

The Crystal Structure of α - $\text{Mg}_2\text{P}_2\text{O}_7$

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The lattice parameters of the α (low temperature) phase of $\text{Mg}_2\text{P}_2\text{O}_7$ are $a=13.198(10)$, $b=8.295(5)$, $c=9.072(5)$ Å, $\beta=104.9(1)^\circ$ and $Z=8$. The space group, $B2_1/c$, although non-primitive, allows an easy comparison of the α and β phases of this compound. A primitive cell could be chosen with space group $P2_1/c$ and $a=6.981(5)$, $b=8.295(5)$, $c=9.072(5)$ Å, $\beta=113.0(1)^\circ$ and $Z=2$. In contrast with the apparently linear P–O–P group found for the β phase, stable above 70°C , this group is bent to an angle of 144° in the α phase. The $\text{P}_2\text{O}_7^{4-}$ ion nearly has C_2 symmetry with average inner and outer P–O bond distances of 1.59 ± 0.02 Å and 1.52 ± 0.02 Å respectively. The diffuse phase transition which occurs between 60 and 70°C appears to be related to the fact that the cations show five- and six-fold coordination in the α phase whereas in the β phase all the cations are equivalent and sixfold coordinated.

Introduction

This paper reports the crystal structure of α - $\text{Mg}_2\text{P}_2\text{O}_7$ and observations related to its phase transformation. $\text{Mg}_2\text{P}_2\text{O}_7$ one is of a series of compounds having the thortveitite structure (Cruikshank, Lynton & Barclay, 1962) for their high temperature (β) form. Among the pyrophosphates this series includes those of Mn (Lukaszewicz & Smajkiewicz, 1961), Zn (Calvo, 1965*a*), Cu (Robertson & Calvo, 1967*a*) (Lukaszewicz, 1966) and Mg (Lukaszewicz, 1961; Calvo, 1965*b*). While this manuscript was under revision a resolution of the structure of α - $\text{Mg}_2\text{P}_2\text{O}_7$ was proposed by Lukaszewicz (1966).

A phase transformation is reported for all these compounds except Mn. In the case of Zn, Mg and Cu pyrophosphates the transformation is inhomogeneous in that the translational periodicity is lost as the transition proceeds. The evidence for this is provided by the appearance of diffuse streaks through some of the reflections in the diffraction pattern of $\text{Cu}_2\text{P}_2\text{O}_7$ (Robertson & Calvo, 1967*a*) and the two non-equivalent electron paramagnetic resonance (e.p.r.) sites for Mn^{2+} in $\text{Zn}_2\text{P}_2\text{O}_7$ between 132° and 155°C (Chambers, Datars & Calvo, 1964). The transformation in $\text{Mg}_2\text{P}_2\text{O}_7$ has been subjected to a number of studies which indicate that it undergoes a diffuse first order transition. Roy, Middleswarth & Hummel (1948) concluded from differential thermal analysis, thermal expansion and powder diffractometric studies that the transition was reversible and occurred at 68° with a considerable volume contraction and with the apparent co-existence of both the α and β phases over an extended temperature interval. Specific heat measurements by Oetting & McDonald (1963) confirmed the broad anomaly. They found a diffuse enthalpy of transformation corresponding to about 730 cal.mole $^{-1}$. Infrared spectroscopic studies by Lazarev (1964) indicated that the anion in the α phase has a symmetry no higher than C_s or C_2 and becomes C_{2h} above the transition as a result of dynamical cen-

tring. Recent single-crystal studies by e.p.r. (Calvo, Leung & Datars, 1967) confirmed the co-existence of both phases while a recent refinement of the structure of β - $\text{Mg}_2\text{P}_2\text{O}_7$ (Calvo, 1965*b*) showed enhanced thermal activity at the central oxygen atom of an apparently linear P–O–P group.

