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X-ray diffraction and electron microscropic studies of tetracopper hydrogentriphosphate

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Tetracopper hydrogentriphosphate, an important copper(II) phosphate in CuO P_2O_5-H_2O phase diagram has been investigated. XRD, scanning electron microscopy and solubility data of copper(II) phosphate indicate the possibility of co-precipitation alongwith its calcium counterpart during calcification because of crystal structure similarities.

It is now known with certainty that traces of copper affect the formation of calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$(CaHA), the crystalline inorganic component of skeletal system under pathologic conditions provided during Wilson's and Hodgkin's diseases *in vivo*[1]. Incorporation of copper in blood and blood plasma has recently been reported to cause kidney stones which contain copper, sarcoma of bones and malignancy of tumours in the inhabitants of Udaipur region of Rajasthan[2].

The presence of copper leads to the formation of sparingly soluble copper(II) phosphates alongwith their calcium counterparts during calcification. Though the stability conditions of such biogenic phosphates of copper have been worked out earlier[3], their characterization has not been well defined. The present note deals with the preparation of well crystallised sample of tetracopper hydrogentriphosphate trihydrate, $Cu_4H(PO_4)_3 \cdot 3H_2O$, its XRD, electron microscopic and solubility data in aqueous medium.

Experimental

A sample of $Cu_4H(PO_4)_3.3H_2O$ was prepared by constant stirring of $CuHPO_4.H_2O$ (1 g) with CH_3CO-ONa-CH_3COOH buffer (200 ml) at *p*H 6.0 for 72 h in an air-tight container. It was filtered, washed with water, acetone and finally dried *in vacuo* for 48 h. The elements Cu and P in the sample were determined complexometrically[4]. The analytical results (Found: Cu, 42.86, wt % P, 15.81 wt %, Cu/P gram atom ratio, 1.33; Reqd. for $Cu_4H(PO_4)_3 \cdot 3H_2O$: Cu, 42, 76 wt % P, 15.66 wt %, Cu/P gram atom ratio, 1.33) corresponded to its desired stoichiometry.

The X-ray diffraction patterns of the sample were obtained by using the model, Phillips Automatic Powder diffractometer, PW 1820 Goniometer and PW 1830 Generator and Cu-K_α radiation. The SEM patterns were obtained using Elmiskope electron microscope. The XRD pattern of the sample using Cu-K_α radiation contained sharp peaks whose *d*-spacings and I/I_o values are presented in Table 1. The values reported by Hayek[5] are also included in Table 1 for comparison. These values were found to be in agreement with those of octacalcium phosphate, $Ca_4H(PO_4)_3.2.5\ H_2O$ (OCP). The calculated lattice parameters of $Cu_4H(PO_4)_3$ included in Table 2, were of comparable order of magnitude with those of OCP. The photomicro-

Table 1—XRD data of $Cu_4H(PO_4)_3 \cdot 3H_2O$

2θ (deg)	*d*-spacings (Å)			I/I_0
Our data	Hayek's data	Our data	Hayek's data	
9.54	9.6	10.35	10.2	41
12.0	12.8	7.3	7.1	15
13.2		6.7		39
15.6		5.7	5.7	30
17.7		5.0		26
18.7		4.7		43
20.6	20.6	4.31	4.31	42
21.2		4.1		38
24.2		3.7		42
25.5		3.5		38
26.9		3.31		33
28.2		3.16		59
29.9	29.9	2.99	3.08	58
30.3		2.94		73
30.9	30.8	2.89	2.84	100
31.4		2.85		67
32.73	33.2	2.73	2.70	89
34.34		2.61		63
37.48		2.39		58
40.84	40.4	2.20	2.13	58
42.8		2.14		56
48.2	47.2	1.89	1.80	58
53.7	53.1	1.71	1.72	68
54.1		1.69		54
55.1		1.68		56
58.9		1.56		54

Table 2—Lattice parameters of $Cu_4H(PO_4)_3.3H_2O$ and OCP [$Ca_4H(PO_4)_3.2.5\ H_2O$]

Lattice constants (Å)	$Cu_4H(PO_4)_3.3H_2O$ calculated	$Ca_4H(PO_4)_3.2.5\ H_2O$
a	19.2	19.7
b	9.72	9.5
c	6.93	6.87

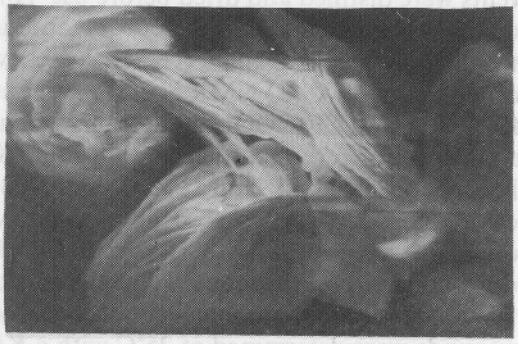

Fig. 1—Electron microscopic pattern of $Cu_4H(PO_4)_3.3\ H_2O$ (magnification × 1800)

graph (SEM) given in Fig. 1 revealed that the crystals of $Cu_4H(PO_4)_3$ were very thin flakes and blade-like in appearance similar to those of OCP[6,7] which is an important transitory phase formed during calcification. The values of solubility product (K_{sp}) of the prepared sample given in Table 3 were calculated by determination of Cu and P contents of the saturated solutions obtained by equilibrating 200 mg of the sample with 250 ml of CH_3COONa-CH_3COOH buffer prepared in 0.165 *M* $NaNO_3$ medium for *p*H in the range 4-5.6 at 25°C. Considering the stability of HPO_4^{-2} ion species within the selected *p*H range, the K_{sp} values were calculated. These values were found to be of the same order as those of CaHA[8]. The following equilibria were considered to be established in aqueous media and this explains the observed increase in solubility with increase of *p*H of the medium.

Table 3—Calculated values of solubility product (K_{sp}) of $Cu_4H(PO_4)_3 \cdot 3H_2O$ at 25°C

*p*H	4.0	4.8	5.6
K_{sp}	3.95×10^{-29}	8.74×10^{-28}	2.13×10^{-27}

$$Cu_4H(PO_4)_3 \overset{aq}{\rightleftharpoons} \underset{(aq)}{4\,Cu^{2+}} + \underset{(aq)}{H^+} + \underset{(aq)}{3\,PO_4^{3-}} \quad \ldots (i)$$

$$3PO_4^{3-} + 3\,H^+ \overset{aq}{\rightleftharpoons} 3\,HPO_4^{2-} \quad \ldots (ii)$$

$$H + OH^- \overset{aq}{\rightleftharpoons} H_2O \quad \ldots (iii)$$

Since $Cu_4H(PO_4)_3.3H_2O$ resembled OCP in crystal morphology and solubility behaviour with CaHA, the possibility of their co-precipitation under special pathologic conditions provided during Wilson's and Hodgkin's diseases can be considered accounting for the significant role played by copper(II) phosphates.

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