051(3)	0.0163(7)
O(14)	0.2172(3)	0.1784(9)	0.2957(3)	0.0187(8)
O(21)	0.5082(2)	0.6104(8)	0.1134(3)	0.0176(7)
O(22)	0.5890(2)	0.2758(8)	0.0767(3)	0.0173(7)
O(23)	0.4334(3)	0.1956(9)	0.0313(3)	0.0193(7)
O(24)	0.5464(3)	0.1521(10)	0.1882(3)	0.0252(9)
		Pb$_3$Cu$_3$(PO$_4$)$_4$ (abbrevation PBP)		
Pb(1)	0.25	0.04062(9)	0.75	0.01597(10)
Pb(2)	0.09460(2)	0.05545(6)	0.85661(2)	0.01620(9)
Cu(1)	0.0	0.0	0.0	0.0128(3)
Cu(2)	0.14757(6)	0.0270(2)	0.52546(7)	0.0136(2)
P(1)	0.03004(12)	0.0062(4)	0.61480(13)	0.0102(3)
P(2)	0.23783(12)	0.0245(4)	0.40044(14)	0.0116(3)
O(11)	− 0.0371(3)	0.1859(12)	0.5433(4)	0.0123(10)
O(12)	0.1152(4)	0.0678(13)	0.6174(4)	0.0176(12)
O(13)	0.0054(4)	− 0.2923(11)	0.5935(4)	0.0155(11)
O(14)	0.0272(4)	0.0827(13)	0.6969(4)	0.0183(12)
O(21)	0.2426(4)	0.3320(12)	0.3911(4)	0.0153(11)
O(22)	0.1671(4)	− 0.0370(13)	0.4278(4)	0.0164(11)
O(23)	0.3223(4)	− 0.0760(13)	0.4671(4)	0.0192(12)
O(24)	0.2085(4)	− 0.1195(15)	0.3156(4)	0.0199(12)
		BaCu$_2$(PO$_4$)$_2$·H$_2$O (abbrevation BAP)		
Ba	0.22942(1)	0.25265(4)	0.28619(1)	0.01376(4)
Cu(1)	0.49879(3)	0.26907(9)	0.48994(2)	0.01203(7)
Cu(2)	0.26181(4)	0.35034(7)	0.02989(2)	0.01136(6)
P(1)	0.05160(7)	0.23248(18)	0.87263(5)	0.01021(12)
P(2)	0.47215(7)	0.26377(19)	0.88259(5)	0.01011(11)
O(11)	− 0.1045(2)	0.2611(6)	0.87514(14)	0.0134(3)
O(12)	0.1118(2)	0.2741(5)	0.77813(15)	0.0173(4)
O(13)	0.0963(2)	− 0.0345(5)	0.91026(17)	0.0143(4)
O(14)	0.1155(2)	0.4440(5)	0.93908(16)	0.0123(4)
O(21)	0.4254(3)	0.2975(4)	0.78528(16)	0.0162(4)
O(22)	0.4037(2)	0.4767(4)	0.94554(17)	0.0119(4)
O(23)	0.6293(2)	0.3038(4)	0.88950(15)	0.0140(4)
O(24)	0.4266(3)	− 0.0024(5)	0.91967(17)	0.0151(5)
Ow	0.2868(3)	0.7337(5)	0.10262(16)	0.0203(4)
H(1)	0.306(5)	0.704(9)	0.152(4)	0.03 (fixed)
H(2)	0.248(5)	0.860(10)	0.100(2)	0.03 (fixed)
		Ba$_2$Cu(PO$_4$)$_2$·H$_2$O (abbrevation BA1)		
Ba	0.07928(1)	0.23223(3)	0.39226(1)	0.01674(5)
Cu	0.75	0.25	0.25	0.01590(8)
P	0.11602(5)	0.26916(13)	0.64771(5)	0.01459(11)
O1	0.1233(2)	0.5029(4)	0.7215(2)	0.0182(4)
O2	0.1327(2)	0.0163(4)	0.7116(2)	0.0211(4)
O3	− 0.0054(2)	0.2623(4)	0.5764(2)	0.0193(4)
O4	0.2020(2)	0.3045(6)	0.5884(2)	0.0337(6)
Ow	0.75	0.1997(12)	0.5	0.100(3)

