

nates^{10,11} the b parameter decreases slightly on going from TmAlO_3 to SmAlO_3 . Starting with NdAlO_3 , the orthoaluminates have the hexagonal perovskite-like arrangement.¹⁰ In the cases of orthoscandates^{2,11} and orthoindates¹² the b parameter increases throughout the series from Lu to La. These results seem to indicate that when the B cation of the ABO_3 perovskite-like compounds is a larger ion such as indium or scandium,

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the substitution of the A cation with a larger rare earth does not have an appreciable effect on the second nearest oxygens. Therefore, the coordination number of the rare earth probably varies across the series REBO_3 when B = Al, Ga, Fe, Cr, or V, whereas it is almost constant when B = Sc or In.

We plan to do the refinements of a number of these perovskite-like structures.

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The Crystal Structure of Lanthanum Carbonate Octahydrate

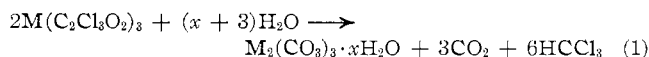
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The crystal structure of lanthanum carbonate octahydrate, $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, has been determined from an X-ray diffraction study of a single-crystal specimen. Four formula units are contained in the orthorhombic unit cell, space group $Pccn$, with lattice parameters $a = 8.984 \pm 0.004$, $b = 9.580 \pm 0.004$, and $c = 17.00 \pm 0.01 \text{ \AA}$ ($\rho_{\text{obsd}} = 2.72 \pm 0.02 \text{ g cm}^{-3}$; $\rho_{\text{calcd}} = 2.732 \text{ g cm}^{-3}$). The final R factor was 0.061 for three-dimensional counter data collected with $\text{Cu K}\alpha$ radiation [$(\sin \theta)/\lambda \leq 0.50$]. $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ crystallizes in an irregular layer type of structure in which the basic layer is formed by alternate rows of carbonate ions and metals. The structure contains two distinctive 10-coordinate metal polyhedra in which coordination sites are occupied both by water molecules and by bidentate and unidentate carbonates. The polyhedra symmetry may be related to a dodecahedron with two sites occupied by bidentate carbonate ions. One-fourth of the water molecules are not bound to the metal ions and are situated between the layers. The average La-O bond is 2.61 \AA ; individual La-O distances range from 2.52 to 2.74 \AA . Hydrogen bonding is apparent.

Introduction

Methods of preparation, thermal decomposition, and structural properties of lanthanon carbonates have been the subject of numerous recent studies.¹⁻¹⁰ Unfortunately, many of these results and their interpretation are contradictory. The inconsistencies are due in part to preparatory difficulties and lack of structural data. A popular method for the preparation of the carbonates is homogeneous precipitation by hydrolysis of the trichloroacetate (eq 1) described first by Salutsky and Quill.¹



By use of this and related methods, normal carbonates, $\text{M}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, have been prepared for all the lan-

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thanons.²⁻⁷ Values reported for x vary from 8 for the lighter metals to 2 or 3 for the heavier ones and also seem dependent on the preparatory conditions. In thermal decomposition studies of the hydrates, intermediate phases have not been observed consistently.^{2-4,6,8} The crystal structures of the lanthanon carbonates are unknown, although many reported lattice parameters are based on values analogous to those obtained from a single crystal of lanthanite¹¹ $\{(\text{La}, \text{Ce})_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}\}$.

In order to determine the structural interrelationships in the lanthanon carbonates and to resolve some of the contradictory reports of their properties, a single-crystal X-ray diffraction study of the inherent structures has been initiated. The structure of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ is described below.

Experimental Section

Crystals of lanthanum carbonate octahydrate, $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, prepared by slow hydrolysis of lanthanum trichloroacetate, were obtained from Dr. L. L. Quill of this department. Composition was determined from carbon and hydrogen analyses (Spang Microanalytical Laboratory, Ann Arbor, Mich.) and from metal analyses by ignition to the oxide. *Anal.* Calcd for $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$: La, 46.15; C, 5.98; H, 2.69. Found:

(11) D. Palache, H. Berman, and C. Frondel, "Dana's Systems of Mineralogy," Vol. II, 7th ed, John Wiley and Sons, Inc., New York, N. Y., 1944.

