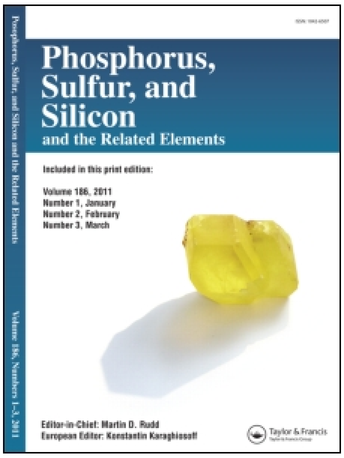

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Two-Dimensional Inorganic Networks in the Crystal Structures of Calcium and Strontium Phosphite Monohydrates

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TWO-DIMENSIONAL INORGANIC NETWORKS IN THE CRYSTAL STRUCTURES OF CALCIUM AND STRONTIUM PHOSPHITE MONOHYDRATES

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The crystal structures of two layered metal phosphites $M(HPO_3)\cdot H_2O$ *where* $M = Ca$ *and Sr are reported. These compounds are the first examples of inorganic phosphites structurally related to metal phosphonates with the general formula of* $M(RPO_3)\cdot H_2O$*. They crystallize in monoclinic system with space group* $P2_1/c$ *and are isostructural. The structures consist of two-dimensional sheets formed by linked metal and phosphorus polyhedra, which are held together by* $O—H\cdots O$ *hydrogen bonds.*

Keywords: Crystal structure; hydrogen bonds; layered structure; metal phosphites; metal phosphonates

INTRODUCTION

The chemistry of metal phosphites and phosphonates has drawn an increasing interest for the design and application of new one-, two-, and three-dimensional materials with requested properties. Researchers have found technological applications in areas such as separations and ion exchange, catalysis to function as a host for intercalation of different compounds and thin films.[1–3] The rational design of metal phosphonates is based on the modification of an inorganic framework of metal phosphite or phosphate by replacing hydrogen or hydroxyl group with

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Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411737 (**CAP**) and CSD-411738 (**SRP**), the name of the authors, and citation of the article.

an organic group. Therefore, the study of structural relationships between metal phosphonates and their purely inorganic analogues would lead to understanding how and to what extent metal ion or organic phosphorus ligand governs the assembling of supramolecular architecture. These relationships are described and tabulated by Mallouk and his coworkers.[1,2]

Our interest in the chemistry of alkaline-earth metal phosphites and phosphonates is to develop new materials for surface modification and to protect different objects such as stones and metals against atmospheric influences, corrosion, and decay.[4] In this study, we present the structures of layered calcium and strontium phosphites monohydrates as the first examples of inorganic phosphites structurally related to metal phosphonates with the formula $M(RPO_3)\cdot H_2O$.

RESULTS AND DISCUSSION

Phosphorus acid is a dibasic acid and reacts with many metal ions to form phosphites with different chemical compositions. There are several reports on the crystal structure of alkaline-earth metal phosphates, while there are just a few structures known for corresponding phosphites. The crystal structures of $Mg(HPO_3)\cdot 6H_2O$[14,15] and $Ca(H_2PO_3)_2\cdot H_2O$[4,16] already have been reported and there is no report on strontium or barium phosphite or hydrogenphosphite. In Table I, we have summarized the structural data for alkaline-earth metal phosphonates and phosphites. No doubt, the structural chemistry of these compounds is dominated by layered types in which the main feature is the formation of inorganic networks from metal and phosphorus polyhedra. The properties of these layered compounds can be altered by modification of organic substituents on phosphorus atom, however, the nature of metal atom and its coordination behavior should not be neglected. In the case of calcium phosphonates, for example, the solubility varies considerably on the changes of organic moiety, and very low solubility could be obtained with phosphonic acids with long organic chains.[6,8] In the case of $Ca(H_2PO_3)_2\cdot H_2O$ and $Ca(HPO_3)\cdot H_2O$ (**CAP**), on the other hand, solubility decreases in the latter case that shows the influence of a compact inorganic framework for **CAP** in comparison to a less compact one for $Ca(H_2PO_3)_2\cdot H_2O$.[4]

In 1979, Rafiq and coworkers described a general route to synthesize alkaline-earth metal phosphites with the formula $M(HPO_3)\cdot xH_2O$.[11] They also reported a preliminary crystallographic data (cell parameters, crystal system, and space group) for calcium and strontium