TABLE 3—*Continued*

Atom	x	y	z	U_{equiv}
		Split model (isotropic displacement parameters, occupation factor 0.5)		
O(4a)	0.2023(4)	0.3371(9)	0.5891(3)	0.0162(8)
O(4b)	0.2014(4)	0.2650(10)	0.5875(4)	0.0227(9)
Ow(a)	0.7488(10)	0.1906(14)	0.4851(6)	0.0184(15)
Ow(b)	0.758(2)	0.230(4)	0.548(2)	0.082(6)

However, a large isotropic displacement parameter of the half occupied position Ow(b) is maintained. Therefore, a detailed discussion of the probable position of the hydrogen atoms is impossible. The Ow(b)$\cdots$O(4a) distance is reduced to 2.44(2) Å, which is not likely for such a hydrogen bond. The other Ow(a, b)$\cdots$O(4a, b) distances are $\geq$ 2.679(9) Å, Ow(a, b)$\cdots$O(3) is $\geq$ 2.82(2) Å.

TOPOLOGY OF Cu^{2+}–(XO_4)$^{3-}$ LAYERS (X = P, As)

The compounds compiled in Table 1 form eight topologically distinct crystal structures, NAP and NAS are isotypic (Fig. 1). Four different types of layers are formed by connecting Cu atoms with XO_4 tetrahedra, BA1 features Cu–PO$_4$ chains (Fig. 2). The fundamental building units are Cu$_3$O$_{12}$ groups formed by a Cu(1) atom on $\bar{1}$ corner-connected to two Cu(2) atoms on a general position (except for BAP and BA1). The central Cu(1) atom is square planar coordinated with average $\langle$Cu(1)–O$\rangle$ bond lengths from 1.943 to 1.986 Å. The Cu(1)–O bonds to the shared corners are longer than to the terminal ones (average values 2.003 and 1.925 Å, respectively). More interesting is the coordination of the terminal Cu(2) atoms (Fig. 3): the five ligands are in a tetragonal pyramidal or in a trigonal bipyramidal environment. In some cases the distribution of the five Cu(2)–O bond lengths is unusual: the formal coordination numbers [3 + 1 + 1] (NAP), [3 + 2] (AGP), and [5] (CAP, PBP) were observed. For the tetragonal pyramids the O–Cu(2)–O angles indicate that the Cu(2) atoms are close to the centre of the basal plane; although the five Cu(2)–O bond lengths are < 2.20 Å (except in the K and Ba compounds), there is no evidence for a transition from the tetragonal pyramidal to the trigonal bipyramidal coordination figure (13). The Cu(2)O$_5$ polyhedra in CAP and PBP belong to the most regular trigonal bipyramidal coordination figures known for Cu(II) atoms: The O–Cu(2)–O bond angles between the two axial ligands are close to 180°, those within the equatorial plane are about 120°. The distribution of the Cu(2)–O bond lengths is well balanced; as a rule, the shortest are to the axial ligands. The terminal Cu(2) atoms

TABLE 4
Interatomic Bond Distances (Å)

