

## The Structure of Synthetic Copper Sodium Phosphate: $\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$

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### Abstract

Synthetic copper sodium phosphate  $\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$  is triclinic,  $P\bar{1}$ , with  $a = 9.3069$  (9),  $b = 8.9152$  (6),  $c = 8.7838$  (8) Å,  $\alpha = 102.25$  (1),  $\beta = 100.20$  (1),  $\gamma = 113.10$  (1)°,  $Z = 1$ . The structure was deduced from Patterson syntheses and refined by the full-matrix least-squares method to  $R = 0.040$  for 2710 observed reflections. The structure contains  $\text{PO}_4$  orthophosphate groups, and six kinds of Cu and three kinds of Na coordination polyhedra. Cu(1), Cu(2) and Cu(3) are at square-planar sites, Cu(4) is at a distorted and elongated octahedral site and Cu(5) and Cu(6) occupy distorted square-pyramidal sites. The coordination polyhedra of the Na atoms are irregular in shape with seven nearest-neighbour O atoms.

### Introduction

It is important from the viewpoint of the systematization of the structures of phosphates and the study of the coordination of divalent copper ions to investigate the structure of copper phosphates. Since the copper phosphates whose structures have been investigated are few, the syntheses of new phases are substantially important. The present paper reports the new crystal structure of copper orthophosphate which has been obtained from hydrothermal syntheses.

Throughout the investigation, calculations were carried out at the Computer Centre of Okayama University, using the modified programs of UNICS (Sakurai, 1971).

### Experimental

The synthesis of this substance was carried out with test-tube-type apparatus (623–873 K, 1000 kg  $\text{cm}^{-2}$ ) with a reagent mixture of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ . Crystals of  $\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$  were greenish with apparent euhedral forms.

The lattice dimensions and diffraction symmetry were estimated from Weissenberg photographs. The intensities of the reflections were collected from a

crystal with approximate dimensions  $0.1 \times 0.1 \times 0.1$  mm, on an automated four-circle diffractometer using the  $2\theta$ - $\omega$  scan technique, and Mo  $K\alpha$  radiation ( $\lambda = 0.70926$  Å) with a graphite monochromator. 2788 intensities were collected up to  $2\theta = 56^\circ$ ; of these, 2710 with  $I > 3\sigma$  above background were classified as observed. The intensities were converted to the structure factors by applying the Lorentz-polarization correction. No absorption corrections were made. The crystal data, such as cell dimensions and their standard deviations measured by the same diffractometer, are given in Table 1.

Table 1. Crystal data

Chemical formula	$\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$ with $Z = 1$	
Space group	$P\bar{1}$	
Lattice dimensions	$a = 9.3069$ (9) Å	$\alpha = 102.25$ (1)°
	$b = 8.9152$ (6)	$\beta = 100.20$ (1)
	$c = 8.7838$ (8)	$\gamma = 113.10$ (1)
Density	$D_m = 3.88, D_x = 3.89 \text{ Mg m}^{-3}$	

Table 2. X-ray powder data

$d$ (obs.)	$I$ (obs.)	$h k l$	$d$ (calc.)
8.18 Å	5	0 0 1	8.216
5.68	18	1 $\bar{1}$ 1	5.674
5.47	35	1 $\bar{1}$ 1	5.480
4.95	10	0 1 1	4.939
4.55	8	2 1 0	4.562
4.10	50	0 0 2	4.108
3.335	17	1 $\bar{2}$ 2	3.327
3.287	38	2 1 2	3.291
3.240	100	0 1 2	3.242
3.161	5	0 2 1	3.161
3.097	14	2 1 0	3.100
3.035	27	3 1 0	3.036
2.947	45	1 $\bar{3}$ 1	2.945
2.855	64	3 0 1	2.858
2.812	60	2 $\bar{3}$ 1	2.810
2.736	55	0 0 3	2.738
2.680	56	1 $\bar{3}$ 2	2.680
2.366	8	0 1 3	2.364
2.179	28	2 4 0	2.177
2.047	15	4 $\bar{3}$ 1	2.047
1.792	6		
1.729	5		
1.639	5		
1.581	12		

The powder diffraction data were collected on a Rigaku powder diffractometer using  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The specimen was mixed with a small amount of silicon powder as internal standard. These data are in Table 2.

