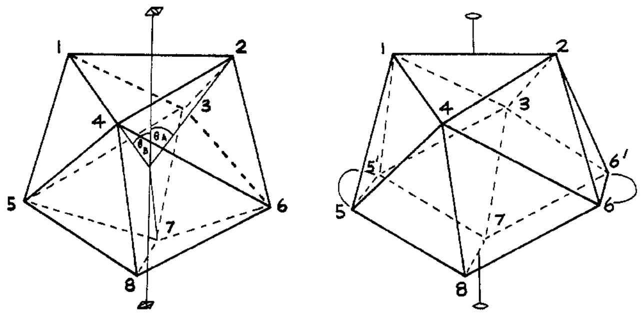

a) D_{2d} b) C_2 or C_{2v}

Figure 4.—Illustration of the relationship between dodecahedral symmetry (a) and the suggested polyhedron model (b) for lanthanum carbonate octahydrate.

θ_A and θ_B for a hard-sphere dodecahedral model are about 37 and 70°, respectively. On the basis of energy considerations, Hoard and Silverton[23] calculated values of 35.2 and 73.5°. The corresponding angles in the present work compare favorably with these values if only the angles involving unidentate ligands are considered. In the La(2) polyhedra θ_A is 35.2° and θ_B is 73.2°. For the La(1) polyhedra the corresponding angles are 32.7 or 32.0 and 73.8°. Thus the polyhedra in question, although distorted from C_{2v} symmetry, approximate that of the suggested dodecahedral derivative model.

All C–O distances in both carbonate groups are of equal length within experimental error and agree with reported values.[24–26] The uncoordinated oxygen atom of the fourfold carbonate ion has a large thermal parameter. An analogous situation was observed with the terminal oxygen of the nitrate ions of $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$[27] and $Th(NO_3)_4 \cdot 5H_2O$.[28] Significant deviation from ideal shape occurs in the carbonate group around the C(2) atom. The distances O–O are shorter if both oxygen atoms are coordinated to the same metal; *i.e.*, they form an edge shared by the carbonate group and the metal coordination polyhedron.

Many of the observed O–O distances involving water molecules are short—an observation which suggests strongly the presence of hydrogen bonds. In the final electron density difference map several residual peaks appeared to be located in positions appropriate for hydrogen bonding. Since attempts to refine these parameters met with only limited success, the hydrogen-bonding scheme must be deduced from stereochemical considerations.

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The Crystal Structure of α-$Ca_2P_2O_7$

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The high-temperature form of calcium pyrophosphate, α-$Ca_2P_2O_7$, crystallizes in the monoclinic space group $P2_1/n$ with lattice parameters a = 12.66 (1) Å, b = 8.542 (8) Å, c = 5.315 (5) Å, and β = 90.3 (1)°. There are four molecules per unit cell yielding a calculated density of 2.95 g/cm^3 compared to a measured value of 2.947 g/cm^3. This structure is closely related to that of α-$Sr_2P_2O_7$, although the latter has orthorhombic symmetry. Both cations show coordination numbers of eight with average cation–oxygen atom bond lengths of 2.54 and 2.51 Å for the individual cation sites. The two ends of the anion deviate by 13° from the eclipsed configuration with a P–O–P angle of 130°. The P–O(–P) bond lengths average 1.60 Å while the terminal ones average to 1.51 Å. The individual P–O bond lengths range from 1.49 to 1.62 Å and have estimated standard deviations of the order of 0.01 Å. The structure was refined by a full-matrix least-squares procedure using 1416 reflections whose intensities were estimated visually. The final value for the conventional R value is 0.098. The diffraction pattern shows a marked orthorhombic character suggesting a high-temperature phase with Pbnm symmetry.

Introduction

The structures of several divalent metal ion pyrophosphates, $M_2P_2O_7$, have been determined recently. All of these show either a bent P–O–P group in the anion[1–4] or considerable disorder at the central oxygen atom of the anion.[5,6] The value of the P–O–P angle has been found to range from 132° (in $Cd_2P_2O_7$[7]) to 156° (in $Cu_2P_2O_7$[4]). These structures seem to divide between those having the terminal ends of the anion in a

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nearly staggered configuration and those having nearly an eclipsed configuration. The former group of compounds is also characterized by cations with radii smaller than 0.9 Å while the latter have cations with large radii.

Among the latter group are the alkaline earth metal ion pyrophosphates. This group was shown by Randby, Mash, and Henderson[8] to be characterized by four phases—α, β, γ, and δ—not all common to all these compounds. The structure of the β phase, common to $Ca_2P_2O_7$ and $Sr_2P_2O_7$, was determined through the former compound by Webb.[3] The two anions in this structure have P–O–P angles of 131 and 138°. The structure of $\alpha\text{-Sr-}_2\text{P}_2\text{O}_7$ has been determined by Grenier and Masse[9] recently. They confirmed that the crystal system is orthorhombic as reported by Randby, *et al.*,[8] and determined the P–O–P angle to be 133.5°. The remaining phases are structurally unknown although there does not appear to be a very close structural relationship among them since the phase transformations do not appear reversible.

