

Fig. 6. Side chain conformation: (a) the angles χ^{11} and χ^{12} for the threonyl group and (b) the angle χ^1 for phenylalanine.

($\chi^1 = 185^\circ$) and in L-phenylalanine hydrochloride (Gurskaya, 1964) it goes into position I ($\chi^1 = 62^\circ$).

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The Crystal Structure of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$

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$\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ crystallizes in the orthorhombic system. The space group is $P2_12_12_1$; the unit-cell parameters are: $a = 6.71$, $b = 9.00$, $c = 7.40$ Å and $Z = 4$. The three positional coordinates together with an isotropic temperature factor for each atom were refined by a three-dimensional least-squares method using 556 reflexions, the final R value being 0.114. The positions of the hydrogen atoms were not determined. The crystal structure is formed by chains consisting of deformed octahedra $\text{Cu}[\text{O}_3(\text{H}_2\text{O})_3]$, which are connected at the vertices. The chains extend parallel to \mathbf{b} and are mutually bonded by PO_3 groups. The structure is closely related to that of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$.

Introduction

The crystal structure of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ was determined as a part of a general study of the structure and

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properties of phosphites. The specimen examined was prepared by Nessler (1964).

The aim of the structure analysis of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ was to elucidate the role of the phosphite group HPO_3^{2-}

in the crystals of the sparingly soluble copper(II) complex. Apart from this it was intended to discover the role of the crystal water in this structure and to determine the coordination of copper.

Experimental

Prismatic clear blue crystals of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ are elongated in the direction of the b axis. The unit-cell dimensions were determined with the aid of rotation

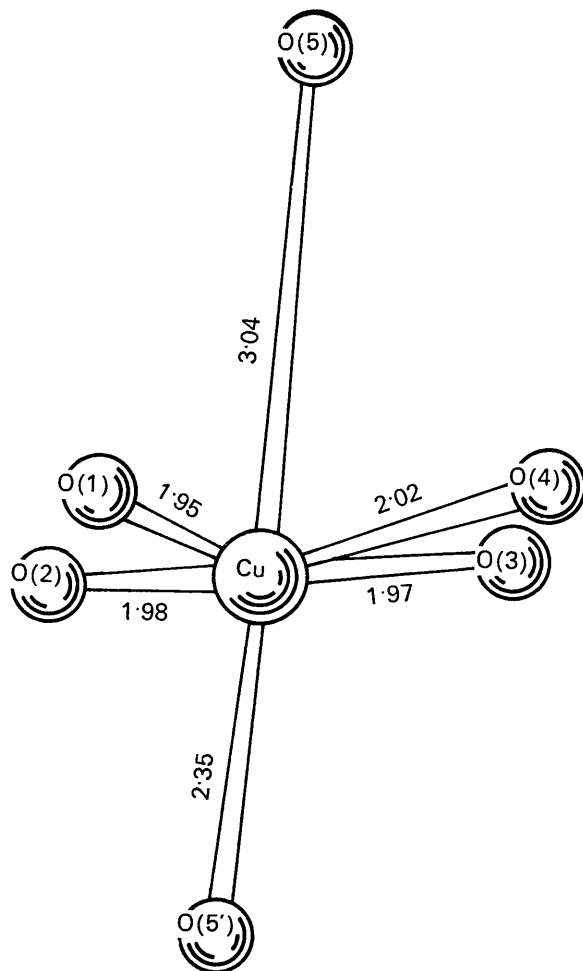


Fig. 1. Coordination octahedron of copper in $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$. The oxygen atoms O(4) and O(5) each belong to a water molecule.

and Weissenberg photographs taken around the b axis and they are:

$$a = 6.71 \pm 0.01, \quad b = 9.00 \pm 0.01, \quad c = 7.40 \pm 0.01 \text{ \AA.}$$

The extinctions identified the non-centrosymmetrical space group $P 2_1 2_1 2_1$ unequivocally. With four formula units in the unit cell, the density calculated from the above data is 2.69 g.cm^{-3} ; the value measured by the suspension method in a bromoform-benzene mixture was 2.66 g.cm^{-3} .

The intensity data were obtained by recording equi-inclination Weissenberg patterns with β -filtered $\text{Cu K}\alpha$ radiation about the b axis and the zero layer line about the a axis. The intensities of stronger reflexions were measured photometrically from integrated photographs, using the multiple-film technique. The weak intensities were estimated visually. The corrections of intensities in individual layer-lines were made for the non-linearity of blackening (Hanic, 1964), for the Lorentz and polarization factor and for absorption. The values of F^2 obtained in this way were then transformed to the common relative scale by comparison of $0kl$ spectra. Thus, 556 independent values were found.

Determination of the structure

The structure model was suggested on the basis of the interpretation of two projections of the Patterson function $-P(uw)$ and $P(vw)$. In these projections the structure was refined with successive Fourier and $F_o - F_c$ syntheses as well as with the least-squares method; the calculations were made on the computer ZRA-1 and Zuse 22 R.