TABLE I Some Structural Data for Alkaline-Earth Metal Phosphonates and Phosphites

Phosphonate compound	Space group	Remark	Ref.	Phosphite compound	Space group	Remark	Ref.
Magnesium							
$Mg(RPO_3)\cdot H_2O$	$Pmn2_1$	Layered	8	$Mg(HPO_3)\cdot 6H_2O$	R3		14, 15
$Mg(RPO_3)\cdot 2H_2O$	$P2_1/c$	Layered	8				
$Mg_3(O_2CRPO_3)_2\cdot 6H_2O$	$P2_1/c$	Extended 3-Dimensional	18				
$Mg(H_3NRPO_3)\cdot 4H_2O$	$P2_1/c$	Layered	19				
$Mg(O_3PRPO_3)_2\ (R_2NH_2)_2\ (H_2O)_2$	$P2_1/c$	Layered	20				
Calcium							
$Ca(RPO_3)\cdot H_2O$	$P2_1/c$	Layered	6	$Ca(HPO_3)\cdot H_2O$	$P2_1/c$	Layered	This study
$Ca(RPO_3H)_2$	C2/c	Layered	4	$Ca(H_2PO_3)_2\cdot H_2O$	P-1	Layered	5, 10
$Ca(RPO_3H)_2$	P-1	Layered	6				
$Ca(O_3PRPO_3)\cdot 2H_2O$	Pnma	Pillared Layered	21				
$Ca(RPO_3)\cdot 2H_2O$	P-1	Layered	22, 23				
$Ca(RPO_3H)_2\cdot 3H_2O$	$Pca2_1$	Layered	24				
$Ca(RPO_3H)_2\cdot 3H_2O$	C2/c	Layered	24				
$Ca(RPO_2\ (OR))_2\cdot H_2O$	$P2_1/c$	Layered	25				
Strontium							
$Sr(HO_3PRPO_3H)_2\cdot 4H_2O$	C2/c	Chains	26	$Sr(HPO_3)\cdot H_2O$	$P2_1/c$	Layered	This study
Barium							
$Ba(RPO_3H)_2$	C2/c	Layered	27	NR			

phosphite monohydrates. Our results confirm their preliminary data and explore the structural details of these compounds.

Crystal Structure of Calcium Phosphite Monohydrate

Calcium phosphite monohydrate, **CAP**, crystallizes in monoclinic system with space group $P2_1/c$ (No. 14). Crystallographic and refinement data are given in Table II. The asymmetric unit consists of one formula unit, $Ca(HPO_3)\cdot H_2O$. The calcium ion is coordinated by seven oxygen atoms forming a distorted pentagonal bipyramid geometry. The Ca–O bond distances are ranging from 2.3156 (13) to 2.6074 (14) Å

TABLE II Crystallographic and Refinement Data

	CAP	SRP
Empirical formula	$Ca(HPO_3)\cdot H_2O$	$Sr(HPO_3)\cdot H_2O$
Formula weight	138.07	185.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a [Å]	7.7091 (1)	7.5906 (5)
b [Å]	6.7212 (1)	7.0502 (4)
c [Å]	7.9582 (8)	8.2156 (5)
β [°]	109.868 (1)	108.459 (1)
V [Å^3]	387.805 (11)	417.04 (4)
Z	4	4
T [K]	297 (2)	183 (2)
ρ (calc.) [g·cm^{-3}]	2.365	2.956
Crystal dimensions [mm]	0.26 × 0.05 × 0.02	0.10 × 0.08 × 0.01
μ [mm^{-1}]	1.889	13.180
F (000)	280	352
Max/min transmission	0.9632/0.6393	0.8795/0.3524
θ range [°]	2.81–32.73	2.83–32.88
Index ranges	$-11 <= h <= 11$	$-11 <= h <= 11$
	$-9 <= k <= 10$	$-10 <= k <= 10$
	$-11 <= l <= 11$	$-12 <= l <= 12$
Reflections collected	5634	7222
Independent reflections	1379	1503
R (int.)	0.0434	0.0775
Reflections obs. [$I > 2\sigma(I)$]	1084	1115
Data/restraints/parameters	1379/3/67	1503/3/67
GooF (F_o^2)	1.028	1.034
R1/wR2[a] for obs. refl.	0.0310/0.0704	0.0448/0.0864
R1/wR2 for all data	0.0469/0.0762	0.0738/0.0952
Weighting scheme[b] x/y	0.0410/0.0118	0.0473/0
Larg. res. Peak/ hole [e·Å^{-3}]	0.412/−0.570	0.976/−1.127