Although the space group reported for α-$Sr_2P_2O_7$ is $Pna2_1$, it was noted that the structure nearly satisfied the requirements of the centric group Pnam.[9] Recently electron paramagnetic resonance on Mn^{2+}-doped α-$Sr_2P_2O_7$ crystals confirmed the latter to be the true space group.[10] In this space group the structure, at least on the average, must have the O–P–O–P–O part of the anion in the mirror plane as well as both cations.

Experimental Section

Crystals of α-$Ca_2P_2O_7$, both pure and doped with Mn^{2+}, were prepared and kindly supplied by Dr. C. W. W. Hoffman, Food Machinery Co., Princeton, N. J. The lattice parameters, except for the β angle, were determined from photographs calibrated by the superposition of reflections from a TiO_2 crystal having the rutile structure. The lattice parameters of TiO_2 were taken as a = 4.5929 (5) and 2.9591 (3) Å.[11] The β angle was determined from a double exposure of the [010] zone taken with the precession camera. The crystal was turned through 180° about the c^* axis between exposures. The β angle was derived from a measurement of the angle between the two a^* axes. These lattice parameters are collected in Table I together with extinction conditions leading to the selection of $P2_1/n$ as the space group. The stronger reflections on the photographs showed a strong orthorhombic character.

The density was measured with a pycnometer at 22.5°. The value obtained, 2.947 g/cm^3, agrees well with the theoretical value and represents a decrease of about 6% over the value of 3.120 g/cm^3 reported by Webb for β-$Ca_2P_2O_7$.

A crystal of dimensions 0.10 × 0.16 × 0.23 mm^3 was mounted so as to rotate about the c axis, coincident with the long axis of the crystal. All of the intensity photographs were taken with Mo Kα radiation and measured visually. Photographs of the type hkn with n = 0–4 were taken with the Weissenberg camera while the [110], [010], and [100] zones were recorded with the precession camera. In addition, the three upper levels of the latter zone were recorded. Lorentz and polarization corrections were applied but absorption corrections were unnecessary since $\mu R \approx 0.2$ for the crystal would lead to relative errors of the order of 1% for the radiation and angular range used. A total of 1416 reflections was estimated of which 997 had observable intensities. About 20% of all the reflections were multiply measured.

Table I

Crystal Data for α-$Ca_2P_2O_7$

a = 12.66 (1) Å β = 90.3 (1)°
b = 8.542 (8) Å Z = 4
c = 5.315 (5) Å
Extinctions $h0l$ $h + l$ odd; $0k0$, k odd
$\rho_{\text{exptl}} = 2.947$ $\rho_{\text{calcd}} = 2.95$
Linear absorption coefficient for Mo radiation = 23.1

Structure Determination

Trial atomic parameters were taken from a draft manuscript on the structure of α-$Sr_2P_2O_7$ available through the kindness of Dr. Grenier. The predicted Patterson peak positions agreed qualitatively with those found on the calculated Patterson projections of α-$Ca_2P_2O_7$. In order to make the structures compatible, the a and b axes must be reversed and the z coordinate shifted by $^1/_4c$. The atomic-scattering curves, corrected for dispersion, for Ca^{2+}, P, and O^- were chosen from the "International Tables."[12] The R value $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ obtained for this trial structure was about 0.3 for the data of the three principal zones.

Further refinement was carried out by a full-matrix least-squares procedure using a program prepared by J. S. Stephens for the IBM 7040 computer. Additional data were added with separate scale constants as they were measured. For the final cycles of refinement, weights, w, were chosen so that $w(\Delta F)^2$ would be independent of the magnitude of F_o. The functional form of w was $(3.0 + 0.075F_o + 0.007F_o^2)^{-1}$. Unobserved reflections were given zero weight if their calculated value did not exceed the minimum observable value in that region of reciprocal space. Otherwise they were given a value 0.9 times the minimum observable value in that region in space. Multiply measured structure factors were averaged and randomly assigned to one of the data sets. When the value of R had dropped to about 0.15, anisotropic thermal parameters replaced the individual isotropic ones. The refinement was terminated when the calculated shifts for the atomic coordinates were one-third or less of their estimated standard deviations. The final atomic parameters, positional and thermal, are collected in Table II. The calculated and observed structure factors are recorded in Table III. The final value of R for all the data is 0.098 while the value of $R_2 = [\Sigma w||F_o|^2 - |F_c|^2|/\Sigma w|F_o|^2]^{1/2}$ is 0.126. No peaks of magnitude greater than 5% of a Ca peak could be detected in the electron density maps prepared at intervals of 0.3 Å along the c axis.

