Zeitschrift für Kristallographie 194, 207–219 (1991)

The crystal structure of monoclinic $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ and its relationship to the triclinic sodium analogue

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Received: April 30, 1990; accepted in final form: August 28, 1990

$Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ / *Synthesis / Crystal structure / Stereochemistry / Very short hydrogen bond / Uncommon* CuO_5 *polyhedron*

Abstract. The crystal structure of $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ was determined from 2611 single crystal X-ray data [$a = 17.725(6)$ Å, $b = 5.162(2)$ Å, $c = 18.584(6)$ Å, $\beta = 125.66(2)°$, space group $C2/c$, $Z = 4$, $R_w = 0.032$, $\sin\theta/\lambda \leq 0.80$ Å^{-1}]. (One part of the PO_4 tetrahedra form dimers via a symmetrically restricted, very short O–H–O bond of 2.428(6) Å). Simultaneously this hydrogen bond is a common edge between two coordination polyhedra of Ag atoms. The Cu(1) atom is in a square planar [4] environment. The Cu(2) atom is tetragonal pyramidal [5] coordinated with an uncommon distribution of Cu–O bond lengths [1.933(2), 1.934(2), 1.976(2), 2.105(2) and 2.180(2) Å]. Monoclinic $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ has topologically the same $[Cu_3(PO_4)_4]^{2-}$ layers as triclinic $Na_5Cu_3(XO_4)_2[(XO_4)H(XO_4)]$ (X = P, As), but a different stacking sequence. In both cases these layers are connected by hydrogen bonds and by Na and Ag atoms, respectively, to a three-dimensional network structure.

Introduction

Recently the crystal structures of the compound $Na_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$ and isotypic arsenate were determined by single crystal X-ray techniques (Effenberger, 1985, 1987a). Both compounds show three interesting crystal chemical features: (i) one Cu(II) atom has a tetragonal pyramidal [4 + 1] coordination with a "short" fifth Cu–O bond; (ii) one part of the XO_4 groups (X = P, As) is connected to dimers by very short symmetrically restricted hydrogen bonds; (iii) in addition the configuration O–H–O is simultaneously a common edge of two Na polyhedra. The substitution of sodium atoms by silver was tried in order to continue studies of these three conspicuous peculiarities and to pursue the variation of the O—H—O bond length in accordance with the space requirement of different cations. Syntheses resulted in the new isochemical compound $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$. Unexpectedly the structure analysis of this Ag(I)-phosphate revealed a new structure type, which is topologically related to the structure of sodium-phosphate and sodium-arsenate [for a preliminary note see Effenberger and Pertlik (1988)]. The synthesis of the silver-arsenate analogue failed up to now.

As a convenience throughout this paper the following abbreviations are used: NAP for $Na_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$, NAS for $Na_5Cu_3(AsO_4)_2[(AsO_4)H(AsO_4)]$, and AGP for $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$. The most relevant details on the crystal structures of NAP and NAS have been described by Effenberger (1985, 1987a). This paper reports the result of crystal structure determination of monoclinic AGP and provides a discussion of the two different structure types.

Synthesis

Crystals of AGP were synthesized under hydrothermal conditions. An aqueous solution of $Cu(NO_3)_2 \cdot 3\,H_2O$ was precipitated with $(NH_4)_2HPO_4$. The precipitate was dried. According to a check by X-ray powder methods it consists predominantly of $Cu_3(PO_4)_2 \cdot 3\,H_2O$ (JCPDS 22-548) and $Cu_2(OH)(PO_4)$ (JCPDS 36-404). 2 g of this precipitate were mixed with 1 g $Ag(NO_3)$ and 0.1 ml 20% HNO_3. This mixture was put into a "Teflon" lined steel vessel (~ 6 ml capacity). H_2O was added to 80% degree of filling. After 3 days reaction time at 500 K (saturation vapour pressure) light green crystals of the title compound were obtained. AGP is monoclinic holohedral, crystals are approximately isometric with $\{100\}$, $\{001\}$, $\{10\bar{1}\}$, $\{110\}$, and $\{11\bar{1}\}$; their diameter is up to 0.4 mm. Both sodium compounds form needle-like, light blue crystals.

