Structural Investigation of a New Series of Long-Chain Polyphosphates. Crystal Structure of AgK(PO$_3$)$_2$ and Crystal Data for AgM(PO$_3$)$_2$ with M = K, Rb, Cs, and Tl

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abstract

Single crystals of four isotypic AgM(PO$_3$)$_2$ compounds (M = K, Rb, Cs, and Tl) have been prepared by flux methods. Crystal structure determination, performed with the silver–potassium salt, shows these four compounds are long-chain polyphosphates. AgK(PO$_3$)$_2$ is monoclinic, $P2_1/a$, with $Z = 4$ and the following unit cell dimensions: $a = 7.490(6)$, $b = 13.175(10)$, $c = 6.037(5)$ Å, $\beta \approx 94.32(6)°$. The final R value is 0.031 for 1887 independent reflections. Infinite (PO$_3$)$_n$ chains are directed along the a direction with a period of four tetrahedra, while associated cations form very corrugated layers waving between the phosphoric chains. © 1993 Academic Press, Inc.

Introduction

A great number of long-chain polyphosphates were characterized during the elaboration of the MPO$_3$–M'PO$_3$ phase-equilibrium diagrams and afterwards structurally investigated.

All the LiPO$_3$–MPO$_3$ systems are now well established. For M = Na and Ag, no intermediate compound appears. The first of these diagrams (*1*) shows the existence of solid solutions, with a minimum on the solid-solution curve for 50% LiPO$_3$ (749 K), while the second one (*2*) is of the eutectic type (30% LiPO$_3$, 683 K). In all the other ones, a 1/1 intermediate compound is observed. In the LiPO$_3$–KPO$_3$ system, first investigated by Mardirosova and Bukhalova (*1*) and later revised by El-Horr *et al.* (*3*), LiK(PO$_3$)$_2$ appears as a congruent melting compound (m. p. = 827 K), with two crystalline forms and

a transition temperature of 582 K. Li PO$_3$–RbPO$_3$ diagram was established by Cavero-Ghersi (*2*), LiPO$_3$–CsPO$_3$, first elaborated by Mardirosova and Bukhalova (*1*), was later revised by Cavero-Ghersi (*2*) and LiPO$_3$–TlPO$_3$ was also elaborated by Cavero-Ghersi (*2*). LiRb(PO$_3$)$_2$ and LiCs(PO$_3$)$_2$ are the only intermediate compounds characterized in the first two systems. Both are congruent melting compounds with m. p. = 893 K (Rb) and 963 K (Cs). The Li PO$_3$–TlPO$_3$ system shows the existence of two polyphosphates, LiTl(PO$_3$)$_2$ and Li$_2$ Tl(PO$_3$)$_3$, both incongruent melting compounds decomposing at respectively 723 and 645 K. In addition, Li$_2$Rb(PO$_3$)$_3$ and Li$_2$Cs(PO$_3$)$_3$ (*4*), not observed in the phase-equilibrium diagrams, were afterwards characterized as long-chain polyphosphates isotypic with Li$_2$NH$_4$(PO$_3$)$_3$ (*5*).

In the domain of the NaPO$_3$–MPO$_3$ sys-

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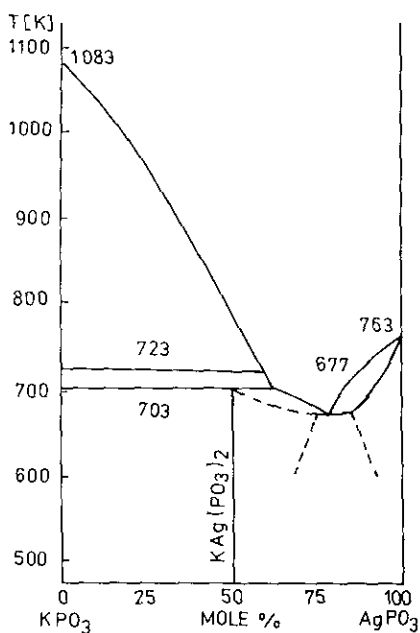All rights of reproduction in any form reserved.