Description of the Structure

The geometry of the anion in $Ca_2P_2O_7$ is shown in Figure 1. The P(1)–O(1)–P(2) bond angle is 130°

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TABLE II

ATOMIC PARAMETERS FOR α-$Ca_2P_2O_7$ (ESD'S IN PARENTHESES)

	Positional parameters		
	x	y	z
Ca(1)	0.7652 (2)	0.8128 (2)	0.7433 (4)
Ca(2)	0.5902 (2)	0.6142 (2)	0.2395 (4)
P(1)	0.0281 (2)	0.2334 (3)	0.7349 (6)
P(2)	0.1798 (2)	0.4863 (3)	0.7699 (6)
O(1)	0.0637 (6)	0.4106 (9)	0.7352 (17)
O(3)	0.0559 (7)	0.1566 (10)	−0.0161 (19)
O(5)	0.0825 (5)	0.1464 (8)	0.5214 (17)
O(7)	−0.0887 (6)	0.2362 (10)	0.6805 (20)
O(2)	0.2411 (7)	0.4611 (10)	0.5241 (19)
O(4)	0.2360 (6)	0.4046 (9)	0.9828 (16)
O(6)	0.1631 (6)	0.6537 (9)	0.8403 (17)

	Thermal parameters, Å² × 10⁴					
	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	221 (10)	217 (10)	190 (22)	13 (7)	−29 (10)	−5 (8)
Ca(2)	232 (9)	184 (9)	200 (21)	18 (7)	17 (9)	−8 (8)
P(1)	138 (11)	90 (11)	184 (21)	1 (8)	−5 (11)	10 (10)
P(2)	147 (12)	119 (12)	140 (23)	−9 (9)	−23 (12)	−28 (11)
O(1)	155 (35)	212 (37)	170 (53)	−25 (27)	−12 (35)	29 (33)
O(3)	280 (44)	267 (44)	240 (57)	77 (33)	−100 (42)	−19 (38)
O(5)	134 (34)	114 (32)	208 (52)	15 (24)	36 (35)	11 (32)
O(7)	182 (38)	210 (42)	439 (68)	11 (30)	−10 (41)	150 (40)
O(2)	268 (45)	198 (39)	295 (62)	−53 (32)	27 (42)	−26 (39)
O(4)	184 (37)	209 (36)	123 (51)	−34 (27)	0 (35)	−56 (32)
O(6)	153 (35)	164 (34)	234 (55)	−62 (26)	−33 (36)	−26 (33)

[a] These values were obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where β_{ij}'s appear as a temperature effect through $\exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$.

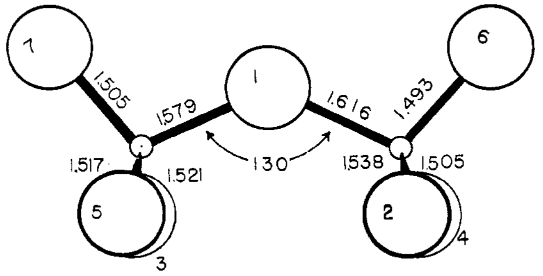

Figure 1.—The geometry of the anion, where the larger circles are the oxygen atoms and the small ones are the phosphorus atoms. The value of the central bond angle and the phosphorus–oxygen atom bond distances in angström units are shown.

compared to 133.5° in α-$Sr_2P_2O_7$ and the values of 133 and 138° found for the two independent anions in β-$Ca_2P_2O_7$. The configuration of the anion deviates significantly from being eclipsed. For example, the angle between the projection of the P(1)–O(7) and P(2)–O(6) vectors on the plane perpendicular to the P(1)–P(2) vector is 13°. In α-$Sr_2P_2O_7$[10] the mirror plane requires an exactly eclipsed configuration for the anion. The phosphorus atoms are slightly displaced out of the same z = constant plane with the two ends of the anion twisted oppositely so that O(6) and O(7) lie on opposite sides of the pseudo-mirror planes at $z = {}^1/_4$ and ${}^3/_4$. These oxygen atoms will be referred to as being *cis* with respect to the central oxygen atom. However, the major component of the P(1)–O(1)–P(2) angle still lies on the *ab* plane as can be seen in Figure 2.