$Sr_3Cu_3(PO_4)_4$	$Pb_3Cu_3(PO_4)_4$	$BaCu_2(PO_4)_2 \cdot H_2O$	$Ba_2Cu(PO_4)_2 \cdot H_2O$
Sr(1)–O(12) = 2.456(4) 2×	Pb(1)–O(24) = 2.340(6) 2×	Ba–O(13) = 2.722(2)	Ba–O(4) = 2.641(2)
Sr(1)–O(24) = 2.474(5) 2×	Pb(1)–O(12) = 2.526(6) 2×	Ba–O(23) = 2.753(2)	Ba–O(4) = 2.737(2)
Sr(1)–O(21) = 2.570(4) 2×	Pb(1)–O(21) = 2.766(6) 2×	Ba–O(21) = 2.768(2)	Ba–O(3) = 2.765(2)
		Ba–O(24) = 2.784(2)	Ba–O(3) = 2.817(2)
Sr(2)–O(14) = 2.488(4)	Pb(2)–O(22) = 2.423(6)	Ba–O(11) = 2.853(2)	Ba–O(1) = 2.835(2)
Sr(2)–O(13) = 2.538(4)	Pb(2)–O(14) = 2.550(7)	Ba–O(12) = 2.892(3)	Ba–O(1) = 2.879(2)
Sr(2)–O(22) = 2.613(4)	Pb(2)–O(14) = 2.647(5)	Ba–O(22) = 3.003(3)	Ba–O(2) = 2.888(2)
Sr(2)–O(21) = 2.615(4)	Pb(2)–O(13) = 2.657(5)	Ba–O(14) = 3.113(3)	Ba–O(3) = 3.011(2)
Sr(2)–O(23) = 2.638(4)	Pb(2)–O(21) = 2.677(4)	Ba–O(12) = 3.129(3)	Ba–O(2) = 3.042(3)
Sr(2)–O(11) = 2.695(4)	Pb(2)–O(11) = 2.730(5)	Ba–O(21) = 3.146(2)	Ba–Ow = 3.124(4)
Sr(2)–O(14) = 2.790(4)	Pb(2)–O(23) = 2.886(7)	Ba–O(21) = 3.215(3)	
Sr(2)–O(22) = 2.836(4)	Pb(2)–O(24) = 2.926(5)		
Sr(2)–O(24) = 2.985(4)	Pb(2)–O(22) = 3.219(6)		
Cu(1)–O(13) = 1.912(4) 2×	Cu(1)–O(13) = 1.917(6) 2×	Cu(1)–O(24) = 1.911(2)	Cu–O(2) = 1.945(2) 2×
Cu(1)–O(11) = 1.980(3) 2×	Cu(1)–O(11) = 1.970(5) 2×	Cu(1)–O(13) = 1.915(2)	Cu–O(1) = 1.956(2) 2×
		Cu(1)–O(14) = 1.995(2)	
Cu(2)–O(22) = 1.952(4)	Cu(2)–O(22) = 1.940(6)	Cu(1)–O(22) = 2.015(2)	
Cu(2)–O(12) = 1.965(3)	Cu(2)–O(12) = 1.968(5)	Cu(1)–Ow = 2.490(3)	
Cu(2)–O(21) = 1.988(3)	Cu(2)–O(23) = 2.019(6)		
Cu(2)–O(11) = 2.042(3)	Cu(2)–O(11) = 2.090(5)	Cu(2)–O(23) = 1.916(2)	
Cu(2)–O(23) = 2.192(4)	Cu(2)–O(21) = 2.102(5)	Cu(2)–O(22) = 1.960(2)	
		Cu(2)–O(11) = 1.984(2)	
		Cu(2)–O(14) = 2.003(2)	
		Cu(2)–Ow = 2.257(3)	
P(1)–O(14) = 1.508(4)	P(1)–O(14) = 1.528(6)	P(1)–O(12) = 1.511(2)	P–O(4) = 1.515(2)
P(1)–O(12) = 1.528(2)	P(1)–O(12) = 1.534(4)	P(1)–O(11) = 1.526(2)	P–O(3) = 1.538(2)
P(1)–O(13) = 1.539(4)	P(1)–O(13) = 1.534(6)	P(1)–O(13) = 1.545(3)	P–O(2) = 1.550(3)
P(1)–O(11) = 1.579(4)	P(1)–O(11) = 1.580(6)	P(1)–O(14) = 1.586(2)	P–O(1) = 1.560(2)
P(2)–O(24) = 1.516(4)	P(2)–O(21) = 1.531(6)	P(2)–O(21) = 1.499(2)	
P(2)–O(23) = 1.530(4)	P(2)–O(24) = 1.534(7)	P(2)–O(24) = 1.541(3)	
P(2)–O(22) = 1.557(3)	P(2)–O(23) = 1.534(6)	P(2)–O(23) = 1.547(2)	P–O(4a) = 1.540(4)
P(2)–O(21) = 1.566(4)	P(2)–O(22) = 1.572(4)	P(2)–O(22) = 1.579(2)	P–O(4b) = 1.507(5)

in SRP and KAS show the usual tetragonal pyramidal [4 + 1] coordination.

In NAP, NAS, AGP, and SRP the Cu_3O_{12} groups are oriented parallel to each other due to translation symmetry (Fig. 2a), they are linked into layers by the phosphate tetrahedra. The layers have orthogonal symmetry in AGP and SRP, but they are triclinic distorted in NAP and NAS, (see (3)). In CAP and PBP, the Cu_3O_{12} groups are arranged in a herring-bone-like pattern; neighboring Cu_3O_{12} groups are approximately at right angles to each other (Fig. 2b). These layers can be derived from the first layer type by rotation of slices in [010] by a twofold axis running parallel b; the layer-formula $[Cu_3(PO_4)_4]$ is maintained. In both types, the central $Cu(1)O_4$ squares are linked parallel to b via two $P(1)O_4$ tetrahedra by sharing corners to form formal $Cu(PO_4)_2$ rows. The connection schema in BAP is obtained by a linkage of the Cu_3O_{12} groups; formally, one terminal Cu(2) atom is shared between two inclined Cu_3O_{12} groups (Fig. 2c). The formation of the zig-zag chains enables the incorporation of the water molecule, which increases the coordination of the Cu atoms to the common $Cu^{[4+1]}O_5$ polyhedron, the composition of the layer is $[Cu_4(PO_4)_4 (Ow)_2]$. Rows obtained by corner-connection of the CuO_4 squares and PO_4 tetrahedra run parallel to a and b. In KAS, the formal connection scheme is distinct from the former cases: Cu_3O_{12} groups are formed but are moderately twisted and form a parquet-like pattern. The central $Cu(1)O_4$ squares are not linked to each other by phosphate tetrahedra (Fig. 2d).

