

Chemical preparation and crystal structure of an adduct between potassium cyclooctaphosphate and telluric acid: $\text{Te}(\text{OH})_6 \cdot \text{K}_8\text{P}_8\text{O}_{24} \cdot 2 \text{H}_2\text{O}$

U. Schülke, M. T. Averbuch-Pouchot and A. Durif

Zentralinstitut für anorganische Chemie, Rudower Chaussee 5,
1199, Berlin-Adlershof, Germany

Laboratoire de Cristallographie, associé à l'Université Joseph Fourier,
CNRS, B.P. 166, 38042, Grenoble-Cédex 09, France

Received: January 6, 1992; in final version: February 19, 1992.

Cyclophosphates / Adducts / Telluric acid / Crystal structures

Abstract. $\text{Te}(\text{OH})_6 \cdot \text{K}_8\text{P}_8\text{O}_{24} \cdot 2 \text{H}_2\text{O}$ is the first example of an adduct between telluric acid and a cyclooctaphosphate. We report its chemical preparation and its atomic arrangement. The title compound is triclinic $P\bar{1}$, $Z = 1$ with the following unit cell dimensions:

$$a = 11.315(9), b = 10.67(1), c = 7.547(3) \text{ \AA} \\ \alpha = 108.72(5), \beta = 100.30(2), \gamma = 66.80(5)^\circ$$

Crystal structure was determined and refined to final $R = 0.028$ for 7265 independent reflections. The atomic arrangement is mainly characterized by the coexistence of independent units of $[\text{P}_8\text{O}_{24}]^{8-}$ ring anions and of $\text{Te}(\text{OH})_6$ groups, both centrosymmetric.

The hydrogen bond scheme is described. In addition, the internal symmetries and the geometries of the rare $[\text{P}_8\text{O}_{24}]^{8-}$ ring anions presently investigated are discussed.

Introduction

The progress in chemistry of cyclophosphates with large ring anions, cyclohexa-, cycloocta-, cyclodeca- and cyclododecaphosphates, whose existence was clearly proved by the thin layer chromatography technique as early as 1955 proceeded slowly. Only when Schiilke and Kayser (1985) published a convenient process for the preparation of large amounts of $\text{Li}_6\text{P}_6\text{O}_{18}$ the crystal chemistry of cyclohexaphosphates could be developed

Table 1. Crystal data and experimental parameters used for the intensity data collection. Strategy and final results of the structure determination.

I. Crystal data	
Formula: $\text{Te}(\text{OH})_6 \cdot \text{K}_8\text{P}_8\text{O}_{24} \cdot 2\text{H}_2\text{O}$	Space group: $P\bar{1}$
Crystal system: triclinic	$F_w = 1210.256$
$a = 11.315(9)$, $b = 10.67(1)$	$V = 792(2) \text{ \AA}^3$
$c = 7.547(3) \text{ \AA}$, $\alpha = 108.72(5)$	$Z = 1$
$\beta = 100.30(2)$, $\gamma = 66.80(5)^\circ$	19 reflections ($10.2 < \theta < 14.6^\circ$)
Refinement of unit cell parameters:	$R(000) = 590$
$\sigma_{\text{pal.}} = 2.537 \text{ g} \cdot \text{cm}^{-3}$	$\mu(\text{AgK}\alpha) = 1.292 \text{ mm}^{-1}$
Linear absorption factor:	Crystal size: $0.24 \times 0.40 \times 0.35 \text{ mm}$
Morphology: short stout triclinic prism	
II. Intensity measurements	
Temperature: 294 K	Wavelength: $\text{AgK}\alpha$ (0.5608 \AA)
Diffractometer: Philips PW 1100	Scan mode: ω
Monochromator: graphite plate	Scan width: 1.20°
Scan speed: $0.02^\circ \cdot \text{s}^{-1}$	Theta range: $3-30^\circ$
Measurement area: $\pm h$, $\pm k$, l	$h_{\text{max}} = 20$, $h_{\text{min}} = 18$, $l_{\text{max}} = 13$
Total background measuring time:	10 s
Total number of scanned reflections:	9904
Total number of non-zero reflections:	8445
Total number of independent reflections:	8004 ($R_{\text{int.}} = 0.01$)
Two intensity and orientation reference reflections:	no variation
III. Structure determination	
Lorentz and polarization corrections	No absorption correction
Program used: SDP [1]	Computer used: Micro-Vax II
Determination:	Direct methods with MULTAN [2]
Hydrogen atoms from difference-Fourier syntheses	
Thermal displacement parameters:	anisotropic for non-H atoms
	isotropic for H atoms
Unique reflections included:	7265 with $I > 4 \sigma(I)$
Weighting scheme: unitary	Refined parameters: 243
Unweighted agreement factor R :	0.028
Weighted agreement factor R_w :	0.032
E.s.d.: 0.845	Largest shift/error = 0.05
Drawings made with STRUPL0 [3]	

[1] Structure Determination Package (1979).

