Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

Crystal Structures of Bis(urea)bis(dihydrogen phosphato)calcium–Bis(urea) and Its Isomorphous Magnesium Analogue, $M[OC(NH_2)_2]_2(H_2PO_4)_2 \cdot 2CO(NH_2)_2$ (M = Ca, Mg)

THOMAS D. HAYDEN, EUNICE E. KIM, and KLAAS ERIKS*

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The crystal structures of bis(urea)bis(dihydrogen phosphato)calcium–bis(urea) and its magnesium analogue, $M(H_2PO_4)_2[CO(NH_2)_2]_4$, have been determined where M = Ca, Mg. The two structures are isomorphous, crystallizing in the space group $P2_1/n$ with $a = 7.404$ (1) Å, $b = 21.534$ (6) Å, $c = 5.657$ (1) Å, $\beta = 91.05$ (1)°, and $V = 901.8$ (4) Å^3 for the calcium compound and $a = 7.352$ (2) Å, $b = 21.502$ (5) Å, $c = 5.370$ (1) Å, $\beta = 91.64$ (2)°, and $V = 848.5$ (4) Å^3 for the magnesium compound, with $Z = 2$. Data were collected with an automated diffractometer, yielding 1694 unique reflections with $I > 3\sigma$ for the Ca compound and 1500 for the Mg compound. Anisotropic least-squares refinement converged to R values of 0.066 and 0.039 for the Ca and Mg compounds, respectively. The structure contains sheets of $M(H_2PO_4)_2[OC(NH_2)_2]_2$, separated by sheets containing only urea with all oriented perpendicular to the crystallographic b axis. The M^{2+} ions are six-coordinated by oxygen atoms, four from phosphate groups and two from urea. The urea molecules occupy trans positions. The octahedron around M^{2+} is almost regular, with an average Ca–O distance of 2.335 Å and Mg–O distance of 2.105 Å. The phosphate group acts as a bidentate ligand, bridging two different M^{2+} ions and thus forming chains of $[M(O_2PO_2H_2)_2]_n$ along the c axis. The urea sheets are held together by hydrogen bonds, and there are also hydrogen bonds between the two types of sheets as well as within the $M(H_2PO_4)_2[OC(NH_2)_2]_2$ sheets. The latter generate a configuration of six-membered rings around M^{2+}.

Introduction

The structure determinations described below were motivated by our interest in the mechanism of biological calcification, particularly the binding of calcium phosphate to connective tissue, to amino acids, and to organic bases. Much work has been done on the structures of the many phases in which calcium phosphate itself can occur, but no such information is available for crystalline solids that contain calcium phosphate along with organic components. The reason for this is, in large part, the extremely low solubility of many of the calcium phosphate phases, so that any attempt to crystallize complexes containing an organic component and calcium phosphate from solutions containing Ca^{2+} ions, phosphate ions, and the organic base result in a precipitate of calcium phosphate in one of its phases.

We did succeed in crystallizing a calcium phosphate and a magnesium phosphate complex with urea as the organic component and determined their crystal structures.

An additional point of importance is the difference in behavior between Ca^{2+} and Mg^{2+} ions, which exhibits itself in many instances concerning biological cells and tissues. This difference is at least in part a result of the difference between the Pauling radii of the two ions (0.99 Å for Ca^{2+}, 0.65 Å for Mg^{2+}), which causes their coordination numbers to be quite different. As a result there are only a few examples in the literature of cases where Ca and Mg compounds have isomorphous structures. For the phosphate–urea compound reported here the Ca and Mg structures were found to be isomorphous, both having six-coordination around the metal ion.

Experimental Section

a. Preparation. The compound $Ca(H_2PO_4)_2[CO(NH_2)_2]_4$ was prepared by following the procedure described by Frazier et al.[1] A saturated solution of $Ca(H_2PO_4) \cdot H_2O$ was saturated with urea and filtered. The adduct was crystallized from the filtrate by slow evaporation of water at room temperature. A number of large crystals, approximately 1 × 1 × 0.5 cm^3, were formed. Attempts to form smaller well-formed crystals failed, perhaps due to the high viscosity and supersaturation of the solutions. Recrystallization of the material from aqueous solution was not possible, because the compound dissolves incongruently and $CaHPO_4 \cdot 2H_2O$ precipitates.[1] For the preparation of $Mg(H_2PO_4)_2[CO(NH_2)_2]_4$, stoichiometric amounts of $Mg(OH)_2$ and urea were added to H_3PO_4 (85% by weight) at 110 °C with vigorous stirring, giving a thick, viscous solution. The solution was divided into portions of 25 mL each. To each portion were added increasing amounts of water, from 6 to 20 mL, and the solutions so diluted were allowed to stand overnight. Two types of crystals formed in the containers with 6 and 8 mL of water, some that were less dense than the solution and floated on top and others that were more dense and formed at the bottom. The lighter crystals were found to be urea, while the heavier ones were used for this study. The latter crystals separated from the bottom of the container only with considerable difficulty.