The three-dimensional structure refinement was performed with the aid of programs supplied by Monsanto Research (Daly, Stephens & Wheatley, 1963) for the computer NE 803B. Altogether, 29 parameters were refined; three positional parameters and one isotropic temperature factor for every atom, except H, as well as the overall scale factor. For unobserved reflexions $\frac{1}{3}$ of the lowest observed F_o was taken.

The Cruickshank weighting scheme was used and five refinement cycles were calculated with the block-diagonal approximation. The final R -value was 11.36%. The agreement between the measured and calculated values of structure factors F_o and F_c may be observed in Table 1, where, in the columns from left to right the values of hkl , $100 F_o$ and $100 F_c$, respectively, are listed.

Table 2. Final positional parameters and isotropic temperature factors (\AA^2) and the estimated standard deviation

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
Cu	0.5164	0.1559	0.2219	0.0003	0.0002	0.0003	0.59	0.03
P	0.7581	0.3976	0.4326	0.0006	0.0004	0.0004	0.65	0.06
O(1)	0.2399	0.2137	0.7199	0.0019	0.0012	0.0016	1.07	0.17
O(2)	0.9579	0.3910	0.5226	0.0017	0.0013	0.0015	0.87	0.17
O(3)	0.2742	0.0536	0.1389	0.0017	0.0013	0.0014	0.77	0.17
O(4) (H_2O)	0.0434	0.2772	0.0378	0.0017	0.0012	0.0015	0.94	0.18
O(5) (H_2O)	0.2890	0.4399	0.3030	0.0020	0.0016	0.0020	2.03	0.23

Discussion

The final atomic parameters and their standard deviations are shown in Table 2.

The coordination polyhedron of copper is an asymmetric octahedron (Fig. 1). In this, the three oxygens O(1), O(2), O(3), situated at the shorter distances (1.95 – 1.98 Å) belong to three different HPO_3^{2-} groups. The remaining oxygen atoms O(4), O(5), O(5') belong to the crystal water.

One of the water molecules in the coordination sphere is at the shorter distance, 2.02 Å, and we may observe that oxygen from the water molecule forms a significantly longer bond than do the oxygens from the HPO_3^{2-} group (Table 3). The coordination sphere is completed by two water molecules such that the distances between Cu and the corresponding oxygen atoms – O(5) and O(5') – are not identical. The central copper atom is shifted from the planar coordination of the oxygen atoms towards the nearer vertex of the octahedron. The water molecules situated at the vertices of the octahedra connect two neighbouring octahedra and in this way form octahedral chains. These are oriented along the *b* axis which is the growth axis of the crystal.

Table 3. *Interatomic bond distances and bond angles in the octahedron of Fig. 1*

	Length	σ
Cu–O(1)	1.952 Å	0.012 Å
Cu–O(2)	1.977	0.011
Cu–O(3)	1.966	0.011
Cu–O(4)	2.022	0.011
Cu–O(5)	3.036	0.014
Cu–O(5')	2.349	0.014

Table 3 (cont.)

	Length	σ
O(1)–O(2)	2.874	0.016
O(2)–O(3)	2.836	0.016
O(3)–O(4)	2.700	0.016
O(4)–O(1)	2.756	0.016

	Angle	σ
O(1)–Cu–O(2)	94.0°	0.5°
O(2)–Cu–O(3)	92.0	0.5
O(3)–Cu–O(4)	85.2	0.5
O(4)–Cu–O(1)	87.8	0.5

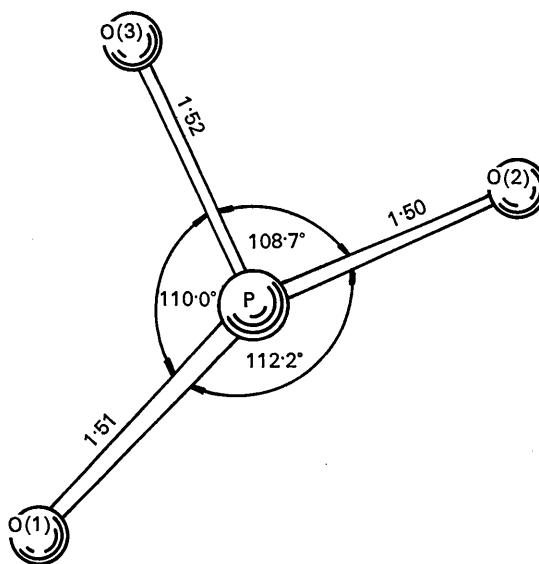


Fig. 2. The HPO_3^{2-} group.

Table 4. *Comparison of the interatomic bond distances and bond angles in the HPO_3 group in the structures of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$ and H_3PO_3*

O(H) means an oxygen atom from an OH group.