[2] Main, P., et al. (1977).

[3] Fischer, R. X. (1985).

in a systematic way. Today, crystal structures of more than fifty cyclohexaphosphates are known. A recent survey, unfortunately already obsolete, of their crystal chemistry has been published by Averbuch-Pouchot and Durif (1991).

In the field of cyclooctaphosphates, things are a little different. As early as 1968 (a, b), Schülke reported a process for the preparation of convenient amounts of hexahydrate of the sodium salt, $\text{Na}_8\text{P}_8\text{O}_{24} \cdot 6\text{H}_2\text{O}$, but in spite of the possibility to use this salt as starting material, the rare

Table 2. Final atomic coordinates for the atomic arrangement of $\text{Te}(\text{OH})_6 \cdot \text{K}_8\text{P}_8\text{O}_{24} \cdot 2\text{H}_2\text{O}$. B_{eq} are given for non-hydrogen atoms, B_{non} for hydrogen atoms. Estimated standard deviations are given in parentheses. $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j a_i \cdot b_j \cdot \beta_{ij}$

Atoms	x	y	z	B_{eq}
Te	0	0	0	1.025(2)
K(1)	0.43872(4)	0.89184(4)	0.25603(6)	1.849(7)
K(2)	0.97620(4)	0.38360(4)	0.08076(6)	1.923(7)
K(3)	0.35586(4)	0.58668(4)	0.84047(6)	1.809(7)
K(4)	0.85018(5)	0.91491(5)	0.36957(7)	2.217(8)
P(1)	0.28028(4)	0.28185(4)	0.43550(6)	1.137(7)
P(2)	0.13583(4)	0.57864(4)	0.43053(6)	1.048(7)
P(3)	0.32757(4)	0.67998(4)	0.37264(6)	1.104(7)
P(4)	0.46645(4)	0.80441(4)	0.70866(6)	1.128(7)
O(1)	0.8625(2)	0.1659(1)	0.9581(2)	1.79(3)
O(2)	0.9751(2)	0.0687(1)	0.2625(2)	1.61(2)
O(3)	0.1156(1)	0.0975(2)	0.0236(2)	1.97(3)
O(L11)	0.3283(2)	0.3206(2)	0.6334(2)	1.99(3)
O(E12)	0.7579(1)	0.8444(1)	0.6360(2)	1.82(3)
O(L12)	0.8396(1)	0.5875(1)	0.6141(2)	1.25(2)
O(L14)	0.3798(1)	0.2693(2)	0.2977(2)	1.75(2)
O(E21)	0.0327(1)	0.6328(1)	0.2944(2)	1.64(2)
O(E22)	0.1220(2)	0.6474(2)	0.6346(2)	1.83(3)
O(L23)	0.7269(1)	0.4350(1)	0.6194(2)	1.87(3)
O(E31)	0.2217(2)	0.8197(1)	0.3887(2)	1.80(3)
O(E32)	0.5928(2)	0.3811(2)	0.7906(2)	2.17(3)
O(L34)	0.5803(2)	0.3168(1)	0.4391(2)	1.97(3)
O(E41)	0.4219(1)	0.9328(1)	0.6414(2)	1.74(2)
O(E42)	0.5618(2)	0.1902(2)	0.1053(2)	2.27(3)
O(W)	0.7776(2)	0.6371(3)	0.0425(3)	4.60(6)
				B_{non}
H(1)	0.160(4)	0.854(5)	0.155(7)	4(1)
H(2)	0.946(4)	0.143(5)	0.281(6)	3(1)
H(3)	0.158(4)	0.113(5)	0.119(6)	4(1)
H(1W)	0.242(5)	0.371(5)	0.841(7)	4(1)
H(2W)	0.728(5)	0.683(5)	0.961(7)	4(1)

cyclooctaphosphates well investigated since that date have been characterized either during elaborations of phase-equilibrium diagrams or during the investigations of various systems by flux methods. At first a series of four isotopic $\text{Cu}_3\text{M}_2\text{P}_8\text{O}_{24}$ compounds was characterized during the elaboration of the $\text{MPO}_3\text{-Cu}_2\text{P}_4\text{O}_{12}$ phase-equilibrium diagrams for $\text{M} = \text{Rb}$, Cs and Tl by Laügt et al. (1968), Laügt and Martin (1972), Laügt (1974a, 1974b) and for the ammonium salt during an investigation of the $\text{CuO-P}_2\text{O}_5\text{-NH}_3\text{-H}_2\text{O}$ system by Laügt and Guitel (1975), afterwards other

Table 3. Main interatomic distances (Å) and bond angles (°) in the associated cation polyhedra, the Te(OH)₆ group and the hydrogen bond scheme.