These anions pack in columns composed of pairs related by centers of symmetry with the *cis* side of the anions adjacent to each other. These columns in turn form sheets parallel to the *ac* plane with the columns in adjacent sheets rotated by nearly 90° and shifted by ${}^1/_2 a$ in order to fit in the interstices between successive columns in the same sheet. The anions sit in interstitial sites between adjacent sheets with Ca(1) bonded to the four *trans*-oxygen atoms of two anions separated by an a-axis translation. These oxygen atoms are $O(\bar{2})$, $O(\bar{4})$, $O(\bar{3})$, and $O(\bar{5})$ around Ca(1) (see Figure 2). The remaining coordination group of this cation consists of the O(2′) and O(6′) edge of a third anion and

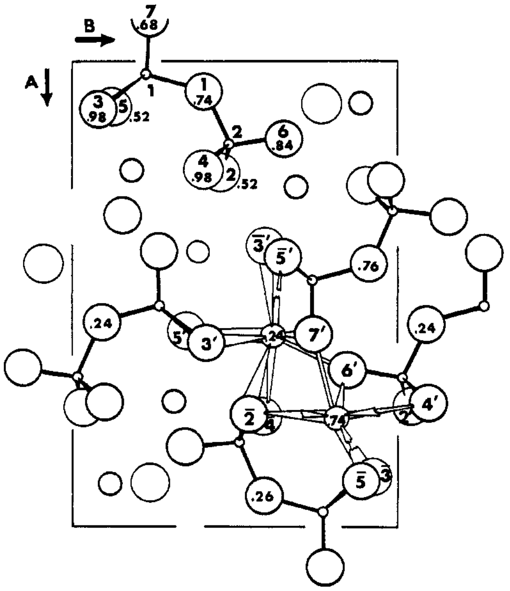

Figure 2.—The structure of α-$Ca_2P_2O_7$ projected onto the xy plane, where the large circles represent oxygen atoms and the small circles represent phosphorus atoms, while the medium-sized circles represent the cations. The decimal numbers represent the z coordinates of the atom. The broken bonds are to oxygen atoms a unit cell length away from those shown in this figure.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR α-$Ca_2P_2O_7$[a]

[a] Unobserved reflections are marked with an asterisk.

O(4′) of a fourth anion removed by a *c*-axis length from the third. The final oxygen atom, O(7′), is shared with the fifth anion. The group of these eight oxygen atoms forms a pseudo-cube about cation 1 with a mean cation–oxygen atom bond length of 2.54 Å with a range in individual distances from 2.360 to 2.807 Å as is shown in Table IV. Cation 2 shares two edges composed of $O(\bar{2})$ and $O(\bar{4})$ with the first anion and $O(\bar{3}')$ and $O(\bar{5}')$ with the second. All of these oxygen atoms are *trans* to the central oxygen atom. An additional edge consists of the *cis*-oxygen atom, O(7′), and the *trans*-oxygen atom, $O(\bar{3}')$ of a third anion. The seventh oxygen atom, $O(\bar{5}')$, comes from the anion one *c*-axis translation removed. The remaining oxygen atom, O(6′), nearly lies in the same z = constant plane as Ca(2). The entire arrangement of these oxygen atoms about the cation forms another distorted cube with a mean Ca(2)–O bond length of 2.51 Å and the range of individual bonds from 2.250 to 2.689 Å. No other oxygen atoms lie within 3 Å of either cation. Each *trans*-oxygen atom is shared between the phosphorus atom and three cations while the *cis*-oxygen atoms are bonded to only two cations in addition to the phosphorus atom. Unlike β-$Ca_2P_2O_7$, O(1), the central oxygen atom of the anion, does not appear within the primary coordination sphere of either cation.

The geometry of the anion in α-$Ca_2P_2O_7$ is similar to that in α-$Sr_2P_2O_7$ and β-$Ca_2P_2O_7$. The P–O(–P) bond lengths are 1.579 (8) and 1.616 (8) Å compared with 1.59 and 1.60 Å in α-$Sr_2P_2O_7$. In β-$Ca_2P_2O_7$ the average value of this bond length is 1.615 Å. The average terminal bond lengths are also very similar in the three compounds. In α-$Ca_2P_2O_7$ this average is 1.521 Å for the *trans* bonds and 1.499 Å for the *cis* bonds while in α-$Sr_2P_2O_7$ the comparable *trans* and *cis* values are 1.51 and 1.47 Å, respectively. In β-$Ca_2P_2O_7$ these distances

TABLE IV

BOND LENGTHS AND ANGLES IN α-$Ca_2P_2O_7$ (THE ESD'S ARE ENCLOSED IN PARENTHESES)