Experimental and structure determination

The quality of the crystal chip used for X-ray structure investigation was checked by Weissenberg film methods first. Crystal data, details on data collection and results of structure refinement are summarized in Table 1. Extinction rules gave evidence for the space groups Cc or $C2/c$, the latter was confirmed by the structure refinement within the limit of accuracy. The atomic coordinates of the Ag atoms were found by direct methods, those of the other atoms by subsequent Fourier and difference Fourier summations. The H atom could not be located by experiments. During the final

Table 1. Crystal data (from least-squares refinement of 75 accurate 2θ-values with range from 42.3° to 50.9°), X-ray intensity measurements and structure refinement for $Ag_5Cu_3(PO_4)_2[(PO_4)H(PO_4)]$.

$a = 17.725(6)$ Å
$b = 5.162(2)$ Å
$c = 18.584(6)$ Å
$\beta = 125.66(2)°$

$V = 1381.5$ Å^3
$Z = 4$
Space group: $C2/c$
Density (calc) = 5.341 g cm^{-3}

Room temperature
$\mu(MoK\alpha) = 113$ cm^{-1}
$2° \leq 2\theta \leq 70°$
130 variables
Goodness of fit = 2.05
$R = 0.031$
$R_w = 0.032$; $w = [\sigma(F_o)]^{-2}$

STOE four-circle diffractometer AED2
program system STRUCSY (1984) on an ECLIPSE S140
crystal size: 0.07 mm × 0.11 mm × 0.22 mm
graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å)
$2\theta/\omega$ scan mode; step width 0.3°; 0.5 of 1.5 s/step
40 steps/reflection (increased for $\alpha_1 - \alpha_2$ dispersion)
6 steps each side for background correction
3 standard reflections (each 2 h); intensity variation ±4.0%
absorption correction according to crystal shape
transmission factors from 0.364 to 0.493
correction for Lorentz- and polarization effects
6245 measured reflections ($+h \pm k \pm l$)
3048 reflections in unique data set
2611 reflections with $F_o > 3\sigma(F_o)$ used for refinement
secondary extinction (Zachariasen, 1967): $g = 3.8(1) \times 10^{-6}$

stage of refinement anisotropic displacement factors were allowed to vary. Complex neutral atomic scattering functions from the *International Tables for X-ray Crystallography* (1974) were employed. A final difference Fourier summation showed maxima and minima of 1.31 and -1.42 eÅ^{-3}. The highest maxima were found near to the positions of the Ag atoms. The structure parameters are given in Table 2[1], some relevant interatomic distances are compiled in Table 3. Labelling of atoms corresponds for NAP, NAS, and AGP in consideration of the topological relations.

Coordination of atoms

The coordination polyhedra of the three crystallographically independent Ag atoms in AGP are irregular. The shortest Ag–O bond is 2.31 Å. The definition of the upper limit for coordination is arbitrary: Up to 3.054 Å (shortest Ag–Ag distance) the atom Ag(1) has eight, the atoms Ag(2) and

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[1] Additional material can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 54238, the names of the authors and the title of the paper.

Table 2. Atomic coordinates and anisotropic displacement parameters defined as $\exp[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\, h_i\, h_j\, a_i^*\, a_j^*]$ for AGP. E.s.d.'s in parentheses.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	0	0.50332(8)	1/4	0.0539(3)	0.0204(2)	0.0175(2)	0	0.0211(2)	0
Ag(2)	0.23892(2)	0.02673(6)	0.12497(2)	0.0224(1)	0.0227(1)	0.0219(1)	0.0053(1)	0.0160(1)	0.0056(1)
Ag(3)	0.17117(2)	0.00207(6)	0.24286(2)	0.0259(1)	0.0235(1)	0.0224(1)	−0.0015(1)	0.0168(1)	−0.0020(1)
Cu(1)	0	0	0	0.0150(2)	0.0091(2)	0.0136(2)	−0.0010(2)	0.0027(2)	0.0008(2)
Cu(2)	0.37542(3)	0.03641(8)	0.02509(2)	0.0114(1)	0.0140(2)	0.0121(1)	−0.0004(1)	0.0067(1)	0.0013(1)
P(1)	0.41082(5)	0.01199(15)	0.37847(5)	0.0100(3)	0.0104(3)	0.0087(3)	0.0001(2)	0.0048(2)	0.0002(2)
P(2)	0.15330(5)	0.05946(16)	0.39762(5)	0.0111(3)	0.0118(3)	0.0113(3)	0.0005(3)	0.0065(3)	0.0003(2)
O(11)	0.4180(2)	−0.1775(5)	0.4477(1)	0.0154(9)	0.0122(9)	0.0126(9)	0.0014(8)	0.0084(8)	0.0026(7)
O(12)	0.4962(2)	−0.0211(5)	0.3777(1)	0.0120(8)	0.0231(12)	0.0130(8)	−0.0020(8)	0.0076(7)	−0.0038(8)
O(13)	0.4027(2)	0.2932(5)	0.4039(2)	0.0159(10)	0.0122(10)	0.0146(10)	0.0016(8)	0.0063(8)	−0.0014(7)
O(14)	0.3239(2)	−0.0464(5)	0.2865(1)	0.0143(9)	0.0203(12)	0.0115(9)	−0.0012(9)	0.0048(8)	−0.0019(8)
O(21)	0.1540(2)	0.3582(5)	0.4000(2)	0.0225(11)	0.0125(10)	0.0238(11)	0.0007(9)	0.0177(10)	0.0002(8)
O(22)	0.2477(2)	−0.0378(5)	0.4221(2)	0.0132(9)	0.0234(13)	0.0152(9)	0.0039(9)	0.0057(8)	−0.0024(8)
O(23)	0.1240(2)	−0.0480(5)	0.4537(2)	0.0255(12)	0.0176(12)	0.0181(10)	0.0006(9)	0.0155(10)	0.0025(8)
O(24)	0.0843(2)	−0.0283(5)	0.2986(1)	0.0139(9)	0.0304(15)	0.0126(9)	−0.0033(9)	0.0062(8)	−0.0039(8)

