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Sodium Copper Pyrophosphate Hexadecahydrate

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Abstract. $Na_6Cu(P_2O_7)_2.16H_2O$: F.W. 677·6, triclinic, $P\bar{1}$, $a=6{\cdot}842(1)$, $b=8{\cdot}759(2)$, $c=12{\cdot}727(3)$ Å, $\alpha=89{\cdot}50(2)$, $\beta=95{\cdot}96(1)$, $\gamma=112{\cdot}58(1)°$, (measured at 22 ± 2 °C), $Z=1$, $d_x=2{\cdot}02$ (by flotation in benzene–methylene iodide), $d_c=1{\cdot}99$ g cm^{-3}, $F(000)=427$, $V=700{\cdot}0$ Å^3. The pyrophosphate anion has a bridge P–O–P angle of 129·7(3)°, a mean P–O (bridge) distance of 1·620 Å and a mean P–O (terminal) distance of 1·515 Å. The copper ion is on a center of symmetry and is surrounded by oxygen atoms in a distorted octahedral arrangement. Two of the sodium atoms are surrounded by six oxygen atoms at mean distances of 2·449 and 2·402 Å while the third sodium is surrounded by five oxygen atoms at a mean distance of 2·390 Å.

Introduction. Deep blue crystals were grown from aqueous solution at room temperature according to the procedure of Bassett, Bedwell & Hutchinson (1936). A crystal of approximate dimensions 0·1 × 0·1 × 0·1 mm was coated with a thin layer of Lubriseal high-vacuum grease to inhibit water loss. Intensity data were collected from 2396 reflections of which 2113 were considered observed by the criterion that the net intensity was greater than twice its standard deviation computed from counting statistics. A four-circle diffractometer was used in the θ–2θ scan mode with nickel-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}54050$ Å). The crystal was mounted so that its [011] direction was parallel to the φ axis of the diffractometer. The standard reflections monitored during the data collection showed no systematic change with time. There was no evidence for symmetry elements on precession-camera photographs and there were no systematic absences. Since no piezoelectric effect was detected the solution of the structure and the refinement were carried out in space group $P\bar{1}$. Absorption corrections were made to each reflection based on the carefully measured shape of the crystal and a calculated absorption coeffieient of $\mu=53{\cdot}75$ cm^{-1}. The maximum absorption factor [exp (μR)] was 1·634 and the minimum was 1·373. Atomic scattering factors for Na^+, Cu^{2+}, P, and O were taken from *International Tables for X-ray Crystallography* (1962) and corrected for anomalous dispersion according to Cromer & Liberman (1970). The scattering factors of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms.

A Patterson map revealed the positions of all the copper and phosphorus atoms and Fourier maps based on the positions of these atoms revealed the location of all the sodium and oxygen atoms. The structure was refined by block-diagonal least-squares calculations with anisotropic thermal parameters, using only reflections considered as observed, to an R index ($R=\sum|\Delta F|/\sum|F_o|$) for the observed data of 0·083. A difference map at this stage revealed 13 out of the 16 hydrogen atom positions and these were introduced into the least-squares refinement with fixed isotropic thermal parameters of 2·5 Å^2. The final R was 0·072 for the observed reflections and 0·093 for all reflections. The weighting scheme was $w=1/\{1+[(|F_o|-P_1)/P_2]^4\}$ where P_1 and P_2 were adjusted to values of 40 and 25 respectively to give an R sensibly independent of $|F_o|$. The final coordinates of the hydrogen atoms are listed in Table 1 and the coordinates and anisotropic thermal parameters for the heavy atoms in Table 2.* The NRC

Table 1. *Hydrogen-atom coordinates*

Estimated standard deviations in this and following tables are indicated in parentheses.

	x	y	z
H(22)	0·244 (14)	0·422 (11)	0·037 (7)
H(23)	0·329 (14)	0·549 (11)	0·096 (7)
H(24)	−0·564 (14)	0·245 (11)	0·142 (7)
H(25)	−0·454 (14)	0·400 (11)	0·172 (7)
H(26)	−0·052 (14)	0·538 (11)	0·334 (7)
H(27)	−0·048 (14)	0·375 (11)	0·334 (7)
H(28)	−0·613 (14)	0·353 (11)	0·360 (7)
H(29)	−0·534 (14)	0·521 (11)	0·343 (7)
H(30)	−0·563 (14)	−0·220 (11)	0·257 (7)
H(31)	−0·740 (14)	−0·201 (11)	0·251 (7)
H(32)	−0·130 (14)	0·811 (11)	0·516 (7)
H(33)	−0·278 (14)	0·146 (11)	−0·066 (7)
H(34)	−0·410 (14)	0·133 (11)	−0·017 (7)