A. P_2O_7 Group

Distance, Å	
P(1)-P(2)	2.896 (4)
P(1)-O(1)	1.579 (8)
P(1)-O(3)	1.517 (10)
P(1)-O(5)	1.524 (9)
P(1)-O(7)	1.505 (8)
P(2)-O(1)	1.616 (8)
P(2)-O(2)	1.538 (10)
P(2)-O(4)	1.505 (9)
P(2)-O(6)	1.493 (8)
O(1)-O(3)	2.545 (12)
O(1)-O(5)	2.537 (11)
O(1)-O(7)	2.453 (11)
O(3)-O(5)	2.484 (14)
O(3)-O(7)	2.526 (13)
O(5)-O(7)	2.454 (11)
O(1)-O(2)	2.551 (12)
O(1)-O(4)	2.544 (11)
O(1)-O(6)	2.491 (11)
O(2)-O(4)	2.487 (13)
O(2)-O(6)	2.554 (12)
O(4)-O(6)	2.436 (12)

Bond angle, deg			
P(1)-O(1)-P(2)	130.0 (4)		
O(1)-P(1)-O(3)	110.5 (5)	O(3)-P(1)-O(5)	109.6 (5)
O(1)-P(1)-O(5)	109.7 (4)	O(3)-P(1)-O(7)	113.4 (5)
O(1)-P(1)-O(7)	105.3 (4)	O(5)-P(1)-O(7)	108.2 (5)
O(1)-P(2)-O(2)	107.9 (5)	O(2)-P(2)-O(4)	109.6 (5)
O(1)-P(2)-O(4)	109.2 (4)	O(2)-P(2)-O(6)	114.8 (5)
O(1)-P(2)-O(6)	106.4 (4)	O(4)-P(2)-O(6)	108.8 (5)

B. Ca–O_8 Group[a]

Distance, Å	
Ca($\bar{1}$)–O(3)	2.693 (9)
Ca($\bar{1}$)–O(5)	2.416 (8)
Ca($\bar{1}$)–O(7')	2.368 (8)
Ca($\bar{1}$)–O(2)	2.739 (9)
Ca($\bar{1}$)–O($\bar{2}'$)	2.460 (9)
Ca($\bar{1}$)–O(4)	2.360 (8)
Ca($\bar{1}$)–O($\bar{4}'$)	2.807 (8)
Ca($\bar{1}$)–O($\bar{6}'$)	2.514 (9)
Ca(2)–O(3')	2.396 (10)
Ca(2)–O($\bar{3}'$)	2.689 (9)
Ca(2)–O(5')	2.598 (8)
Ca(2)–O($\bar{5}'$)	2.511 (8)
Ca(2)–O(7')	2.464 (10)
Ca(2)–O(2)	2.555 (9)
Ca(2)–O(4)	2.508 (8)
Ca(2)–O(6')	2.250 (8)

Bond angle, deg			
O(3)–Ca($\bar{1}$)–O(5)	68.3 (3)	O(5)–Ca($\bar{1}$)–O(7')	153.7 (3)
O(3)–Ca($\bar{1}$)–O(7')	136.6 (3)	O(5)–Ca($\bar{1}$)–O(2)	81.0 (3)
O(3)–Ca($\bar{1}$)–O(2)	112.7 (3)	O(5)–Ca($\bar{1}$)–O($\bar{2}'$)	110.0 (3)
O(3)–Ca($\bar{1}$)–O($\bar{2}'$)	72.8 (3)	O(5)–Ca($\bar{1}$)–O(4)	118.8 (3)
O(3)–Ca($\bar{1}$)–O(4)	75.7 (3)	O(5)–Ca($\bar{1}$)–O($\bar{4}'$)	72.1 (2)
O(3)–Ca($\bar{1}$)–O($\bar{4}'$)	106.9 (2)	O(5)–Ca($\bar{1}$)–O($\bar{6}'$)	84.0 (3)
O(3)–Ca($\bar{1}$)–O($\bar{6}'$)	151.1 (3)	O(7')–Ca($\bar{1}$)–O(2)	80.0 (3)
O(2)–Ca($\bar{1}$)–O($\bar{2}'$)	169.0 (3)	O(7')–Ca($\bar{1}$)–O($\bar{2}'$)	89.5 (3)
O(2)–Ca($\bar{1}$)–O(4)	69.3 (3)	O(7')–Ca($\bar{1}$)–O(4)	70.5 (3)
O(2)–Ca($\bar{1}$)–O(4')	118.4 (3)	O(7')–Ca($\bar{1}$)–O($\bar{4}'$)	101.5 (3)
O(2)–Ca($\bar{1}$)–O($\bar{6}'$)	69.0 (3)	O(7')–Ca($\bar{1}$)–O($\bar{6}'$)	72.2 (3)
O(4)–Ca($\bar{1}$)–O($\bar{4}'$)	168.5 (3)	O($\bar{4}'$)–Ca($\bar{1}$)–O($\bar{6}'$)	54.2 (2)
O(4)–Ca($\bar{1}$)–O($\bar{6}'$)	127.6 (3)	O($\bar{2}'$)–Ca($\bar{1}$)–O(4)	104.1 (3)
O($\bar{2}'$)–Ca($\bar{1}$)–O($\bar{6}'$)	111.2 (3)	O($\bar{2}'$)–Ca($\bar{1}$)–O(4')	66.9 (3)
O($\bar{3}'$)–Ca(2)–O($\bar{3}'$)	72.9 (3)	O($\bar{3}'$)–Ca(2)–O(5')	102.2 (3)
O($\bar{3}'$)–Ca(2)–O(5')	70.2 (3)	O($\bar{3}'$)–Ca(2)–O($\bar{5}'$)	57.0 (3)
O($\bar{3}'$)–Ca(2)–O($\bar{5}'$)	112.9 (3)	O($\bar{3}'$)–Ca(2)–O(7')	143.2 (3)
O($\bar{3}'$)–Ca(2)–O(7')	119.3 (3)	O($\bar{3}'$)–Ca(2)–O(2)	71.5 (3)
O($\bar{3}'$)–Ca(2)–O(2)	112.5 (3)	O($\bar{3}'$)–Ca(2)–O(4)	108.5 (3)
O($\bar{3}'$)–Ca(2)–O(4)	168.7 (3)	O($\bar{3}'$)–Ca(2)–O($\bar{6}'$)	135.2 (3)
O($\bar{3}'$)–Ca(2)–O($\bar{6}'$)	92.2 (3)	O(5')–Ca(2)–O(5')	79.4 (2)
O($\bar{5}'$)–Ca(2)–O(7')	87.5 (3)	O(5')–Ca(2)–O(7')	57.9 (3)
O($\bar{5}'$)–Ca(2)–O(2)	91.9 (3)	O(5')–Ca(2)–O(2)	171.3 (3)
O($\bar{5}'$)–Ca(2)–O(4)	76.0 (2)	O(5')–Ca(2)–O(4)	119.6 (3)
O($\bar{5}'$)–Ca(2)–O($\bar{6}$)	154.9 (3)	O(5')–Ca(2)–O($\bar{6}'$)	112.1 (3)
O(7')–Ca(2)–O(2)	123.7 (3)	O(2)–Ca(2)–O(4)	58.8 (3)
O(7')–Ca(2)–O(4)	66.6 (3)	O(2)–Ca(2)–O(6')	76.4 (3)
O(7')–Ca(2)–O($\bar{6}'$)	81.0 (3)	O(4)–Ca(2)–O($\bar{6}'$)	79.0 (3)