Table I. Summary of Crystal Data

	$Ca(H_2PO_4)_2$-$[CO(NH_2)_2]_4$	$Mg(H_2PO_4)_2$-$[CO(NH_2)_2]_4$
cryst size, mm^3	0.28 × 0.22 × 0.13	0.41 × 0.37 × 0.20
a, Å	7.404 (1)	7.352 (2)
b, Å	21.534 (6)	21.502 (5)
c, Å	5.657 (1)	5.370 (1)
β, deg	91.05 (1)	91.64 (2)
V, Å^3	901.8 (4)	848.5 (4)
Z, formula units/cell	2	2
fw	474.28	458.50
D(calcd), g/cm^3	1.746	1.795
D(measd), g/cm^3 (at 23 ± 1 °C)	1.745	1.77
temp of data collection	25 ± 1 °C	20 ± 1 °C
wavelength of Mo Kα radiation, Å	$\alpha_1 = 0.70926$	$\alpha = 0.71069$
scan range, deg	2.0–2.3	2.0–2.1
scan rate, deg min^{-1}	1.0	2.02–29.3
total bkgd/scan time	0.17	0.5
max 2θ, deg	55.0	60.13
no. of reflctns measd	2625	5621
no. of unique reflctns	2079	2571
no. of unique reflctns with $I > 3\sigma$	1694	1500
check reflctns; % decay	(800), (080), (008); none	$(1\bar{6}\bar{1})$, $(27\bar{1})$; none
diffractometer used	FACS-1 Picker	Syntex $P2_1$

b. Data Collection. A roughly prismatic fragment (0.28 × 0.22 × 0.13 mm^3) of a large $Ca(H_2PO_4)_2[CO(NH_2)_2]_4$ crystal was put into a glass capillary (0.7-mm diameter) and was mounted on an automated Picker four-circle diffractometer (FACS-1 system) equipped with a Mo tube and graphite monochromator. Preliminary unit cell parameters were obtained from 12 centered reflections. They agreed with results obtained by Frazier et al.[1] and with parameters calculated from powder data determined earlier by us. Accurate unit cell parameters were calculated from 12 centered reflections with 2θ values between 51 and 66°. Unit cell parameters, along with all other pertinent crystal data, are given in Table I. Systematic extinctions

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(1) A. W. Frazier, J. R. Lehr, and J. P. Smith, *J. Agric. Food Chem.*, **15**, 345 (1967).

Table II. Final Positional Parameters with Isotropic Thermal Parameters for Hydrogens