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* Tables of the coordinates of the corners of the crystal and observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30545 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic coordinates and thermal parameters for the heavy atoms*

The B_{ij} are coefficients in the expression $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\times 10^{-4}]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0·0	0·0	0·0	99 (3)	30 (2)	6 (1)	−14 (4)	11 (2)	−1 (2)
Na(2)	−0·1314 (4)	0·3703 (4)	0·1006 (2)	125 (7)	140 (5)	30 (2)	144 (10)	43 (5)	45 (5)
Na(3)	−0·4534 (4)	0·1288 (3)	0·3014 (2)	111 (6)	81 (4)	36 (2)	74 (8)	26 (5)	25 (4)
Na(4)	−0·2533 (4)	0·4817 (3)	0·4966 (2)	122 (7)	82 (4)	26 (2)	94 (8)	8 (5)	−15 (4)
P(5)	−0·2017 (2)	−0·2515 (2)	0·1740 (1)	59 (3)	25 (2)	10 (1)	16 (4)	10 (3)	2 (2)
P(6)	0·0276 (2)	0·0962 (2)	0·2432 (1)	55 (3)	25 (2)	8 (1)	12 (4)	3 (3)	−2 (2)
O(7)	−0·1342 (7)	−0·0945 (5)	0·2549 (3)	125 (11)	33 (6)	12 (2)	−4 (13)	31 (8)	−5 (6)
O(8)	−0·2092 (6)	−0·1893 (5)	0·0614 (3)	138 (12)	34 (6)	8 (2)	9 (13)	−4 (8)	5 (6)
O(9)	−0·4229 (6)	−0·3608 (5)	0·1990 (3)	60 (10)	32 (6)	24 (3)	−22 (12)	10 (8)	11 (6)
O(10)	−0·0407 (7)	−0·3294 (5)	0·1961 (3)	128 (12)	87 (7)	29 (3)	133 (16)	25 (9)	7 (7)
O(11)	0·1178 (6)	0·1043 (5)	0·1377 (3)	84 (11)	46 (6)	14 (2)	−38 (13)	15 (8)	−16 (6)
O(12)	−0·1052 (6)	0·1977 (5)	0·2484 (3)	105 (11)	51 (6)	31 (3)	94 (14)	6 (9)	7 (7)
O(13)	0·2023 (6)	0·1317 (5)	0·3339 (3)	90 (11)	52 (6)	15 (2)	55 (13)	−12 (8)	−3 (6)
O(14)	−0·2984 (16)	0·1423 (9)	−0·0259 (5)	1037 (49)	169 (13)	44 (5)	528 (43)	73 (23)	−17 (12)
O(15)	0·2149 (7)	0·4797 (5)	0·0487 (3)	111 (12)	69 (7)	34 (3)	72 (15)	−17 (9)	−20 (7)
O(16)	−0·4600 (7)	0·3105 (5)	0·1624 (4)	100 (11)	54 (7)	41 (3)	59 (14)	13 (10)	2 (7)
O(17)	−0·0299 (7)	0·4761 (5)	0·3680 (3)	159 (12)	67 (7)	21 (3)	129 (15)	−7 (9)	0 (7)
O(18)	−0·5484 (7)	0·4620 (5)	0·3784 (3)	127 (12)	52 (6)	23 (3)	38 (14)	19 (9)	0 (6)
O(19)	−0·1027 (8)	0·7845 (6)	0·4771 (3)	212 (14)	86 (8)	21 (3)	120 (17)	32 (10)	0 (7)
O(20)	−0·3225 (8)	0·1799 (6)	0·4868 (4)	179 (14)	100 (8)	37 (3)	45 (17)	28 (11)	26 (8)
O(21)	−0·6170 (8)	−0·1568 (6)	0·2812 (5)	135 (14)	82 (8)	112 (6)	77 (18)	70 (14)	−44 (11)

computer programs (Ahmed, Hall, Huber, Pippy, Saunderson & Singh, 1966) were used for data processing, structure determination and refinement.