[a] Atom x(i') is generated from atom x(i) by the n-glide operation and atom x($\bar{i}$) by the inversion operation.

are 1.529 and 1.497 Å. Although the *cis* bond lengths in any compound cannot be regarded as different from the *trans* values at the 1% level of significance, the correlation among the compounds is a strong one.

The angle between the *cis*-oxygen atom and the central oxygen atom at the phosphorus atom is smaller than the comparable angle involving the *trans*-oxygen atoms. The O–P–O angles at the terminal end of the anion are significantly larger than those involving the central oxygen atom.

Discussion

The fact that α-$Ca_2P_2O_7$ has monoclinic rather than orthorhombic symmetry, as reported by Randby, *et al.*,[8] was apparently noted as early as 1956.[13] Although it is possible that an orthorhombic phase having the α-$Sr_2P_2O_7$ structure with space group Pbnm can be obtained for $Ca_2P_2O_7$, it is likely to be only stable at high temperatures and will transform reversibly and rapidly

[13] J. R. Lehr, private communication.

Table V

Summary of Some Geometric Characteristics of the Anion in Various Pyrophosphates

A. Eclipsed Group

	α-$Ca_2P_2O_7$	β-$Ca_2P_2O_7$[a]	$Cd_2P_2O_7$
P–O–P angle, deg	130	131 138	132
Dihedral angle I,[h] deg	13	6 11	28
⟨P–O⟩ [*n*] for terminal bonds and constant number, *n*, of cation ligands, Å	1.521 [3] 1.499 [2]	1.529 [3] 1.527 [2] 1.480 [1]	1.521 [2] 1.450 [1]
Average bond angles at the phosphorus atom			
(i) With central oxygen atoms, deg	108.2	105.9	106
(ii) With terminal oxygen atoms, deg	110.7	112.6	112

B. Staggered Group

	α-$Cu_2P_2O_7$[c]	α-$Mg_2P_2O_7$[d]	α-$Ni_2P_2O_7$[e]	α-$Co_2P_2O_7$[f]	$Na_4P_2O_7 \cdot 10H_2O$[g]
P–O–P angle, deg	156.8	144.1	137.0	143	130.2
Dihedral angle II,[i] deg	3	15	15	14	13
⟨P–O⟩ [*n*] for terminal bonds and constant number, *n*, of cation ligands, Å	1.533 [2] 1.508 [1]	1.525 [2] 1.472 [1]	1.541 [2] 1.516 [1]	1.518 [2] 1.506 [1]	
Average bond angles at the phosphorus atom					
(i) With central oxygen atoms, deg	106.6	106.6	105.6	107.5	105.8
(ii) With terminal oxygen atoms, deg	112.0	112.3	112.9	111.3	113.0