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR2 = [\sum[W(F_o^2 - F_c^2)^2] / \sum (F_o^2)^2]^{1/2}$.
[b] $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$.

and are comparable with those found for $Ca(H_2PO_3)_2{\cdot}H_2O$, ranging from 2.3531 (10) to 2.5331 (10) Å [5] and for $Ca(O_3PCH_3){\cdot}H_2O$ ranging from 2.305 (2) to 2.707 (2).[6] The phosphite group is chelated by O1 and O2 atoms to the Ca ion, while bridging to other Ca ions through oxygen atoms, including O3. The coordination environment of Ca and P atoms is shown in Figure 1 and selected bond distances and angles are given in Table III. The structure exhibits a two-dimensional inorganic network formed by linking Ca and P polyhedra, aligned parallel to *bc* plane. The phosphite groups are arranged in such a way that the (P—)H atoms are sticking out from the layers which is similar to the case of $Ca(O_3PCH_3){\cdot}H_2O$,[6] where (P—)R groups are pointing out from the layers. Between these layers, the O3 atom is involved in a hydrogen bond with the H41 of the closest water molecule, while within the layer, the O1 atom, forms a hydrogen bond with the H42 of water. These

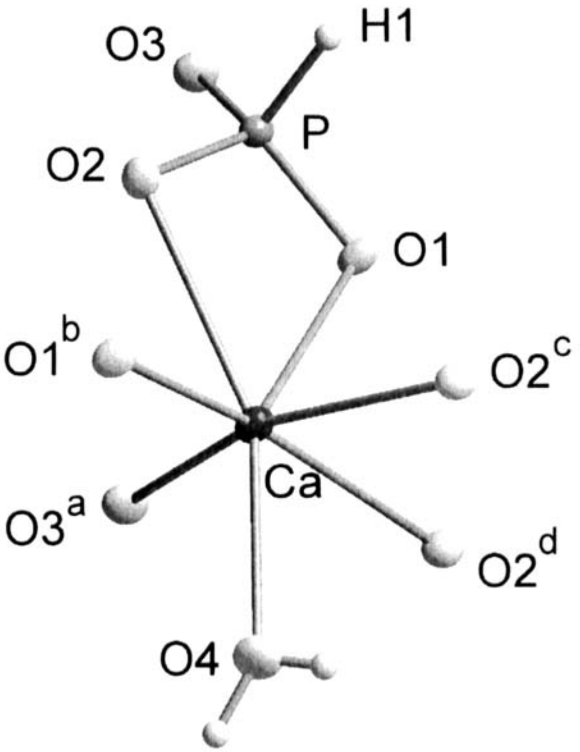


FIGURE 1 The coordination geometry of calcium atom in the crystal structure of **CAP** including atom-labeling scheme. Displacement ellipsoids are shown at 50% probability level. Symmetry codes are listed in Table II.

TABLE III Selected Bond Distances and Angles [Å, °]

CAP			
Ca–O1	2.4870 (14)	O1–Ca–O2	58.34 (4)
Ca–O2	2.6072 (14)	O3^{a}–Ca–O1^{b}	113.89 (5)
Ca–O3^{a}	2.3155 (13)	O1^{b}–Ca–O2^{c}	86.01 (5)
Ca–O4	2.3926 (17)	O3^{a}–Ca–O2^{d}	80.16 (5)
Ca–O1^{b}	2.3777 (14)	O2^{c}–Ca–O2^{d}	79.38 (5)
Ca–O2^{c}	2.4163 (13)	O1–P–O2	107.77 (8)
Ca–O2^{d}	2.4786 (14)	O1–P–O3	114.81 (8)
P–O1	1.5331 (14)	O2–P–O3	112.59 (8)
P–O2	1.5431 (14)		
P–O3	1.5145 (14)		
P–H1	1.254 (14)		
SRP			
Sr–O1	2.630 (3)	O2–Sr–O1	55.60 (9)
Sr–O2	2.711 (3)	O3^{e}–Sr–O1^{f}	126.48 (10)
Sr–O3^{e}	2.488 (3)	O1^{f}–Sr–O2^{g}	84.86 (10)
Sr–O4	2.567 (4)	O3^{e}–Sr–O2^{h}	74.96 (10)
Sr–O1^{f}	2.525 (3)	O2^{g}–Sr–O2^{h}	73.88 (11)
Sr–O2^{g}	2.568 (3)	O1^{f}–Sr–O4^{i}	55.41 (10)
Sr–O2^{h}	2.632 (3)	O3^{e}–Sr–O4^{i}	71.33 (10)
Sr–O4^{i}	3.187 (4)	O2–P–O1	108.94 (19)
P–O1	1.529 (3)	O2–P–O3	113.23 (19)
P–O2	1.532 (3)	O1–P–O3	113.98 (18)
P–O3	1.518 (3)		
P–H1	1.325 (19)		