FIG. 1. Equilibrium diagram of the system KPO_3–$AgPO_3$ as determined by (1). The $\alpha \rightarrow \beta$ transformation of KPO_3 appears at 723 K on the left part of the diagram.

at 435°C. No assumption was made as to the nature of the anion. The last study found in the previous literature is the investigation of the $AgPO_3$–$NaPO_3$ system (8). Once more, only one intermediate phase was characterized, again the 1 : 1 compound, $AgNa(PO_3)_2$ melting congruently at 530°C. Figure 3 reports this diagram.

In the present work, we describe a process for the preparation of single crystals of the $AgM(PO_3)_2$ compounds for $M = K$, Rb, Cs, and Tl, and show, through a systematic crystallographic investigation, they are isotypes. The crystal structure determination of the silver–potassium salt confirms the previous assumption of (6) by the nature of the phosphoric anion. In the case of lithium, as would be expected from the Ag PO_3–$LiPO_3$ phase diagram elaborated by (9) which is a simple eutectic system ($LiPO_3$ 50%, 476°C), no compound could be obtained. All attempts to reproduce the silver-

tems, it is interesting to note that no long-chain polyphosphate has been observed as an intermediate compound. All the characterized compounds, $Na_2KP_3O_9$, $Na_2RbP_3O_9$, ..., are cyclotriphosphates.

Previous to the present investigation, a few $AgPO_3$–MPO_3 phase-equilibrium diagrams have been elaborated but never complemented by crystal data. The Ag PO_3–KPO_3 system, reported in Fig. 1, was examined by Savenkova et al. (6). It shows the existence of only one compound, Ag $K(PO_3)_2$, melting incongruently at 430°C. By chromatographic and spectroscopic considerations, the authors assumed this compound was a long-chain polyphosphate. A second phase diagram, studied by Savenkova et al. (7), examines the $AgPO_3$–$RbPO_3$ system and is depicted in Fig. 2. Here also, the only observed intermediate phase was a 1 : 1 compound, $AgRb(PO_3)_2$, decomposing
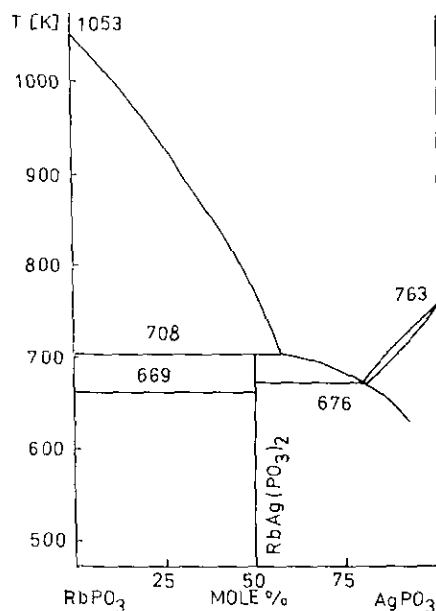

FIG. 2. Phase diagram of the system $RbPO_3$–$AgPO_3$ as determined by (2). The $\alpha \rightarrow \beta$ transformation of $RbPO_3$ appears at 669 K on the left part of the diagram.

TABLE I

OPTIMIZED RATIOS OF STARTING COMPONENTS FOR THE CRYSTAL GROWTH OF THE $AgM(PO_3)_2$ COMPOUNDS, WITH M = K, Rb, Cs, Tl

Metal	M_2CO_3 (g)	Ag_2O (g)	H_3PO_4 (cm³)
K	1.2	2.0	3.5
Rb	1.7	1.0	3.5
Cs	2.0	1.0	3.0
Tl	2.5	1.0	3.0

sodium salt failed. All the crystals were proven to belong to various terms of a solid solution between silver and sodium polyphosphates.

Experimental

A. Chemical Preparations and Crystal Data

All the crystals were prepared by a flux method involving, as starting materials, silver oxide (Ag_2O), H_3PO_4 monophosphoric acid and the corresponding alkali or thallium carbonates. All starting materials were analytical reagent chemicals: H_3PO_4, (85%) Prolabo-R. P. Normapur; Ag_2O, (>99%) Aldrich-Chemie; K_2CO_3, (>99%) Prolabo-R. P. Normapur; Rb_2CO_3, (99%) Prolabo-R. P. Rectapur; Tl_2CO_3, (98%) Merck.