[a] Reference 3. [b] Reference 7. [c] Reference 4. [d] Reference 5. [e] Reference 1. [f] C. Calvo, unpublished results. [g] W. S. McDonald and D. W. J. Cruickshank, *Acta Cryst.*, **22,** 43 (1967). [h] Dihedral angle I is the angle through which one end of the anion has to be rotated about the P–P vector in order to have the *cis*-oxygen atoms superimposed when viewed down this axis. [i] Dihedral angle II is the angle through which each end of the anions has to be rotated about the P–P vector in order that the two P–O_{11} vectors are collinear when viewed down this axis.

to the phase described here as the temperature is lowered.

In order that α-$Ca_2P_2O_7$ adopts the higher symmetry structure, each cation must replace one strong bond to a *cis*-oxygen atom with two weaker ones to the pair of oxygen atoms related by the mirror plane. Thus for Ca(1) there will be two equivalent bonds to the pair of O($\overline{6}'$) one unit cell removed at a Ca–O bond distance no less than 2.65 Å ($= {}^1/_2c$) while for Ca(2) a pair of oxygen atoms, O($\overline{7}'$), will be similarly involved. These oxygen atoms are also a unit cell apart. If the only changes in atomic positions are those that are needed to create the mirror planes at $z = {}^1/_4$ and ${}^3/_4$ from the present α-$Ca_2P_2O_7$ structure, these latter bond distances would nearly be 3 Å long, and therefore one can regard them to be so weak as to be broken.

A comparison of the values determined for the *c* axis of the α phases of the alkaline pyrophosphates with twice the expected cation–oxygen atom bond length might indicate why α-$Ca_2P_2O_7$ adopts a monoclinic unit cell while the others could be orthorhombic. In order to support bonds of reasonable strength normal to the mirror plane in the orthorhombic unit cell, the minimum possible cation–oxygen atom bond length, fixed at ${}^1/_2c$, must be comparable to or less than previously found cation–oxygen atom bond lengths. In α-$Sr_2P_2O_7$ Grenier and Masse[9] found a *c*-axis length of 5.39 Å while twice the average cation bond length is 5.28 Å and therefore α-$Sr_2P_2O_7$ can easily support the orthorhombic phase based upon this criterion. The comparable values are 5.315 and 5.06 Å in α-$Ca_2P_2O_7$, respectively. Randby, *et al.*,[8] reported α-$Ba_2P_2O_7$ to be orthorhombic with a *c*-axis length of 5.61 Å while the average Ba–O bond length reported in the "International Tables"[14] is 2.81 Å. Thus, one would expect $Ca_2P_2O_7$ to be energetically unstable, at a fixed volume and unit cell size, in space group Pbnm com-

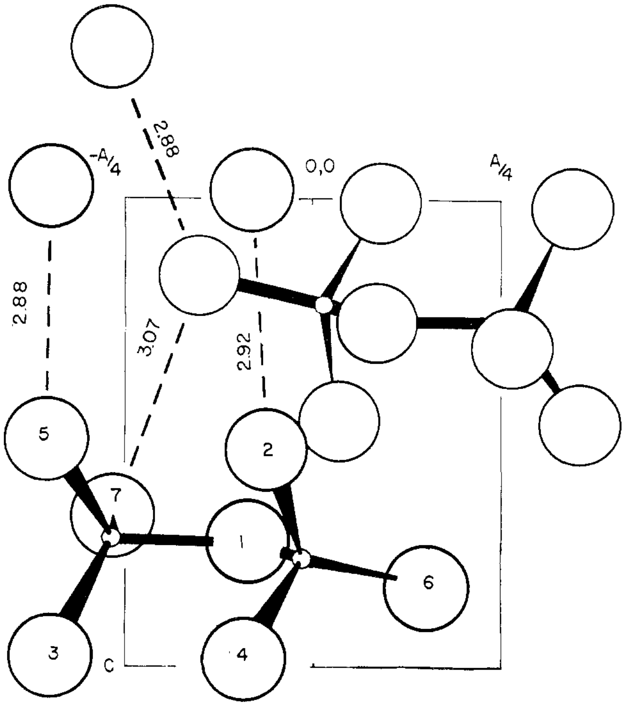

Figure 3.—The interactions of the anions near the *ac* plane, where the large circles represent oxygen atoms and the small circles are the phosphorus atoms. The dashed lines represent the nearest interanion distances.