Since various members of this series of pyrophosphates show pronounced individuality in their low temperature forms despite having isostructural high temperature modifications, it is of interest to determine the effect of the anion's environment upon its geometry. Among the low temperature pyrophosphates $\text{Mg}_2\text{P}_2\text{O}_7$ is a convenient choice for this study since it does not have a space group ambiguity. The low scattering power of the cation and the readily accessible transition temperature provide added advantages.

Experimental

Crystals of $\text{Mg}_2\text{P}_2\text{O}_7$, doped with 0.1% Cu^{2+} for subsequent e.p.r. studies, were grown from a melt prepared from the decomposition product obtained from MgNH_4PO_4 . The morphology of the crystals was that of flat plates of diamond-shaped cross-section with the b axis parallel to the shorter diagonal. The large faces correspond to $\pm(001)$. A portion of one of these plates (0.08 mm \times 0.12 mm \times 0.15 mm) was mounted and aligned to rotate about the b axis and used throughout the crystallographic studies reported here. Weissenberg photographs containing reflections indexed as hnl , $0 \leq n \leq 5$ were taken with Mo $K\alpha$ radiation. The $\{100\}$, $\{001\}$, $\{101\}$, $\{10\bar{1}\}$ and $\{102\}$ zones (containing reflections of the types $0kl$, $hk0$, hkh , $hk\bar{h}$ and $2hk\bar{h}$ respectively) were photographed with the precession camera using Mo $K\alpha$ radiation. Accurate parameters were determined from films calibrated with TiO_2 reflections whose unit-cell dimensions were taken as $a=4.5929(5)$, $c=2.9591(3)$ (Cromer & Herrington, 1955). The parameters obtained for α - $\text{Mg}_2\text{P}_2\text{O}_7$ at 22°C are $a=13.198(10)$, $b=8.295(5)$, $c=9.072(5)$ Å and $\beta=$

104.9(1)°. The density was determined with a pycnometer to be 3.14 g.cm⁻³ where 3.18 g.cm⁻³ is predicted for eight molecules per unit cell. The space group, $B2_1/c$, was determined from extinction of those reflections of type hkl with $h+l$ odd, $h0l$ with h and l odd and $0k0$ with k odd. This non-primitive cell was chosen in order to maintain a simple relationship between the axes of the α and β phases. The latter phase is also monoclinic with $a=6.494(7)$, $b=8.28(1)$, $c=4.522(5)$ Å and $\beta=103.8(1)^\circ$ with $Z=2$ and space group $C2/m$.

The intensities of the reflections were measured by visual comparison, corrected for Lorentz and polarization effects and converted to relative structure factors. No absorption corrections were applied since with a linear absorption coefficient of $\mu=12$ cm⁻¹ they would amount to less than 1%.

The reversible nature of the phase transition indicated that the α and β structures were closely related. Therefore the gross structural features would be expected to be preserved through the transformation. The unit cell of the β form can be generated from that of the α form by the addition of two elements of symmetry. These elements are a mirror plane at $y=\frac{1}{2}$, which in combination with the c -glide and the B centring halves both the a and c axes, and alone would yield the space group $P2_1/m$, and an additional centre of symmetry at $\frac{1}{2}, 0, 0$ in the α cell. The origin of the unit cell of the β phase is at this centre of symmetry.

The initial trial structure was based upon the structure of β -Mg₂P₂O₇. The x and z coordinates for all the atoms were refined first with the atom positions differing from those of the β phase only in that one of the Mg²⁺ ions was displaced by 0.25 Å in the $[10\bar{1}]$ direction from its β -phase position. This displacement coincided in direction with that found for the cations in the α forms of Zn₂P₂O₇ (Robertson & Calvo, 1967*b*) and Cu₂P₂O₇ (Robertson & Calvo, 1967*a*) and its magnitude was estimated from the peak broadening of the Patterson function. Refinement was then pursued using difference syntheses until the $R(=\sum ||F_o| - |F_c|| / \sum |F_o|)$ value fell to about 0.20. The y parameters were found by trial and error displacements from the β structure where the anion was displaced out of the glide plane and the P-O-P group bent. Subsequently the agreement improved to the point where full-matrix