The KOn polyhedra				
K(1) O ₂ polyhedron				
K(1)—O(E11)	2.916(1)	K(1)—O(E32)	2.975(2)	
K(1)—O(E12)	2.789(1)	K(1)—O(E41)	2.829(2)	
K(1)—O(E31)	3.239(2)	K(1)—O(E41)	2.748(2)	
K(1)—O(F42)	2.582(2)			
K(2)O ₄ polyhedron				
K(2)—O(i)	2.909(2)	K(2)—O(E21)	2.881(2)	
K(2)—O(3)	2.757(1)	K(2)—O(E21)	2.766(2)	
K(2)—O(L12)	2.842(1)	K(2)—O(E22)	2.749(2)	
K(2)—O(W)	2.816(3)	K(2)—O(W)	2.997(3)	
K(3)O ₅ polyhedron				
K(3)—O(1)	3.002(1)	K(3)—O(L23)	3.386(2)	
K(3)—O(E11)	2.877(2)	K(3)—O(E32)	2.710(1)	
K(3)—O(E22)	2.768(2)	K(3)—O(E32)	2.678(2)	
K(3)—O(L34)	2.926(2)	K(3)—O(F42)	2.773(2)	
K(4)O ₄ polyhedron				
K(4)—O(2)	2.904(2)	K(4)—O(E21)	2.842(1)	
K(4)—O(2)	3.106(1)	K(4)—O(E31)	2.723(1)	
K(4)—O(3)	3.015(2)	K(4)—O(F41)	2.860(1)	
K(4)—O(F12)	2.836(2)	K(4)—O(W)	3.472(3)	
The Te(OH) ₆ group				
2 × Te—O(1)	1.915(1)			
2 × Te—O(2)	1.910(1)			
2 × Te—O(3)	1.922(2)			
The hydrogen bonds				
O—H...O	O—H	H...O	O—H...O	O—O
O(1)—H(1)...O(E31)	0.82(5)	1.88(5)	156(5)	2.652(2)
O(2)—H(2)...O(E22)	0.71(4)	1.97(4)	172(4)	2.677(2)
O(3)—H(3)...O(E12)	0.80(4)	1.93(4)	173(5)	2.719(2)
O(W)—H(1W)...O(E11)	0.98(6)	1.82(5)	157(3)	2.746(3)
O(W)—H(2W)...O(L14)	0.89(5)	2.20(5)	162(4)	3.062(3)
H(1W)—O(W)—H(2W)	131(4)			

compounds of general formula $M_2K_2P_8O_{24}$ ($M = Al, Fe, Ga, V$) were discovered by Grunze et al. (1983), Lavrov et al. (1981) and Palkina et al. (1979) during investigations of the corresponding $K_2O \cdot P_2O_5 \cdot M_2O_3$ systems by flux methods. In all these cases, the true nature of the anion was recognized during the structural investigations. Recently, we started a systematic investigation of this family of salts and described crystal structures of two of them, $Na_8P_8O_{24} \cdot 6H_2O$ (Schülke et al., 1992a) and $Ag_8NaP_8O_{24}(NO_3)_2 \cdot 4H_2O$ (Averbuch-Pouchot and Durif, 1992). In the present study, we describe the first example of an adduct between a cyclooctaphosphate and telluric acid, $Te(OH)_6 \cdot K_8P_8O_{24} \cdot 2H_2O$, provid-

Table 4. Main interatomic distances (Å) and bond angles (°) in the four independent PO₄ tetrahedra building the ring anion. Estimated standard deviations are given in parentheses.