Of interest are the stacking sequences (see Fig. 1); succeeding layers are identical in NAP, NAS, CAP, PBP, and KAS, but they form an *ABAB* stacking sequence in AGP, SRP, and BAP. NAP (NAS) and AGP are polytypes. The essential arrangement of the *Me* atoms in PBP and CAP
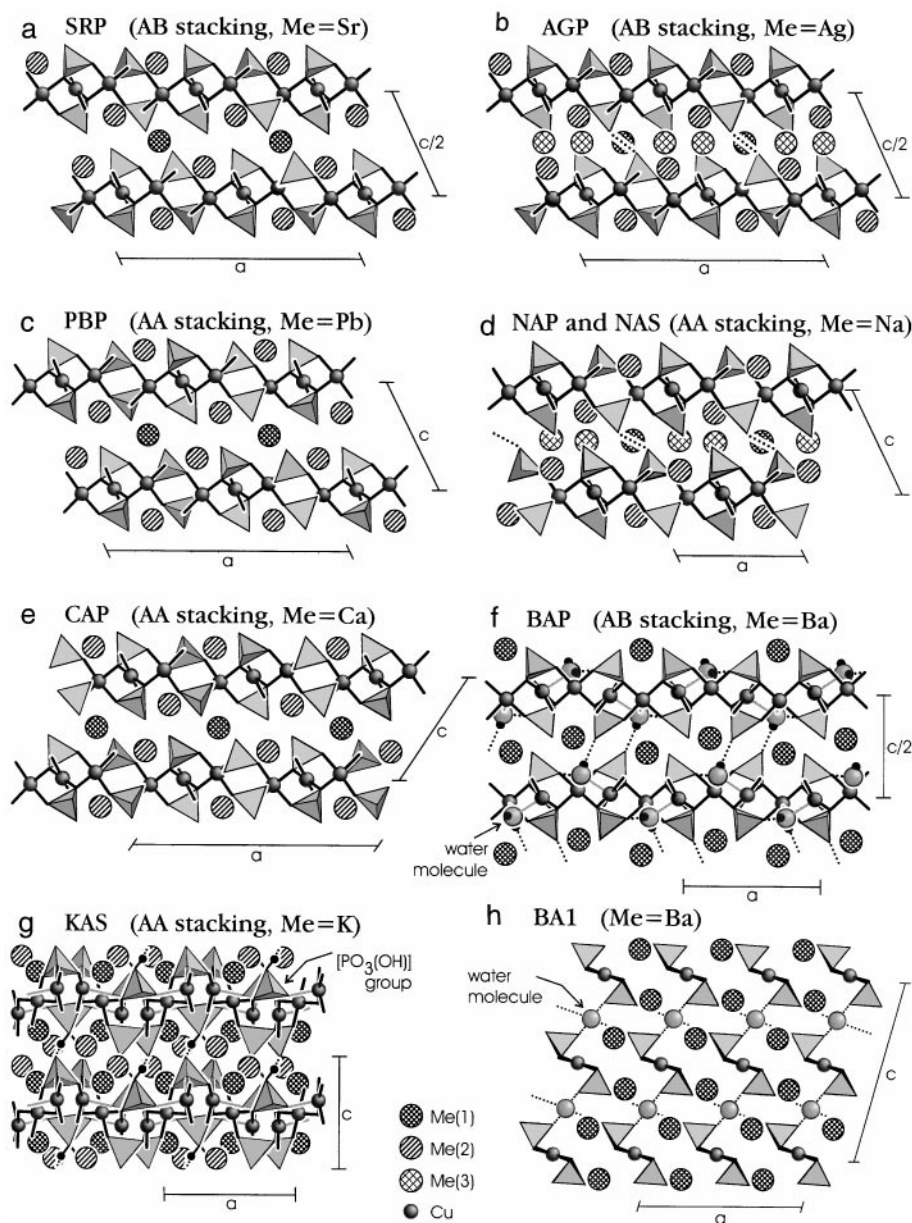
FIG. 1. Stacking variants of (a)–(e) and (g) $[Cu_3(PO_4)_4]$ layers and (f) $[Cu_4(PO_4)_4(Ow)_2]$ layers and the connection of the layers by alkali, alkaline earth, Pb, or Ag atoms and hydrogen bonds. (h) Connection of the $Cu(PO_4)_2$ chains by Ba atoms and water molecules. Hydrogen bonds are dotted; for the abbrevation of compounds see Table 1. Program ATOMS (12).