Symmetry transformations used to generate equivalent atoms:
$^{a}-x+1, -y+1, -z+1.$
$^{b}-x+1, y-1/2, -z+1/2.$
$^{c}x, -y+1/2, z-1/2.$
$^{d}-x+1, y+1/2, -z+1/2.$
$^{e}-x+1, -y+2, -z+1.$
$^{f}-x+1, y-1/2, -z+3/2.$
$^{g}x, -y+3/2, z+1/2.$
$^{h}-x+1, y+1/2, -z+3/2.$
$^{i}x, -y+3/2, z-1/2.$

hydrogen bonds are stabilizing the inorganic network. The geometry of the hydrogen bonds is given in Table IV.

Crystal Structure of Strontium Phosphite Monohydrate

Strontium phosphite monohydrate, **SRP**, crystallizes in monoclinic system with space group $P2_1/n$ (No. 14) (see Table II for more details on crystal data). The asymmetric unit consists of one formula unit, $Sr(HPO_3)\cdot H_2O$. The coordination environment of the strontium ion is shown in Figure 3, in which the Sr atom is coordinated by seven oxygen

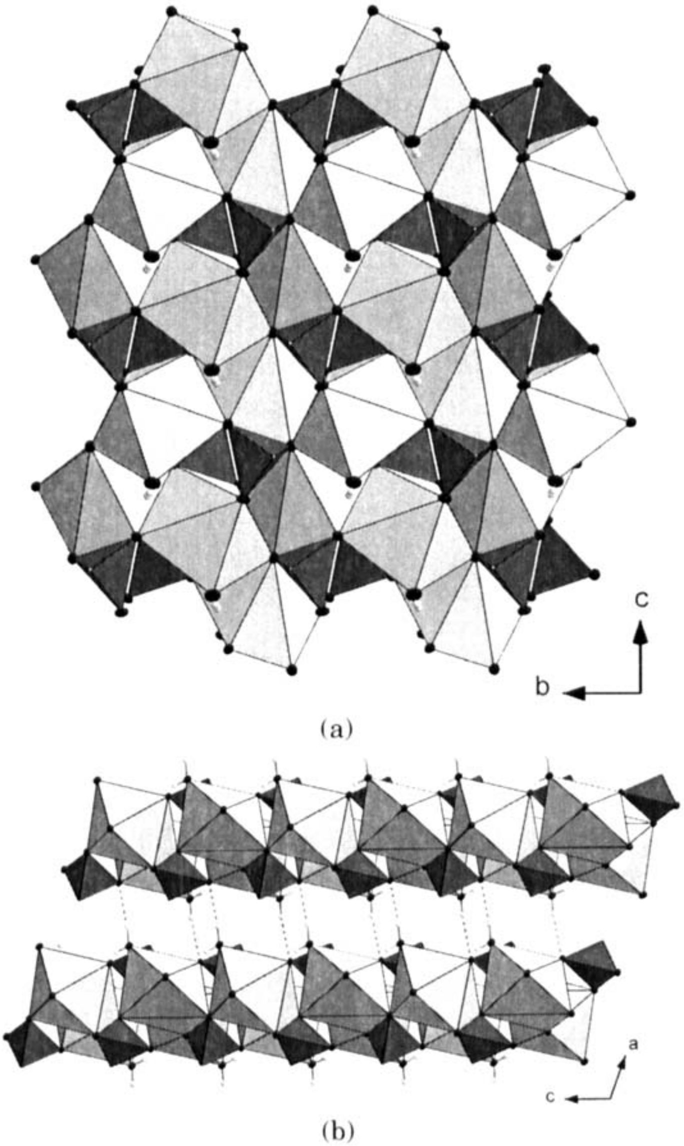


FIGURE 2 Two-dimensional inorganic network of **CAP** formed by linking Ca and P polyhedra: (a) top view; (b) side view, showing interlayer hydrogen bonds.