	$Ca(H_2PO_4)_2[CO(NH_2)_2]_4$				$Mg(H_2PO_4)_2[CO(NH_2)_2]_4$			
atom	*x*	*y*	*z*	100*U*, Å^2	*x*	*y*	*z*	100*U*, Å^2
Ca/Mg	0.00	0.00	0.00		0.00	0.00	0.00	
P	0.1101 (1)	0.0947 (4)	0.5037 (2)		0.1024 (1)	0.0842 (0)	0.5108 (1)	
O(1)	0.1524 (3)	0.0442 (1)	0.3151 (4)		0.1343 (3)	0.0379 (1)	0.3072 (3)	
O(2)	0.1447 (3)	0.0710 (1)	0.7555 (4)		0.1331 (3)	0.0630 (1)	0.7756 (3)	
O(3)	0.2209 (4)	0.1511 (1)	0.4537 (5)		0.2320 (3)	0.1407 (1)	0.4645 (3)	
O(4)	−0.0969 (3)	0.1095 (1)	0.4834 (5)		−0.0987 (3)	0.1099 (1)	0.4833 (4)	
O(5)	−0.2345 (3)	0.0728 (1)	0.0642 (5)		−0.2189 (3)	0.0660 (1)	0.0553 (3)	
O(6)	0.2496 (4)	0.2301 (1)	0.8019 (5)		0.2568 (3)	0.2245 (1)	0.8165 (4)	
C(1)	−0.3909 (5)	0.0794 (2)	−0.0221 (7)		−0.3791 (4)	0.0731 (1)	−0.0302 (5)	
C(2)	0.1293 (5)	0.2391 (2)	0.9517 (7)		0.1313 (4)	0.2366 (1)	0.9612 (5)	
N(1)	−0.4426 (5)	0.0490 (2)	−0.2156 (7)		−0.4365 (4)	0.0442 (1)	−0.2356 (5)	
N(2)	−0.5091 (5)	0.1186 (2)	0.0734 (9)		−0.4958 (5)	0.1122 (2)	0.0770 (7)	
N(3)	−0.0069 (5)	0.1997 (2)	0.9788 (7)		−0.0093 (4)	0.1984 (1)	0.9917 (6)	
N(4)	0.1278 (5)	0.2911 (2)	1.0804 (8)		0.1297 (4)	0.2900 (1)	1.0890 (6)	
H(3)	0.225 (6)	0.181 (2)	0.561 (9)	7.0 (16)	0.233 (6)	0.167 (2)	0.569 (7)	7.3 (14)
H(4)	−0.163 (7)	0.095 (2)	0.374 (10)	7.5 (18)	−0.145 (6)	0.098 (2)	0.340 (8)	9.8 (15)
H(11)	−0.366 (6)	0.017 (2)	−0.278 (8)	4.6 (13)	−0.365 (5)	0.018 (2)	−0.308 (6)	5.2 (10)
H(12)	−0.540 (6)	0.051 (2)	−0.252 (9)	5.9 (17)	−0.557 (9)	0.046 (3)	−0.275 (10)	13.2 (23)
H(21)	−0.607 (6)	0.121 (2)	0.017 (9)	6.3 (17)	−0.610 (6)	0.117 (2)	0.023 (7)	6.9 (15)
H(22)	−0.467 (5)	0.136 (2)	0.213 (7)	3.2 (11)	−0.459 (5)	0.129 (2)	0.206 (6)	4.0 (11)
H(31)	−0.004 (6)	0.165 (2)	0.937 (8)	5.4 (15)	0.004 (6)	0.167 (2)	0.932 (7)	5.8 (15)
H(32)	−0.077 (6)	0.210 (2)	1.076 (8)	4.9 (14)	−0.095 (6)	0.213 (2)	1.099 (7)	5.9 (13)
H(41)	0.069 (7)	0.294 (2)	1.203 (10)	7.5 (19)	0.058 (6)	0.295 (2)	1.208 (7)	6.2 (13)
H(42)	0.207 (6)	0.311 (2)	1.068 (8)	4.6 (15)	0.223 (5)	0.312 (2)	1.084 (6)	4.2 (11)

occurred for $h0l$ with $h + l = 2n + 1$ and for $0k0$ with $k = 2n + 1$, which uniquely determine the space group as $P2_1/n$, a nonstandard setting of $P2_1/c$ (space group No. 14 in Vol. 1 of ref 2).

A total of 2625 reflections were measured at 25 ± 1 °C. These included check reflections after every group of 50 reflections, 75 space group extinctions, and 197 equivalent pairs. The reflections were collected in two sets: the first set for $2° < 2\theta < 50°$, the second for $50° < 2\theta < 55°$. All reflections were corrected for Lorentz and polarization factors. No absorption corrections were applied since for the crystal used $\mu r = 0.08$ (approximately).

An $Mg(H_2PO_4)_2[CO(NH_2)_2]_4$ crystal of dimensions 0.41 × 0.37 × 0.20 mm^3 was mounted on the tip of a glass fiber with epoxy cement. The crystal was centered on a Syntex $P2_1$ diffractometer, equipped with a Mo tube and graphite monochromator. Unit cell determination and preliminary unit cell parameters showed that the structure is isomorphous with that of the calcium compound. Final unit cell parameters were calculated from 15 reflections with high 2θ values. The 5621 measured reflections included check reflections after every group of 42 reflections, 94 space group extinctions, and 2496 equivalent pairs. The range of 2θ covered was 2–60°. *Lp* corrections were applied but no absorption corrections ($\mu r \approx 0.05$).