### Structure determination and refinement

Three-dimensional Patterson syntheses were carried out, and the structure determination was attempted in space group  $P\bar{1}$ , because the Wilson statistics show that this substance has a centre of symmetry. The positions of six independent Cu atoms were found from the maps. The positions of four P atoms were found from the Fourier maps with the phases given by these Cu atoms. The positions of three Na atoms and sixteen O atoms were obtained from further Fourier maps calculated with six Cu and four P positional parameters.

In order to refine the atomic coordinates and isotropic temperature factors, three cycles of full-matrix least-squares calculation were carried out, and the  $R$  value was reduced to 0.070. Three further cycles of

refinement with anisotropic temperature factors reduced  $R$  to 0.040.\*

Scattering factors corresponding to neutral atoms were used throughout the calculations (*International Tables for X-ray Crystallography*, 1974). The final positional parameters are shown in Table 3.

### Description of the structure and discussion

Fig. 1 shows the structure of  $\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$  viewed along  $[100]$ . Cu(1), Cu(2) and Cu(3) are at special positions and have square-planar coordination, which is in accord with the  $dsp^2$  hybrid-orbital model. The average Cu—O distances are 1.961, 1.980 and 1.974  $\text{\AA}$ . These values are slightly longer than the average Cu—O distance of 1.94  $\text{\AA}$  in square-planar coordinations calculated statistically by Kawamura, Kawahara & Iiyama (1978). Cu(4) is at a distorted and elongated octahedral site. The average value of four nearest Cu—O distances is 1.966  $\text{\AA}$  and two longer Cu—O distances are 2.584  $\text{\AA}$  for O(5) and 2.638  $\text{\AA}$  for O(10). Cu(5) and Cu(6) are at distorted and elongated square-pyramidal sites. The fifth O atoms weakly coordinated to Cu(5) and Cu(6) are at distances of 2.403 and 2.370  $\text{\AA}$ . The distortion of the Cu(5) and Cu(6) coordination polyhedra is probably due to these relatively short Cu—O distances.

Table 3. Atomic parameters ( $\times 10^5$  for Cu,  $\times 10^4$  for other atoms) and isotropic temperature factors ( $B_{\text{eq}}$ ) for  $\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$

	$x$	$y$	$z$	$B_{\text{eq}} (\text{\AA}^2)$
Cu(1)	0	0	0	0.635
Cu(2)	50000	50000	0	0.563
Cu(3)	0	50000	50000	0.762
Cu(4)	42624 (8)	87689 (8)	71034 (7)	0.752
Cu(5)	55093 (8)	29835 (8)	66178 (7)	0.605
Cu(6)	6194 (8)	27281 (8)	80292 (7)	0.644
Na(1)	633 (3)	9313 (3)	6448 (3)	1.190
Na(2)	2580 (3)	7024 (3)	9950 (3)	1.382
Na(3)	3445 (3)	3059 (3)	3295 (3)	1.144
P(1)	911 (2)	3762 (2)	1664 (2)	0.506
P(2)	2727 (2)	4263 (2)	6604 (2)	0.544
P(3)	2902 (2)	9456 (2)	3935 (2)	0.459
P(4)	3512 (2)	1225 (2)	9610 (2)	0.453
O(1)	702 (5)	2041 (5)	1929 (4)	0.783
O(2)	9979 (5)	3377 (5)	9885 (4)	1.088
O(3)	142 (5)	4611 (5)	2760 (5)	1.219
O(4)	2736 (5)	4865 (5)	1947 (5)	0.883
O(5)	2320 (5)	5525 (5)	5885 (5)	1.421
O(6)	2986 (5)	4741 (5)	8485 (4)	0.767
O(7)	1245 (5)	2481 (5)	6006 (5)	1.026
O(8)	4227 (4)	4221 (5)	6175 (4)	0.811
O(9)	2695 (5)	8957 (5)	5463 (4)	1.056
O(10)	3377 (5)	8307 (5)	2788 (4)	0.932
O(11)	1346 (4)	9455 (5)	3032 (4)	0.703
O(12)	4327 (4)	1305 (4)	4423 (4)	0.557
O(13)	4592 (4)	2634 (5)	8968 (4)	0.747
O(14)	3322 (4)	9448 (5)	8751 (4)	0.864
O(15)	4261 (5)	1709 (5)	1438 (4)	0.960
O(16)	1821 (4)	1213 (5)	9258 (4)	0.773