La, 46.32; C, 6.04; H, 2.70. Analysis of samples dried in air for a period of weeks indicated a small loss of water corresponding to less than 0.3 mol per formula. Single crystals used in the structure analysis were coated with Canada balsam to minimize loss of water during data collection. The colorless, clear crystals cleaved micaceously parallel to (001).

The orthorhombic symmetry and unit cell were established from Weissenberg and precession photographs using Cu K α radiation (λ_{α} 1.5418 Å). Systematic absences occurred for $h00$, $0k0$, and $00l$ when h , k , or $l = 2n + 1$, for $0kl$ and $h0l$ when $l = 2n + 1$, and for hkl when $h + k = 2n + 1$. Therefore, Pccn is a possible space group. In addition, hkl reflections, where $l = 2n + 1$, were very weak or absent. The lattice parameters obtained by least-squares refinement of powder diffractometric data were: $a = 8.984 \pm 0.004$ Å, $b = 9.580 \pm 0.004$ Å, and $c = 17.00 \pm 0.01$ Å. The density (2.732 g cm $^{-3}$) calculated for four formula units agreed with the density observed pycnometrically (2.72 ± 0.01 g cm $^{-3}$ at 26°). For four formula units, the metal atoms and at least four oxygen and carbon atoms must be on the twofold axes or at the symmetry centers and on the twofold axes.

A preliminary set of intensity data was collected from equi-inclination Weissenberg photographs taken of the $h0l$ to $h6l$ levels using the multiple-film technique. A crystal of the approximate dimensions $0.16 \times 0.15 \times 0.05$ mm was exposed 60 hr per level with Cu K α radiation. The relative intensities of the 705 observed reflections were estimated visually by comparison with a calibrated intensity strip. The reduced data set, uncorrected for absorption effects, was used to determine the metal positions and part of the light-atom structure. Intensities used in the final refinement were obtained with a General Electric XRD-5 scintillation counter equipped goniostat at 26° using a tabular crystal ($0.16 \times 0.15 \times 0.11$ mm) oriented with its b axis parallel to the instrument ϕ axis. Copper K α radiation was used in the sphere [$(\sin \theta)/\lambda \leq 0.5$]; the take-off angle was 4°, and the counter aperture size, 10°. Mosaicity of the crystal was checked by narrow-source, open-counter scans for which the average half-width was approximately 0.2°. Intensities of 749 reflections, measured with the stationary-crystal, stationary-counter technique, were recorded as the difference in 10-sec counts with balanced Ni and Co filters to measure total and background intensities, respectively. Intensities of 116 reflections were recorded as zero. Of these 108 had $l = 2n + 1$ as did 94 of the 125 reflections with intensities less than 2 cps. The intensity of several standard reflections measured repeatedly during the experiment did not change. The data were corrected for Lorentz and polarization effects.

When the structure was essentially solved, an absorption correction was computed with a FORTRAN program DATA2, written by Coppens, Leiserowitz, and Rabinovich.¹³ The absorption coefficient, μ , was 444 cm $^{-1}$ and the effects of absorption were severe. For this computation the crystal was defined by eight boundary planes and the correction was calculated using a $12 \times 12 \times 10$ grid. Correction factors varied from 12 to 64. Their validity was checked by a comparison of experimentally determined and calculated absorption effects on ($0k0$) reflections measured at $\chi = 90^\circ$. Over a 90° range in ϕ , absorption decreased the intensity of the (040) and (080) reflections by factors of 0.51 and 0.47, respectively. The calculated factors were 0.47 and 0.45.

Calculations were made on CDC 3600 and 6600 computers using full-matrix least-squares, Fourier, and distance and angle programs written by A. Zalkin. Stereo drawings were made using a program written by A. C. Larson. In the least-squares treatment the function $\sum w(|F_o| - |F_c|)^2$ was minimized. Unit or zero weights, w , were assigned as indicated in the following section.

Scattering factors used were: La $^{+3}$ and C, as given by Cromer and Waber;¹³ O $^{2-}$, as reported by Tokonami.¹⁴ The corrections

$\Delta f' = -2.1$ and $\Delta f'' = 8.9$ for lanthanum¹⁵ were included in the calculations.