c. Structure Determination and Refinement. The structure of $Ca(H_2PO_4)_2[CO(NH_2)_2]_4$ was solved from a Patterson map and subsequent difference Fourier calculations. After the Ca atoms were placed at inversion centers (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$), all the other non-hydrogen atoms could be located. Least-squares refinement with isotropic temperature factors led to R $(=\sum||F_o| - |F_c||/\sum|F_o|) = 0.10$ and R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}) = 0.099$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, and weights were taken as $w = [\sigma(F_o)]^{-1/2}$. Further refinement with anisotropic temperature factors for the heavy non-hydrogen atoms gave $R = 0.077$. At this point all hydrogen atoms were located at chemically reasonable positions from a difference Fourier map. Least-squares refinement was continued with inclusion of the H atoms, with isotropic temperature factors. Convergence was reached at final values of $R = 0.066$ and $R_w = 0.059$. A total of 1694 reflections with $|F_o| \geq 3\sigma(F_o)$ contributed to the calculations.

The isomorphous Mg structure was refined with use of the atomic parameters of the Ca structure as starting point. Hydrogen atoms were again located from a difference Fourier map, and subsequent least-squares refinement identical with that used for the Ca structure led to $R = 0.039$ and $R_w = 0.040$. In this refinement 1500 reflections with $|F_o| \geq 3\sigma(F_o)$ were used. All calculations were performed by using the program X-RAY 76.[3] Scattering factors for all heavier atoms were taken from Cromer and Mann[4] and those for hydrogen from Stewart et al.[5] Final atomic parameters for both the Ca and the Mg structure are listed in Table II. Calculated interatomic distances and angles for both compounds are listed in Table III, and data concerning the hydrogen bonds are given in Table 3 of the supplementary material. Tables of F_o and F_c values are available.[6]

In the following description and discussion of the structures statements are made about the calcium complex. Since the structure of the magnesium complex is isomorphous, these statements apply to the magnesium complex as well.

Description of the Structures

The compound $Ca(H_2PO_4)_2[CO(NH_2)_2]_4$ exhibits a layer structure, in which sheets of calcium–urea–phosphate alternate with sheets of urea molecules, the two types of sheets being oriented perpendicular to the crystallographic *b* axis. There are two crystallographically distinct types of urea molecules, hereafter referred to as the *ligand* urea and the *lattice* urea molecules. The structural results show that the proper name for the compound is bis(urea)bis(dihydrogen phosphato)calcium–bis(urea).

Each *calcium ion* links together four different phosphate groups through oxygen atoms, and each phosphate group is bonded to two different calcium ions through its oxygen atoms O(1) and O(2). Thus infinite chains of calcium phosphate are formed, which run parallel to the *c* axis of the crystal. Figure 1, which represents a projection of part of the structure down the reciprocal axis a^*, shows these chains. They appear at $y = 0$ and again at $y = {}^1/_2$. In addition to the four phosphate oxygens the calcium ion is coordinated by the oxygen atoms of two *ligand* urea molecules that are located on opposite sides of the flat calcium phosphate chains. Table III lists interatomic distances and angles for the calcium (and magnesium) octahedra, which appear to have only very minor distortions: the average Ca–O distance is 2.335 Å with an average deviation of 0.024 Å, while the average deviation of the angles from 90° is 1.56°. For the magnesium compound

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(2) "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England, 1965.

(3) J. M. Stewart, P. A. Machin, C. W. Dickenson, H. L. Ammon, H. Heck, and H. Flack, Eds., Technical Report TR446, University of Maryland, College Park, MD, 1976.

(4) D. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **A24**, 321 (1968).

(5) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(6) See paragraph at the end of the paper regarding supplementary material.

