

# The Crystal Structure of Magnesium Tetrametaphosphate, $\text{Mg}_2\text{P}_4\text{O}_{12}$

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The crystal structure of  $\text{Mg}_2\text{P}_4\text{O}_{12}$  has been determined by means of direct methods and refined from three-dimensional X-ray diffractometer data ( $R=6.0\%$  for 781 independent reflections).  $\text{Mg}_2\text{P}_4\text{O}_{12}$  crystallizes in the monoclinic space group  $C2/c$  with  $Z=4$ . The cell constants are  $a=11.756(2)$ ,  $b=8.285(1)$ ,  $c=9.917(1)$  Å,  $\beta=118.96(2)^\circ$ ,  $V=845$  Å<sup>3</sup>. The calculated density is 2.865 g/cm<sup>3</sup>. The  $\text{PO}_4$  tetrahedra in the structure are linked together in a ring to form  $\text{P}_4\text{O}_{12}^{4-}$  ions with P—O—P angles of 134.2 and 138.8°. The magnesium ions are always six-coordinated.

The phase diagram of the system  $\text{MgO}-\text{P}_2\text{O}_5$  was published in 1958 by Berak.<sup>1</sup> The crystal structures for three of the four compounds occurring in this system were determined some years ago, viz.  $\alpha\text{-Mg}_2\text{P}_2\text{O}_7$ ,<sup>2</sup>  $\beta\text{-Mg}_2\text{P}_2\text{O}_7$ ,<sup>3</sup> and  $\text{Mg}_3(\text{PO}_4)_2$ .<sup>4</sup> The structure of the remaining compound, magnesium metaphosphate, has been unknown to date. However, on the basis of spectroscopic measurements<sup>5</sup> and paper-chromatographic analysis<sup>6,7</sup> it has earlier been postulated that magnesium metaphosphate contains tetrametaphosphate ( $\text{P}_4\text{O}_{12}^{4-}$ ) ions. Furthermore, it has been known since about 1956 that  $\text{Mg}_2\text{P}_4\text{O}_{12}$  belongs to a family of isomorphous tetrametaphosphates  $\text{M}^{\text{II}}_2\text{P}_4\text{O}_{12}$  with  $\text{M}=\text{Mg}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Mn}$ ,  $\text{Zn}$  ( $\alpha$ -phase),  $\text{Cd}$  ( $\alpha$ -phase).<sup>6,7</sup> In order to establish the crystal structure of these compounds, a crystallographic study of  $\text{Mg}_2\text{P}_4\text{O}_{12}$  was undertaken.

## EXPERIMENTAL

A sample of  $\text{Mg}_2\text{P}_4\text{O}_{12}$  was prepared by mixing  $\text{MgCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  in the molar ratio 1:2. The mixture was then slowly heated

to 900 °C. A quantitative analysis by means of X-ray fluorescence spectroscopy, with  $\text{MgO}$  and  $\text{Li}_3\text{PO}_4$  as standards, confirmed the empirical formula  $\text{Mg}(\text{PO}_3)_2$ . The  $d$ -values and relative intensities obtained from a Guinier powder photograph also agreed with those reported earlier in the literature for magnesium metaphosphate.<sup>7-9</sup> Good single crystals were then prepared in a sealed thin-walled platinum tube from the melt (m.p. 1165 °C)<sup>1</sup> allowed to solidify very slowly during a period of two weeks. An almost spherically shaped ( $r=0.050\pm 0.004$  mm) single crystal was selected from the sample. With this, the unit cell dimensions were determined and refined by an PW1100 automatic diffractometer on the basis of 25 strong but distinct reflections. The cell constants are:  $a=11.756(2)$ ,  $b=8.285(1)$ ,  $c=9.917(1)$  Å,  $\beta=118.96(2)^\circ$ ,  $V=845$  Å<sup>3</sup>.  $Z=4$  gives a calculated density of 2.865 g/cm<sup>3</sup>. This is in agreement with values published by Beucher and Grenier.<sup>8</sup> The PW1100 diffractometer (graphite monochromator;  $\text{CuK}\alpha$  radiation,  $\lambda=1.5405$  Å) was also used for the collection of single-crystal data. 786 independent non-extinct reflections were measured up to  $\theta=70^\circ$ . Of these 52 reflections had  $\sigma(I)/I > \frac{1}{2}$  and might be regarded as "insignificant". Nevertheless they were included in all the following calculations. The net

Table 1. Basic set used for solving the triple relations.

$hkl$	$E$	Sign	Comment
022	2.92	—	variable
357	2.87	+	def. of origin
914	2.65	+	def. of origin
444	2.58	+	variable
044	1.94	+	from $\sum_1$ relations

Table 2. Fractional atomic coordinates and thermal parameters from the isotropic refinement of  $\text{Mg}_2\text{P}_4\text{O}_{12}$ . The estimated standard deviations (within parentheses) refer to the last digit of the respective values.