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(14) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

pared with $P2_1/n$, because of the long *c* axis and only to become stable if the entropy contribution at high temperature can reverse the sign of the free energy difference.

In Figure 3 the packing of adjacent anions around the center of symmetry is shown. These anions form the columns referred to above. The packing at the *cis* end of the centrosymmetrically related molecules is determined by steric interaction of the oxygen atoms since the pair O(6)–O(7) distances are 2.86 and 3.08 Å apart. The nearest *trans*-oxygen atom separations between anions lying at the *c*-axis length apart are 2.88 Å for the O(3)–O(5) pair and 2.92 Å for the O(2)–O(4) pair. Therefore the *c* axis cannot be substantially contracted, as would be required in the orthorhombic form of this phase with normal Ca(1)–O($\bar{6}'$) and Ca(2)–O(7′) bonds, without a substantial loss in energy from the compression of the oxygen atoms.

The nonreversible transformation between the β and α phases of $Ca_2P_2O_7$ reported by Parodi, Hickok, Segelken, and Cooper[15] is consistent with their large structural difference. In β-$Ca_2P_2O_7$ the P–P vectors of the angle make angles of 55 and 56° with the *ab* plane and adjacent anions pack by fitting at the terminal ends rather than *cis* to *cis* across the center of symmetry. In addition, considerable cation–anion rearrangement would be necessary in order to carry through this proposed transformation.

The anions themselves differ slightly. In β-$Ca_2P_2O_7$ the anions deviate by 6 and 11° from the eclipsed configuration whereas this angle is 13° in α-$Ca_2P_2O_7$. Since the larger of these angles in β-$Ca_2P_2O_7$ occurs on the anion showing a P–O–P bond angle farthest removed from that in α-$Ca_2P_2O_7$, there does not appear to be a simple relationship between this bond angle and the deviation from the eclipsed configuration. As is summarized in Table V, those pyrophosphates with cations having small radii show a large dispersion in their P–O–P angles while the deviation from a staggered configuration is minimal. Those pyrophosphates where the cations have larger radii, including Na^+, all show P–O–P bond angles near 130° but with variable deviations from the eclipsed configuration. All of the nearly eclipsed structures, however, show on the average positive deviations from the ideal tetrahedral angle at the terminal oxygen atoms and negative deviations for those O–P–O angles involving the central oxygen atom. Furthermore, these structures show a correlation between the oxygen atom coordination number and the P–O bond length, implying a greater bond strength (shorter P–O distance) as the coordination number decreases.

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[15] J. A. Parodi, R. L. Hickok, W. G. Segelken, and J. R. Cooper, *J. Electrochem. Soc.*, **112**, 688 (1965).

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Electron-Deficient Bonding with Sulfur Atoms. III. Crystal and Molecular Structure of Bis(thiourea)silver(I) Chloride

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The crystal structure of bis(thiourea)silver(I) chloride, $Ag[SC(NH_2)_2]_2Cl$, was determined from 1679 intensities measured by counter methods at room temperature. The crystals are monoclinic $P2_1/a$ with cell constants $a = 36.70\ (4)$, $b = 8.24\ (1)$, $c = 5.87\ (1)$ Å, and $\beta = 92°\ 50' \pm 15'$. With eight molecules (two crystallographically independent formula units) per cell the calculated and observed densities are 2.22 and 2.18 g cm^{-3}, respectively. Refinement by full-matrix least-squares including anisotropic temperature factors converged to a conventional R of 0.062. The structure is composed of almost trigonal-planar $Ag(S)_3$ units bonded together by sulfur bridges to form a spiraling linear polymer. The fourth coordination position of each Ag is completed by long axial Ag–Cl distances of 2.854 (5) and 3.035 (5) Å, respectively. The Ag–Ag distances alternate between a long 4.709 (2) Å and a short 3.132 (2) Å with accompanying Ag–S–Ag bridge angles of 133.4 (2) and 77.3 (2)°, respectively. The sharp bridge bond can be interpreted as an Ag–S–Ag three-center, two-electron, electron-deficient bridge bond. However, the broad-angle bridge is readily understandable in terms of two electron-pair donor–acceptor linkages. The Ag–S distances fall into the range of 2.49–2.59 Å with individual standard deviations of ±0.004 Å.

Introduction

Thiourea (hereafter, tu) is a chemically interesting ligand in that it has several different possible modes of binding to a metal ion. It may coordinate through the mostly nonbonding electron pairs of the nitrogen[1] (this has not been conclusively established by single-crystal structure studies, but only inferred from the infrared spectra) or *via* the sulfur atom. The sulfur itself may donate electrons by two different means: (a) electrons from the nonbonding sp^2 lobes or (b)

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[1] T. J. Lane, D. N. Sen, and J. V. Quagliano, *J. Chem. Phys.*, **22**, 1855 (1954).