corresponds to that in SRP. The layers in PBP and CAP are mutualy shifted. Worth mentioning is the structural analogy between AGP and SRP: They have topologically the same layer and the same stacking sequence. The layers are linked by five Ag(I) atoms and one symmetrically restricted hydrogen bond p.f.u. (per formula unit) in AGP but by three Sr(II) atoms in SRP. The Sr(II) atoms occupy three of the former five Ag(I) positions p.f.u., the two additional Ag(I) positions and the position of the H atoms are vacant in SRP.

In BAP, the phosphate tetrahedra are twisted with respect to the other layer structures due to the interchanged ratio $Cu:PO_4 = 1:1$ instead of $3:4$ (Fig. 1f). BAP bears the strongest resemblance to SRP; the $Me(1)$ position in SRP is vacant in BAP. One of the two hydrogen bonds of the water molecule in BAP is within the layer, the other connects two layers. The layers in KAS maintain the ratio $Cu:PO_4$ $= 1:1$ but they are slightly undulating and nested (Fig. 1g). BA1 forms rows by corner connection of the CuO_4 squares
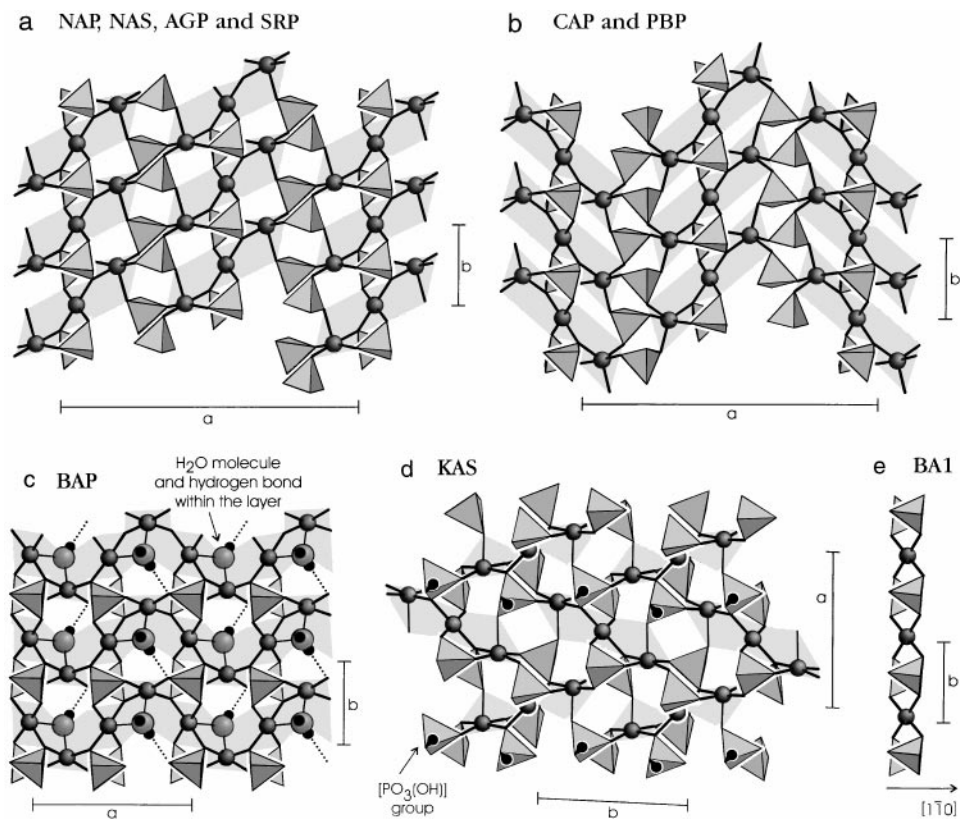
FIG. 2. The connection of the Cu(II) atoms and phosphate (arsenate) tetrahedra: the Cu_3O_{12} groups are arranged (a) parallel to each other, (b) in a herring-bone pattern, and (d) in a parquet-like pattern, and (c) connected among each other forming $Cu_4O_{12}(Ow)_2$ chains linked by phosphate tetrahedra and hydrogen bonds. In (e) the $Cu(PO_4)_2$ chain represents a part of the layers shown in (a)–(c). For the abbrevation of compounds see Table 1. Program ATOMS (12).
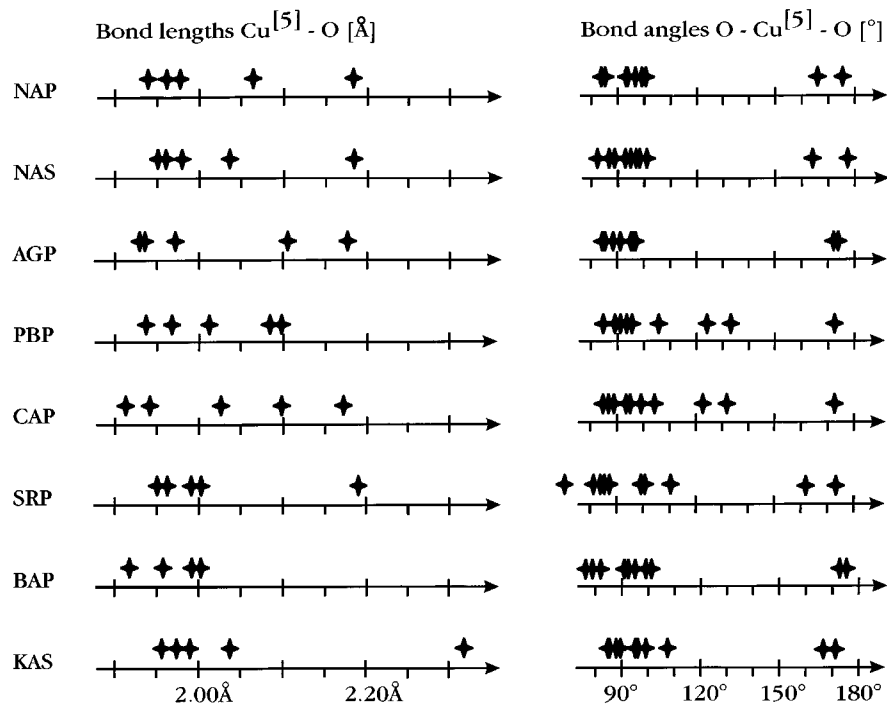