Table 3. Selected interatomic distances (Å) and bond angles (°) for AGP. Ag–O bonds < 3.50 Å and Cu–O bonds < 3.0 Å are given. *c* = central atom, *l* = ligand.

Ag(1)^{1}–O(12)^{7,8}	2.416(2)	Ag(2)^{1}–O(21)^{12}	2.366(2)	Ag(3)^{1}–O(24)^{1}	2.308(2)
Ag(1)^{1}–O(21)^{1,4}	2.629(2)	Ag(2)^{1}–O(22)^{11}	2.473(2)	Ag(3)^{1}–O(14)^{1}	2.343(2)
Ag(1)^{1}–O(24)^{2,5}	2.705(2)	Ag(2)^{1}–O(14)^{1}	2.480(2)	Ag(3)^{1}–O(14)^{11}	2.407(2)
Ag(1)^{1}–O(24)^{1,4}	3.001(3)	Ag(2)^{1}–O(13)^{12}	2.545(2)	Ag(3)^{1}–O(13)^{12}	2.480(2)
		Ag(2)^{1}–O(23)^{3}	2.595(2)	Ag(3)^{1}–O(22)^{1}	2.777(2)
		Ag(2)^{1}–O(11)^{11}	2.740(2)	Ag(3)^{1}–O(14)^{12}	2.894(2)
		Ag(2)^{1}–O(22)^{12}	3.091(3)	Ag(3)^{1}–O(11)^{11}	3.354(2)
		Ag(2)^{1}–O(14)^{11}	3.307(3)	Ag(3)^{1}–O(12)^{11}	3.483(3)
		Ag(2)^{1}–O(24)^{11}	3.453(3)		