least-squares procedures could finish the refinement. The program used was written by J.S. Stephens of this laboratory. Unit weights were assigned initially, but in the final stages weights were assigned as $\omega=(1+0.05F_o + 0.009F_o^2)^{-1}$ where the coefficients were chosen so that the mean value of $\omega(\Delta F)^2$ was independent of the magnitude of F_o . This form had been suggested by Cruickshank *et al.* (1961). Unobserved reflections were considered to be in agreement and omitted from the refinement if the calculated structure factors were less than the minimum observable value. The atomic form factors for Mg²⁺, P and O⁻ were taken from *International Tables for X-ray Crystallography* (1962).

Initially it was found that a number of the atoms developed non-positive definite matrices for their temperature factors during the refinement and therefore the structure was first refined with isotropic temperature factors. The average B values obtained for each species were 0.34 Å² for the magnesium, 0.16 Å² for the phosphorus and 0.49 Å² for six of the seven oxygen atoms. The seventh, O_{III}(2*c*), had a value of 0.08 Å². When anisotropic temperature factors were used the R value dropped from 0.093 to 0.082 but at the expense of a non-positive definite thermal matrix for this last oxygen atom. The value of the residual $R_2 = \{\sum \omega ||F_o|^2 - |F_c|^2| / \sum \omega F_o^2\}^{\frac{1}{2}}$ is 0.112.

The final atomic positional parameters are listed in Table 1 and the thermal parameters are in Table 2. The observed and calculated structure factors adjusted to half the contents of the unit cell and then multiplied by 10 are in Table 3.

Table 1. Atomic parameters, with estimated standard errors, in α -Mg₂P₂O₇

	x	y	z
Mg(1)	0.3669 (1)	0.9301 (3)	0.2562 (2)
Mg(2)	0.3993 (2)	0.5598 (3)	0.2267 (2)
P(1)	0.2780 (1)	0.2329 (3)	0.0389 (1)
P(2)	0.4844 (1)	0.2271 (3)	-0.0480 (1)
O _I	0.3757 (3)	0.1744 (8)	-0.0239 (4)
O _{II} (1)	0.5625 (3)	0.2364 (7)	0.1097 (4)
O _{II} (2)	0.1882 (3)	0.2418 (7)	-0.1070 (4)
O _{III} (1 <i>c</i>)	0.2611 (3)	0.0989 (7)	0.1420 (4)
O _{III} (1 <i>t</i>)	0.3042 (4)	0.3867 (8)	0.1210 (5)
O _{III} (2 <i>c</i>)	0.5084 (3)	0.0910 (7)	-0.1471 (4)
O _{III} (2 <i>t</i>)	0.4745 (3)	0.3889 (7)	-0.1293 (4)

Table 2. Mean-square atomic vibrations ($\times 10^4$) (with estimated standard deviations)

	U_{11}^*	U_{22}	U_{33}	U_{13}	U_{23}	U_{13}
Mg(1)	29 (6)	35 (17)	34 (7)	9 (9)	-5 (5)	-5 (10)
Mg(2)	63 (7)	24 (16)	49 (7)	-12 (10)	4 (6)	-2 (10)
P(1)	21 (4)	29 (13)	16 (4)	3 (6)	-10 (3)	9 (6)
P(2)	64 (5)	21 (13)	3 (4)	-2 (6)	1 (3)	8 (6)
O _I	26 (13)	120 (36)	36 (13)	44 (17)	-2 (10)	5 (17)
O _{II} (1)	91 (13)	75 (35)	10 (11)	29 (21)	-5 (9)	-9 (17)
O _{II} (2)	54 (11)	45 (30)	42 (11)	33 (20)	2 (9)	21 (17)
O _{III} (1 <i>c</i>)	32 (11)	58 (32)	33 (11)	-8 (17)	-6 (9)	40 (17)
O _{III} (1 <i>t</i>)	150 (18)	42 (35)	61 (11)	-37 (22)	-30 (11)	-7 (20)
O _{III} (2 <i>c</i>)	38 (11)	22 (30)	7 (11)	5 (18)	15 (8)	-33 (16)
O _{III} (2 <i>t</i>)	122 (16)	34 (32)	56 (14)	54 (21)	24 (11)	16 (18)

* These values were obtained from $\beta_{ij} = 2\pi b_i b_j U_{ij}$ where β_{ij} 's appear as the effect of temperature through $\exp[-(\beta_{11}h + 2\beta_{12}hk + \dots)]$ in the structure factor expression and the b_i are the reciprocal lattice vectors.

