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Silver–Potassium Cyclodecaphosphate Decahydrate, $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$: A New Example of a Phosphoric 10-Member Ring Anion

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Chemical preparation and atomic arrangement of $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$ are described. The title compound is triclinic, space group $P\bar{1}$, with $a = 14.267(7)$, $b = 7.305(1)$, and $c = 10.319(4)$ Å, $\alpha = 105.38(5)°$, $\beta = 101.03(5)°$, $\gamma = 87.51(5)°$, and $Z = 1$. The main structural interests rest on the existence in the atomic arrangement of a rare type of phosphoric ring anion, $(P_{10}O_{30})^{10-}$, and on an arrangement of Ag_4O_{10} clusters in which silver atoms have a very unusual fourfold coordination. The phosphoric ring anion observed in the title compound is the first example of a centrosymmetrical $(P_{10}O_{30})^{10-}$ group. A comparison of the geometries of the three $(P_{10}O_{30})^{10-}$ presently known is given.

Introduction

Cyclodecaphosphates are very rare compounds. Until recently, the only reported example was $Ba_2Zn_3P_{10}O_{30}$, characterized during the investigation of the BaO–ZnO–P_2O_5 system (*1*). When attempting to prepare by a flux method single crystals of $Ba_2Zn(PO_3)_2$, a long-chain polyphosphate appearing in the $Ba(PO_3)_2$–$Zn(PO_3)_2$ phase-equilibrium diagram, the authors obtained a new species they identified as being probably a cyclodecaphosphate, $Ba_2Zn_3P_{10}O_{30}$. The geometrical nature of the anion was confirmed by the crystal structure determination (*2, 3*), confirming the first assumption. It is worth noting that this compound does not appear in the phase diagram. All attempts to elaborate from this compound a starting material permitting convenient preparations of cyclodecaphosphates failed until very recently when Schülke (*4*) succeeded in producing alkali salts in a reproducible way. Since the elaboration of this process, an accurate structure determination of the potassium salt $K_{10}P_{10}O_{30} \cdot 4H_2O$ has been performed by the present authors (*5*).

It is well known that the major developments in the crystal chemistry of water-

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TABLE I

CRYSTAL DATA AND EXPERIMENTAL PARAMETERS USED FOR THE INTENSITY DATA COLLECTION AND STRATEGY AND FINAL RESULTS OF THE STRUCTURE DETERMINATION

I. Crystal data	
Formula: $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$	F_w = 1635.944
Crystal system: triclinic	Space group: $P\bar{1}$
a = 14.267(7), b = 7.305(1), c = 10.319(4) Å	V = 1017.8(1.5) Å^3
α = 105.38(5)°, β = 101.03(5)°, γ = 87.51(5)°	Z = 1
Unit cell refined from 18 reflections ($10.3° < \theta < 14°$)	
ρ_{cal} = 2.669 g · cm^{-3}	$F(000)$ = 792
Linear absorption factor: $\mu(AgK\alpha)$ = 1.511 mm^{-1}	
Morphology: triclinic plate	
Crystal size: 0.64 × 0.64 × 0.24 mm	
II. Intensity measurements	
Temperature: 293 K	Wavelength: $AgK\alpha$ (0.5608 Å)
Diffractometer: Philips PW1100	Scan mode: $\omega/2\theta$
Monochromator: graphite plate	Scan width: 1.20°
Scan speed: 0.02° · sec^{-1}	θ range: 3°–25°
Total background measuring time: 10 sec	
Total number of scanned reflections: 9285	
Total number of nonzero reflections ($\pm h \pm k l$): 6746	
Number of unique reflections: 6600 (h_{max} = 23, k_{max} = 12, l_{max} = 15)	
Intensity and orientation reference reflections, every 4 hr: no variation	
III. Structure determination	
Lorentz and polarization corrections	No absorption correction
Program used: SDP (*7*)	Computer used: MicroVax II
Determination: direct methods with MULTAN (*8*)	
f, $\Delta f'$, and $\Delta f''$ from "International Tables for X-Ray Crystallography" (*9*)	
Unique reflections included: 3987 with $I > 9\sigma(I)$	
Weighting scheme: unitary	Refined parameters: 271
Unweighted agreement factor R: 0.046	
Weighted agreement factor R_w: 0.053	
e.s.d.: 2.274	Largest shift/error = 0.01
Drawings made with STRUPLO (*10*)	

soluble cyclophosphates were bonded to the generalization of the metathesis reaction described by Boullé (*6*) involving the silver salt as starting material. With the purpose of applying this type of reaction to the syntheses of new cyclodecaphosphates, we began investigations to produce a convenient silver salt. During these attempts we identified a mixed monovalent cation compound, $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$. The description of its atomic arrangement is the aim of the present paper.