Atom	$x$	$y$	$z$	$B$
Mg(1)	0 <sup>a</sup>	0.0513(2)	$\frac{1}{4}$ <sup>a</sup>	0.36(4)
Mg(2)	$\frac{1}{4}$ <sup>a</sup>	$\frac{1}{4}$ <sup>a</sup>	$\frac{1}{2}$ <sup>a</sup>	0.38(4)
P(1)	0.0089(1)	0.2627(1)	-0.0242(1)	0.33(3)
P(2)	0.1967(1)	0.4915(1)	0.1968(1)	0.34(3)
O(1)	0.2329(3)	0.4198(4)	0.3469(3)	0.77(5)
O(2)	0.2988(3)	0.5809(4)	0.1765(3)	0.48(5)
O(3)	0.0779(3)	0.6102(4)	0.1554(3)	0.81(5)
O(4)	0.1421(3)	0.3589(4)	0.0643(3)	0.73(5)
O(5)	-0.0491(3)	0.2410(4)	0.0811(3)	0.56(5)
O(6)	0.0316(3)	0.1200(4)	-0.0952(3)	0.79(5)

<sup>a</sup> Parameter fixed by symmetry.

intensities were corrected for Lorentz, polarization, and absorption ( $\mu=104 \text{ cm}^{-1}$ ) effects. The latter correction was performed assuming the crystal to be spherical with  $r=0.050 \text{ mm}$ .

#### DETERMINATION AND REFINEMENT OF THE STRUCTURE

The systematic extinctions, confirmed by diffractometer measurements as well as from Weissenberg photographs, are:  $hkl$ ,  $h+k \neq 2n$ ;  $h0l$ ,  $l \neq 2n$ ; and  $0k0$ ,  $k \neq 2n$ . The distribution of the  $|E|$  values and some statistical tests applied, e.g. the  $N(z)$  test,<sup>10</sup> indicated space group  $C2/c$  rather than  $Cc$ , and the former symmetry was indicated throughout the work.

The structure was solved by means of direct methods utilizing a program system developed by Norrestam<sup>11</sup> based on the variance-weighted phase-sum formula for phase determination. The 113 highest  $|E|$  values ( $|E| > 1.4$ ) were used to generate 591 triple relations. As a basic set five reflections were selected (see Table 1). The  $E$  map based on 112 determined phases revealed almost all atomic positions. The structure determination was then completed by Fourier methods and least-squares refinements.

The refinements were performed with a local modification of the full-matrix least-squares program LALS. The atomic scattering factors applied were those for  $\text{Mg}^{2+}$ ,  $\text{P}^0$ , and  $\text{O}^-$  from the *International Tables for X-Ray Crystallography*,<sup>12</sup> with the real part of the anomalous dispersion included. The 52 "insignificant" reflections with  $\sigma(I)/I > \frac{1}{2}$  were given zero

weight, while Hughes' weighting function<sup>13</sup> (with  $h=4$  and  $F_{o,\min}=8$ ) was applied to the other reflections. Initially all 786 reflections were used in the refinements, but prior to the final refinements, five strong low-angle reflections (022, 220, 310, 400,  $\bar{2}02$ ) were omitted as severely suffering from extinction effects. The  $R$  value, defined as  $R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$ , fell to 6.0 % for the isotropically- and to 5.5 % for the anisotropically-refined structure (781 reflections). Since the atomic positional parameters obtained in these two final refinements are very similar and the anisotropic vibrations seem to be small, only the results of the 6.0 % isotropic refinement are considered below. The parameters obtained in this refinement are given in Table 2.

A three-dimensional difference Fourier synthesis calculated with the parameters in Table 2 at points 0.2 Å apart showed no maxima or minima greater than 15 % of the average oxygen peak in the electron density map. The observed and calculated structure factors from the isotropic refinement are shown in Table 3. The reflections with  $\sigma(I)/I > \frac{1}{2}$  are marked with an asterisk.

Two summary papers of the crystallographic programs used in this work have been published at this institute.<sup>14,15</sup>

#### DISCUSSION

The crystal structure of magnesium tetrametaphosphate consists of  $\text{PO}_4$  tetrahedra and





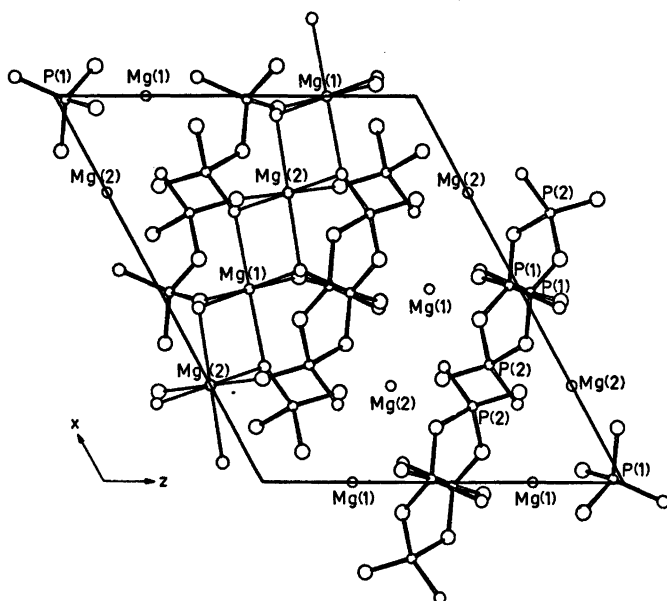


Fig. 1. Projection of the  $Mg_2P_4O_{12}$  structure down the  $b$  axis.