The P(1)O ₄ tetrahedron			
P(1)—O(F11)	1.479(1)	P(1)—O(E12)	1.484(2)
P(1)—O(L12)	1.609(1)	P(1)—O(L14)	1.605(2)
O(E11)—P(1)—O(E12)	119.2(1)	O(E12)—P(1)—O(L12)	106.75(8)
O(E11)—P(1)—O(L12)	111.25(7)	O(E12)—P(1)—O(L14)	108.70(9)
O(E11)—P(1)—O(L14)	110.7(1)	O(L12)—P(1)—O(L14)	98.08(8)
The P(2)O ₄ tetrahedron			
P(2)—O(L12)	1.611(1)	P(2)—O(E22)	1.485(1)
P(2)—O(E21)	1.474(1)	P(2)—O(L23)	1.604(2)
O(L12)—P(2)—O(E21)	106.31(8)	●(E21)—P(2)—●(E22)	120.17(8)
O(L12)—P(2)—O(E22)	109.63(9)	O(E21)—P(2)—●(L23)	111.3(1)
O(L12)—P(2)—O(E23)	98.95(7)	O(E22)—P(2)—●(L23)	108.34(9)
The P(3)O ₄ tetrahedron			
P(3)—O(L23)	1.595(2)	P(3)—O(E31)	1.484(1)
P(3)—O(F32)	1.474(2)	P(3)—O(L34)	1.605(1)
O(L23)—P(3)—O(F31)	110.32(9)	●(F31)—P(3)—O(F32)	118.1(1)
O(L23)—P(3)—O(F32)	107.9(1)	O(F31)—P(3)—O(L34)	110.38(7)
O(L23)—P(3)—O(L34)	99.16(9)	O(E32)—P(3)—O(L34)	109.19(9)
The P(4)O ₄ tetrahedron			
P(4)—O(F41)	1.605(1)	P(4)—O(F41)	1.483(2)
P(4)—O(L34)	1.612(2)	P(4)—O(E42)	1.474(2)
O(L14)—P(4)—O(L34)	101.84(7)	O(L34)—P(4)—O(E41)	110.50(8)
O(L14)—P(4)—O(E41)	109.3(1)	O(L34)—P(4)—O(E42)	105.8(1)
O(L14)—P(4)—O(F42)	105.07(9)	O(F41)—P(4)—O(F42)	122.30(9)
P(1)—P(2)	2.9465(6)	P(1)—O(L12)—P(2)	132.43(9)
P(1)—P(4)	2.9389(7)	P(1)—O(L14)—P(4)	132.6(1)
P(2)—P(3)	2.9255(8)	P(2)—O(L23)—P(3)	132.25(8)
P(3)—P(4)	2.9532(6)	P(3)—O(L34)—P(4)	133.3(1)
P(2)—P(1)—P(4)	107.43(2)		
P(1)—P(2)—P(3)	105.14(2)		
P(2)—P(3)—P(4)	117.49(2)		
P(1)—P(4)—P(3)	101.10(2)		

The O—O distances have been deposited.¹

ing a new example of a P₈O₂₄ ring geometry and showing by this first example the generality of the formation of such adducts with all kinds of water soluble alkali phosphates.

The larger phosphoric anion, [P₁₀O₃₀]¹⁰⁻, was first separated and first characterized in Ba₂Zn₃P₁₀O₃₀ by Bagieu-Beucher et al. (1981, 1982). Schülke developed a reproducible process for the preparation of a good starting material, K₁₀P₁₀O₃₀ · 4H₂O. The crystal structure of this compound was recently determined by the authors (Schülke et al., 1992b).

Table 5. Least-squares plane for the phosphoric ring anion.

Crystallographic equation of the mean-plane for phosphorus atoms only and atom distances (Å) from this plane:

$$2.211x + 2.157y - 7.473z = 0$$

$$P(1) -0.474 \quad P(2) -0.116 \quad P(3) 0.959 \quad P(4) 0.977$$

Crystallographic equation of the mean-plane for both phosphorus atoms and bonding oxygen atoms. Atom distances (Å) from this plane are reported below its equation:

$$2.646x + 2.790y - 7.506z = 0$$

P(1)	-0.706	O(L12)	-0.286
P(2)	-0.223	O(L23)	0.530
P(3)	1.002	O(L34)	0.158
P(4)	0.806	O(L14)	0.556

No general process of preparation exists for the highest observed rings $[P_{12}O_{36}]^{12-}$, up to now observed in only one class of compounds, whose crystal structure was solved using $V_3C_3P_{12}O_{36}$, (Lavrov et al., 1981).

A comparison of the geometries of the rings observed in the previously investigated cyclooctaphosphates with that found in the title compound will be given in the last section of the present work.

Experimental

Chemical preparation

Chemical preparation of this adduct was performed in two steps. In the first stage, an aqueous solution of $Na_8P_8O_{24} \cdot 6H_2O$ was transformed at room temperature into cyclooctaphosphoric acid by using an Amberlite IRN 77 ion-exchange resin. This acid was then immediately neutralized by a stoichiometric amount of potassium carbonate. The so obtained aqueous solution of potassium cyclooctaphosphate was then concentrated by slow evaporation at room temperature during several days and finally added in stoichiometric proportion to a concentrated aqueous solution of telluric acid. After some days of controlled evaporation, at room temperature, the resulting solution produces large stout triclinic prisms of $Te(OH)_6 \cdot K_8P_8O_{24} \cdot 2H_2O$.