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35482 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

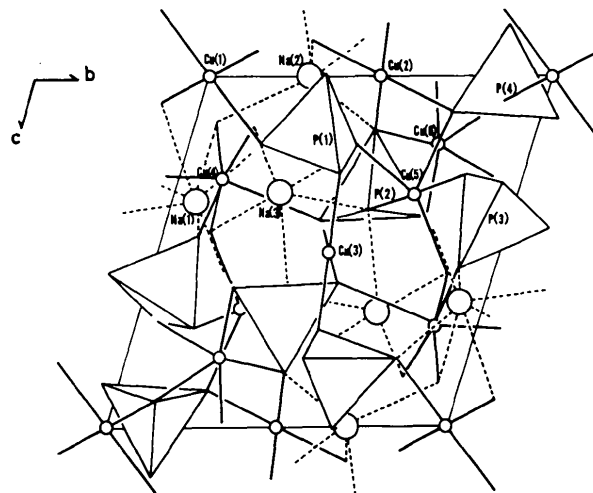


Fig. 1. The structure of  $\text{Cu}_9\text{Na}_6(\text{PO}_4)_8$  viewed along  $[100]$ . The small circles represent Cu atoms and solid lines Cu—O bonds. The large circles represent Na atoms and dashed lines Na—O bonds. P—O tetrahedra are shown.

Table 4. *Interatomic distances (Å) and angles (°) with standard deviations in parentheses*

Cu polyhedra			
Cu(1)—O(1)	1.994 (4)	O(1)—Cu(1)—O(16)	88.7 (2)
O(16)	1.928 (4)		
Cu(2)—O(6)	1.996 (4)	O(6)—Cu(2)—O(13)	93.1 (2)
O(13)	1.963 (4)		
Cu(3)—O(3)	1.962 (5)	O(3)—Cu(3)—O(5)	92.2 (2)
O(5)	1.986 (5)		
Cu(4)—O(5)	2.584 (4)	O(5)—Cu(4)—O(9)	83.4 (2)
O(9)	1.945 (5)	O(10)	154.9 (1)
O(10)	2.638 (4)	O(12)	93.5 (1)
O(12)	2.044 (4)	O(14)	101.1 (2)
O(14)	1.929 (4)	O(15)	90.1 (2)
O(15)	1.944 (5)	O(9)	O(10) 92.0 (2)
			O(12) 91.5 (2)
			O(14) 90.3 (2)
			O(15) 172.8 (2)
		O(10)	O(12) 61.9 (1)
			O(14) 103.6 (1)
			O(15) 92.6 (2)
		O(12)	O(14) 165.4 (1)
			O(15) 85.7 (2)
		O(14)	O(15) 94.1 (2)
Cu(5)—O(4)	1.929 (3)	O(4)—Cu(5)—O(8)	88.3 (2)
O(8)	1.961 (5)	O(10)	92.9 (2)
O(10)	1.916 (5)	O(12)	150.7 (2)
O(12)	1.975 (3)	O(13)	86.4 (2)
O(13)	2.403 (4)	O(10)	173.6 (2)
		O(12)	89.5 (2)
		O(13)	90.4 (2)
		O(12)	92.5 (2)
		O(13)	83.4 (2)
		O(12)	O(13) 122.8 (1)
Cu(6)—O(2)	1.887 (4)	O(2)—Cu(6)—O(6)	103.9 (1)
O(6)	2.124 (4)	O(7)	167.7 (2)
O(7)	1.961 (5)	O(11)	95.9 (2)
O(11)	1.958 (3)	O(16)	91.7 (2)
O(16)	2.370 (5)	O(7)	71.8 (1)
		O(11)	160.1 (2)
		O(16)	89.4 (2)
		O(11)	89.3 (1)
		O(16)	99.7 (2)
		O(11)	O(16) 87.8 (2)
P polyhedra			
P(1)—O(1)	1.543 (5)	O(1)—P(1)—O(2)	107.8 (2)
O(2)	1.540 (4)	O(3)	110.5 (3)
O(3)	1.540 (5)	O(4)	107.5 (3)
O(4)	1.533 (4)	O(2)	O(3) 107.5 (3)
			O(4) 109.4 (3)
		O(3)	O(4) 114.0 (2)
P(2)—O(5)	1.536 (6)	O(5)—P(2)—O(6)	111.9 (3)
O(6)	1.565 (4)	O(7)	110.7 (3)
O(7)	1.540 (4)	O(8)	108.4 (3)
O(8)	1.521 (5)	O(6)	O(7) 101.2 (2)
			O(8) 111.6 (2)
		O(7)	O(8) 112.9 (3)
P(3)—O(9)	1.521 (4)	O(9)—P(3)—O(10)	113.4 (3)
O(10)	1.528 (5)	O(11)	110.1 (3)
O(11)	1.523 (4)	O(12)	109.3 (2)
O(12)	1.563 (3)	O(10)	O(11) 109.9 (2)
			O(12) 105.5 (2)
		O(11)	O(12) 108.4 (2)
P(4)—O(13)	1.555 (4)	O(13)—P(4)—O(14)	112.3 (2)
O(14)	1.528 (5)	O(15)	108.9 (2)
O(15)	1.524 (4)	O(16)	106.0 (3)
O(16)	1.545 (5)	O(14)	O(15) 110.2 (3)
			O(16) 109.2 (2)
		O(15)	O(16) 110.2 (3)