c	l	$c-l$	l_1	l_2	l_1-l_2	l_1-c-l_2
Cu(1)^{1}	O(13)^{9,12}	1.927(2)	O(13)^{9}	O(13)^{12}	3.854(5)	180
Cu(1)^{1}	O(11)^{10,11}	2.045(2)	O(13)^{9}	O(11)^{10}	2.819(3)	90.4(1)
Cu(1)^{1}	O(23)^{3,4}	2.800(2)	O(13)^{9}	O(11)^{11}	2.801(4)	89.6(1)
			O(13)^{12}	O(11)^{10}	2.801(4)	89.6(1)
			O(13)^{12}	O(11)^{11}	2.819(3)	90.4(1)
			O(11)^{10}	O(11)^{11}	4.091(5)	180
Cu(2)^{1}	O(22)^{3}	1.933(3)	O(22)^{3}	O(12)^{6}	3.854(4)	170.8(2)
Cu(2)^{1}	O(12)^{6}	1.934(3)	O(22)^{3}	O(21)^{12}	2.848(4)	93.5(1)
Cu(2)^{1}	O(21)^{12}	1.976(2)	O(22)^{3}	O(11)^{3}	2.861(4)	90.1(1)
Cu(2)^{1}	O(11)^{3}	2.105(2)	O(22)^{3}	O(23)^{11}	2.992(4)	93.2(1)
Cu(2)^{1}	O(23)^{11}	2.180(3)	O(12)^{6}	O(21)^{12}	2.653(4)	85.4(1)
			O(12)^{6}	O(11)^{3}	2.853(4)	89.8(1)
			O(12)^{6}	O(23)^{11}	3.059(4)	95.9(1)
			O(21)^{12}	O(11)^{3}	4.070(4)	171.6(2)
			O(21)^{12}	O(23)^{11}	3.360(4)	107.8(1)
			O(11)^{3}	O(23)^{11}	2.740(4)	79.5(1)
P(1)^{1}	O(14)^{1}	1.522(2)	O(14)^{1}	O(12)^{1}	2.486(4)	109.1(2)
P(1)^{1}	O(12)^{1}	1.531(3)	O(14)^{1}	O(13)^{1}	2.496(4)	108.2(2)
P(1)^{1}	O(13)^{1}	1.559(2)	O(14)^{1}	O(11)^{1}	2.527(4)	110.1(2)
P(1)^{1}	O(11)^{1}	1.562(2)	O(12)^{1}	O(13)^{1}	2.560(4)	111.9(2)
			O(12)^{1}	O(11)^{1}	2.524(4)	109.4(2)
			O(13)^{1}	O(11)^{1}	2.526(3)	108.1(1)
P(2)^{1}	O(23)^{1}	1.514(3)	O(23)^{1}	O(22)^{1}	2.579(4)	115.3(2)
P(2)^{1}	O(22)^{1}	1.539(3)	O(23)^{1}	O(21)^{1}	2.509(4)	110.3(2)
P(2)^{1}	O(21)^{1}	1.543(2)	O(23)^{1}	O(24)^{1}	2.540(4)	110.8(2)
P(2)^{1}	O(24)^{1}	1.570(2)	O(22)^{1}	O(21)^{1}	2.511(4)	109.2(2)
			O(22)^{1}	O(24)^{1}	2.431(4)	102.8(2)
			O(21)^{1}	O(24)^{1}	2.519(4)	108.0(2)

O(24)–H–O(24) = 2.428(6)

Symmetry code: 1: x,y,z; 2: $x,1+y,z$; 3: $x,-y,-1/2+z$; 4: $-x,y,1/2-z$; 5: $-x,1+y,1/2-z$; 6: $1-x,y,1/2-z$; 7: $1/2-x,1/2+y,1/2-z$; 8: $-1/2+x,1/2+y,z$; 9: $-1/2+x,1/2-y,-1/2+z$; 10: $-1/2+x,-1/2-y,-1/2+z$; 11: $1/2-x,1/2+y,1/2-z$; 12: $1/2-x,-1/2+y,1/2-z$.

Table 4. Volume of the space filling polyhedra and coordination numbers (referred to Hoppe, 1970; O'Keeffe, 1979) for the atoms Me (= Na, Ag), Cu and H in NAP, NAS, and AGP. The calculations include the H atom in the middle of the hydrogen bridges O(24)–O(24). The ratios for all the atomic radii are set equal to 1.0. Calculations were performed with program KRISTALLCHEMIE (Nowotny and Zobetz, 1982).

		NAP	NAS	AGP
Me(1)	volume (Å^3)	14.70	15.50	15.78
	coordination numbers	6.64/6.40	6.24/5.75	6.62/6.38
Me(2)	volume (Å^3)	14.05	14.32	15.39
	coordination numbers	6.33/6.38	5.77/5.81	6.00/5.93
Me(3)	volume (Å^3)	14.46	15.10	15.90
	coordination numbers	5.58/5.72	5.55/5.68	5.71/5.59
Cu(1)	volume (Å^3)	12.19	12.05	11.48
	coordination numbers	5.09/4.80	5.04/4.77	5.11/4.84
Cu(2)	volume (Å^3)	10.11	10.46	10.17
	coordination numbers	5.31/5.11	5.34/5.17	5.21/5.02
H	volume (Å^3)	9.83	10.30	10.63
	coordination numbers	3.75/3.14	3.69/3.11	3.89/3.16

Ag(3) have six oxygen neighbours. Table 3 lists Ag–O bonds up to 3.50 Å including three additional neighbours for the Ag(2) and two additional neighbours for the Ag(3) atom. The coordination number for the Me(1) atom (Me = Na, Ag) may be characterized by [2 + 4 + 2] in the title compound, for NAP it is [4 + 4] and for NAS it is [2 + 2 + 2]. The Me(2) and Me(3) atoms have coordination numbers [5 + 1] and [2 + 2 + 2] in the title compound and [5 + 2] and [5 + 1] in both the triclinic sodium compounds.