Crystal structure determination

The parameters used for the X-ray diffraction data collection as well as the strategy for the crystal structure determination and its final results are reported in Table 1.

The final atomic coordinates, the values of B_{eq} for non-H atoms and B_{iso} for H-atoms are given in Table 2. The values of the thermal anisotropic

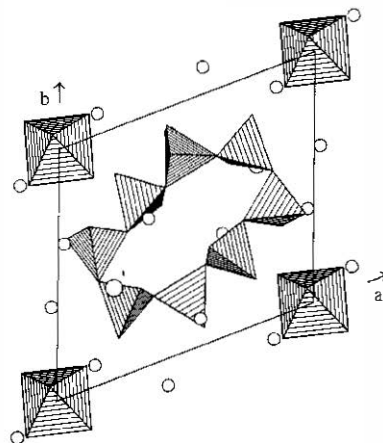


Fig. 1. Projection of the atomic arrangement of $Te(OH)_6 \cdot K_8P_8O_{24} \cdot 2H_2O$ along c . The smaller empty circles represent the potassium atoms and the larger ones water molecules.

displacement parameters refined for non-H atoms and the list of structure factors are deposited.¹

Structure description

As always observed in adducts between monovalent cation phosphates and telluric acid, the phosphoric anion and the $Te(OH)_6$ group are independent entities and so do not share any oxygen atom.

In the present atomic arrangement, the $Te(OH)_6$ group is located around the inversion centre (0, 0, 0). The six oxygen atoms build an almost regular octahedron around the central tellurium atom with three Te-O distances ranging from 1.910 to 1.922 Å and O-Te-O angles spreading between 87.61 and 89.18° (Table 3). The three observed Te-O-H angles, 105, 106 and 120° are in accordance with all the values previously observed in such groups.

¹ Additional material to this paper can be ordered referring to the no. CSD 54239, names of the authors and citation of the paper at Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Four independent PO_4 tetrahedra build the centrosymmetric P_8O_{24} ring anion located around the inversion centre ($1/2, 1/2, 1/2$). Inside this ring the four independent PO_4 tetrahedra have geometrical features quite comparable with all previously reported condensed phosphoric anions. Table 4 summarizes their main characteristics. We shall compare, in the last section of this article, the main features of the present ring with the few other examples of such anions. Table 5 gives the equations of the least-squares planes of the ring calculated for phosphorus atoms only and for a set of atoms including both phosphorus and bonding oxygen atoms. Atom distances from the L. S. planes are in both cases less than 1.002 Å.

Figure 1 gives in projection along the c direction the respective locations of the main components of this atomic arrangement.

The main numerical values observed for distances and bond angles in the hydrogen bond network are reported in Table 3. The telluric groups are not interconnected by H -bonds, all their hydrogen atoms establish, in a three dimensional way, H -bonds with external oxygen atoms of their adjacent phosphoric rings. So, H(1) and H(2) establish H -bridges connecting $Te(OH)_6$ and P_8O_{24} entities along the c direction, while H(3) performs the same type of connections in the (a, b) plane. The two hydrogen atoms of the water molecule connect phosphoric rings along the c direction. It is worth reporting that one of the two hydrogen bonds involving the water molecule is established with a bonding oxygen atom of the phosphoric ring. O(L14), this type of oxygen is rarely observed as acceptor in condensed phosphate crystal chemistry.

The four independent potassium atoms have, within a range of 3.50 Å for the $K-O$ distance, sevenfold for K(1) and eightfold coordinations for K(2), K(3) and K(4). Inside these various polyhedra, the $K-O$ distances vary from 2.582 to 3.472 Å (Table 3). The water molecule is involved in the $K(2)O_8$ and $K(4)O_8$ coordination polyhedra.

The P_8O_{24} ring anion

As said above, only four structural studies of cyclooctaphosphates have been reported before. What we consider as the main geometrical features of a ring framework, $P-P$ distances, $P-O-P$ and $P-P-P$ angles for the five P_8O_{24} rings presently known are reported in Table 6. In front of so few examples, any kind of discussion similar to what was possible with a large number of examples for other smaller rings, P_6O_{18} for instance (Averbuch-Pouchot and Durif, 1991) seems here fruitless. Nevertheless, one can notice that among the five rings presently investigated two have a $2/m$ internal symmetry and three are centrosymmetric. Among the numerical data reported in Table 6 the $P-P$ distances ranging from 2.818 to 3.018 Å and the $P-O-P$ angles spreading from 123.1 to 146.3° are within

Table 6. Main geometrical features in the five $[P_8O_{24}]^{8-}$ ring anions presently investigated.