Table 4 (cont.)

Bond distances about Na			
Na(1)—O(1)	2.283 (5)	Na(3)—O(1)	2.327 (5)
O(7)	1.781 (5)	O(4)	2.407 (6)
O(7)'	2.295 (4)	O(8)	2.376 (4)
O(9)	2.341 (6)	O(8)'	2.415 (4)
O(11)	2.546 (6)	O(11)	2.965 (5)
O(14)	2.870 (5)	O(12)	2.340 (5)
O(16)	2.444 (4)	O(15)	2.238 (5)
Na(2)—O(2)	2.302 (6)		
O(3)	2.775 (4)		
O(4)	2.892 (6)		
O(6)	2.368 (6)		
O(10)	2.354 (4)		
O(13)	2.507 (5)		
O(14)	2.512 (5)		

Na(1), Na(2) and Na(3) have seven nearest-neighbour O atoms. The Na—O distances range from 2.238 to 2.965 Å. The coordination polyhedra of the Na atoms are irregular. Na(1) and Na(3) coordination polyhedra each occur in pairs across an inversion centre, sharing the O(7)—O(7) and O(8)—O(8) edges respectively.

PO<sub>4</sub> tetrahedra fill the interstices of the Cu and Na coordination polyhedra with edge and corner sharing, and are isolated from other PO<sub>4</sub> tetrahedra. The P—O distances are in the range 1.521 to 1.565 Å and O—P—O angles are in the range 101.2 to 114.0°. The distortion indices of each tetrahedron are close to the average index of 64 tetrahedra in orthophosphates (Baur, 1974).

The values of the interatomic distances and angles are given in Table 4. These agree with those in CuKPO<sub>4</sub>·H<sub>2</sub>O (Läugt & Tordjman, 1976), Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (Shoemaker, Anderson & Kostiner, 1977), Cu<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>4</sub> (Anderson, Shoemaker, Kostiner & Ruszala, 1977), Cu<sub>5</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> (Läugt & Guitel, 1977) and Cu<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O (Anderson, Shoemaker & Kostiner, 1978; Läugt, Durif & Guitel, 1978).