Discussion. This investigation was undertaken as part of a continuing study of the influence of cation coordination on the conformation of polyphosphate ions in the solid state. The crystal structure is shown in the stereoscopic drawing (Johnson, 1965) in Fig. 1. The copper ion is at a center of symmetry and is chelated by two pyrophosphate anions to give four close oxygen neighbors at an average distance of 1·939 Å in a nearly square planar configuration. Two water molecules lie on opposite sides of this square at a distance of 2·764(11) Å (Table 3). A similar bidentate coordination has been found in manganese pyrophosphate dihydrate (Schneider & Collin, 1973). Each Na(2) and Na(4) atom is surrounded by six oxygen atoms with a distorted octahedral arrangement. The Na(3) atom is surrounded by five oxygen atoms with Na–O distances lying between 2·319 and 2·443 Å (Table 3). The Na(4) octahedra are joined by sharing edges to form a chain parallel to the *a* axis. The Na(2) and Na(3) Na–O distances lying between 2·325 and 2·725 Å in

Table 3. *Coordination about copper and sodium*

Cu(1)–O(8)	1·948 (4) Å	Na(3)–O(13)	2·443 (5) Å
Cu(1)–O(11)	1·930 (4)	Na(3)–O(16)	2·378 (5)
Cu(1)–O(14)	2·764 (11)	Na(3)–O(20)	2·417 (6)
Na(2)–O(10)	2·725 (5)	Na(3)–O(21)	2·319 (6)
Na(2)–O(12)	2·438 (5)	Na(4)–O(17)	2·366 (5)
Na(2)–O(14)	2·410 (8)	Na(4)–O(17)	2·372 (5)
Na(2)–O(15)	2·353 (6)	Na(4)–O(18)	2·340 (5)
Na(2)–O(15)	2·443 (5)	Na(4)–O(18)	2·364 (5)
Na(2)–O(16)	2·325 (6)	Na(4)–O(19)	2·470 (5)
Na(3)–O(12)	2·391 (5)	Na(4)–O(20)	2·502 (6)

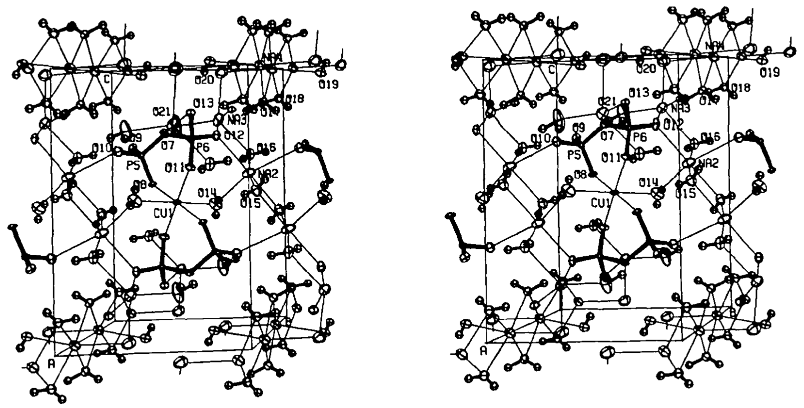

Fig. 1. A stereoscopic view of sodium copper pyrophosphate hexadecahydrate. The origin used for the fractional coordinates in Table 1 is located on the copper atom at the center of the unit cell.

polyhedra also are linked together by sharing edges to form chains that run through the structure.

The bond distances and angles in the pyrophosphate ion are normal and shown in Table 4. The bridging oxygen atom, O(7), is not bonded to either sodium or copper atoms. Its nearest neighbor outside the pyrophosphate ion is the oxygen atom O(19) of a water molecule at 3·027 Å, somewhat long for a hydrogen bond. The terminal oxygen atoms of the pyrophosphate ion appear about 14° from the perfectly staggered conformation when viewed along the P–P axis.

Table 4. *Distances* (Å) *and angles* (°) *in the pyrophosphate ion*

P(5)–P(6)	2·933 (2)	O(7)—P(5)–O(9)	103·7 (2)
P(5)–O(7)	1·613 (4)	O(7)—P(5)–O(10)	107·6 (2)
P(5)–O(8)	1·532 (4)	O(8)—P(5)–O(9)	110·5 (2)
P(5)–O(9)	1·513 (5)	O(8)—P(5)–O(10)	113·0 (2)
P(5)–O(10)	1·506 (5)	O(9)—P(5)–O(10)	113·6 (2)
P(6)–O(7)	1·627 (4)	O(7)—P(6)–O(11)	106·9 (2)
P(6)–O(11)	1·525 (4)	O(7)—P(6)–O(12)	105·5 (2)
P(6)–O(12)	1·501 (5)	O(7)—P(6)–O(13)	105·9 (2)
P(6)–O(13)	1·514 (4)	O(11)–P(6)–O(12)	113·5 (2)
P(5)–O(7)—P(6)	129·7 (3)	O(11)–P(6)–O(13)	110·5 (2)
O(7)–P(5)—O(8)	107·9 (2)	O(12)–P(6)–O(13)	114·0 (2)

The proposed hydrogen-bond scheme is shown in Table 5. The water molecule that contains O(14) is bonded to both Cu(1) and Na(2) and the next closest oxygen atoms are another O(14) at 3·054 Å and O(15) at 3·152 Å. If these atoms are involved in hydrogen bonding the interactions must be weak. The two hydrogen atoms attached to O(20) and one attached to O(19) were not located in the structure determination.