Formula	P-P (Å)	P-O-P (°)	P-P (Å)	Symmetry	Ref.
$K_2Ca_2P_8O_{24}$	131.4	123.1	2.818	$2/m$	[1]
	138.0	134.4	2.933		
		136.0	2.947		
$Cu_3(NH_4)_2P_8O_{24}$	119.9	129.1	2.888	$\bar{1}$	[2]
	92.1	134.8	2.928		
	112.2	146.3	2.930		
	123.3	134.9	3.018		
$Na_8P_8O_{24} \cdot 6 H_2O$	123.9	138.4	3.011	$\bar{1}$	[3]
	121.0	126.3	2.880		
	147.8	127.3	2.891		
	146.7	128.5	2.902		
$Ag_8NaP_8O_{24}(NO_3)_2 \cdot 4 H_2O$	102.5	133.9	2.958	$2/m$	[4]
	108.7	129.5	2.889		
		128.8	2.900		
		132.4	2.946		
$Te(OH)_6 \cdot K_8P_8O_{24} \cdot 2 H_2O$	107.4	132.4	2.946	$\bar{1}$	[5]
	105.1	132.6	2.939		
	117.5	132.2	2.925		
	111.1	133.3	2.953		

[1] Palkina et al. (1979) [2] Laügt et al. (1975) [3] Schülke et al. (1992a, in press) [4] Averbuch-Pouchot et al. (1992, in press) [5] Present work.

the ranges commonly observed in the cyclophosphate crystal chemistry. The angular deviations of the $P-P-P$ angles from their ideal value for a planar regular ring (135°) are more interesting to examine. In small rings, P_3O_9 , P_4O_{12} , such angles never depart of more than some degrees from their ideal values, 60 or 90° , but when the ring size increases the deviations become very important. So, the $P-P-P$ angles for the P_6O_{18} anions in cyclohexaphosphates (Averbuch-Pouchot and Durif, 1991) vary from 85.9 to 142.8° and are in fact quite comparable with those observed in the few examples of P_8O_{24} rings reported in Table 6 where they spread from 92.1 to 146.7° . These large deviations can be interpreted by the fact that the geometric strains decrease when the ring size increases and so favour the tendency of rings to twist as to become as compact as possible.

References

- Averbuch-Pouchot, M. T., Durif, A.: Present state of cyclohexaphosphate crystal chemistry. *Eur. J. Solid State Chem.* **28** (1991) 9-22.
 Averbuch-Pouchot, M. T., Durif, A.: Structure of silver-sodium cyclooctaphosphate-nitrate tetrahydrate: $Ag_8NaP_8O_{24}(NO_3)_2 \cdot 4 H_2O$. *Acta Crystallogr.* (1992, in press).
 Bagieu-Bucher, M., Durif, A., Guitel, J. C.: $Ba_2Zn_3P_{16}O_{30}$ the first example of a decametaphosphate ring. *J. Solid State Chem.* **40** (1981) 248.