The sum of the electrostatic charges calculated with the parameters of Brown & Wu (1976) is satisfactory.

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## Etude de Chromates, Molybdates et Tungstates Hydratés. III. Etude Structurale du Molybdate de Zinc Dihydraté

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### Abstract

The crystal structure of  $\text{ZnMoO}_4 \cdot 2\text{H}_2\text{O}$  has been determined by X-ray diffraction from 3506 independent reflexions collected on an automatic four-circle diffractometer.  $\text{ZnMoO}_4 \cdot 2\text{H}_2\text{O}$  crystallizes in the monoclinic system, space group  $P2_1$ , with  $a = 8.546$  (15),  $b = 10.263$  (21),  $c = 5.887$  (7) Å,  $\beta = 90.57$  (14)°,  $Z = 2$ ,  $V = 516.3$  Å<sup>3</sup>,  $d_m = 3.38$ ,  $d_x = 3.36$  Mg m<sup>-3</sup>. The structure was solved by the heavy-atom method and full-matrix least-squares refinement gave  $R = 0.041$  and  $R_w = 0.052$ . The structure consists of groups of two  $[\text{ZnO}_4(\text{H}_2\text{O})_2]$  octahedra linked together in the  $ab$  plane by  $[\text{MoO}_4]$  tetrahedra. The two-dimensional feature of this arrangement clearly shows the very important role of water molecules.

### Introduction

L'étude cristallographique des chromates, molybdates, tungstates et sulfates hydratés de métaux  $M$  bivalents, de formule générale  $MM'O_4 \cdot n\text{H}_2\text{O}$ , montre l'existence de types structuraux différents en fonction d'une part du degré d'hydratation et d'autre part de la taille respective des tétraèdres  $M'O_4$  et des octaèdres  $MO_6$  (Bars, Le Marouille & Grandjean, 1980). Afin de préciser cette étude nous avons entrepris la détermination structurale du molybdate de zinc dihydraté,  $\text{ZnMoO}_4 \cdot 2\text{H}_2\text{O}$ . En effet, avec  $\text{MgMoO}_4 \cdot 2\text{H}_2\text{O}$  qui lui est isotype, c'est le molybdate de métal bivalent au plus bas degré d'hydratation dont la structure ait été résolue.

### Partie expérimentale

Le molybdate de zinc dihydraté a été préparé par Meullemeestre & Penigault (1975) à partir d'un mélange équimolaire de molybdène et d'oxyde de zinc en suspension aqueuse à température ambiante. Les cristaux se déposent sous la forme de petits prismes très réguliers. Les paramètres de maille ont été affinés par moindres carrés à partir des diagrammes de poudre (groupe d'espace  $P2_1$  ou  $P2_1/m$ ).

Les intensités diffractées par un monocristal de dimensions  $0,06 \times 0,06 \times 0,16$  mm ont été enregistrées sur diffractomètre automatique Nonius CAD-4 dans les conditions suivantes: longueur d'onde 0,70926 Å (monochromateur de graphite); balayage  $\omega/2\theta$ ; angle de balayage  $(1,5 + 0,5 \text{ tg } \theta)^\circ$ ; ouverture de la fente compteur  $(3 + 0,5 \text{ tg } \theta)$  mm; vitesse de balayage  $2^\circ \text{ min}^{-1}$ .

Les 3506 réflexions non nulles indépendantes ont été corrigées des facteurs de Lorentz et polarisation; aucune correction d'absorption n'a été effectuée ( $\mu_1 = 7,1 \text{ mm}^{-1}$ ).

Le test de centrosymétrie (Karle, Dragonnette & Brenner, 1965) basé sur la statistique des facteurs de structure normalisés indique l'absence de centre de symétrie:

	centrosymétrique	non centrosymétrique
$\langle  E ^2 \rangle = 1,000$	1,000	1,000
$\langle  E ^2 - 1 \rangle = 0,761$	0,968	0,736
$\langle  E  \rangle = 0,881$	0,798	0,886.

L'interprétation de la fonction de Patterson conduit dans le groupe  $P2_1$  à positionner les atomes de zinc et