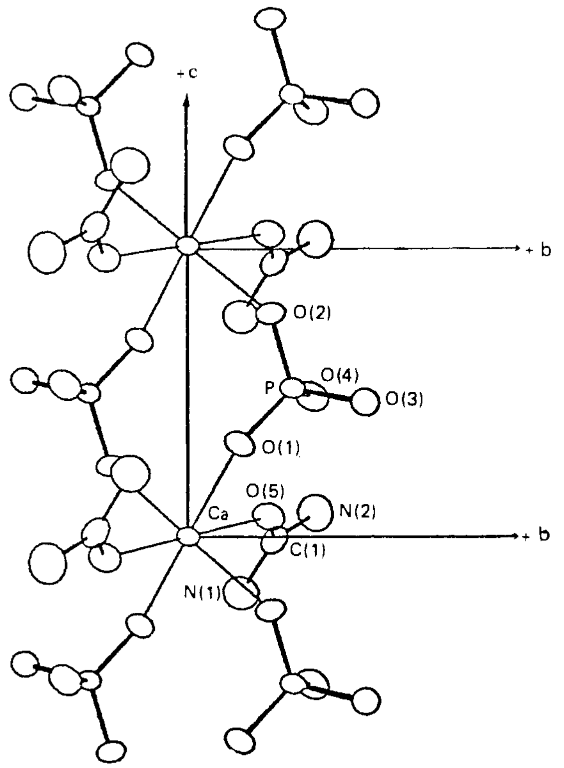

Figure 1. Representation of the $[Ca(H_2PO_4)_2]_n$ chains parallel to the *c* axis, with the view along the reciprocal axis *a**. The atoms of the asymmetric unit are labeled.

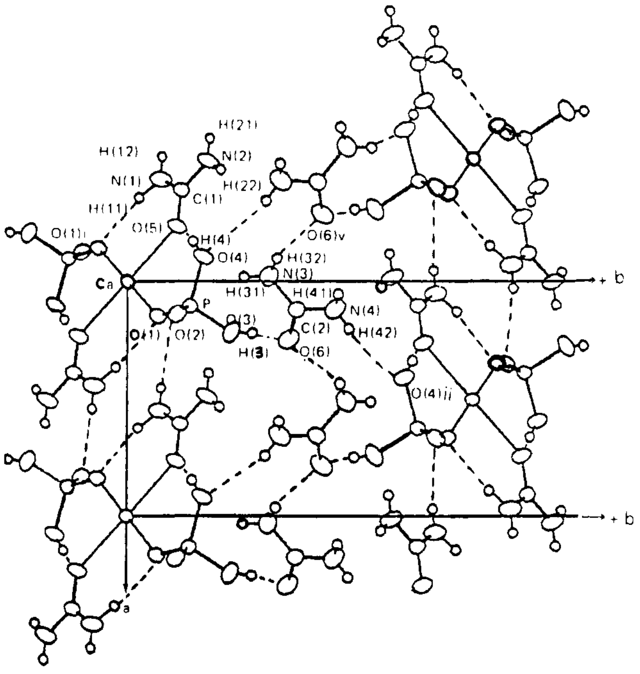

Figure 2. Projection along the reciprocal axis *c**, showing the $Ca(H_2PO_4)_2[CO(NH_2)_2]_2$ sheet at $y = 0$ and the urea sheet at $y = {}^1/_4$. Atoms of the asymmetric unit are labeled. Dashed lines indicate hydrogen bonds.

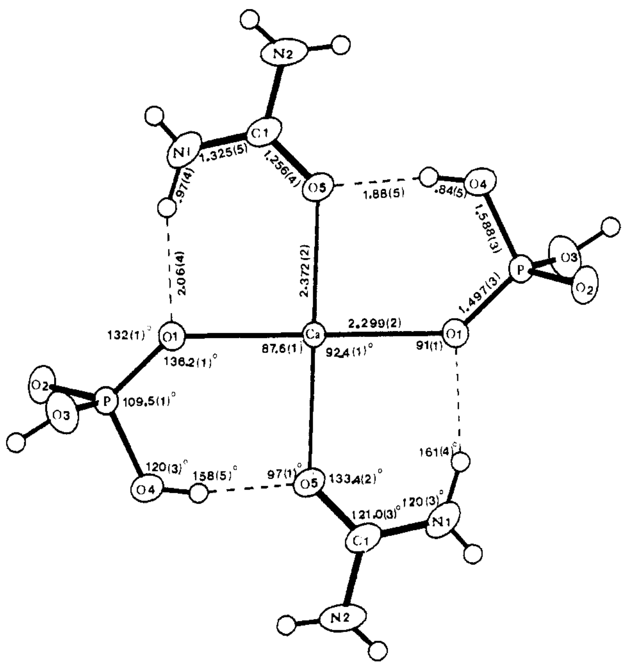

Figure 3. Interligand hydrogen-bonded structure around Ca (Mg), showing the four six-membered rings.

the values are Mg–O(av) = 2.105 ± 0.045 Å and 90 ± 1.1°.