Table 3. Observed and calculated structure factors (x 5)
Unobserved reflections are marked with an asterisk (to be read as 'less than').

Table with multiple columns for observed (Fobs) and calculated (Fcalc) structure factors, organized by reflection indices (h, k, l) and symmetry-equivalent reflections. Includes various numerical values and asterisks indicating unobserved reflections.

Crystal structure

The bonding in α -Mg₂P₂O₇ in many respects is similar to that found in the β phase. In the latter phase the cations are found to be in irregular octahedra with oxygen atoms at the corners. These octahedra share an edge with mirror plane related MgO₆ groups and additional edges with octahedra related by the centring operations $\frac{1}{2}, \frac{1}{2}, 0$ and $-\frac{1}{2}, \frac{1}{2}, 0$. These groups form sheets parallel to the *ab* plane where the cations lie in two-thirds of the octahedral holes of approximately close-packed oxygen atoms. Every oxygen atom in these sheets is bonded to two cations. The linear P–O–P groups lie between these sheets and opposite the empty octahedral sites.

In the α phase the central bond angle is bent to 144° with the greatest component of this displacement of the central oxygen atom from linearity lying along the *b* direction. The magnitude of the displacement from collinearity with the P(1)–P(2) vector is about 0.5 Å whereas the component in the *ac* plane is about 0.1 Å. Adjacent P₂O₇⁴⁻ groups along a *z*-constant plane are related alternately by a centre of symmetry or a two-fold screw axis. Thus the direction of the component of this displacement of the central oxygen atom parallel to the *ac* plane alternates sequentially while the displacement along the *b* axis alternates after every second anion. This feature can be seen in Fig. 1, where the α -Mg₂P₂O₇ structure is projected on to the *x, z* plane.

The terminal oxygen atoms are displaced from their β phase positions so as to maintain a pseudo threefold axis lying nearly along the inner P–O bond. This is accompanied by a small rotation of the terminal groups in the same sense when looking towards the central oxygen atom leaving the O_{II} atom at a slightly different *y* value from the P atoms. The P–O bond distances involving these oxygen atoms are identical, being 1.536 Å both on side 1 and on side 2. The e.s.d. for all the P–O bonds is 0.01 Å. In comparison with the β phase, the PO₄ groups of the anion are rotated in the opposite sense about an axis through the phosphorus atom and lying in the *ac* plane. This leaves the anion more open on the side corresponding to the displacement of the central oxygen atom from its β -phase position. The O_{III} oxygen atoms on this side of the glide plane (called *cis*) subtend P–O bond distances of 1.506 Å on side 1 and 1.526 Å on side 2 of the anion, whereas the *trans* oxygen atoms subtend bond distances of 1.473 Å on side 1 and 1.521 Å on side 2. The larger P–O–(P) bond (1.612 Å) lies on the same side as this short terminal P–O bond whereas the P–O–(P) bond on side 2 is 1.569 Å. The average values found for these bonds are 1.532 Å and 1.538 Å for sides 1 and 2 respectively. These bond distances are tabulated in Table 4 and the anion geometry of the α phase is compared with that of the β phase in Fig. 2.

In detail the bonding about the cations differs from that found in the β phase. The cations still form a hexagonal network of edge-shared octahedra but only

if an anomalously large cation–oxygen bond is included. This bond, Mg(2)–O_{III}(1*t*), has a value of 2.15 Å in the β phase as compared with 3.35 Å in the α phase. The eleven 'normal' Mg–O bond distances have an average value of 2.08 Å [2.10 Å about Mg(1) and 2.04 Å about Mg(2)] as compared with 2.07 Å in the β phase.