Experimental

$Ag_4K_6P_{10}O_{30} \cdot 10H_2O$ was prepared by addition of a diluted silver nitrate aqueous solution to a solution of potassium decacyclophosphate until the apparition of a persistent very light turbidity. The crystals appear as large triclinic plates, very often imbricated, after some days of controlled evaporation at room temperature. For the X-ray data collection a small rectangular parallelepiped was cut from such a crystal. All the main

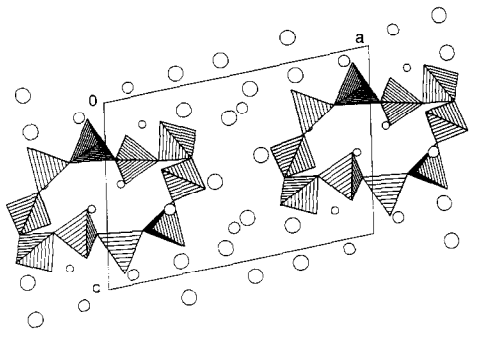

FIG. 1. Projection along the *b* direction of the atomic arrangement of $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$. The smallest circles symbolize the silver atoms, the intermediate ones the potassium atoms, and the largest ones the water molecules.

crystalline characteristics and experimental conditions for the X-ray data collection as well as the strategy and results of the crystal structure are summarized in Table I. Crystals are not stable for a long time at room temperature and an important fading of the intensity reference reflections (25%) was observed during intensity data collection and corrected during data reduction. Final atomic coordinates and B_{eq} are given in Table II.

TABLE II

FINAL ATOMIC COORDINATES AND B_{eq} FOR $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$

Atoms	*x*	*y*	*z*	B_{eq}
Ag(1)	0.05641(4)	0.30269(8)	−0.55180(6)	2.44(1)
Ag(2)	0.85582(4)	0.79115(8)	0.83806(6)	2.20(1)
K(1)	0.9061(1)	0.3866(2)	0.0538(1)	1.84(2)
K(2)	0.2388(1)	0.6756(2)	0.6427(2)	2.52(3)
K(3)	0.5207(1)	0.7270(3)	0.1867(2)	2.71(3)
P(1)	−0.0937(1)	0.3093(2)	−0.3273(2)	1.19(2)
P(2)	−0.0459(1)	−0.0597(2)	0.2020(2)	1.24(2)
P(3)	0.2144(1)	0.2049(2)	−0.2636(2)	1.48(3)
P(4)	0.2918(1)	0.1917(2)	−0.5052(2)	1.53(3)
P(5)	0.2713(1)	−0.1719(2)	0.2826(2)	1.39(3)
O(E11)	0.0746(4)	0.6466(6)	0.4527(4)	1.84(8)
O(L12)	0.0370(4)	0.8796(6)	0.3120(5)	1.73(8)
O(L15)	0.7981(3)	0.2346(6)	0.6308(4)	1.70(8)
O(E12)	0.0798(4)	0.5412(6)	0.1958(5)	1.80(9)
O(E21)	−0.0232(4)	0.1390(6)	0.2077(5)	2.00(9)
O(E22)	0.0623(4)	0.2102(6)	0.9291(4)	1.86(9)
O(L23)	0.1354(3)	0.0468(6)	0.7234(5)	1.77(8)
O(E31)	0.1690(4)	0.3873(6)	0.7251(5)	2.4(1)
O(E32)	0.7076(4)	0.8009(8)	0.1460(5)	2.6(1)
O(L34)	0.7480(4)	0.9019(6)	0.4014(5)	2.13(9)
O(E41)	0.2116(4)	0.2807(7)	0.4182(5)	2.5(1)
O(E42)	0.3761(4)	0.3083(8)	0.5694(5)	2.7(1)
O(E51)	0.2129(4)	0.8893(7)	0.1658(5)	2.07(9)
O(E52)	0.6546(4)	0.3190(7)	0.7440(5)	2.14(9)
O(L45)	0.3258(3)	0.0051(6)	0.3967(5)	1.63(8)
O(W1)	0.6971(4)	0.6965(8)	0.8673(6)	2.9(1)
O(W2)	0.5535(5)	0.340(1)	0.0924(7)	4.2(2)
O(W3)	0.7233(5)	0.1437(8)	0.0722(5)	3.0(1)
O(W4)	0.5867(5)	0.3375(9)	0.4548(7)	3.6(1)
O(W5)	0.4706(5)	0.1086(9)	0.2226(7)	4.1(2)

Note. Estimated standard deviations are given in parentheses. $B_{eq} = \frac{4}{3} \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{b}_j \cdot \beta_{ij}$.