The *ligand urea molecules* connect the calcium phosphate chains together, in the *a* direction of the cell, by the N(1)–H···O(2) and N(2)–H···O(2) hydrogen bonds to phosphate oxygen atoms, to form a two-dimensional sheet perpendicular to the *b* axis. This can be seen in Figure 2, which represents a projection of the structure along the reciprocal axis *c**. In addition, these urea molecules are involved in the formation of the interligand hydrogen bonds: their oxygen atoms are acceptors of a hydrogen bond from the H–O(4) group of phosphate, and one of the nitrogen atoms donates a hydrogen bond N(1)–H to O(1) of the phosphate group. In this manner four six-membered rings are formed around the calcium atom, as shown in Figure 3. The rings are almost planar, as can be seen from the data in Table 4 of the supplementary material. The largest deviation from the plane through O(4) and P is for the atom O(4) (0.17 Å), while for the plane through N(1) and C(1) the largest deviation is for C(1) (0.06 Å). The two planes are at dihedral angles at 6.7°.

Interleaved between the layers described above are layers containing only *lattice urea molecules*, located at $y = {}^1/_4$ and $y = {}^3/_4$. The molecules in this layer are hydrogen bonded head to tail between O(6) and N(3) and between O(6) and N(4), at N–H···O distances of 2.997 and 3.120 Å, respectively (Figure 2). The bonding between the phosphate urea layers, $Ca(H_2PO_4)_2[CO(NH_2)_2]_2$, and the lattice urea layers is provided by five hydrogen bonds, the strongest of which are (a) O(3)–H(3)···O(6) between the oxygen of lattice urea and a hydroxyl group of the $H_2PO_4^-$ group, of length 2.608 Å, and (b) N(4)–H(42)···O(4)^{II} between the second nitrogen atom of the lattice urea and the hydroxyl group of the $CaPO_4$ chain at $y = {}^1/_2$, of length 3.010 Å. The interlayer hydrogen bonding is relatively weak, which explains the pronounced cleavage of the crystals perpendicular to the crystallographic *b* axis.

The *phosphate group* acts as a bidentate bridging ligand coordinated to calcium. The $H_2PO_4^-$ group is tetrahedral with only minor distortions. The O–P–O angles range from 106.7 to 117.1°. The average value of the angles is 109.4°, with mean deviation 2.6° (see Table III). There are clearly two short P–O distances, averaging 1.500 Å (1.504 Å in Mg), and two longer ones, averaging 1.579 Å (1.575 Å in Mg). The short distances correspond to the P═O bonds, while the long ones correspond to the P—O(H) bonds. This is confirmed by the hydrogen-bonding scheme, as described above, in which O(4) is connected to the O(5) of the ligand urea by a hydrogen bond of length 2.682 Å, while O(3) is connected to O(6) of the lattice urea by a hydrogen bond of length 2.608 Å. Clearly O(3) and O(4) must provide the H atoms for these two hydrogen bonds. The largest O–P–O angle (117.1°) is the one involving the two short P–O distances (O(1)–P–O(2)), as expected.