atoms: six from phosphite groups and one from water molecules with the bond distances ranging from 2.488 (3) to 2.711 (3) Å. There is a long Sr—O bond distance of 3.187 Å to the O4 atom of water molecule at (x, −y + 3/2, z −1/2), while to O4 of the other water molecule is 2.567

TABLE IV The Geometry of Hydrogen Bonds [Å,°]

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
CAP				
O4–H42···O1[a]	0.71 (4)	2.10 (4)	2.803(2)	170 (5)
O4–H41···O3[b]	0.82 (3)	1.99 (3)	2.801 (2)	168 (3)
SRP				
O4–H42···O1[c]	0.79 (2)	2.14 (5)	2.719 (5)	130 (6)
O4–H41···O3[d]	0.81 (2)	1.96 (2)	2.760 (5)	172 (6)

Symmetry transformations used to generate equivalent atoms:
[a] −x + 1, −y + 1, −z.
[b] x − 1, y, z − 1.
[c] −x + 1, −y + 2, −z + 2.
[d] x + 1, y, z + 1.

(4) Å. This bond may be regarded as a weak coordination to metal atom and there is a significant increase in the angle O3^{v}-M-O1^{vi} of 126.48 (10)° for **SRP** in comparison to the respective angle of 113.89 (5)° for **CAP**. Furthermore, long Sr–O distances of 2.906 (4) and 3.084 (5) Å

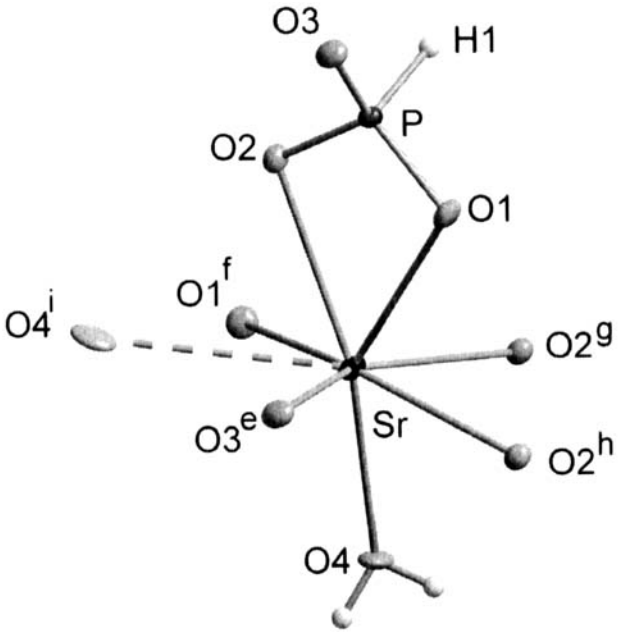
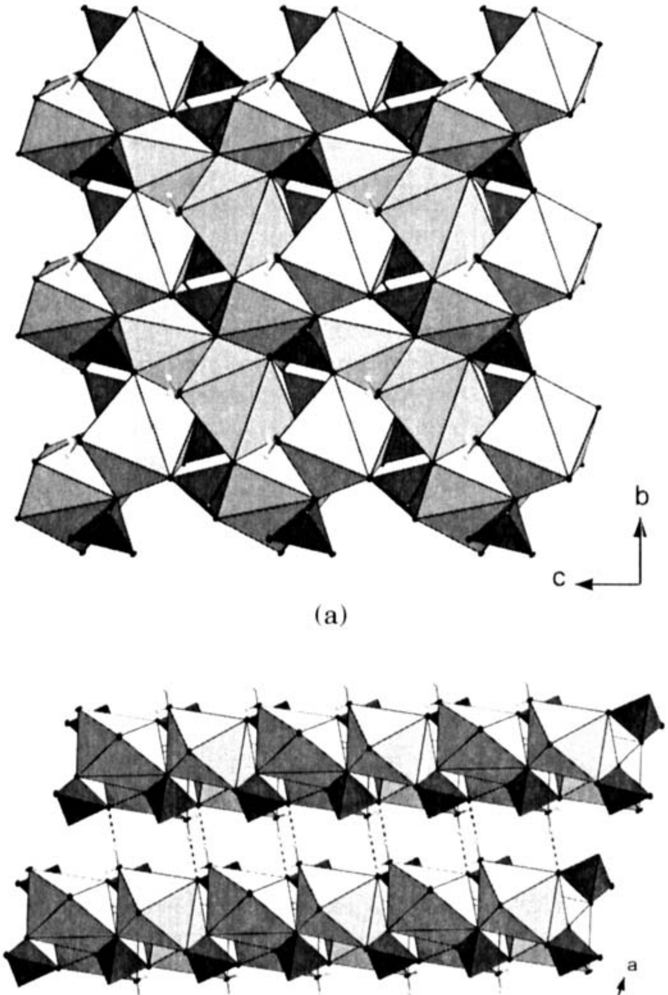