$MgO_6$  octahedra which share corners forming a three-dimensional framework. An ORTEP<sup>16</sup> plot of the structure is shown in Fig. 1.

Most metaphosphate compounds have been found to have their  $PO_4$  tetrahedra linked together in infinite chains. In  $Mg_2P_4O_{12}$  four  $PO_4$  tetrahedra are linked together in a ring to form  $P_4O_{12}^{4-}$  ions, in accordance with the previously-mentioned postulations.<sup>5,6,7</sup> Only few metaphosphate structures with such anions have been found and determined to date.<sup>17-20</sup> The first of these structures was  $Al_4(P_4O_{12})_3$ , determined by Pauling and Sherman.<sup>17</sup>

Table 5. Interatomic distances (Å) in the magnesium-oxygen coordination octahedra. The e.s.d. of each Mg—O distance is  $\pm 0.003$  Å.

Mg(1)—O(6) ( $\times 2$ )	1.990
—O(2) ( $\times 2$ )	2.125
—O(5) ( $\times 2$ )	2.161
Average	2.092
Mg(2)—O(1) ( $\times 2$ )	2.007
—O(2) ( $\times 2$ )	2.094
—O(5) ( $\times 2$ )	2.095
Average:	2.065

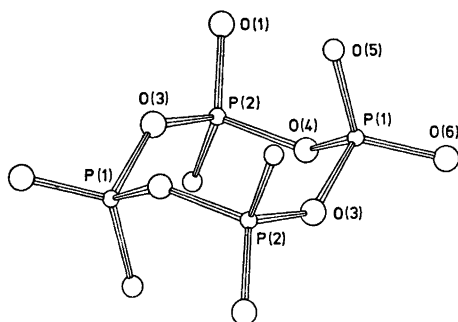


Fig. 2. The tetrametaphosphate ion.

The  $P_4O_{12}^{4-}$  ions in  $Mg_2P_4O_{12}$  have a crystallographically imposed  $\bar{1}$  symmetry. (Cf. Fig. 2.) The shortest oxygen-oxygen distance between two different anions is 2.737 Å. Some interatomic distances and angles of the anion are given in Table 4. The  $PO_4$  tetrahedra are fairly regular with O—O distances ranging from 2.455 to 2.563 Å. The bridging P—O distances (1.590–1.599 Å) are significantly longer than the terminal P—O distances (1.461–1.510 Å). The two different P—O—P angles are 134.2 and 138.8°, respectively. The tetrametaphosphate

ion dimensions (distances and angles) found in  $\text{Mg}_2\text{P}_4\text{O}_{12}$  are in good agreement with those published for other tetrametaphosphates, e.g.  $(\text{NH}_4)_4\text{P}_4\text{O}_{12}$ ,<sup>18</sup>  $\text{Na}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ ,<sup>19</sup> and  $\text{SrK}_2\text{P}_4\text{O}_{12}$ .<sup>20</sup> However, the configuration of the anions are different. In  $\text{Al}_4(\text{P}_4\text{O}_{12})_3$ <sup>17</sup> as well as in  $\text{SrK}_2\text{P}_4\text{O}_{12}$ <sup>20</sup> the anions have  $\bar{4}$  point symmetry. In the ammonium phosphate the anion symmetry is  $2/m$ ,<sup>18</sup> whereas in the sodium phosphate the  $\text{P}_4\text{O}_{12}$  rings, besides having point symmetry  $\bar{1}$ , show strong pseudosymmetry  $2/m$ .<sup>19</sup>

The magnesium ions in  $\text{Mg}_2\text{P}_4\text{O}_{12}$  are always surrounded by six oxygen atoms thus forming rather regular  $\text{MgO}_6$  octahedra of two different types: one with 2 point symmetry (around  $\text{Mg}(1)$ ), the other with  $\bar{1}$  symmetry [around  $\text{Mg}(2)$ ]. The Mg—O distances range from 1.990 to 2.161 Å. Some interatomic distances for the magnesium-oxygen coordination octahedra are given in Table 5.

Octahedral coordination is the most common coordination for magnesium ions and it also occurs in the three previously mentioned magnesium phosphates.<sup>2-4</sup> However, two of these structures,  $\alpha\text{-Mg}_2\text{P}_2\text{O}_7$ ,<sup>3</sup> and  $\text{Mg}_3(\text{PO}_4)_2$ ,<sup>4</sup> also contain magnesium ions with the quite unusual coordination number of five.

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