Solution of the Structure

The locations of the eight lanthanum atoms were deduced from a three-dimensional Patterson function. Metals are located in two fourfold sets: $4c$, $\pm(1/4, 1/4, z)$, $\pm(1/4, 1/4, 1/2 + z)$; $4d$, $\pm(1/4, 3/4, z')$, $\pm(1/4, 3/4, 1/2 + z')$. The Patterson synthesis yields two non-equivalent solutions for the z parameters: solution 1, $z = 0.000$, $z' = 0.033$; solution 2, $z = 0.250$, $z' = 0.283$. The first solution, found subsequently to be incorrect, was chosen in the initial search for light-atom positions. The z parameters, over-all scale factor, and isotropic thermal parameters of the metal atoms were refined by the least-squares technique with all of the observed reflections assigned unit weights ($R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.26$). The resulting thermal parameters were nonpositive definite since the data were uncorrected for absorption.¹⁶

An electron density difference function which exhibited duplicate images because of the Pmmn symmetry was calculated with structure factors based on the refined metal parameters and $l = 2n$ intensity data. The structure was solved by selecting various peaks in the difference function for trial atoms and testing the behavior of the isotropic thermal parameters by least-squares calculations. In subsequent cycles the parameters of the acceptable light atoms were included in the structure factor calculation and all data were used in the difference syntheses. After a fourfold carbonate ion and three eightfold water molecules had been located ($R = 0.21$), it became apparent that the symmetry of the carbonate ions required the shift of all atoms $+0.250$ along z (solution 2 for the metals). Subsequently, the remaining eightfold carbonate ion and eightfold water molecule were placed correctly. When absorption-corrected goniostat data were used, the isotropic thermal parameters became positive definite, and R was reduced to 0.08.

In the final least-squares refinement the 125 observed reflections with intensities less than 2 cps and 10 reflections with intensities less than background were given zero weight to remove the effect of such a large body of low reliability data. Zero weighting was also given to eight strong reflections for which the observed structure factors were significantly lower than the calculated values, perhaps because of extinction. No other attempt was made to eliminate extinction effects. These changes altered positional parameters only slightly but did affect some of the thermal parameters significantly. Thermal parameters were allowed to refine anisotropically using factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$, where $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. Since some of the anisotropic thermal parameters of carbonate atoms became negative, only the metal and water oxy-

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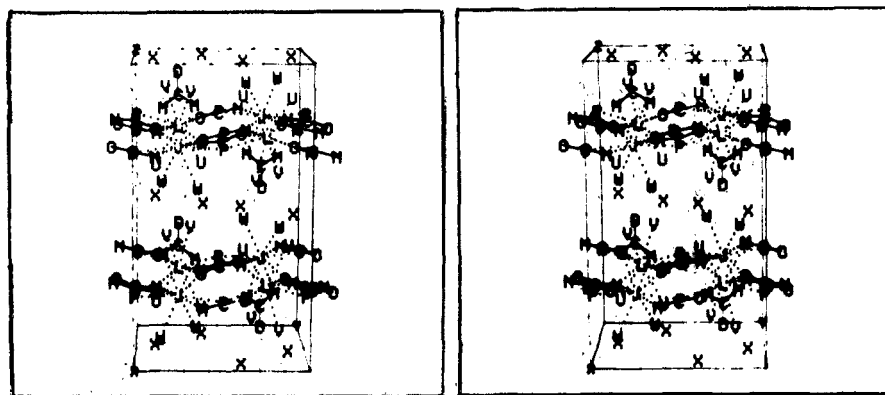
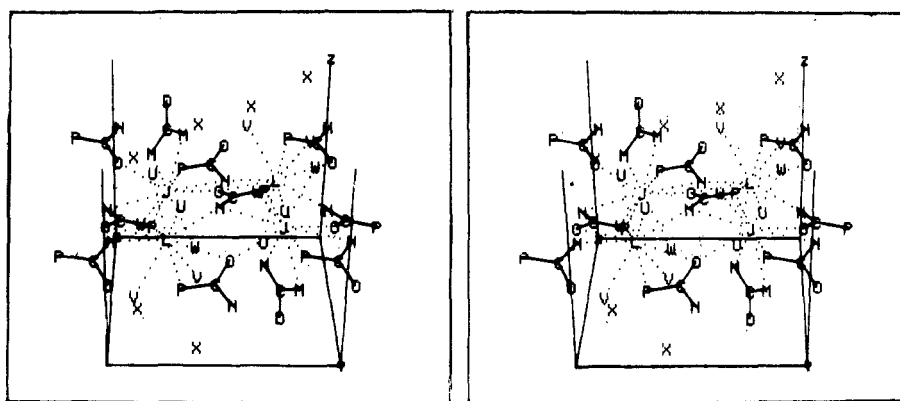
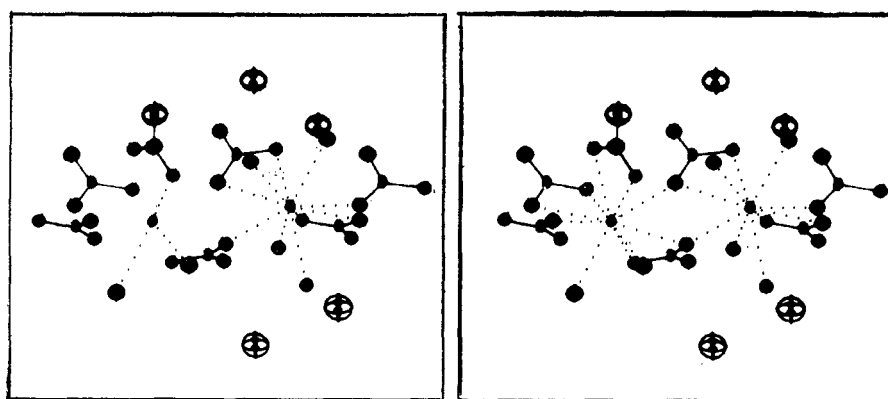
Figure 1.—Stereoscopic illustration of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.Figure 2.—Stereoscopic illustration of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ half-cell.