An analysis of the surrounding of the Me atoms (Table 4) reveals a slight increase of the volume of space filling polyhedra of the Me atoms from NAP to NAS and to AGP. The coordination numbers for the Me atoms calculated according to Hoppe (1970) and to O'Keeffe (1979) respectively are similar. Slightly smaller values are observed for NAS than for NAP and AGP which is significant at least for the Me(1) and Me(2) atoms; the coordination numbers of the Me(1) atoms are practically equivalent in NAP and AGP and of the Me(3) atoms in all the three compounds.

The Cu(1) atom (site symmetry $\bar{1}$) is exactly planar coordinated by four O atoms with an average Cu(1)–O bond length of 1.986 Å. Two additional O atoms at 2.80 Å complete the coordination polyhedron to an elongated tetragonal dipyramid. In NAP and NAS the Cu(1) atoms have comparable coordinations with average Cu(1)–O bond lenghts to the four nearest neighbours of 1.982 Å and 1.986 Å, the additional ligands are at ~3.0 Å.

The coordination polyhedron of the Cu(2) atom is of greater interest: four O atoms form a distorted square with the Cu(2) atom near to the centre, in AGP the average Cu(2)–O bond length is 1.987 Å; it should be mentioned that one of these four bond lengths, Cu(2)–O(11), is 2.105 Å,

Table 5. Distortion of the XO_4 tetrahedra in NAP, AGP, and NAS. Mean square relative deviation from average bond length: $\Delta = 1/4 \sum_{i=1}^{4} [(XO_i - XO_m)/XO_m]^{2\,a}$; bond angle variance: $\sigma^2 = 1/5 \sum_{i=1}^{6} (OXO_i - 109.47°)^{2\,a}$; distortion parameter for bond lengths: $DI(XO) = \left(\sum_{i=1}^{4} |XO_i - XO_m|\right)/4(XO_m)^{b}$; distortion parameter for bond angles: $DI(OXO) = \left(\sum_{i=1}^{6} |OXO_i - OXO_m|\right)/6(OXO_m)^{b}$; distortion parameter for edges: $DI(OO) = \left(\sum_{i=1}^{6} |OO_i - OO_m|\right)/6(OO_m)^{b}$.

		NAP	AGP	NAS
Δ	$X(1)O_4$	0.000189	0.000126	0.000172
	$X(2)O_4$	0.000182	0.000166	0.000149
σ^2	$X(1)O_4$	1.93	1.96	3.67
	$X(2)O_4$	19.73	16.44	42.81
DI(XO)	$X(1)O_4$	0.0117	0.0110	0.0123
	$X(2)O_4$	0.0109	0.0097	0.0101
DI(OXO)	$X(1)O_4$	0.0101	0.0093	0.0126
	$X(2)O_4$	0.0298	0.0250	0.0487
DI(OO)	$X(1)O_4$	0.0077	0.0076	0.0102
	$X(2)O_4$	0.0134	0.0124	0.0261

XO, OO and OXO signifies X – O and O – O bond lengths and O – X – O angles; index *i* indicates individual values, index *m* the mean value for the polyhedron. For references cf. [a] Robinson, Gibbs and Ribbe (1971), Brown and Shannon (1973) and Fleet (1976); [b] Baur (1974).

whereas the others range from 1.933 Å to 1.976 Å. A fifth O atom – O(23) – completes the coordination figure to a tetragonal pyramid; the Cu(2) – O(23) bond length is only 2.180 Å, which is conspicuously short for the fifth O neighbour in a tetragonal pyramidal coordination polyhedron around divalent copper atoms. Similarly in NAP and NAS the average Cu(2) – O bond lengths are 1.984 Å and 1.980 Å within the basal plane and 2.183(4) Å and 2.189(2) Å to the apices. In both these compounds Cu(2) – O(11) is somewhat shorter than in AGP [2.064(3) Å and 2.040(3) Å], whereas the other Cu(2) – O bond lengths within the basal plane are in the same range as those of AGP: 1.937(4) Å to 1.975(2) Å. Although the coordination figures around the Cu(2) atoms are similar in the three compounds under discussion the distortion towards a [3 + 1 + 1] coordination is more strongly pronounced in AGP.

The O – Cu – O angles between opposite corners in the basal plane of the tetragonal pyramid range from 164.4° to 177.7° indicating only a moderate angular distortion. Tetragonal pyramids CuO_5 with five Cu – O bonds

< 2.20 Å are rare. Especially one long of the four Cu – O bonds in the basal plane has seldomly been described in inorganic crystal structures. On the contrary such a distribution of Cu(II) – O bonds is the rule for the rare trigonal bipyramidal coordination (Effenberger, 1988).