Structure Description

Figures 1 and 2 give two different projections of this atomic arrangement, one along the *b* axis the other one along *c*.

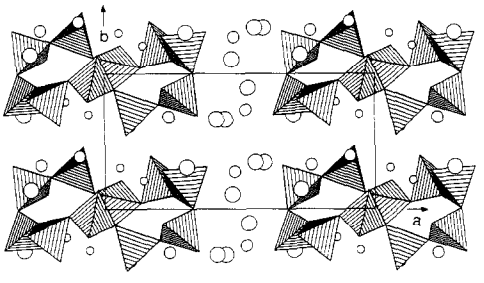

FIG. 2. Projection along the *c* direction of the atomic arrangement of $Ag_4K_6P_{10}O_{30} \cdot 10H_2O$. The smallest circles symbolize the silver atoms, the intermediate ones the potassium atoms, and the largest ones the water molecules.

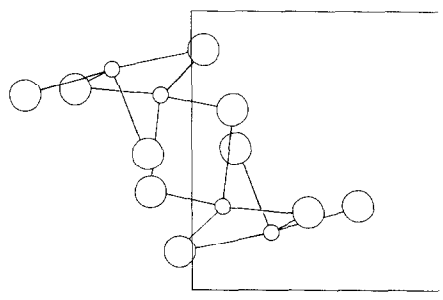

FIG. 3. Projection along the *c* direction of the Ag_4O_{10} cluster situated around the $(0, \frac{1}{2}, \frac{1}{2})$ inversion center.

TABLE III

MAIN INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN THE $(P_{10}O_{30})^{10-}$ RING

The $P(1)O_4$ tetrahedron				
P(1)	O(E11)	O(L12)	O(L15)	O(E12)
O(E11)	1.488(5)	2.496(7)	2.433(7)	2.571(6)
O(L12)	107.8(3)	1.598(5)	2.478(6)	2.549(6)
O(L15)	103.9(3)	101.6(3)	1.599(5)	2.534(6)
O(E12)	119.7(3)	111.5(2)	110.5(3)	1.485(4)
The $P(2)O_4$ tetrahedron				
P(2)	O(L12)	O(E21)	O(E22)	O(L23)
O(L12)	1.609(5)	2.464(7)	2.548(6)	2.473(7)
O(E21)	105.5(2)	1.484(5)	2.593(6)	2.459(8)
O(E22)	110.8(2)	121.7(3)	1.485(4)	2.533(7)
O(L23)	100.8(3)	105.7(3)	110.3(3)	1.600(5)
The $P(3)O_4$ tetrahedron				
P(3)	O(L23)	O(E31)	O(E32)	O(L34)
O(L23)	1.611(5)	2.548(7)	2.517(7)	2.386(8)
O(E31)	111.1(3)	1.479(5)	2.574(8)	2.546(7)
O(E32)	108.5(3)	120.2(3)	1.490(5)	2.500(7)
O(L34)	95.7(3)	111.1(3)	107.5(3)	1.608(5)
The $P(4)O_4$ tetrahedron				
P(4)	O(L34)	O(E41)	O(E42)	O(L45)
O(L34)	1.610(6)	2.533(8)	2.504(8)	2.436(7)
O(E41)	109.6(3)	1.488(5)	2.541(7)	2.524(7)
O(E42)	108.8(3)	118.5(3)	1.467(5)	2.480(6)
O(L45)	99.3(3)	110.3(2)	108.6(3)	1.587(4)
The $P(5)O_4$ tetrahedron				
P(5)	O(L15)	O(E51)	O(E52)	O(L45)
O(L15)	1.608(6)	2.529(7)	2.523(7)	2.466(7)
O(E51)	109.4(3)	1.489(5)	2.566(7)	2.562(6)
O(E52)	109.3(3)	119.3(3)	1.485(5)	2.463(6)
O(L45)	100.1(2)	111.5(3)	105.4(2)	1.609(4)

P(1)–P(2)	2.986(2)	P(1)–O(L15)–P(5)	131.5(3)
P(1)–P(5)	2.925(2)	P(2)–O(L23)–P(3)	130.1(3)
P(2)–P(3)	2.911(3)	P(3)–O(L34)–P(4)	127.9(3)
P(3)–P(4)	2.891(3)	P(4)–O(L45)–P(5)	134.2(3)
P(4)–P(5)	2.945(2)	P(1)–O(L12)–P(2)	137.1(3)

P(2)–P(1)–P(5)	99.83(7)
P(1)–P(2)–P(3)	96.01(7)
P(2)–P(3)–P(4)	136.90(7)
P(3)–P(4)–P(5)	116.34(8)
P(1)–P(5)–P(4)	99.40(7)

Note. Estimated standard deviations are given in parentheses.