Figure 3.—Stereoscopic illustration of lanthanum coordination.

These molecules and ions project out from the primary layer described above. The metals and coordinated ligands form a series of widely spaced layers. A hydrogen bond apparently exists between the terminal oxygen of the fourfold carbonate ion and the water molecules in the next layer. The remaining water molecules (X in the illustrations) which are situated between the layers furnish additional hydrogen bonding. The facile cleavage observed along (001) supports this conjecture. The lanthanum atoms are situated in two somewhat different environments. La(1) is coordinated by four water molecules and two unidentate and two bidentate carbonate groups; in La(2) the fourfold carbonate ions acting as bidentates replace two water molecules. Bond distances of less than 3.2 Å are pre-

sented in Table III, and selected bond angles in Table IV. The average lanthanum to oxygen distances are 2.61 and 2.60 Å for La(1) and La(2), respectively. The longest La-O bond for each metal involves an oxygen of a bidentate carbonate ion. The average La-O(Aq) distance, 2.63 Å, is consistent with reported La-O(Aq) distances for 9-coordinate metal, which range from 2.58 Å in $\text{KLaZ} \cdot 8\text{H}_2\text{O}$,¹⁷ where Z is the ethylenediaminetetraacetate ion, to 2.74 Å in $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.¹⁸ The La-O(carboxylate) distances reported for $\text{KLaZ} \cdot 8\text{H}_2\text{O}$ and $\text{HLaZ} \cdot 7\text{H}_2\text{O}$,¹⁹ where the

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(18) E. B. Hunt, Jr., R. E. Rundle, and A. J. Stosick, *Acta Cryst.*, **7**, 106 (1954).