The mean P(1) – O bond lengths in AGP and NAP are identical within limits of error: 1.544 Å and 1.543 Å, whereas in AGP the mean P(2) – O bond length (1.542 Å) is significantly longer than in NAP (1.536 Å). These values are in accordance with literature: Baur (1974) found in a survey average P – O distances from 1.506 Å to 1.572 Å with a mean value of 1.537 Å. Compilations by Corbridge (1971) and Shannon and Calvo (1973) revealed identical results.

The reason for the good agreement of ⟨P(1) – O⟩ but different ⟨P(2) – O⟩ bond lengths in NAP and AGP is not completely clear: Variations of the mean bond lengths in PO_4 tetrahedra were considered to be due to (i) the coordination number of the oxygen atoms, (ii) the different electronegatives of cations, and (iii) the degree of distortion of the tetrahedra (Shannon and Calvo, 1973; Brown and Shannon, 1973; Baur, 1974); Coordination of oxygen atoms is similar in NAP and AGP; the electronegativities of Na (0.9) and Ag (1.8) should cause for both the phosphate tetrahedra a shift of the average bond lengths in comparable amounts. Only the distortion parameters (Table 5) indicate a difference: the degree of distortion is smaller for both phosphate tetrahedra in AGP as compared with NAP, this effect is more pronounced for the $P(2)O_4$ tetrahedra. This might be the reason for the different average P(2) – O bond lengths. It should be mentioned that the distortion is very large for the $X(2)O_4$ tetrahedra in all three compounds.

The hydrogen bond

Neither in the title compound nor in the two triclinic compounds the H atom was located by experiments. Due to crystal chemical considerations a symmetry restricted hydrogen bond O(24) – H – O(24) is assumed for the three compounds NAP, NAS, and AGP.

Excluding the contribution of bond strengths from the H atom in AGP the sum of bond valences at the oxygen atoms O(11) to O(22) range from 1.96 v.u. (valence units) to 2.04 v.u. (Table 6). The calculated value for O(23) is somewhat small for an oxygen atom (1.76 v.u.), but it is definitely too small for O(24) (1.57 v.u.). The same trend has been observed for the corresponding O atoms in NAP and NAS. The low values for O(23) are obviously caused by their coordination to one Na/Ag, one Cu (apical ligand only), and one P/As atom. The insufficient saturations of the O(23) atoms are responsible for the extremely short Cu(2) – O(23) bond lengths to the apices of the tetragonal pyramidal coordination figures of $Cu(2)O_5$. In

Table 6. Bond valences (s; in valence units) calculated from bond lengths (r) in AGP according to Brown and Altermatt (1985). $s = \exp[(r_o - r)/B]$, $B = 0.37$, $r_o(\mathrm{Ag}) = 1.842$, $r_o(\mathrm{Cu}) = 1.679$, $r_o(\mathrm{P}) = 1.617$ Å.

s	Ag(1)	Ag(2)	Ag(3)	Cu(1)	Cu(2)	P(1)	P(2)	Σ
O(11)	–	0.09	0.02	0.37	0.32	1.16	–	1.96
O(12)	0.21	–	0.01	–	0.50	1.26	–	1.98
O(13)	–	0.15	0.18	0.51	–	1.17	–	2.01
O(14)	–	0.18 0.02	0.26 0.22 0.06	–	–	1.29	–	2.03
O(21)	0.13	0.24	–	–	0.45	–	1.22	2.04
O(22)	–	0.18 0.03	0.08	–	0.50	–	1.24	2.03
O(23)	–	0.13	–	0.05	0.26	–	1.32	1.76
O(24)	0.10 0.04	0.01	0.28	–	–	–	1.14	1.57
Σ	0.96	1.03	1.11	1.86	2.03	4.88	4.92	

addition X(2)–O(23) is the smallest bond length to any X atom within each of the three compounds.

Atom O(24) is coordinated to two Ag and to one P. The sum of bond valences for O(24) is 2.07 v.u. including the hydrogen bond O(24)–H–O(24). For discussion of this hydrogen bond the P(2)–O(24) bond length is of special interest: in AGP it is 1.570 Å and significantly longer than in NAP [1.559(4) Å] which correlates with the hydrogen bond lengths of 2.428 Å and 2.388 Å (Ferraris and Ivaldi, 1984; Ichikawa, 1987). In addition the short P(2)–O(24) bond lengths support the assumption of the hydrogen bond O(24)–H–O(24); at least a free hydrogen bond or a so-called "weak" hydrogen bond with an O(24)–H...O distance beyond ~2.60 Å seems impossible.

The hydrogen bond is symmetrically restricted by a twofold axis in AGP, and by a center of symmetry in NAP and NAS. A slight dislocation of the H atom towards an only apparently symmetric hydrogen bond with local violation of symmetry (either statistically or ordered causing a lowering of space group symmetry or multiplication of cell content) is expected.

The O–H–O configuration is simultaneously a common O–O edge between the coordination polyhedra of two silver atoms. Comparable structural units have been found not only in NAP and in NAS but also in $K_3Cu_2[(P_2O_7)H(P_2O_7)]$ (Effenberger, 1987b) and in $KCu_3(OH)_2[(AsO_4)H(AsO_4)]$ (Effenberger, 1989). In these five compounds a very short, sym-

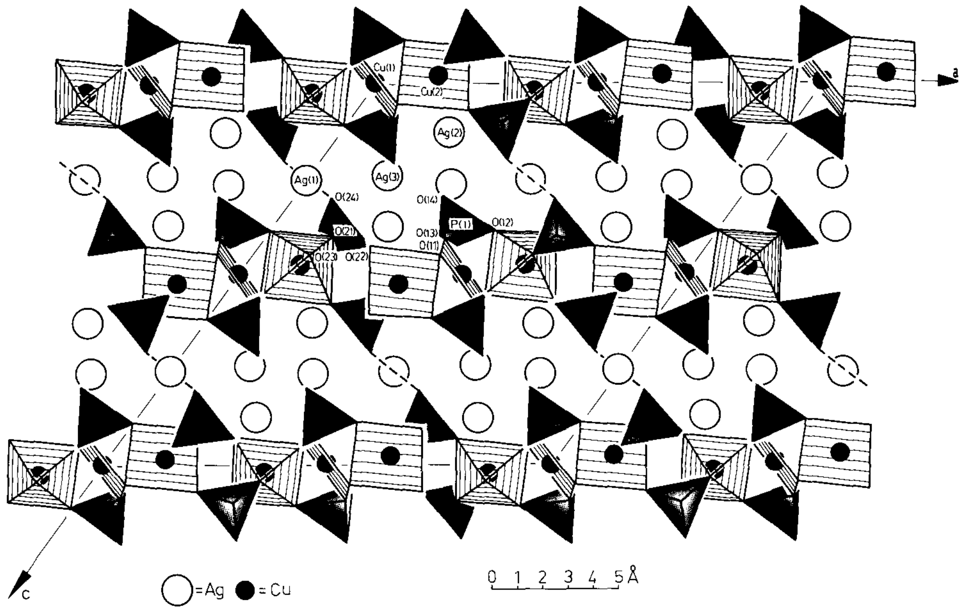

Fig. 1. Projection of the crystal structure of AGP in a projection onto (010). $Cu(1)O_4$ and $Cu(2)O_5$ coordination polyhedra are hatched, PO_4 tetrahedra are dotted. The O(24)–H–O(24) bond is indicated by a broken line.

metrically restricted O–H–O bond connects each two oxoanion groups to a dimer. Simultaneously O–H–O is a common O–O edge of two coordination polyhedra around potassium atoms.

The crystal structure

The crystal structures of AGP and of NAP and NAS are characterized by the corner connection of a $Cu(1)O_4$ square with two $Cu(2)O_5$ polyhedra to Cu_3O_{12} groups. The XO_4 tetrahedra link these groups to $^2_\infty[Cu_3(PO_4)_4]$ units which are interconnected by the O–H–O bond and by the Ag (Na) atoms to a three-dimensional network. Figure 1 depicts the atomic arrangement of AGP. For a comparison with NAP see Effenberger (1985).

The relation between the triclinic structure of NAP (and NAS) – space group $P\bar{1}$ – and monoclinic AGP – space group $C2/c$ – is visualized by a transformation according to

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{monoclinic}} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{triclinic}} \cdot \begin{pmatrix} \bar{1} & \bar{2} & \bar{2} \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

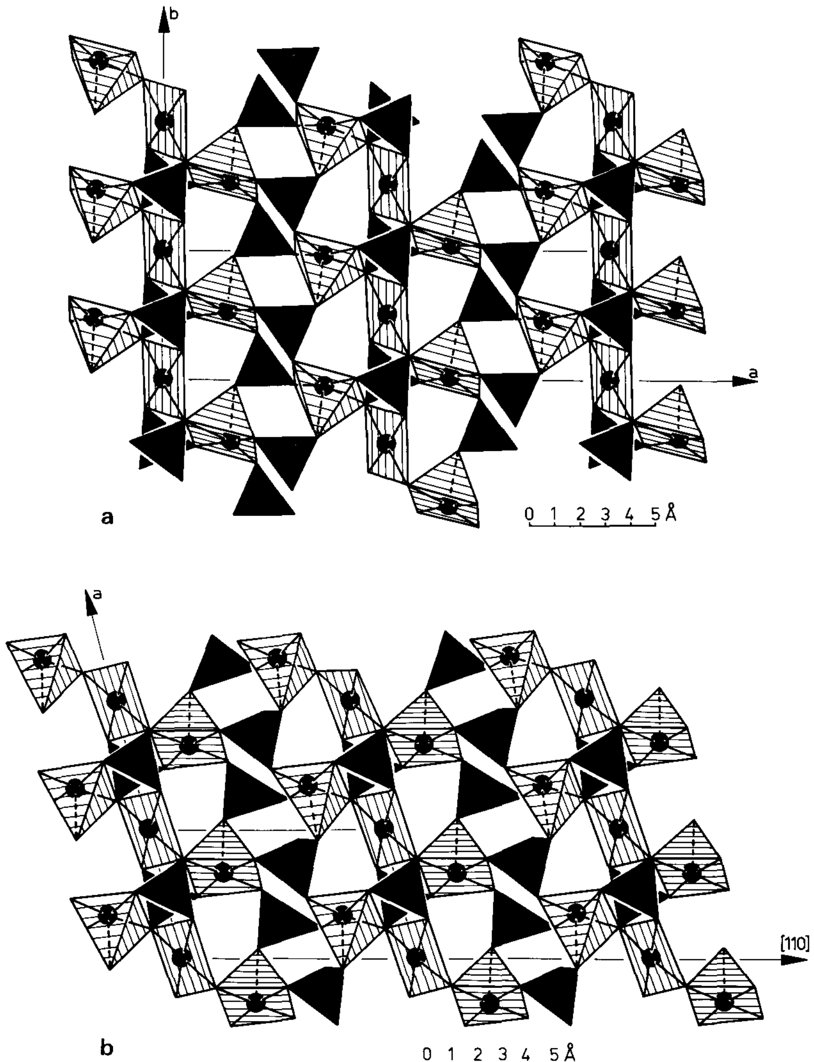

Fig. 2. The $^{2}_{\infty}[Cu_3(PO_4)_4]$ units in (a) monoclinic AGP and (b) triclinic NAP.

This yields a cell with fourfold cell content and the following lattice parameters for NAP/NAS: $a = 18.010/18.388$ Å, $b = 5.106/5.275$ Å, $c = 18.104/18.594$ Å, $\alpha = 90.09/90.04°$, $\beta = 126.79/126.75°$, $\gamma = 91.40/92.33°$. These parameters show the pronounced pseudomonoclinic cell geometry of these two compounds.

The $^2_\infty[Cu_3(PO_4)_4]$ units with symmetry $\bar{1}$ are topologically identical in both structure types; they show only minor differences depending on weak torsions of the individual coordination polyhedra (Fig. 2). Although both structure types contain only one kind of these layer-like units, they have a different stacking order: in NAP all layers have the same orientation, in AGP they are combined by a twofold axis resulting in a stacking sequence ...ABABAB.... This causes an interchange of the orientation of the coordination polyhedra in subsequent $^2_\infty[Cu_3(PO_4)_4]$ units. Surprisingly, in both structure types the coordination polyhedra of the Na and Ag atoms show only minor differences. This is caused by the pseudo-special atomic coordinates of the majority of atoms: with the exception of the three atoms O(11), O(13), and O(21) the parameters y/b are close to 0.00 or 0.50, the largest deviation is 0.307 Å for the atom P(2). Though all the three Me atoms have ligands in two neighbouring units, their coordination polyhedra are similar with respect to ligands, Me – O distances and O – Me – O angles. This helds especially for the Me(2) and Me(3) atoms; the largest differences were found for the coordination polyhedra around the Me(1) atoms which obviously is caused by the hydrogen bond.

Acknowledgements. The authors thank Prof. Dr. H. Fuess (Darmstadt, FRG) for revision of the manuscript and Mag. M. Wildner (Vienna) for instructions in handling the computer program "KRISTALLCHEMIE". The syntheses were supported by the "Hochschuljubiläumsstiftung der Stadt Wien".

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