Phase transformation

A series of X-ray photographs of Mg₂P₂O₇ were taken between 58 and 75°C. The crystal was heated by an air flow along the axis of the Weissenberg camera and the temperature was monitored by a thermocouple attached to the collimator and lying on the rotation axis of the crystal but displaced by about 1 cm from it. The

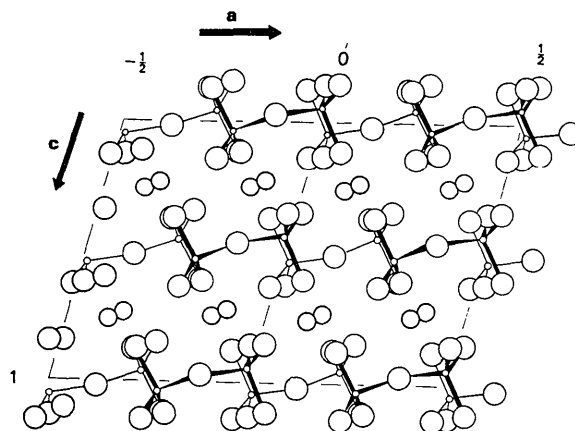


Fig. 1. The structure of α -Mg₂P₂O₇ projected onto the *x, z* plane. The smallest circles represent the phosphorus atoms, the intermediate circles the Mg ions, and the largest circles the oxygen atoms. The bold anions all lie near the same plane and about $\frac{1}{2}b$ from the remaining anions.

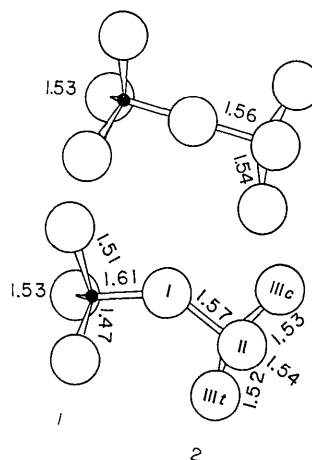


Fig. 2. The anion geometry in the α and β modifications of Mg₂P₂O₇ are compared. The upper diagram represents the anion in the β phase and the lower one the anion in the α phase. The *b* axis is vertical and the bond distances are in Å. The two ends of the anion are labelled 1 and 2.

temperature stability of the system was better than 1 °C per hour although the absolute temperature was known to an accuracy no better than 2 or 3 °C. In one sequence of photographs consisting of a 40° section of the second layer line for a crystal aligned about the *b* axis, reflections from the α and β phase were found to co-exist at 65 ± 1 °C, but only the α -phase reflections existed at 62 ± 1 °C and only the β -phase at 69 ± 1 °C. The weak reflections characterizing the α phase were missed previously owing to the short duration of the exposures (Calvo, 1965*b*). A second sequence of photographs containing *h*0*l* reflections indicated that the α and β phases co-existed from 62° to 65° with the intensity of the α -phase reflections relative to those arising from the β phase decreasing with increasing temperature. In each of the three photographs in this sequence the $h=0 \pmod{4}$ α -phase reflections and $h=0 \pmod{2}$ β -phase reflections were distinctly separated at moderate and high scattering angles, indicating a volume discontinuity at the transformation. No evidence of changes in spot shape could be detected.

A larger crystal of the same composition was examined under a microscope with ordinary illumination while the crystal was heated through the phase transformation. The surface of the crystal, indexed as (001), had striations parallel to the *b* axis. As the transformation proceeded lines of index of refraction discontinuities were seen to develop parallel to the *b* axis and move across the crystal.

