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Preparation and Properties of Two Strontium Orthophosphates— $Sr_3(PO_4)_2 \cdot 4H_2O$ and $Sr_6H_3(PO_4)_5 \cdot 2H_2O$

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Two new strontium orthophosphates have been prepared by precipitation from aqueous solution at room temperatures or below. $Sr_3(PO_4)_2 \cdot 4H_2O$ was prepared by adding a $Sr(NO_3)_2$ solution to a solution containing an excess of K_2HPO_4 and made basic with KOH. This new compound, a gelatinous material, appears to have a layer structure. $Sr_6H_3(PO_4)_5 \cdot 2H_2O$ was prepared by adding a $Sr(NO_3)_2$ solution to a KH_2PO_4 solution which had been adjusted to pH 7.7. X-Ray diffraction data are reported for both compounds.

IN THE COURSE OF STUDIES on mixed crystal formation between calcium and strontium hydroxyapatite, two phases of strontium phosphate have been found with characteristic x-ray diffraction patterns distinct from any previously reported. Both compounds precipitate from aqueous solution at room temperatures or below.

EXPERIMENTAL

All chemicals were reagent grade. The distilled water was boiled to remove excess CO_2 and was cooled under a soda-lime trap.

Preparation of $Sr_3(PO_4)_2 \cdot 4H_2O$. This preparation, until the final drying period, was carried out at 10° to prevent hydrolysis of the compound to strontium hydroxyapatite. Precautions were taken to minimize CO_2 absorption during the precipitation and washing. To a vigorously stirred solution of 20 grams K_2HPO_4 and 15 ml. of 1*N* KOH was added to 100 ml. of a solution containing 1 gram $Sr(NO_3)_2$. The gelatinous precipitate was stirred for ½hr. and washed by centrifugation in cold water. Finally, the precipitate was either washed with ethanol and ether or dried in a vacuum desiccator over Drierite. The water content was variable and depended on the method of drying. The amount found by weight loss on heating to 900° varied between slightly under 4 to 5 moles of water per mole of $Sr_3(PO_4)_2$. The weight per cent analysis of a typical preparation was: calcd. for $Sr_3(PO_4)_2 \cdot 4H_2O$—Sr, 50.08; P, 11.79; H_2O, 13.72. Found—Sr, 50.09; P, 12.09; H_2O (weight loss on heating to 900°), 12.84.

On heating the compound to 900° it transformed to pure $Sr_3(PO_4)_2$, as revealed by its x-ray pattern. X-Ray emission analysis showed a small potassium contamination amounting to less than 0.5%.

Precipitates showing identical diffraction patterns could be made using wide variations in amount of K_2HPO_4 and $Sr(NO_3)_2$, but it was noticed that, unless K_2HPO_4 was in excess of $Sr(NO_3)_2$, Sr/P ratios in the precipitate slightly greater than 1.5 could be obtained. Presumably the gelatinous precipitate has an affinity for strontium ions.

Preparation of $Sr_6H_3(PO_4)_5 \cdot 2H_2O$. A solution of 20 grams KH_2PO_4 in 1 liter of water was adjusted to pH 7.70 with 1*N* KOH. To this vigorously stirred solution at room temperature was added 100 ml. of water containing 2 grams $Sr(NO_3)_2$. A large excess of KH_2PO_4 was used to keep the pH moderately constant during the precipitation. The gelatinous precipitate was allowed to stand quitely for at least 2 hours during which it transformed to a more crystalline form. The precipitate was washed extensively with water and finally with alcohol and ether. It was dried to constant weight at 150°. On heating this compound to 900° it broke down into a mixture of α-$Sr_2P_2O_7$ and $Sr_3(PO_4)_2$. The ratio of α-$Sr_2P_2O_7$ to $Sr_3(PO_4)_2$, as determined by a careful intensity estimate of characteristic x-ray lines of these compounds and a comparison with intensity estimates on known mixtures of α-$Sr_2P_2O_7$ and $Sr_3(PO_4)_2$, corresponded to a Sr/P ratio of 1.20 ± 0.005 in the original sample. Anal: Calcd. for $Sr_6H_3(PO_4)_5 \cdot 2H_2O$—Sr, 50.57; P, 14.90; weight loss on conversion to α-$Sr_2P_2O_7$ and $Sr_3(PO_4)_2$, 6.06. Found—Sr, 50.36; P, 14.64; weight loss on heating to 900°, 5.53. Contamination by potassium was less than 0.5%.