The $(P_{10}O_{30})^{10-}$ Ring Anion

The phosphoric ring is centrosymmetrical, located around the (0, 0, $\frac{1}{2}$) inversion center and so is built of five independent PO_4 tetrahedra. Interatomic distances and bond angles in this ring given in Table III are not significantly different from those observed in the two previously reported cyclodecaphosphates.

The Ag_4O_{10} Clusters

The silver atoms are not dispersed inside the atomic arrangement but assemble around the inversion centers to form clusters containing four silver atoms. Inside such a cluster the Ag–Ag distances are 3.265 and 3.321 Å. Each silver atom has four oxygen neighbors assembled to establish a unusual coordination. Inside an AgO_4 entity the silver atom and three of the oxygen atoms are almost coplanar with O–Ag–O angles close to 90° while the fourth oxygen atom establishes an Ag–O bond almost perpendicular to this plane (Table IV). These AgO_4 groups are connected by edge-sharing to build a centrosymmetrical cluster of formula Ag_4O_{10}. Such an assembly is represented in Fig. 3 in projection along the *c* axis. As far as we know such a configuration has not yet been observed in silver salts.

The KO_n Polyhedra

The three independent potassium atoms have different coordination polyhedra (Table IV). Within a range of 3.50 Å, one of them, K(1), has a sevenfold coordination made by six oxygen atoms and one water molecule; the second one, K(2), has eight neighbors, including two water molecules; and the last one, K(3), has only six neighbors, among which are three water molecules. In this last polyhedron, the six K–O distances are relatively shorter than those in the first two polyhedra. It is to be noticed that in the coordination polyhedron of K(2) are involved two bonding oxygen atoms of the phosphoric ring, O(L15) and O(L23), a fact not very common in condensed phosphates.

Geometry of the $P_{10}O_{30}$ Ring Anions

As we said before, $P_{10}O_{30}$ ring anions are very rare. Including the ring observed in the title compound, one can only report three examples. So with so few data, any kind of

TABLE IV

MAIN INTERATOMIC DISTANCES (Å) IN THE COORDINATION POLYHEDRA OF SILVER AND POTASSIUM ATOMS

The AgO_4 polyhedra			
Ag(1)–O(E11)	2.524(5)	Ag(1)–O(E21)	2.519(4)
Ag(1)–O(E11)	2.269(5)	Ag(1)–O(E41)	2.287(6)
O(E11)–Ag(1)–O(E11)	94.3(2)	O(E11)–Ag(1)–O(E21)	106.0(2)
O(E11)–Ag(1)–O(E41)	84.0(2)	O(E11)–Ag(1)–O(E21)	98.8(2)
O(E11)–Ag(1)–O(E41)	162.1(2)	O(E21)–Ag(1)–O(E41)	98.8(2)
Ag(2)–O(E12)	2.518(4)	Ag(2)–O(E21)	2.618(6)
Ag(2)–O(E41)	2.555(5)	Ag(2)–O(W1)	2.491(7)
O(E12)–Ag(2)–O(E21)	82.4(1)	O(E12)–Ag(2)–O(E41)	89.6(2)
O(E12)–Ag(2)–O(W1)	93.4(2)	O(E21)–Ag(2)–O(E41)	89.8(2)
O(E21)–Ag(2)–O(W1)	174.9(1)	O(E41)–Ag(2)–O(W1)	87.4(2)
The KO_n polyhedra			
K(1)–O(E12)	2.746(5)	K(1)–O(E31)	2.804(5)
K(1)–O(E12)	2.807(5)	K(1)–O(E51)	2.912(4)
K(1)–O(E22)	2.872(5)	K(1)–O(W3)	3.279(7)
K(1)–O(E22)	2.953(5)		
K(2)–O(E11)	2.727(5)	K(2)–O(E41)	3.170(5)
K(2)–O(L15)	3.009(5)	K(2)–O(E42)	3.262(6)
K(2)–O(L23)	3.024(5)	K(2)–O(W3)	2.843(5)
K(2)–O(E31)	2.758(6)	K(2)–O(W4)	2.847(8)
K(3)–O(E32)	2.873(6)	K(3)–O(W2)	2.782(7)
K(3)–O(E42)	2.732(6)	K(3)–O(W2)	2.790(7)
K(3)–O(E52)	2.785(6)	K(3)–O(W5)	2.793(7)
The water molecule organization			
O(W1)–O(E32)	2.749(8)	O(W2)–O(W3)	2.777(10)
O(W1)–O(E52)	2.753(7)	O(W2)–O(W5)	2.839(12)
O(W1)–O(W5)	2.858(9)		
O(W3)–O(E32)	2.833(9)	O(W4)–O(E42)	2.748(9)
O(W3)–O(E51)	2.727(8)	O(W4)–O(E52)	2.994(9)