Conclusions

In an earlier paper (Robertson & Calvo, 1967*a*) it was suggested that the doubled *c* with the *c*-glide plane replacing the β phase mirror plane, which is common to all the α phases in this series, arises from the twist that the bent anions place upon the octahedra of the cations through their shared oxygen atoms. The sense of the rotation given to cation octahedra adjacent along the *c* axis is opposite since they are attached at opposite ends of the same anion. For rigid octahedra rotated about an axis (a pseudo threefold axis of the octahedron) through the cation adjacent anions along *c* will have opposite displacements along the *b* axis, thus creating the *c*-glide plane with a doubled periodicity along the *c* direction.

The phase transformation in α -Cu₂P₂O₇ is of the second order but it transforms inhomogeneously. The *l*-odd reflections of α -Cu₂P₂O₇ become diffuse along the *a** direction, suggesting that the disordering mechanism involves perfect coherence in layers parallel to the *b* and *c* axes but a temperature dependent number of stacking faults with translational component $\frac{1}{2}c$ along the *a** axis. This stacking fault arises when adjacent anions along *a** have their P–O–P angle acute in opposite sense along the *b* axis. A completely random stacking leads, in the case of Cu₂P₂O₇, to the β phase.

In contrast with Cu₂P₂O₇, Mg₇P₂O₇ does not satisfy the Landau (1937) criterion, as modified by Haas

Table 4. *Interatomic distances and angles in α -Mg₂P₂O₇ (uncorrected for the effects of thermal motion)*

P ₂ O ₇ ⁴⁻ group				
Bond distances (Å)				
P(1)–P(2)	3.026	(3.105)*		
P(1)–O _I	1.612	(1.557)	O _I –O _{II} (1)	2.459
P(2)–O _I	1.569		O _I –O _{II} (2)	2.506
P(1)–O _{II} (1)	1.533	(1.534)	O _I –O _{III} (1 <i>t</i>)	2.521
P(2)–O _{II} (2)	1.539		O _I –O _{III} (2 <i>t</i>)	2.534
P(1)–O _{III} (1 <i>c</i>)	1.507	(1.542)	O _I –O _{III} (1 <i>c</i>)	2.473
P(2)–O _{III} (2 <i>c</i>)	1.527		O _I –O _{III} (2 <i>c</i>)	2.408
P(1)–O _{III} (1 <i>t</i>)	1.472		O _{II} (1)–O _{III} (1 <i>c</i>)	2.513
P(2)–O _{III} (2 <i>t</i>)	1.521		O _{II} (2)–O _{III} (2 <i>c</i>)	2.557
			O _{II} (1)–O _{III} (1 <i>t</i>)	2.538
			O _{II} (2)–O _{III} (2 <i>t</i>)	2.522
			O _{III} (1 <i>t</i>)–O _{III} (1 <i>c</i>)	2.473
			O _{III} (2 <i>t</i>)–O _{III} (2 <i>c</i>)	2.524
Angles (°)				
P(1)–O _I –P(2)	144°			
		Side 1	Side 2	
O _I –P–O _{II}		103	108	
O _I –P–O _{III} (<i>t</i>)		110	110	
O _I –P–O _{III} (<i>c</i>)		105	102	
O _{II} –P–O _{III} (<i>t</i>)		115	111	
O _{II} –P–O _{III} (<i>c</i>)		111	113	
O _{III} (<i>c</i>)–P–O _{III} (<i>t</i>)		112	112	
MgO ₆ group				
Bond distances (Å)				
Mg(1)–O _{II} (1)	2.073	(2.05)	Mg(2)–O _{II} (1)	2.037
–O _{II} (2)	2.084		–O _{III} (2)	2.054
–O _{III} '(2 <i>c</i>)	2.135	(2.15)	–O _{III} '(2 <i>t</i>)	2.120
–O _{III} '(1 <i>c</i>)	2.137		–O _{III} '(1 <i>t</i>)	3.350
–O _{III} '(2 <i>t</i>)	2.142	(2.02)	–O _{III} '(1 <i>t</i>)	1.985
–O _{III} (1 <i>c</i>)	2.059		–O _{III} '(2 <i>c</i>)	2.024

* Bond distances in parenthesis are those found in β -Mg₂P₂O₇.