Table III. Interatomic Distances and Angles

	bond dist, Å[a]			bond angles, deg	
	M = Ca	M = Mg		M = Ca	M = Mg
		M Octahedron			
M-O(1)	2.299 (2)	2.066 (2)	O(1)-M-O(2)$^{\text{VII}}$	87.9 (1)	89.1 (1)
M-O(2)$^{\text{VII}}$	2.335 (2)	2.076 (2)			
M-O(5)	2.372 (2)	2.172 (2)	O(2)$^{\text{VII}}$-M-O(5)	90.2 (1)	90.9 (1)
O(1),O(2)$^{\text{VII}}$	3.217 (3)	2.905 (2)	M$^{\text{III}}$-O(2)-P	132.2 (1)	133.3 (1)
O(1),O(5)	3.232 (3)	2.956 (3)			
O(1),O(2)$^{\text{VIII}}$	3.335 (3)	2.953 (3)			
O(1),O(5)$^{\text{I}}$	3.372 (4)	3.039 (3)			
O(5),O(2)$^{\text{VII}}$	3.333 (3)	3.030 (3)			
O(5),O(2)$^{\text{VIII}}$	3.321 (3)	2.980 (3)			
		PO_4 Tetrahedron			
P-O(1)	1.497 (3)	1.503 (2)	O(2)-P-O(3)	108.8 (1)	108.0 (1)
P-O(2)	1.502 (3)	1.505 (2)	O(2)-P-O(4)	106.7 (1)	108.0 (1)
P-O(3)	1.570 (3)	1.568 (2)	O(2)-P-O(1)	117.1 (1)	117.6 (1)
P-O(4)	1.588 (3)	1.581 (2)	O(3)-P-O(4)	106.3 (1)	106.6 (1)
			O(3)-P-O(1)	107.9 (1)	106.8 (1)
			O(4)-P-O(1)	109.5 (1)	109.2 (1)
O(1),O(2)	2.559 (3)	2.573 (2)			
O(1),O(3)	2.479 (4)	2.466 (3)			
O(1),O(4)	2.520 (4)	2.514 (3)			
O(2),O(3)	2.498 (4)	2.486 (3)			
O(2),O(4)	2.480 (4)	2.497 (3)			
O(3),O(4)	2.526 (4)	2.524 (3)			
		Ligand Urea			
C(1)-O(5)	1.256 (4)	1.261 (3)	O(5)-C(1)-N(1)	121.0 (3)	121.2 (2)
C(1)-N(1)	1.325 (5)	1.325 (4)	O(5)-C(1)-N(2)	121.3 (3)	121.5 (3)
C(1)-N(2)	1.336 (5)	1.342 (4)	N(1)-C(1)-N(2)	117.6 (3)	117.3 (3)
N(1)-H(11)	0.97 (4)	0.87 (4)			
N(1)-H(12)	0.75 (5)	0.91 (6)			
N(2)-H(21)	0.79 (5)	0.89 (5)			
N(2)-H(22)	0.93 (4)	0.82 (3)			
		Lattice Urea			
C(2)-O(6)	1.255 (5)	1.251 (4)	O(6)-C(2)-N(3)	121.9 (3)	122.4 (3)
C(2)-N(3)	1.328 (5)	1.335 (4)	O(6)-C(2)-N(4)	120.7 (3)	121.0 (3)
C(2)-N(4)	1.335 (5)	1.337 (4)	N(3)-C(2)-N(4)	117.3 (3)	116.6 (3)
N(3)-H(31)	0.79 (5)	0.75 (4)			
N(3)-H(32)	0.79 (5)	0.92 (4)			
N(4)-H(41)	0.83 (5)	0.85 (4)			
N(4)-H(42)	0.73 (4)	0.84 (4)			

[a] Symmetry operations are indicated by roman numerals: (no symbol) x, y, z; (I) $-x, -y, -z$; (II) $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (III) $x, y, 1 + z$; (IV) $-1 + x, y, 1 + z$; (V) $-^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (VI) $-^1/_2 + x, {}^1/_2 - y, -^1/_2 + z$; (VII) $x, y, -1 + z$; (VIII) $-x, -y, 1 - z$.

The two types of urea molecules are identical in their interatomic distances and angles, within the accuracy of the structure determination. This is true in spite of the fact that they are crystallographically different and serve quite different purposes in the structure. As shown in Table 4 of the supplementary material, both types of molecules are planar with all hydrogen atoms lying within 0.2 Å of the calculated planes.

Discussion

The hoped-for coordination of Ca or Mg to nitrogen did not materialize in these structures. Although there are quite a few examples of Ca–N coordination, coordination to oxygen is almost always preferred. The nitrogen atom N(1) nearest the Ca ion lies at a distance of 3.63 Å, much too far to be considered part of the Ca coordination sphere. Urea, when coordinated to metal ions, almost always coordinates through its oxygen atom. The one notable exception is $Co[OC(NH_2)_2]_4(NO_3)_2$, which contains, aside from two oxygen-bound urea molecules, two bridging bidentate urea molecules, which are bonded through oxygen and nitrogen.[7]

A notable feature of the structure is the absence of PO-H···OPO hydrogen bonds as observed in $Ca(H_2PO_4)$,[8] $Ca(H_2PO_4)\cdot H_2O$,[9,10] $CaHPO_4$,[11,12] NaH_2PO_4,[13] methylguanidinium dihydrogen phosphate,[14] procaine dihydrogen phosphate,[15] and imidazolium dihydrogen phosphate.[16] Yet the bond angles and distances are in agreement with the ones observed in these dihydrogen phosphate salts.