Note. Estimated standard deviations are given in parentheses.

discussion similar to what was possible with a good number of compounds for other smaller rings, P_6O_{18} for example (*11*), seems fruitless here. Nevertheless we report in Table V what we consider the main geometrical features of a ring framework, P–P distances, and P–O–P and P–P–P angles for the three rings presently known.

Among the numerical values reported in Table V, the P–P distances ranging from 2.870 to 3.011 Å and the P–O–P angles between 123.3° and 144.3° are within the ranges commonly observed in the cyclophosphate crystal chemistry. The values reported in the same table for the P–P–P angles can appear very dispersed since they vary from 86.6° to 136.9° but are in fact quite comparable to the range of values observed in cyclohexaphosphates (85.9° to 142.8°) (*11*).

Two of the three rings reported in Table V have a twofold internal symmetry but have in fact fundamentally different geometries; in $Ba_2Zn_3P_{10}O_{30}$ the binary axis is perpendicular to the mean plane formed by the phosphorus atoms, while in the case of

TABLE V

MAIN GEOMETRICAL DATA OF THE $P_{10}O_{30}$ RING ANIONS

Formula	P–P–P (°)	P–O–P (°)	P–P (Å)	Symmetry	Ref.
$Ba_2Zn_3P_{10}O_{30}$	112.9	130.0	2.915	2	(3)
	102.1	133.8	2.915		
	131.9	144.3	3.002		
	99.7	123.3	2.838		
	126.6	128.6	2.870		
$K_{10}P_{10}O_{30} \cdot 4H_2O$	86.6	137.1	3.011	2	(5)
	111.5	133.1	2.950		
	133.3	128.9	2.911		
	107.1	131.3	2.936		
	90.5	134.9	2.963		
		138.2	3.006		
$Ag_4K_6P_{10}O_{30} \cdot 10H_2O$	99.8	131.5	2.986	$\bar{1}$	Present study
	96.0	130.1	2.925		
	136.9	127.9	2.911		
	116.3	134.2	2.891		
	99.4	137.1	2.945		

$K_{10}P_{10}O_{30} \cdot 4H_2O$ the binary axis is parallel to this mean plane after passing through two centrosymmetrical bonding oxygen atoms of the ring.

Additional materials, lists of anisotropic thermal parameters, and calculated and observed structure factors can be obtained on request to the authors.

References

1. M. BAGIEU-BEUCHER AND N. EL. HORR, private communication.
2. M. BAGIEU-BEUCHER, A. DURIF, AND J. C. GUITEL, *J. Solid State Chem.* **40,** 248 (1981).
3. M. BAGIEU-BEUCHER, A. DURIF, AND J. C. GUITEL, *J. Solid State Chem.* **45,** 159 (1982).
4. U. SCHÜLKE, to be published.
5. U. SCHÜLKE, M. T. AVERBUCH-POUCHOT, AND A. DURIF, *Z. Anorg. Allg. Chem.*, in press.
6. A. BOULLE, *C.R. Acad. Sci.* **206,** 517 (1938).
7. "Structure Determination Package," Version RSX11M. Enraf–Nonius, Delft, The Netherlands (1977).
8. P. MAIN, L. LESSINGER, M. M. WOOLFSON, G. GERMAIN, AND J. P. DECLERQ, "MULTAN77: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Universities of York, England, and Louvain, Belgium (1977).
9. D. T. CROMER AND J. T. WEBER, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England (1974).
10. R. X. FISCHER, *J. Appl. Crystallogr.* **18,** 258 (1985).
11. M. T. AVERBUCH-POUCHOT AND A. DURIF, *Eur. J. Solid State Inorg. Chem.* **28,** 9 (1991).