TABLE III

INTERATOMIC DISTANCES UNCORRECTED FOR THERMAL MOTION^a

Atom 1-Atom(s) 2	Dist, Å	Atom 1-atom(s) 2	Dist, Å
A. Coordination Sphere La(1)			
La(1)-2O(5)	2.52 (4)	O(3)-Aq(1)	3.04 (6)
La(1)-2O(3)	2.54 (4)	O(3)-Aq(1)	3.38 (6)
La(1)-2Aq(2)	2.62 (4)	O(3)-Aq(2)	3.09 (6)
La(1)-2Aq(1)	2.66 (4)	O(3)-O(4)	2.72 (6)
La(1)-2O(4)	2.73 (4)	O(3)-O(5)	3.24 (6)
Aq(1)-Aq(1)	2.81 (8)	O(4)-Aq(1)	3.07 (6)
Aq(2)-Aq(2)	2.82 (8)	O(4)-Aq(2)	3.06 (6)
O(5)-Aq(1)	3.22 (6)	O(4)-O(5)	2.18 (6)
O(5)-Aq(2)	2.82 (6)		
B. Coordination Sphere La(2)			
La(2)-2O(1)	2.53 (4)	O(4)-Aq(3)	3.04 (6)
La(2)-2O(4)	2.55 (4)	O(4)-O(1)	3.01 (6)
La(2)-2O(5)	2.56 (4)	O(4)-O(1)	3.15 (6)
La(2)-2Aq(3)	2.62 (4)	O(4)-O(3)	2.72 (6)
La(2)-2O(3)	2.74 (4)	O(4)-O(5)	3.09 (6)
Aq(3)-Aq(3)	3.02 (9)	O(5)-Aq(3)	3.00 (6)
O(1)-O(1)	2.14 (8)	O(5)-O(1)	3.00 (6)
O(3)-Aq(3)	3.26 (6)	O(5)-O(3)	2.17 (6)
O(3)-O(1)	3.05 (6)		
C. Carbonates			
C(1)-2O(1)	1.25 (6)	O(1)-O(1)	2.14 (8)
C(1)-O(2)	1.3 (1)	O(1)-O(2)	2.21 (8)
C(2)-O(3)	1.29 (8)	O(3)-O(4)	2.30 (6)
C(2)-O(4)	1.28 (8)	O(3)-O(5)	2.17 (6)
C(2)-O(5)	1.28 (6)	O(4)-O(5)	2.18 (6)
D. Aqueous O-O			
Aq(1)-O(1)	2.68 (6)	Aq(2)-O(1)	2.68 (6)
Aq(1)-Aq(4)	2.74 (8)	Aq(2)-O(5)	2.82 (6)
Aq(1)-Aq(1)	2.81 (8)	Aq(2)-Aq(4)	2.82 (8)
Aq(1)-Aq(3)	2.85 (6)	Aq(2)-Aq(2)	2.82 (8)
Aq(3)-O(2)	2.61 (8)	Aq(4)-Aq(1)	2.74 (8)
Aq(3)-Aq(1)	2.85 (6)	Aq(4)-Aq(2)	2.82 (8)
Aq(3)-O(5)	3.00 (6)	Aq(4)-Aq(4)	3.0 (1)
Aq(3)-Aq(2)	3.16 (8)	Aq(4)-Aq(2)	3.16 (8)

^a Two times the standard deviation of the last digit is indicated in parentheses.

latter is 10-coordinate, are 2.507 and 2.537 Å respectively, and seem shorter than the observed average La-O(CO₃) distance, 2.60 Å. However, when the two longer bonds are excluded, the average La-O(CO₃) distance is 2.54 Å.

Decacoordination is somewhat unusual. The few examples structurally established include the EDTA complex of lanthanum, YbSb₂,²⁰ and tetrakis(acetato)uranium(IV).²¹ In the latter case the oxygen atoms are arrayed at the corners of a bicapped square antiprism. YbSb₂ is related to the square antiprism and the lanthanum complex to the dodecahedron. The ground-state configuration for decacoordination of unidentate ligands is unknown. Muettterties and Wright²² suggest that either a bicapped square antiprism or a bicapped dodecahedron is the proper symmetry for a sp³d⁵f hybrid model. In the present case,