RESULTS

$Sr_3(PO_4)_2 \cdot 4H_2O$. The x-ray pattern from $Sr_3(PO_4)_2 \cdot 4H_2O$ is shown in Figure 1. This pattern bears no similarity to that of strontium hydroxyapatite. Many of the peaks are

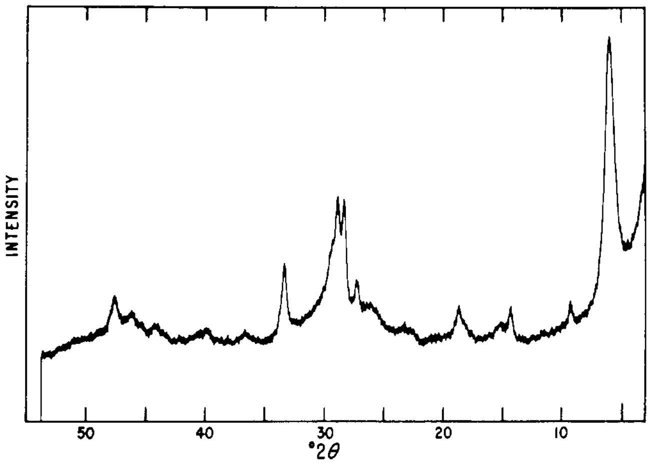

Figure 1. The x-ray diffraction pattern of $Sr_3(PO_4)_2\cdot 4H_2O$ taken with an x-ray diffractometer and CuKα radiation

broad and poorly resolved. Of particular interest is the strong peak at $2\theta = 6°$ whose position and intensity are sensitive to water content. Partial dehydration shifts the peak to higher angles (smaller spacings) and causes a decrease in intensity. This dehydration is reversible below 400°, and the structure giving the x-ray pattern with the strong $2\theta = 6°$ peak can be regenerated by suspending the sample in water for a few minutes.

In boiling water $Sr_3(PO_4)_2\cdot 4H_2O$ hydrolyzes rapidly to a solid giving a strontium hydroxyapatite x-ray pattern but with a Sr/P ratio below that of strontium hydroxyapatite (theor. 1.67). The hydrolysis also proceeds at room temperature, but at a lower rate.

$Sr_6H_3(PO_4)_5\cdot 2H_2O$. The x-ray data for $Sr_6H_3(PO_4)_5\cdot 2H_2O$ are recorded in Table I. This is a crystalline compound with sharp diffraction lines and is stable on heating to 200°. In boiling water it transforms to $Sr_3(PO_4)_2$ but is perfectly stable in water at room temperature for periods of at least three months.

Table I. Powder x-Ray Diffraction Pattern of $Sr_6H_3(PO_4)_5\cdot 2H_2O$[a]

d, A.	*I*	*d*, A.	*I*	*d*, A.	*I*
7.13	5	2.43	6	1.709	2
6.44	2	2.39	13	1.684	9
5.74	4	2.37	7	1.669	5
4.79	6	2.33	7	1.650	4
4.66	2	2.29	4	1.614	2
4.38	11	2.26	7	1.593	3
3.96	2	2.22	5	1.585	6
3.89	14	2.17	6	1.550	6
3.54	14	2.14	16	1.516	7
3.42	16	2.10	3	1.496	2
3.41	14	2.04	9	1.455	2
3.32	57	2.02	8	1.417	3
3.19	100	1.98	10	1.392	2
3.03	44	1.94	29	1.378	2
2.98	22	1.93	13	1.336	3
2.92	14	1.90	9	1.296	4
2.85	40	1.88	9	1.249	1
2.77	33	1.85	2	1.232	2
2.67	6	1.83	2	1.215	1
2.63	2	1.81	7	1.199	2
2.45	16	1.73	6	1.182	2

[a] Pattern obtained with an x-ray diffractometer, CuKα radiation, $\lambda = 1.5418$ A. The interplanar spacings, in angstroms, are given under *d*, and the relative intensities (referred to the strongest line as 100) are given under *I*. The intensities were derived from measurement of peak height above background.

DISCUSSION

A review of the alkaline earth phosphates has recently been assembled by Mooney and Aia (*4*). The following strontium orthophosphates appear well substantiated and can be precipitated from solution at or below 100°: $Sr(H_2PO_4)_2$, $Sr(H_2PO_4)_2\cdot H_2O$, α- and β-$SrHPO_4$, and $Sr_{10}(OH)_2(PO_4)_6$ (strontium hydroxyapatite). $Sr_3(PO_4)_2$ may not precipitate directly from solution below 100°, but it has been made by slow hydrolysis of $SrHPO_4$ (*5*). X-Ray patterns for these compounds have been tabulated by Ropp and coworkers (*6*).

A hydrated tristrontium phosphate with a hydroxyapatite x-ray pattern has been reported (*1*, *2*), but there is disagreement as to whether this, and its calcium analog, should be considered as definite compounds (*4*). Our hydrated tristrontium phosphate is distinct from such preparations since its x-ray pattern is different from that of strontium hydroxyapatite in all respects. A critical feature of our preparative procedure is the use of low temperatures. If the preparation is carried out at room temperature or above, contamination with a phase giving the x-ray pattern of strontium hydroxyapatite occurs.

The strong reflection at $2\theta = 6°$, which occurs in $Sr_3(PO_4)_2\cdot 4H_2O$ and corresponds to an interplanar spacing of 14 A, and its angular variation with water content, suggests that this compound probably has a layer structure with a variable number of water molecules held between the strontium phosphate layers. The repeat distance perpendicular to the layers would be 14 A. A similar situation is found in octacalcium phosphate (*3*), $Ca_8H_2(PO_4)_6\cdot 5H_2O$, where layers resembling sections of hydroxyapatite are interleaved with water molecules to give a layer repeat distance of 18.7 A. These two compounds do not appear to be isostructural since their x-ray patterns, aside from the presence of the intense peak at low angles, are dissimilar.

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