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# A New Investigation of the Structure of Silver Orthophosphate

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**Abstract.** $Ag_3PO_4$ (grown in ammonia solution), cubic, $P\bar{4}3n$, $a = 6{\cdot}004\ (2)$ Å, $Z = 2$, $D_x = 6{\cdot}42$ g cm$^{-3}$. The structure was refined by the full-matrix least-squares method to $R_2 = 0{\cdot}016$. The regular $PO_4$ tetrahedra with a P–O distance of 1·539 Å form a body-centred-cubic (b.c.c.) lattice. The six $Ag^+$ ions are disordered among twelve sites with twofold symmetry.

**Introduction.** $Ag_3PO_4$ was precipitated from an aqueous solution of $AgNO_3$ and $Na_3HPO_4.12H_2O$. It was filtered and re-dissolved in concentrated ammonia solution which was slowly evaporated in a temperature bath held at 60°C. Yellow crystals up to 0·5 mm were obtained. A good quality single crystal was ground into a sphere of radius 0·075 mm for intensity measurements on a Syntex $P2_1$ automatic diffractometer. Graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) was used with a $\theta$–$2\theta$ scan and a variable scan rate. 915 reflections up to $2\theta \le 65°$ were collected. Subsequent averaging led to a unique set of 82 reflections, of which 80 had intensities exceeding three times their standard deviations based on counting statistics. The data were corrected for Lorentz, polarization and absorption effects ($\mu = 133{\cdot}15$ cm$^{-1}$). The lattice parameter was obtained from a least-squares fit to the $2\theta$ values of 15 reflections ($25° < 2\theta < 65°$) carefully measured on the diffractometer. The trial structure was based on the model of Helmholz (1936) in the space group $P\bar{4}3n$. The systematic absences of $hkl$ with $h$, $k$ and $l$ all odd and $hhl$ for $l$ odd were verified. In this model the P was placed at (0,0,0), Ag at $(\frac{1}{4},0,\frac{1}{2})$ and O at $(u,u,u)$ with $u = 0{\cdot}16$ so that there was only one adjustable positional parameter. A full-matrix least-squares program, *CUDLS*, written locally, was used for the refinement. The $R$ factor was 0·12 with individual isotropic temperature factors. The structure failed to refine when highly anisotropic temperature factors were used for the Ag atom as proposed by Helmholz. With the Ag atoms placed in these six special positions with $\bar{4}$ symmetry, additional systematic absences of $hkl$ with $h - k = 4n$ and $l$ odd should be observed. However, as pointed out by Helmholz, this condition was observed to be violated. As neither P nor O in their special positions contribute to the intensity of these reflections, the violation must have arisen from the Ag occupying sites of lower symmetry. In view of the random distribution of Ag among equivalent sites found in a number of its compounds with halogens, the six Ag atoms in the present case were assigned the 12($h$) positions in space group $P\bar{4}3n$. This means that each Ag atom at $(\frac{1}{4},0,\frac{1}{2})$ actually occupies one of the two sites at $(x,0,\frac{1}{2})$ and $(\frac{1}{2} - x, 0, \frac{1}{2})$ on the twofold axis. The structural amplitudes of the three strongest reflections (038, 014 and 126) that violate the above systematic-extinction conditions were calculated for different values of $x$ between 0·25 and 0·15. The best agreement between $|F_o|$ and $|F_c|$ was obtained for $x = 0{\cdot}22$. Refinement of the structure was then resumed using this value of $x$ as the initial parameter for the Ag position. The structure readily refined to a final $R_2$ $\{=[\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}\}$ of 0·016, where the weighting function $w = 5{\cdot}0 - 0{\cdot}03F_o + 0{\cdot}0001F_o^2$. The two adjustable positional parameters were $x = 0{\cdot}231\ (1)$ and $u = 0{\cdot}148\ (1)$. A parameter for correcting the effect of secondary extinction (Larson, 1967) was also refined and its value was $4{\cdot}1\ (2) \times 10^{-7}$. The positional

Table 1. *Positional parameters of* $Ag_3PO_4$

| | Position | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| Ag* | 12($h$) | 0·231 (1) | 0 | $\frac{1}{2}$ |
| P | 2($a$) | 0 | 0 | 0 |
| O | 8($e$) | 0·148 (1) | $x$ | $x$ |

* Half-occupancy.

Table 2. *Bond distances* (Å) *and angles* (°) *of* $Ag_3PO_4$ (*e.s.d.'s in parentheses*)

| | | | |
|---|---|---|---|
| P–O | 1·539 (4) ×4 | O–P–O | 109·47 |
| Ag–O | 2·345 (3) ×2 | O–Ag–O | 93·66 (7) |
| | 2·403 (4) ×2 | | 145·0 (5) |
| Ag–Ag | 2·77 (1) | | 155·5 (5) |
| | 3·00 (1) | | |

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* Deceased.

parameters are shown in Table 1, and bond distances and angles in Table 2.*

**Discussion.** The structure of $Ag_3PO_4$ was first investigated by Helmholz (1936) based on the ideal structure proposed by Wyckoff (1925). In order to fit the observed intensity data, Helmholz invoked the concepts of anisotropic thermal vibration for the Ag atom and concluded that its oscillation along the fourfold axis had an amplitude 1·46 times as large as that perpendicular to this direction. A rather long P—O distance of 1·61 Å was obtained, which was interpreted as being due to covalent bonding between Ag and O. The O parameter was later revised by Vegard (1947) to give a P—O distance of 1·56 Å. However, anisotropic thermal motion of the Ag atom cannot account for the observed intensity of reflections $hkl$ with $h - k = 4n$ and $l$ odd. A bond-valence analysis using the method of Brown & Shannon (1973) gave a bond-valence sum of only 4·13 for P, considerably less than the atomic valence of $P^{5+}$. The structure of $Ag_3PO_4$ was therefore reinvestigated to settle these problems.

The present refinement shows that the structure consists of regular tetrahedra of phosphate ions forming a b.c.c. lattice. The P—O distance is 1·539 (4) Å. Each $Ag^+$ ion occupies one of two possible sites on either side of the ideal site so that its site symmetry is lowered from fourfold to twofold. The distance between these two possible sites is 0·23 (1) Å so that simultaneous occupation of them will not be possible. The $Ag^+$ ion is bonded to four O atoms belonging to four different phosphate groups to form an irregular tetrahedron. Each O is in turn bonded to three $Ag^+$. The O—Ag—O angles range from 93·67 (7) to 155·5 (5)° and the average Ag—O distance is 2·374 (3) Å. A bond-valence analysis now gives a valence sum of 0·95 around $Ag^+$ and 4·94 around $P^{5+}$.

Some features of the present structure are common among a number of Ag compounds characterized by high ionic conductivity (Wiedersich & Geller, 1970). It is particularly closely related to the structure of β-$Ag_3SI$ (Reuter & Hardel, 1965), where the anions are ordered to form a b.c.c. lattice and the three $Ag^+$ ions are disordered among 12 tetrahedral sites. However, the replacement of the chalcogenide and halide ions with phosphate groups destroys the face-sharing arrangement of the tetrahedral sites available for the Ag. This, together with a stronger bonding between Ag and O, is probably responsible for $Ag_3PO_4$ being a non-conducting solid (Takahashi, Ikeda & Yamamoto, 1972).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33160 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.