FIG. 3. Distribution of the Cu(2)–O bond distances and O–Cu(2)–O bond angles.

with each two phosphate tetrahedra (Fig. 1h). These $Cu(PO_4)_2$ rows compare to the interconnection of the Cu(1) atoms by PO_4 in NAP, NAS, SRP, CAP, PBP, and BAP. However, in BA1 the $Cu(PO_4)_2$ rows are linked only by the Ba atoms and by the water molecules (Fig. 2e).

The cell choices and transformations allowed a and b to be within the $[Cu_3(PO_4)_4]$ and $[Cu_4(PO_4)_4(Ow)_2]$ layers. With the exception of KAS, the unit-cell parameter b (i.e., the direction of the $Cu(PO_4)_2$ rows) varies from 4.900 Å in CAP to 5.162 Å in AGP. a is 17.275 to 18.035 Å for the phosphate layers with a parallel or herring-bone pattern of the Cu_3O_{12} groups. As expected a and b are increased in NAS due to the larger AsO_4 tetrahedron. The distance between succeeding layers (i.e., d_{001} or $d_{001}/2$) correlates with the ionic radii of the Me atoms and amounts from 7.248 Å in NAP to 7.970 Å in PBP; an increase was observed for the waved layers in KAS (8.365 Å), a decrease for the layers engaged with each other in BAP (7.283 Å).

A number of additional copper(II)-phosphate layers interconnected by alkali or alkaline earth atoms (and hydrogen bonds) have already been described. Many of these compounds are of interest concerning, e.g., the environment of the Cu atoms, but the connection schemes are distinct from those under discussion, even if the chemical formulas —e.g., $BaCu_2(PO_4)_2$ (14)—might indicate close structural relationships.

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