The optimized initial ratios are reported in Table I. All the experiments were run in open graphite crucibles at 350°C. Crystals appeared in the flux after 1 day of heating at
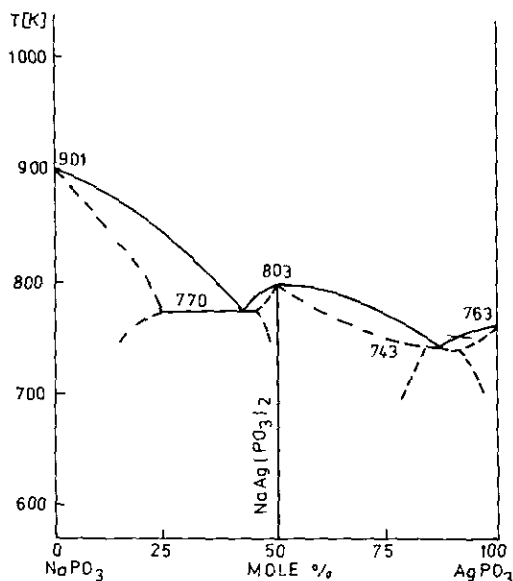

FIG. 3. The $NaPO_3$–$AgPO_3$ system as determined by (3).

this temperature. They were then isolated by removing the excess of the phosphoric flux with hot water and filtration. In all cases, they were monoclinic prisms with a pseudo-hexagonal section. The crystals had a relatively high hardness and all attempts to grind them produced very resistant fibers, prohibiting the collection of X-ray diffraction powder diagrams; therefore the unit-cell dimensions of these compounds were determined using a CAD4 four-cycle diffractometer operating with Ag ($K\alpha$) radiation. These data are presented in Table II.

TABLE II

CELL PARAMETERS OF THE $AgM(PO_3)_2$ COMPOUNDS, WITH M = K, Rb, Cs, Tl

Formula	a(Å)	b(Å)	c(Å)	β(°)	V(Å³)
$AgK(PO_3)_2$	7.490(6)	13.175(10)	6.037(5)	94.32(6)	594(1)
$AgRb(PO_3)_2$	7.512(6)	13.355(10)	6.183(5)	95.76(6)	617(1)
$AgCs(PO_3)_2$	7.398(6)	13.602(10)	6.434(5)	97.42(6)	642(1)
$AgTl(PO_3)_2$	7.436(6)	13.331(10)	6.161(5)	96.13(6)	607(1)

TABLE III

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

Crystal data

Formula: $AgK(PO_3)_2$ F_w = 304.912
Crystal system: monoclinic   Space group: $P2_1/a$
a = 7.490(6), b = 13.175(10) V = 594(1) Å^3
c = 6.037(5) Å, β = 94.32(6)° Z = 4
Unit cell refined from 18 reflections (10.50 < θ < 11.40°)
ρ_{cal} = 3.409 g cm^{-3} $F(000)$ = 576
Linear absorption factor: $\mu(AgK\alpha)$ = 2.289 mm^{-1}
Morphology: colorless monoclinic prism
Crystal size: 0.19 × 0.22 × 0.24 mm

Intensity measurements

Temperature: 294 K   Wavelength: $AgK\alpha$ (0.5608 Å)
Diffractometer: Philips PW1100   Scan mode: $\bar{\omega}$
Monochromator: graphite plate   Scan width: 1.30°
Scan speed: 0.02° sec^{-1} Theta range: 3–30°
Total background measuring time: 10 sec
Maximum number of scans by reflection: 2
Measurement area: $\pm h, k, l$ h_{max} = 13, k_{max} = 23, l_{max} = 10
Total number of scanned reflections: 3867
Total number of nonzero reflections: 2435
Number of collected unique reflections: 2279
Intensity and orientation reference reflections (002, 131), every 4 hr: no variation

Structure determination

Lorentz and polarization corrections   No absorption correction
Program used: SDP (10)   Computer used: Micro-Vax II
Determination: Direct methods with MULTAN (11)
Unique reflections included: 1887 with $I > 4\sigma(I)$
Weighting scheme: unitary   Refined parameters: 92
Secondary extinction coefficient: 3.38 × 10^{-7} (12)
Unweighted agreement factor R: 0.031
Weighted agreement factor R_w: 0.034
Esd: 1.348   Largest shift/error = 0.00
Max. residual density: 1.174 e Å^{-3}
Drawings made with STRUPLO (13)

B. Structure Determination

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

The final atomic coordinates and the values of B_{eq} are given in Table IV. The values of the thermal anisotropic displacement parameters and the list of observed and calculated structure factors are available on request to the author.