	$\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$		H_3PO_3		
	Length	σ	<i>a</i>	<i>b</i>	
P–O(1)	1.514 Å	0.012 Å	P–O(H)	1.545 Å	1.526 Å
P–O(2)	1.498	0.012	P–O	1.540	1.544
P–O(3)	1.516	0.012	P–O(H)	1.482	1.451
O(1)–O(2)	2.500	0.016	P–O(H)	1.509	1.485
O(2)–O(3)	2.449	0.016	O–O(H)	1.552	1.535
O(3)–O(1)	2.481	0.016	O–O(H)	1.558	1.552
			O–O(H)	2.561	
			O–O(H)	2.567	
			O–O(H)	2.545	
			O(H)–O(H)	2.546	
			O(H)–O(H)	2.424	
			O(H)–O(H)	2.398	
			O(H)–P–O	114.4°	114°
O(1)–P–O(2)	112.2°	0.7°	O(H)–P–O	114.3	111
O(2)–P–O(3)	108.7	0.6	O–P–O	103.0	103
O(3)–P–O(1)	110.0	0.6	O–P–O	101.5	101
			O(H)–P–O	114.0	114
			O(H)–P–O	113.6	117

a. Loopstra (1958).

b. Furberg & Landmark (1957).

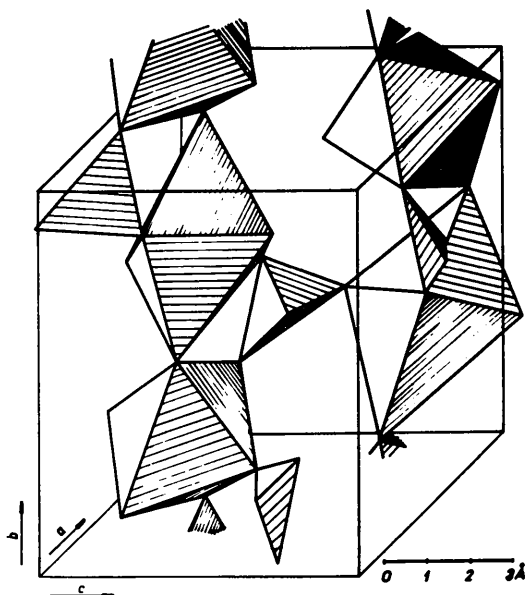


Fig. 3. The arrangement of chains and their bonding.

The configuration of the phosphorus and oxygen atoms belonging to the HPO_3^{2-} group in this compound and in the structure of phosphorous acid (Furberg & Landmark, 1957) have been found to be very similar (Table 4.). In the latter compound the position of the hydrogen atom in the corner of a deformed tetrahedron HPO_3 was determined by neutron diffraction (Loopstra, 1958). Thus, there is good reason to assume that a hydrogen atom completes the deformed tetrahedral coordination of the HPO_3^{2-} group in the structure of $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$.

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Liaisons de Superposition des Molécules Cycliques

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Certain cyclic molecules possessing a similar topology are very different with regard to their chevron or stacking structures. These differences in structure reveal the non-identical properties of the electronic configuration of these molecules. The superposition is linked to the existence in the structure of π electron clouds and a bonding group or polar atom. The close-packing conditions are satisfied. Application of Hartman & Perdok's periodic bond chain theory proves the existence of very energetic bonds; these bonds are charge-transfer interactions and in extreme cases polar interactions. These compounds of stacked molecules are self-complex and are not fundamentally different from common complexes. The existence of these self-complexing cases in certain chemical series implies other complexation cases between non-identical molecules. The stacking bonds explain certain mechanical or physical properties and certain chemical reactions in solution. With these results one can form hypotheses concerning the mechanism of the biological activity of certain therapeutic agents.

L'organisation cristalline des composés appartenant à certaines séries chimiques comme purines et pyrimidines, naphthoquinones α et β , hydroxy-coumarine, an-

Since the oxygen atoms from the group HPO_3^{2-} belong to three different octahedra $\text{Cu}[\text{O}_3(\text{H}_2\text{O})_3]$, the octahedral chains are linked with each other by means of the group HPO_3^{2-} and this accounts for the sparing solubility of this compound. It means that this compound is a coordination polymer.

The results of the structure analysis have shown a close resemblance between the crystal structures $\text{CuHPO}_3 \cdot 2\text{H}_2\text{O}$, $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ (Gattow, 1958) and $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$ (Zemann & Zemann, 1962). In these three structures, a deformed octahedron about the copper atom represents the coordination polyhedron. In $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$, the four short $\text{Cu}-\text{O}$ distances, occupied by the oxygen atoms from the three SeO_3 groups and from the water molecule are: 1.98, 1.97, 1.94 and 1.94 Å (H_2O), respectively. The $\text{Cu}-\text{O}(\text{H}_2\text{O})$ distances directed toward the vertices of the octahedra are 2.27 and 3.21 Å. In $\text{CuTeO}_3 \cdot 2\text{H}_2\text{O}$, the distances in the square planar coordination are as follows: 1.99, 1.79, 1.93, and 1.97 (H_2O) Å. The two longer bonds are 2.35 and 3.34 Å.

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thraquinones α et méso, et quelques dérivés du naphthalène est caractérisée par l'empilement des molécules en colonnes à axes parallèles. Ce 'stacking' doit être rap-