(1965), for a second order phase transformation which requires that the change in symmetry (including the translational factor group) correspond to a single irreducible representation of the space group of higher symmetry. In the case of Mg₂P₂O₇ two irreducible representations are involved and by Landau's criterion these changes would have to be successive rather than simultaneous. This theory, as Birman (1966) has remarked, seems to give the proper symmetry constraints although it fails in its analytical predictions. On the other hand specific heat studies show the transformation in Mg₂P₂O₇ to be non-isothermal (McDonald & Oetting, 1963), and although the lattice parameters change sharply there are hysteresis effects (Roy *et al.*, 1948). Transformations of this sort have been studied by Ubbelohde (1966) and called anomalous first order by Mayer & Streeter (1939).

The differences between the transitions in Cu₂P₂O₇ and Mg₂P₂O₇ seem to be related to the formation of the sixth Mg–O bond and further lead to the α and β phase domains found during the transformation. Although the axial oxygen atoms around Mg(2) are roughly the same distance apart in α -Mg₂P₂O₇ (5.40 Å) as found in α -Cu₂P₂O₇ (5.26 Å), in the latter case the cation is more equally ligated to these oxygen atoms. It appears that the ability of Cu²⁺ to form axial bonds of variable lengths is a major factor preventing the two α phases from being isostructural. Further there is no evidence that α -Mg₂P₂O₇, in becoming the β phase, becomes disordered in the same way as α -Cu₂P₂O₇ since the e.p.r. lines of the β phase do not grow out of those of the α phase (Calvo, Leung & Datars, 1967). Thus, in contrast, if α -Mg₂P₂O₇ is a positionally disordered phase like β -Cu₂P₂O₇ it must be based upon a Mg₂P₂O₇ structure where the both cations are sixfold coordinated to oxygen atoms at normal Mg–O bond distances. It appears that the transformation is triggered by the formation of the sixth Mg(2)–O bond and further that the α phases feature a bent pyrophosphate anion at the expense of the bond energy in one cation–oxygen bond.

The values of the average inner and outer P–O bond distances compare favorably with those predicted by Cruickshank (1961). His values are 1.64 and 1.58 Å for the inner bond and 1.51 and 1.53 Å for P–O–P bond angles of 120° and 180° respectively. The values found here are 1.591 and 1.516 Å. Thermal corrections as suggested by Busing & Levy (1964) would raise these values by a minimum of 0.001 and 0.003 Å and a maximum of 0.010 and 0.013 Å respectively. In detail, since the e.s.d.'s for all the bonds are 0.01 Å, the difference between the inner P–O distances appear to be significant. Further, the short P(2)–O_{III}(2*t*), involving the oxygen atom supporting only one strong cation oxygen bond, is significantly shorter than the average terminal bond length of 1.525 Å when this short bond is excluded. One is tempted to associate this shortened bond with the fact that this oxygen atom is ligated strongly to only one cation rather than two as is the case for the remaining terminal oxygen atoms of the anion. This environmental effect seems rather large since, even with the maximum correction, a linear bond distance order bond relationship would imply a bond order of only 1.2.

A further indication of some electron delocalization from the anion to the cations is provided by the fact that all the oxygen atoms ligated to two cations in addition to the phosphorus atom are found to be nearly coplanar with these atoms. This result is summarized in Table 5.

The structure obtained by Lukaszewicz (1966), based upon 205 observed reflections, shows similar bond distances to those reported here although some of the atomic positions differ by more than 3 standard deviations. His P(1)–O(P) and P(2)–O(P) bond distances are 1.630 and 1.593 Å respectively with a central bond angle of 140°. The average terminal P–O bond distances are 1.530 and 1.526 Å for sides 1 and 2 respectively.