- Bagieu-Beucher, M., Durif, A., Guitel, J. C.: Crystal Structure of a Barium-Zinc Decametaphosphate $Ba_2Zn_3P_{10}O_{30}$. *J. Solid State Chem.* **45** (1982) 159–163.
- Fischer, R. X.: A Fortran Plot Program for Crystal Structure Illustrations in Polyhedral Representation. *J. Appl. Crystallogr.* **18** (1985) 258–262.
- Grunze, I., Chudinova, N. N., Palkina, K. K.: Production of potassium aluminium cyclooctaphosphate $K_2Al_2P_8O_{24}$ and potassium iron cyclooctaphosphate $K_2Fe_2P_8O_{24}$. *Izv. Akad. Nauk SSSR, Neorg. Mater.* **19** (1983) 1943–1945.
- Laügt, M.: Etude du système hinaire $RbPO_3$ - $Cu(PO_3)_2$. *C. R. Acad. Sci.* **278C** (1974a) 1197–1200.
- Laügt, M.: Etude du système binaire $TiPO_3$ - $Cu(PO_3)_2$. *C. R. Acad. Sci.* **278C** (1974b) 1497–1500.
- Laügt, M., Guitel, J. C.: Structure de l'octamétaphosphate de cuivre-ammonium $Cu_3(NH_4)_2P_8O_{24}$. *Z. Kristallogr.* **141** (1975) 203–216.
- Laügt, M., Martin, C.: Etude du système métaphosphate de césium métaphosphate de cuivre. *Mat. Res. Bull.* **7** (1972) 1525–1534.
- Laügt, M., Scory, M., Durif, A.: Etude des systèmes $Cu(PO_3)_2$ - $TiPO_3$ et $Cu(PO_3)_2$ - $RbPO_3$. Données cristallographiques sur $CuTi(PO_3)_3$ et $CuRb(PO_3)_3$. *Mat. Res. Bull.* **3** (1968) 963–970.
- Lavrov, A. V., Nikolacv, V. P., Sadikov, G. G., Voitenkov, M. Ya.: Crystal structure of the cycloduoocaphosphate $Cs_3V_3P_{12}O_{36}$. *Dokl. Akad. Nauk SSSR.* **259** (1981) 103–106.
- Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P., Woolfson, M. M.: MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univ. of York, England, and Louvain, Belgium (1977).
- Palkina, K. K., Maksimova, S. I., Kusnetsov, V. G., Chudinova, N. N.: Crystal structure of the double octametaphosphate $K_7Ga_2P_8O_{24}$. *Dokl. Akad. Nauk SSSR* **245** (1979) 1386–1389.
- Schülke, U.: Preparation of Octometaphosphates, $M_8^I P_8 O_{24}$. *Angew. Chem., Internat. Edit.* **7** (1968a) 71.
- Schülke, U.: Darstellung von Oktametaphosphaten, $M_8^I P_8 O_{24}$. *Z. Anorg. Allg. Chem.* **360** (1968b) 231–246.
- Schülke, U., Averbuch-Pouchot, M. T., Durif, A.: Crystal structure of sodium cyclooctaphosphate hexahydrate, $Na_8P_8O_{24} \cdot 6 H_2O$. *J. Solid State Chem.* (1992a, in press).
- Schülke, U., Averbuch-Pouchot, M. T., Durif, A.: Preparation and crystal structure of potassium cyclodécaphosphate tetrahydrate, $K_8P_8O_{24} \cdot 4 H_2O$. *Z. Anorg. Allg. Chem.* (1992b, in press).
- Schülke, U., Kayser, R.: Zur thermischen Dehydratisierung von Lithiumdihydrogenphosphat, -hydrogendiphosphat und -cyclophosphat-hydraten. *Z. Anorg. Allg. Chem.* **531** (1985) 167–176.
- Structure Determination Package RSX11M 1979 Version, Enraf-Nonius, The Netherlands.

Zeitschrift für Kristallographie

International Journal for Structural, Physical,
and Chemical Aspects of Crystalline Materials

Editors-in-Chief: H. Schulz, H. G. von Schnering.
With the assistance of W. Hönle

Editorial Board: G. Bergerhoff, E. F. Bertaut, G. Ferguson, M. L. Fornasini,
H. Fuess, M. Hart, P. Hartman, S. Haussühl, R. J. Hill,
K. Huml, R. A. Jacobson, Jiang Min-hua, F. Liebau,
E. Parthé, P. Paufler, S. Rundqvist, L. A. Shuvalov,
J. J. Stezowski, Y. Takéuchi, E. Tillmanns

Please send manuscripts to one of the following addresses:

Professor Dr. G. Bergerhoff Institut für Anorganische Chemie, Universität Bonn
Gerhard-Domagk-Straße 1, W-5300 Bonn 1, F.R.G.

Professor Dr. E. F. Bertaut Laboratoire de Cristallographie, CNRS Grenoble, 25, Avenue
des Martyrs, B.P. 166X, Centre de Tri, F-38042 Grenoble Cedex, France

Professor Dr. G. Ferguson Department of Chemistry, University of Guelph,
Ontario N1G 2W1, Canada

Professor Dr. M. L. Fornasini Università di Genova, Istituto di Chimica Fisica
Corso Europa 26, I-16132 Genova, Italy

Professor Dr. H. Fuess Fachbereich Materialwissenschaften, Fachgebiet Strukturforchung,
Technische Hochschule Darmstadt, Petersenstr. 20,
W-6100 Darmstadt 1, F.R.G.

Professor Dr. M. Hart FRS Department of Physics, Schuster Laboratory
The University, Manchester M13 9PL, U.K.

Professor Dr. P. Hartman Instituut voor Aardwetenschappen
Budapestlaan 4, Postbus 80 021, NL 3508 TA Utrecht, Netherlands

Professor Dr. S. Haussühl Institut für Kristallographie, Universität Köln
Zùlpicher Straße 49, W-5000 Köln 1, F.R.G.

Dr. R. J. Hill CSIRO Division of Mineral Products,
P.O. Box 124, Port Melbourne, Victoria 3207, Australia

Dr. W. Hönle Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1, W-7000 Stuttgart 80, F.R.G.

Professor Dr. K. Huml Institute of Macromolecular Chemistry, Czechoslovak
Academy of Sciences, CSFR-16206 Prague 6, Czechoslovakia

Professor Dr. R. A. Jacobson Iowa State University, Department of Chemistry, Gilman Hall,
Ames, Iowa 50011-3111, USA

Professor Jiang Min-hua Institute of Crystal Materials, Shandong University
Jinan Shandong, P.R.C.

Professor Dr. F. Liebau Mineralogisch-Petrographisches Institut
Schlaugstraße 40-60, W-2300 Kiel, F.R.G.

Professor Dr. Dr. h.c. E. Parthé Laboratoire de Cristallographie aux Rayons X, Université de Genève,
24 quai Ernest Ansermet, CH-1211 Genève, Switzerland.

Professor Dr. P. Paufler Abteilung Physik, Fakultät für Naturwissenschaften und Mathematik,
Technische Universität Dresden, Mommsenstr. 13, D-8027 Dresden, F.R.G.

Professor St. Rundqvist University of Uppsala, Institute of Chemistry
Box 531, S-751 21 Uppsala 1, Sweden.

Professor Dr. Dr. h.c. H. G. von Schnering Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1, W-7000 Stuttgart 80, F.R.G.

Professor Dr. H. Schulz Institut für Kristallographie und Mineralogie der Universität
München, Theresienstraße 41, W-8000 München 2, F.R.G.

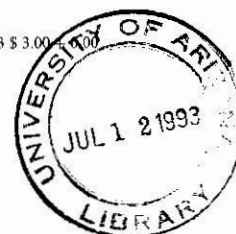
Professor Dr. L. A. Shuvalov Institute of Crystallography, Academy of Sciences of the USSR
Leninsky pr. 59, Moscow 117333, CIS

Professor Dr. J. J. Stezowski Department of Chemistry, University of Nebraska,
Hamilton Hall, Lincoln NE 68588-0304, USA

Professor Dr. Y. Takéuchi Department of Earth Sciences, Nihon University 3-25-40 Sakurajosui,
Setagayaku, Tokyo 156, Japan. Telex: Nichidai J 29496

Professor Dr. E. Tillmanns Institut für Mineralogie und Kristallographie, Universität Wien,
Dr.-Karl-Lueger-Ring 1, A-1010 Wien, Österreich

Zeitschrift für Kristallographie 203, 1-15 (1993)
© by R. Oldenbourg Verlag, München 1993 - 0044-2968/93 \$ 3.00



X-ray powder diffraction of Ag_2Te at temperatures up to 1123 K

J. Schneider and H. Schulz

Institut für Kristallographie und Mineralogie, Universität München, Theresienstraße 41,
D-8000 München 2, Federal Republic of Germany

Received: April 4, 1991, in revised form October 10, 1991

**Ag_2Te / X-ray diffraction / Rietveld refinement / Fast ion conductors /
Anharmonic temperature factors**

Abstract. X-ray powder diffraction was performed on $\beta\text{-Ag}_2\text{Te}$ at room temperature, on ion conducting $\alpha\text{-Ag}_2\text{Te}$ at 523 K, 723 K and 923 K respectively and on $\gamma\text{-Ag}_2\text{Te}$ at 1123 K.

Rietveld profile refinement of $\beta\text{-Ag}_2\text{Te}$ confirmed the space group $P2_1/c$ and the positional parameters of the model of Fröhlich (Z. Kristallogr. 112 (1959) 44-52).

For the α -modification in space group $Fm\bar{3}m$, best results were obtained for a model with a statistical distribution of Ag ions: about 60% of the available Ag ions were placed into $32f(x,x,x)$ positions around the tetrahedral $8c(1/4, 1/4, 1/4)$ sites and the remainder on the $48i(x,x,1/2)$ positions. The probability density function (PDF) calculated with these formal structure parameters suggests next neighbour jumps of Ag ions via the $48i$ sites.

The first structure refinement of $\gamma\text{-Ag}_2\text{Te}$ showed it to crystallize in space group $Im\bar{3}m$ and to be iso-structural to $\alpha\text{-AgI}$. Third order anharmonic coefficients of the temperature factor of the Ag ions could be refined from our X-ray powder data. Corresponding PDF maps show Ag-densities bridging next nearest as well as second next nearest neighbours.

Introduction

Fast silver ion conductors exhibiting the cubic body centered structure like $\alpha\text{-AgI}$ and its structural derivatives, $\alpha\text{-Ag}_2\text{S}$ or $\alpha\text{-Ag}_2\text{Se}$, have attracted much attention (Chandra, 1981). The cubic face centered compound $\alpha\text{-Ag}_2\text{Te}$ however, was investigated to a much lesser extent. According to

4 33866 SDI: JRC
35 U/A 10/06/94 526-