TABLE IV

SELECTED BOND ANGLES

Atom 1	Atom 2	Atom 3	Angle, ^a deg
A. Coordination Sphere La(1)			
Aq(1)	La(1)	Aq(1)	63.9 (0.9)
Aq(1)	La(1)	O(3)	71.6 (0.7)
Aq(1)	La(1)	O(4)	69.4 (0.6)
Aq(1)	La(1)	O(5)	76.7 (0.7)
Aq(2)	La(1)	Aq(2)	65.3 (1.0)
Aq(2)	La(1)	O(3)	73.5 (0.7)
Aq(2)	La(1)	O(4)	69.8 (0.7)
Aq(2)	La(1)	O(5)	66.5 (0.7)
O(3)	La(1)	O(4)	62.0 (0.7)
O(3)	La(1)	O(5)	79.5 (0.7)
O(3)	La(1)	O(3)	147.6 (1.0)
O(4)	La(1)	O(5)	48.9 (0.6)
B. Coordination Sphere La(2)			
Aq(3)	La(2)	Aq(3)	70.3 (1.0)
Aq(3)	La(2)	O(4)	72.0 (0.7)
Aq(3)	La(2)	O(5)	70.8 (0.7)
O(1)	La(2)	O(1)	50.0 (0.9)
O(1)	La(2)	O(3)	70.6 (0.7)
O(1)	La(2)	O(4)	76.9 (0.7)
O(1)	La(2)	O(4)	72.7 (0.7)
O(1)	La(2)	O(5)	72.2 (0.7)
O(3)	La(2)	O(4)	61.9 (0.7)
O(3)	La(2)	O(5)	48.3 (0.6)
O(4)	La(2)	O(5)	74.7 (0.7)
O(4)	La(2)	O(4)	146.9 (1.0)
C. Carbonates			
O(1)	C(1)	O(2)	121.0 (2.0)
O(1)	C(1)	O(1)	118.0 (4.0)
O(3)	C(2)	O(4)	127.2 (2.5)
O(3)	C(2)	O(5)	115.7 (2.6)
O(4)	C(2)	O(5)	117.1 (2.7)

^a Standard deviation in parentheses.

suggested models are useless since the coordination polyhedron has only C₂ symmetry and no ligands are on C₂. A somewhat more appropriate model may be derived from the dodecahedron. Using the numbering rules suggested by Muettterties and Wright (Figure 4a), sites 5 and 6 are occupied by bidentate carbonates which split each site, Figure 4b. Splitting the sites alone lowers the model symmetry to C_{2v}. The symmetry of the polyhedron is actually lower since the orientation of the carbonates as well as that of the other ligands prohibits the presence of mirror planes and reduces the symmetry to C₂. An ideal dodecahedron may be visualized as two interpenetrating orthogonal trapezoids. In the present case the trapezoids are neither quite planar nor orthogonal. The best least-squares planes, given by the equation $Ax + By + Cz = D$, were calculated through the two trapezoids about each metal. The appropriate coordinates of C(2) were used as the positions of substituted bidentates and coordinate errors were not included. The mean deviations from the least-squares planes are 0.03 and 0.26 Å for the La(1) and 0.13 and 0.02 Å for the La(2) case. The angles between the planes are 86 and 87°, respectively, for the La(1) and La(2) coordinations. Normally a dodecahedron is described by two angles, θ_A and θ_B , as indicated in Figure 4a. The predicted values of

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(20) R. Wang, R. Bodnar, and H. Steinfink, *Inorg. Chem.*, **5**, 1468 (1966).

(21) I. Jelenić, D. Grdenić, and A. Bezjak, *Acta Cryst.*, **17**, 758 (1964).

(22) E. L. Muettterties and C. M. Wright, *Quart. Rev. (London)*, **21**, 109 (1967).

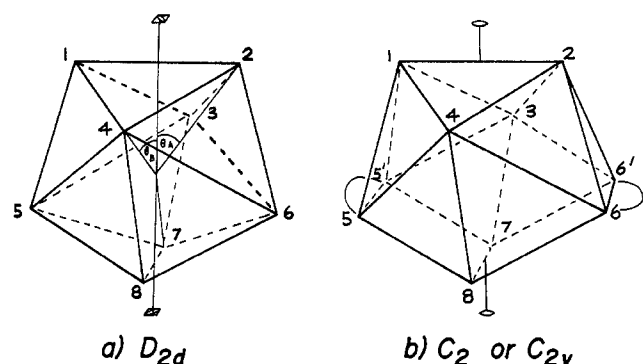


Figure 4.—Illustration of the relationship between dodecahedral symmetry (a) and the suggested polyhedron model (b) for lanthanum carbonate octahydrate.

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 Silverton²³ 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

(23) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

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 -Ca₂P₂O₇

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The high-temperature form of calcium pyrophosphate, α -Ca₂P₂O₇, 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 $\beta = 90.3$ (1)°. There are four molecules per unit cell yielding a calculated density of 2.95 g/cm³ compared to a measured value of 2.947 g/cm³. This structure is closely related to that of α -Sr₂P₂O₇, 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 Cd₂P₂O₇) to

156° (in Cu₂P₂O₇). These structures seem to divide between those having the terminal ends of the anion in a

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