Structure Description

As said above, the phosphoric anion present in this arrangement, is an infinite $(PO_3)_n^{n-}$ chain. The unit cell is crossed by
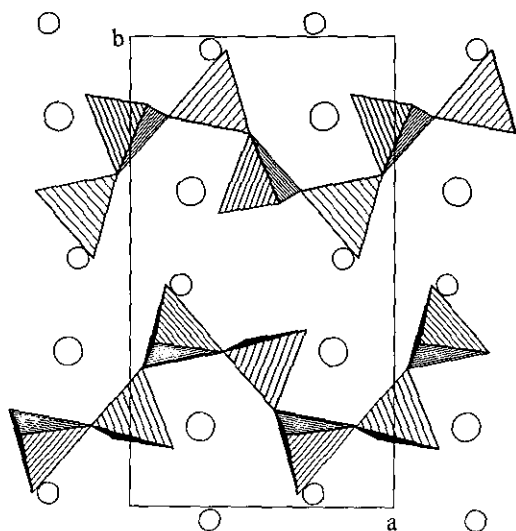
FIG. 4. Projection, along the c direction, of the atomic arrangement of $AgK(PO_3)_2$. Small circles represent silver, the other ones potassium atoms.

TABLE IV

FINAL ATOMIC COORDINATES AND B_{eq} FOR THE ATOMIC ARRANGEMENT OF $AgK(PO_3)_2$

Atoms	x	y	z	$B_{eq}{}^a$
Ag	0.69526(5)	0.02801(2)	0.81253(6)	1.690(4)
K	0.7681(1)	0.33005(7)	0.7033(2)	1.79(1)
P(1)	0.6512(1)	0.13196(7)	0.3143(2)	0.96(1)
P(2)	0.5065(1)	0.32610(7)	0.1516(2)	1.09(1)
O(E11)	0.3627(4)	0.9719(2)	0.7847(5)	1.61(4)
O(E12)	0.0918(4)	0.3481(2)	0.5395(4)	1.38(4)
O(L1)	0.0477(4)	0.2941(2)	0.1358(5)	1.31(4)
O(L2)	0.8544(4)	0.1715(2)	0.3244(5)	1.34(4)
O(E21)	0.6659(4)	0.3766(2)	0.2614(6)	2.07(5)
O(E22)	0.4353(4)	0.3543(3)	0.9246(5)	1.97(5)

Note. Estimated standard deviations are given in parentheses.

$^a B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j a_i \cdot b_j \cdot \beta_{ij}$.

two of these chains spreading parallel to the a direction. The period of the chain corresponds to four PO_4 tetrahedra, but due to the presence of the a glide plane is in fact built by only two crystallographically independent tetrahedra. Figure 4 illustrates a projection along the c direction with the respective locations of phosphoric chains and associated cations. In this view, the zig-zag configuration of the chain is apparent, in contrast to its rather straight aspect reported by Fig. 5, the projection of an isolated chain along the b direction. The main internal geometrical features of this phosphoric anion are given in Table V. They are quite compa-
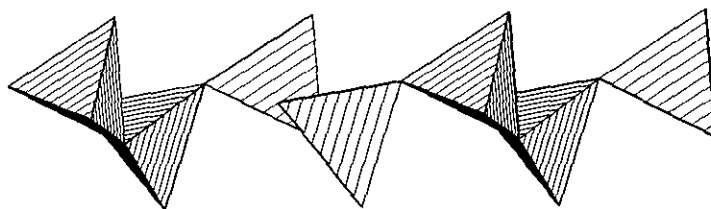
rable to previously measured infinite anions or oligophosphoric anions (*14*).