In summary, although the anion has nearly C₂ symmetry, it does deviate significantly. The central bond angle is 144° and the average inner and outer bond

Table 5. Bond angles about terminal oxygen atoms in α -Mg₂P₂O₇

At O _{II} (1)		At O _{II} (2)	
Mg(1)–O _{II} (1)–Mg(2)	98.9	Mg(1)–O _{II} (2)–Mg(2)	98.0
Mg(1)–O _{II} (1)–P(1)	131.5	Mg(1)–O _{II} (2)–P(2)	132.4
Mg(2)–O _{II} (1)–P(1)	129.1	Mg(2)–O _{II} (2)–P(2)	128.2
	Sum 359.5		Sum 358.6
At O _{III} (1 <i>c</i>)		At O _{III} (2 <i>c</i>)	
Mg(1)–O _{III} (1 <i>c</i>)–Mg'(1)	102.5	Mg(1)–O _{III} (2 <i>c</i>)–Mg(2)	102.0
Mg(1)–O _{III} (1 <i>c</i>)–P(1)	127.7	Mg(1)–O _{III} (2 <i>c</i>)–P(2)	129.4
Mg'(1)–O _{III} (1 <i>c</i>)–P(1)	128.6	Mg(2)–O _{III} (2 <i>c</i>)–P(2)	124.4
	Sum 358.8		Sum 355.8
At O _{III} (1 <i>t</i>)		At O _{III} (2 <i>t</i>)	
Mg(2)–O _{III} (1 <i>t</i>)–Mg'(2)	100.3	Mg(1)–O _{III} (2 <i>t</i>)–Mg(2)	98.7
Mg(2)–O _{III} (1 <i>t</i>)–P(2)	155.2	Mg(2)–O _{III} (2 <i>t</i>)–P(2)	144.8
Mg(2)–O _{III} (1 <i>t</i>)–P(2)	102.4	Mg(1)–O _{III} (2 <i>t</i>)–P(2)	113.6
	Sum 357.9		Sum 357.1

distances differ by 0.08 Å as compared with 0.05 Å for α -Cu₂P₂O₇ where the bond angle is 157° (Robertson & Calvo, 1967a). A significantly shortened terminal P–O bond length is tentatively attributed to the fact that this oxygen atom fails to complete the sixfold coordination about one of the cations.

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Structure Cristalline du Bisdiéthylthiocarbamate de Phénylarsine

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(Reçu le 10 janvier 1967)

The crystal structure of phenylarsenic bisdiethylthiocarbamate, C₆H₅As[S₂CN(C₂H₅)₂]₂, at room temperature, has been determined by three-dimensional methods, and refined by isotropic least-squares methods. There are four formula units in the monoclinic cell, $a = 14.82$, $b = 9.48$, $c = 16.63$ Å, $\beta = 112^\circ 40'$, space group $P2_1/c$. Arsenic has two strong bonds (2.33 Å) and two weak bonds (2.87 Å)

with sulphur atoms and a fifth bond with the phenyl ring (1.96 Å). Each group S₂CN is planar.

$\begin{matrix} (-) & (+) \\ \text{S}_2\text{C}=\text{NR}_2 \end{matrix}$ is an important canonical form in the structure. The coordination of arsenic is discussed.

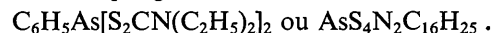
Introduction

Les dithiocarbamates sont des complexes qui ont été très étudiés. De nombreuses publications ont paru, notamment au sujet de leur intérêt en analyse minérale et de leur grande activité biologique (surtout comme fongicides). Thorn & Ludwig (1962) ont essayé de faire une synthèse des informations actuelles chimiques et physico-chimiques. Malgré cela le mécanisme des propriétés des dithiocarbamates est encore très mal connu. La recherche de leur structure cristalline devrait fournir des renseignements appréciables. Plusieurs laboratoires étrangers s'y intéressent.

En ce qui nous concerne, le premier composé étudié dans notre laboratoire a été le diéthylthiocarbamate de cuivre (Bally, 1963, 1966). Le second, qui fait l'objet de cette publication, est le bisdiéthylthiocarbamate de phénylarsine (Bally, 1965, 1966).

Partie expérimentale

Le bisdiéthylthiocarbamate de phénylarsine a pour formule chimique globale:



La répartition électronique suivant les espèces atomiques indique: