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Crystal data and crystal structure for silver cyclohexaphosphate monohydrate: $Ag_6P_6O_{18} \cdot H_2O$

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Condensed inorganic phosphate* / $Ag_6P_6O_{18} \cdot H_2O$ / *Crystal structure* / *Ring anion

Abstract. The chemical preparation and the crystal structure of $Ag_6P_6O_{18} \cdot H_2O$ arc reported. The title compound is trigonal ($R\bar{3}$) with $a = 14.807(10)$ Å, $c = 6.597(7)$ Å ($a_{rh} = 8.827$ Å, $\alpha_{rh} = 114.01°$), $V = 1257(3)$ Å^3, $Z = 3$, $M_w = 1139.05$ amu and $D_x = 4.515$ g cm^{-3}. The structure has been solved using 1073 independent data with a final R value of 0.035. The P_6O_{18} anions have $\bar{3}$ symmetry. They alternate along the $\bar{3}$ axis with rings of six loosely bounded silver atoms. Each Ag_6 ring is connected to its six neighbours by a short Ag–Ag distance (3.003 Å).

Introduction

The chemistry of cyclohexaphosphates is relatively little developed. In spite of a very clear and detailed process described by Griffith and Buxton (1965) for the chemical preparation of $Li_6P_6O_{18}$ and $Na_6P_6O_{18} \cdot 6H_2O$, these compounds have up to now never been used extensively as starting materials for the preparation of new cyclohexaphosphates. The chemical literature reports some chemical preparations and thermal behaviour for Ba, Ga, Y, Cu, Co, Ni, Cd and Mn cyclohexaphosphates (Lazarevski et al., 1980, 1981, 1982a, b). Structural investigations are rare. One can only report four:

- $Na_6P_6O_{18} \cdot 6H_2O$ (Jost, 1965),
- $Cu_2Li_2P_2O_{18}$ (Laügt, 1974),
- $Cr_2P_6O_{18}$ (Bagieu-Beucher and Guitel, 1977),
- $Cs_2(UO_2)P_6O_{18}$ (Linde et al., 1978),

Table 1. Crystallographic data for known cyclohexaphosphates.

Formula	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	Space group
$Na_6P_6O_{18} \cdot 6H_2O$	11.58	18.54	10.48	*Ccma*
$Cu_2Li_2P_6O_{18}$	9.485 111.73	9.419 106.25	9.379 106.80	$P\bar{1}$
$Cs_2(UO_2)P_6O_{18}$	6.988	10.838 104.25	13.309	$P2_1/n$
$Cr_2P_6O_{18}$	8.311	15.221 105.85	6.220	$P2_1/a$

It is worth noticing that three of these compounds have been characterized by indirect methods:

(a) $Cu_2Li_2P_6O_{18}$ during attempts to prepare single crystals of a long chain polyphosphate: $CuLi(PO_3)_3$, characterized during the determination of the $Cu_2P_4O_{12}-LiPO_3$ phase diagram (Laügt, 1969);

(b) $Cr_2P_6O_{18}$ and $Cs_2(UO_2)P_6O_{18}$ during systematic investigations of the $Cr_2O_3-P_2O_5$ and $Cs_2O-UO_2-P_2O_5$ systems by flux methods.

Table 1 reports crystallographic data for these four compounds.

The process reported by Griffith and Buxton for the preparation of $Li_6P_6O_{18}$ has recently been improved and simplified by Schülke and Kayser (1985). In the present paper we describe the chemical preparation and the crystal structure of a new cyclo-hexaphosphate $Ag_6P_6O_{18} \cdot H_2O$ using $Li_6P_6O_{18}$ as starting material. This silver salt seems to be a promising material for the preparation of water soluble cyclohexaphosphate, by a process similar to that described by Boullé (1938) for the preparation of cyclotriphosphates.

Chemical preparation

The title compound is prepared as a pure compound in a reproducible way and with good yield by mixing aqueous solutions of silver nitrate (31 g in 350 cm^3) and lithium cyclohexaphosphate (19 g in 225 cm^3), these quantities corresponding to a molar ratio 6/1. After some hours of standing at room temperature, elongated prismatic crystals appear in the solution.

When more diluted solutions are used, the precipitation occurs after one day and one observes the formation of four kinds of crystals (including the title compound) corresponding probably to various hydrates of $Ag_6P_6O_{18}$. Experiments are in run to characterize the three other species, unfortunately appearing most of time as twinned crystals.

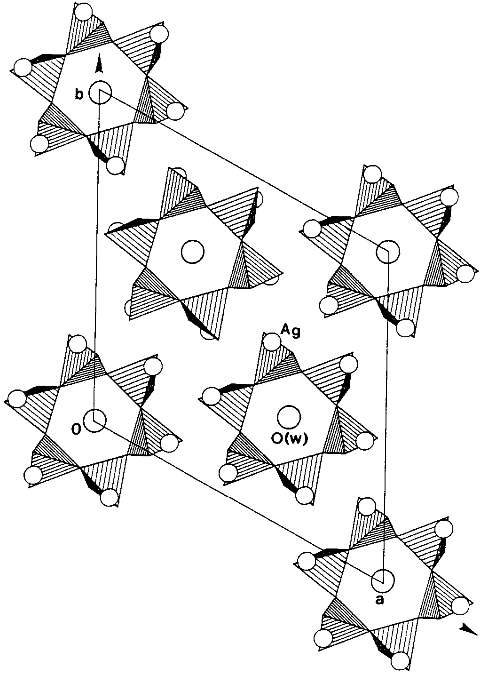

Fig. 1. Projection of the atomic arrangement of $Ag_6P_6O_{18} \cdot H_2O$ along the c axis. Drawing executed with STRUPLO (R. X. Fischer 1985).

Crystal data

A preliminary study by the Weissenberg method shows this compound to be trigonal. The only observed existence condition is: $-h+k+l=3\,n$, so five space groups are possible: $R3$, $R\bar{3}$, $R32$, $R3m$ and $R\bar{3}m$.

A careful examination of the intensity of reflexions shows that in fact only space groups $R3$ or $R\bar{3}$ are possible.

Crystal structure determination

Experimental conditions used during the intensity data collection and various physical data are listed in Table 2. The lattice parameters are

Table 2. Parameters used for the X-ray data collection.

Apparatus	Enraf-Nonius CAD4
Wavelength	Ag$K\bar{\alpha}$ (0.5608 Å)
Monochromator	Graphite plate
Scan mode	ω
Theta range	3 – 30°
Scan width	1.20°
Scan speed	from 0.02 to 0.04° s^{-1}
Total background measuring time	14 to 27 s
Reference reflexions	731, $\overline{731}$ (orientation), 006, 00$\bar{6}$ (intensity)
Total number of measured reflexions	5226 ($\pm h, \pm k, l$)
Number of independent reflexions, $R_{int.}$	1632, 0.015
Crystal size	0.32 × 0.16 × 0.21 mm
μ (Ag$K\bar{\alpha}$)	37.51 cm^{-1}
$F(000)$	1578
Experiment temperature	294 K

obtained by least-squares refinement from the angular settings of 20 reflexions $10 < \theta < 14.75°$. The intensities have been corrected for Lorentz and polarization effects, but no correction for absorption has been applied. The structure determination, first run in the less symmetrical $R3$ space group, by direct methods (Main et al., 1977) shows the existence of higher symmetry and led to the space group $R\bar{3}$. After final refinement cycles using anisotropic thermal parameters the R value converged to 0.035 ($R_w = 0.038$) for a set of 1073 reflexions such that $I > 9\ \sigma_I$. This same R factor is 0.057 for the total set of 1632 measured reflexions. The extinction coefficient is refined to $g = 1.72 \times 10^{-7}$. The formula used for the extinction correction is taken from Stout and Jensen (1968). Atomic scattering factors for neutral atoms, f' and f'' are taken from International Tables for X-ray Crystallography (1974). Anomalous dispersion has been taken into account. Full-matrix refinements have been run on F, using a unitary weighting scheme. All the calculations have been done using the SDP system (1977), the computer being a Micro Vax II. Table 3 reports the final atomic coordinates. The lists of hkl, F_{obs}, F_{calc} and of the anisotropic parameters have been deposited.[1]

Structure description

The P_6O_{18} ring anion

The phosphoric ring is built up by six corner-sharing PO_4 tetrahedra. Being located around the $\bar{3}$ axis with a z value close by zero, this ring has a $\bar{3}$ symmetry and so is constructed by only one crystallographic independent PO_4 tetrahedron. Its main geometrical features (interatomic distances and bond angles) are reported in Table 4 and are quite comparable to what is usually observed in condensed phosphates, cyclic or linear.

Table 3. Final atomic coordinates for $Ag_6P_6O_{18} \cdot H_2O$. E.s.d. are given in parentheses $B_{eq} = 4/3 \sum_i \sum_j \vec{a}_i \cdot \vec{a}_j \cdot \beta_{ij}$.