The calcium is six-coordinated, and that is clearly the reason that in this case the Ca and Mg structures can be isomorphous. Magnesium rarely shows a coordination higher than six, as a result of its small ionic radius (0.65 Å). If the radius of oxygen is taken as 1.45 Å, making the Mg–O distance 2.10 Å (almost precisely equal to the average of the Mg–O distances in the present structure), then the O–O separation in the octahedron surrounding Mg is $2.10(2^{1/2}) = 2.97$ Å. This means that in the Mg octahedron the oxygen atoms almost

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touch each other, and there certainly would not be room for a seventh oxygen around Mg. By contrast the ionic radius of Ca^{2+} is 0.99 Å, and so the Ca–O distance would be 2.44 Å (compared with an average of 2.36 Å in the present structure) and O–O separations in an octahedron around Ca^{2+} would be 3.45 Å, much larger than the 2.9 Å for touching oxygen atoms. Even a cubic eight-coordination for Ca^{2+} would have a O–O separation of 2.82 Å, indicating of course that Ca^{2+} is capable of accommodating more oxygen atoms around it than Mg^{2+}. Consequently, it is highly likely that isomorphisms between calcium and magnesium compounds will be found only in those cases where the calcium ion is six-coordinated, as is the case in the present study, and such isomorphism is in fact rather rare. Examples of cases where it is found are Ca_2GeO_4,[17] Mg_2GeO_4,[18] and $Ca(NH_3)_6X_2$ and $Mg(NH_3)_6X_2$, where X = Cl, Br, I.[19] In the last example the six-coordination of the cations is obvious. Aside from these examples isomorphous Ca and Mg compounds are hard to find. Even in very simple compounds it does not occur, e.g., $CaSO_4$–$MgSO_4$,[20,21] $Ca(H_2O)_6X_2$–$Mg(H_2O)_6X_2$ (with X = Cl, Br, I),[22,23] or $CaWO_4$–$MgWO_4$.[24,25] The results found here may therefore be considered to be unusual in that they represent another case of isomorphous Ca and Mg compounds.

The direction in the crystal that is most directly affected by the difference in the ionic radii of Ca^{2+} and Mg^{2+} is the *c* axis (as can be seen from Figures 1 and 2), because it is in this direction that CaO_6 octahedra are linked by the phosphate groups to form chains. Thus the rather large difference in the length of the *c* axis in the two compounds is readily understood.

The hydrogen bonding responsible for holding the various components of the structure together was already described above. One observation to be added is that N(3)–H(31) is apparently involved in a bifurcated hydrogen bond: to O(2) of the phosphate group (N(H)···O length 3.25 Å, angle 154°) and to O(5) of the ligand urea (length 3.25 Å, angle 126°).

The formation of the six-membered rings in the coordination sphere of calcium is not uncommon and is apparently a stabilizing feature in some Ca–PO_4 structures. Although formation of five-membered rings is perhaps a preferred interaction,[26] formation of six-membered rings is observed in $Ca(H_2PO_4)_2$ as $\overline{\mathrm{Ca{-}O{-}P{-}O\cdots H\cdots O}}\mathrm{{-}P}$, where the hydrogen bond is very strong and the hydrogen is effectively centered,[7] in $Ca(H_2PO_4)_2{\cdot}H_2O$ as $\overline{\mathrm{Ca{-}O{-}P{-}O\cdots H{-}O}}\mathrm{{-}H}$,[8,9] and in $CaHPO_4$ as $\overline{\mathrm{Ca{-}O{-}P{-}O\cdots H\cdots O}}\mathrm{{-}P}$, where the hydrogen is disordered.[11,12]

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Registry No. $Ca[OC(NH_2)_2]_2(H_2PO_4)_2{\cdot}2CO(NH_2)_2$, 60892-69-5; $Mg[OC(NH_2)_2]_2(H_2PO_4)_2{\cdot}2CO(NH_2)_2$, 82918-04-5.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table 1), all interatomic distances (Table 2), hydrogen bonds (Table 3), calculated least-squares planes and deviations of atoms from these planes (Table 4), and final values of $|F_o|$ and $|F_c|$ for both $Ca(H_2PO_4)[CO(NH_2)_2]_2{\cdot}2CO(NH_2)_2$ and $Mg(H_2PO_4)[CO(NH_2)_2]_2{\cdot}2CO(NH_2)_2$ (39 pages). Ordering information is given on any current masthead page.

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