FIGURE 3 The coordination geometry of strontium atom in the crystal structure of **SRP** including atom-labeling scheme. Displacement ellipsoids are shown at 50% probability level. Symmetry codes are listed in Table II.



(a)

(b)

FIGURE 4 Two-dimensional inorganic network of **SRP** formed by linking Sr and P polyhedra: (a) top view; (b) side view, showing interlayer hydrogen bonds.

have been already reported in the crystal structure of α-SrHPO$_4$.[13] Therefore the coordination of strontium ion may be regarded as 7 + 1. The phosphite group is chelated by 01 and 02 atoms to the Sr ion, while bridging to other Sr ions through oxygen atoms, including 03. The selected bond distances and angles are given in Table III. The structure exhibits a two-dimensional inorganic network formed by linking Sr and

P polyhedra, aligned parallel to *bc* plane. The arrangement of phosphite groups and hydrogen bonding scheme are similar to **CAP**. The geometry of the hydrogen bonds is given in Table IV.

CONCLUSION

Both **CAP** and **SRP** crystallize with the same space group $P2_1/c$ and very similar unit cell parameters and they are isostructural. Nevertheless, they differ slightly from each other. The Ca ion in **CAP** is only 7 coordinated, while the Sr ion in **SRP** is 7 + 1 coordinated, with one long Sr—O bond distance. This behavior can be described as a high tendency of strontium ion to higher coordination numbers. In the crystal structures of **CAP** and **SRP** the phosphite group acts as chelating-bridging ligand in coordination to metal ions. Thus, it behaves differently in comparison to the coordination of phosphonate group in monoclinic Ca $(O_3PCH_3)\cdot H_2O$.[6] and orthorhombic $Cu(PhPO_3)\cdot H_2O$,[7] where no chelation occurs, but acts similarly for other orthorhombic members of the $M(RPO_3)\cdot H_2O$ family (M = Mn, Zn, Ni, Co, Mg, Cd, and Fe), where the phosphonate group is chelating.[8–12]

The geometry of hydrogen bonds for both **CAP** and **SRP** is given in Table IV. Obviously, both hydrogen bonds for **CAP** are strong, while one of them for **SRP** is weaker than other one. This can be attributed to a distortion by weak coordination of water molecules within two Sr ions.

EXPERIMENTAL

Synthesis

The crystals of **CAP** or **SRP** suitable for single-crystal X-ray diffraction analysis were obtained by hydrothermal reaction of calcium or strontium carbonate with phosphorous acid at autogenous pressure. $CaCO_3$ or $SrCO_3$ was added to a solution of H_3PO_3 (with ratio 1:1) in deionized water in a quartz cell of an stainless steel autoclave. The pH of the solution was adjusted to 6 using potassium hydroxide. It was sealed and placed in an oven operating at 423 K for overnight. Then it was allowed to cool at 5 °C/h to room temperature. Colorless plate-like crystals suitable for X-ray diffraction were found on the wall of the quartz cell and carefully taken out.

Crystal Structure Determination

Data were collected using a Siemens SMART CCD diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). Full spheres of reciprocal lattice were scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and exposure time 20 s per frame. Preliminary orientation matrices were obtained from the first frames using SMART.[28] The frames were integrated using the preliminary orientation matrices which were updated every 100 frames. Final cell parameters were obtained by refinement on the positions of reflections (3209 for **CAP**; 3151 for **SRP**) with $I > 10\sigma(I)$ after integration of all the frames using SAINT.[28] The data were empirically corrected for absorption and other effects using SADABS[29] based on the method of Blessing.[30] The structures were solved by the Patterson method and refined by full-matrix least squares on all F^2 data using SHELXTL.[31] The non-H atoms were refined anisotropically. The hydrogen atoms of water molecules and on phosphorus atoms (P—H) were located from difference on a Fourier map and refined isotropically with restrain bond distances of 0.8 Å and 1.3 Å, respectively.

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