The associated cations establishing the three-dimensional cohesion between the phosphoric chains also have similar behaviors. Within a limit of 3.5 Å, the potassium atom has an eightfold oxygen coordination with K–O distances ranging from 2.697(3) to 3.256(3) Å. The silver atom is surrounded by five oxygen atoms with Ag–O distances varying from 2.309(3) to 2.592(3) Å. Main interatomic distances in these two coordination polyhedra are given in Table V.

Very often in the description of long-chain polyphosphates, the most appropriate way to understand the atomic arrangement is to examine it in a projection along the chain direction. For the title structure, a projec-

FIG. 5. Projection, along the b axis, of one isolated $(PO_3)_n$ chain.

TABLE V

MAIN INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN
THE PHOSPHORIC ANION AND IN THE COORDINATION POLYHEDRA
OF POTASSIUM AND SILVER ATOMS

P(1)O$_4$ tetrahedron				
P(1)	O(E11)	O(E12)	O(L1)	O(L2)
O(E11)	1.493(3)	2.589(4)	2.474(4)	2.546(4)
O(E12)	120.8(2)	1.485(3)	2.537(4)	2.451(4)
O(L1)	105.7(2)	110.1(2)	1.608(3)	2.527(4)
O(L2)	110.5(2)	104.9(1)	103.7(1)	1.605(3)
P(2)O$_4$ tetrahedron				
P(2)	O(L1)	O(L2)	O(E21)	O(E22)
O(L1)	1.617(3)	2.500(4)	2.512(4)	2.448(4)
O(L2)	101.9(1)	1.601(3)	2.474(4)	2.555(4)
O(E21)	108.4(2)	106.8(2)	1.479(3)	2.584(4)
O(E22)	104.4(2)	111.9(2)	121.6(2)	1.480(3)
P(1)–P(2)	2.919(1)		P(2)–P(1)–P(2)	92.59(4)
P(2)–P(1)	2.957(1)		P(1)–P(2)–P(1)	111.88(4)
	P(1)–O(L1)–P(2)	129.6(2)		
	P(1)–O(L2)–P(2)	134.5(2)		

AgO$_5$ polyhedron				
Ag–O(E11)	2.592(3)		Ag–O(E21)	2.309(3)
Ag–O(E11)	2.502(3)		Ag–O(E11)	2.431(3)
Ag–O(E12)	2.406(3)			

KO$_8$ polyhedron				
K–O(E11)	2.739(3)		K–O(L2)	3.200(3)
K–O(E12)	2.697(3)		K–O(E21)	2.788(4)
K–O(E12)	2.835(3)		K–O(E22)	2.933(3)
K–O(L1)	3.256(3)		K–O(3)	3.000(3)

Note. Estimated standard deviations are given in parentheses.

tion along the *a* direction, as given by Fig. 6, clearly illustrates this rule showing how the phosphoric chains are nestled between very corrugated layers built by the associated cations.

The present study does not put an end to the systematic investigation of the MPO_3–$M'PO_3$ systems, since as far as we know nothing has been reported for systems including combinations of K, Rb, Cs, and Tl monovalent cations. In addition, and from the author's experience, evidence exists for the existence of mixed NH_4–M^1 long-chain polyphosphates, of which only a unique example, $Li_2NH_4(PO_3)_3$, has been reported until now.
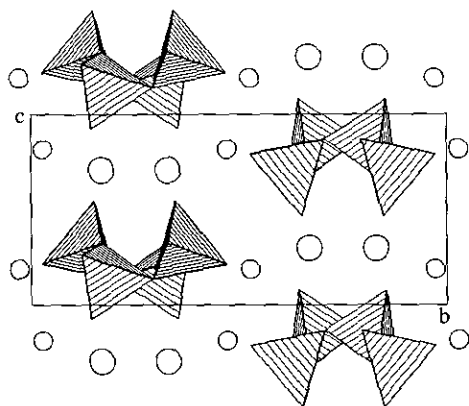

FIG. 6. Projection, along the *a* direction, of the atomic arrangement of $AgK(PO_3)_2$. Smaller circles denote silver atoms, the larger ones potassium atoms.

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