Atoms	x (σ)	y (σ)	z (σ)	B_{eq} (σ) [$Å^2$]
Ag	0.92873(3)	0.39399(2)	0.91249(5)	2.525(6)
P	0.96039(6)	0.16535(6)	0.0630(1)	1.37(1)
O(L)*	0.5474(2)	0.3769(2)	0.4238(4)	1.91(5)
O(E1)*	0.5762(2)	0.5492(2)	0.2874(5)	2.18(5)
O(E1)*	0.8609(2)	0.3226(2)	0.5968(4)	2.30(6)
O(W)*	0	0	0.478(4)	12.8(6)

* (L) corresponds to a linking oxygen atom, (E) to end standing oxygen atom and (W) to the oxygen atom of H_2O.

Table 4. Main interatomic distances (Å) and bond angles (°) of the atomic arrangement.

The PO_4 tetrahedron

P	O(L)	O(L)	O(E1)	O(E2)
O(L)	*1.597(2)*	2.469(4)	2.532(4)	2.474(4)
O(L)	100.7(2)	*1.609(3)*	2.490(4)	2.526(4)
O(E1)	110.5(2)	107.1(2)	*1.485(4)*	2.584(4)
O(E2)	109.3(1)	109.3(1)	120.8(2)	*1.487(3)*

P – P 2.909(1) P – P – P 112.19(4)°
P – O(L) – P 130.3(2)°

The least-squares plane involving O(L) and P
departure from the plane: P ± 0.415 (Å)
O(2) ± 0.622 (Å)

The silver atom network

Ag – Ag	3.670(1) Å	(in the [Ag_6] ring)
Ag – Ag	3.003(1) Å	(connections between rings)
Ag – Ag	3.666(1) Å	(around 3_1 axes)
Ag – Ag – Ag	112.2(1)°	(in the ring)

The silver atom coordination

Ag – O(E1)	2.523(3)	Ag – O(E2)	2.324(3)
Ag – O(E1)	2.540(3)	Ag – O(E2)	2.717(3)
Ag – O(E1)	2.685(3)	Ag – O(E2)	2.583(4)
Ag – O(L)	2.888(3)		

The silver atom network

The arrangement of the silver atoms inside the structure can be compared with the situation of the phosphorus atoms. They are arranged as to build

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[1] Additional material to this paper can be ordered referring to the no. CSD 53562, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

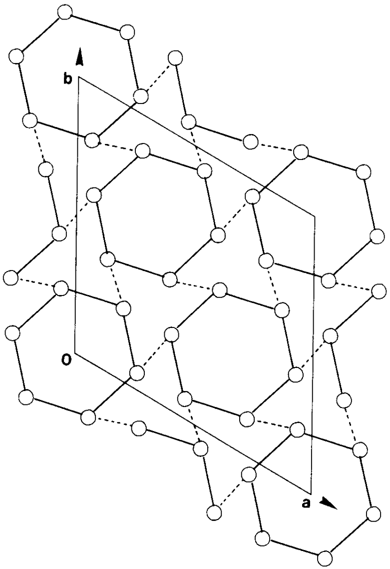

Fig. 2. Projection of the silver atom network along the *c* direction. The short Ag–Ag distance connecting the [Ag$_6$] rings is represented by a dotted line.

a six-member ring of symmetry $\bar{3}$ around the $\bar{3}$ axis, separated by a distance of $c/2$ of the phosphoric ring. Three types of Ag–Ag distances are observed. Inside the [Ag]$_6$ ring silver atoms are separated by a distance of 3.670 Å. Each of this ring is interconnected to its six neighbours by a rather short distance of 3.003 Å, and the spiral of silver atoms around each 3_1 axis corresponds to an Ag–Ag distance of 3.666 Å. Figure 2 reports in projection along the *c* direction this silver atoms network. Within a range of 3 Å the silver atom has a sevenfold coordination with Ag–O distances spreading in a range of 2.324 Å to 2.888 Å. The largest Ag–O distance [Ag–O(L)] corresponding to a connection with a bonding oxygen of the phosphoric ring is probably not to be taken into consideration, by comparison with what is commonly observed in condensed phosphate crystal chemistry where O(L) oxygen atoms are generally not involved in cation coordination.

The water molecule

A water molecule, not involved in the cation coordination is located on the $\bar{3}$ axis close by an inversion center. This water molecule is statistically distributed on a sixfold position $(0,0,\pm z)$ with $z = 0.478$. The refinement of the occupancy rate shows no significant deviation from 0.500(7). It is to be noticed that this water molecule lies approximately at the center of the [Ag]$_6$ ring.

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SDP, Structure determination package, version RSX11M, September 1977; Enraf-Nonius, Delft.