The large standard deviations for the O(14) coordinates and the large thermal vibration parameters for this oxygen induced us to compute a difference map based on F_o calculated with O(14) and its associated hydrogen atoms H(33) and H(34) omitted. A single difference electron density peak of 6·3 e Å^{-3} occurred at the position of the omitted O(14) and there were no other peaks significantly above background. A subsequent least-squares refinement omitting O(14), H(33) and H(34) failed to reduce R below 0·115. These tests suggest that O(14) is correctly located but suffers from considerable disorder. Another possibility is that the space group is actually $P1$ and the position deduced for O(14) is the mean of two non-centrosymmetric mates. We have not attempted refinement in space group $P1$.

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Table 5. *Water geometry and hydrogen-bond distances and angles*

Only approaches under 3·00 Å are tabulated. (Approximate estimated standard deviations are as follows: 0·1 Å in O–H distances; 0·006 Å in O–O distances; 12° in H–O–H angles; 10° in O–H···O angle.) The superscripts to the atom number denote the symmetry-related atoms, as follows: (i) $-X, -Y, -Z$; (ii) $X, 1-Y, Z$; (iii) $-X, 1-Y, 1-Z$; (iv) $X-1, Y, Z$; (v) $1-X, 1-Y, Z$.

A···H(1)–*B*–H(2)···*C*					H(1)–*B*	H(2)–*B*	H(1)–*B*–H(2)	*A*···*B*	*A*···H(1)	*B*–H(1)···*A*	*B*···*C*	*C*···H(2)	*B*–H(2)···*C*
O(8^{i})	H(22)	O(15)	H(23)	O(9^{vi})	0·62 Å	0·94 Å	103°	2·900 Å	2·33 Å	153°	2·856 Å	1·94 Å	165°
O(11^{iv})	H(24)	O(16)	H(25)	O(9^{ii})	0·74	0·78	120	2·742	2·05	156	2·830	2·05	177
O(10^{ii})	H(26)	O(17)	H(27)	O(12)	0·74	0·94	117	2·773	2·10	154	2·732	1·81	169
O(13^{iv})	H(28)	O(18)	H(29)	O(9^{ii})	0·66	0·91	122	2·764	1·87	167	2·772	2·17	153
O(13^{iii})	H(32)	O(19)		O(20^{iii})	0·61			2·747	2·15	169	2·793		
		O(20)		O(19^{iii})							2·793		
O(9)	H(30)	O(21)	H(31)	O(10^{iv})	0·84	0·83	99	2·863	2·02	177	2·806	1·98	172
	H(33)	O(14)	H(34)		0·55	0·76	120						

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9α-Chlorocortisol, an Active Cortisol Derivative

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Abstract. $C_{21}H_{29}ClO_5$, monoclinic, $P2_1$, $a=12{\cdot}580$ (6), $b=7{\cdot}658$ (4), $c=10{\cdot}687$ (6) Å, $\beta=115{\cdot}03$ (5)°, $Z=2$, $M=396{\cdot}92$, $D_c=1{\cdot}41$, $D_m=1{\cdot}43$g cm^{-3}, m.p. 190°C (with decomposition). The molecular conformation, including the *A*-ring and C(17) side-chain orientations, is similar to that of cortisol and 9α-bromocortisol.

Introduction. The crystal structure of 9α-chlorocortisol was determined as part of a study of structure-activity relationships among the 9α-derivatives of cortisol. A crystal with dimensions $0{\cdot}05\times0{\cdot}2\times1{\cdot}0$ mm was used for the X-ray measurements of the lattice parameters and intensities. The systematic absences ($0k0$; $k=2n+1$) indicated the space group to be $P2_1$ (C_2^2, No. 4), and the cell constants were determined by a least-squares analysis of the 2θ values for 31 reflections having 2θ in the range 50–60° [at 20°C; λ(Cu $K\alpha$)$=1{\cdot}54178$ Å]. The intensities of the 1678 independent reflections with $2\theta<130°$ were measured on a GE XRD-5 diffractometer by the stationary-counter stationary-crystal technique using Cu $K\alpha$ radiation monochromated by balanced nickel and cobalt filters. After the Lorentz and polarization corrections $[(1+\cos^2 2\theta)/2 \sin 2\theta]$ had been applied, normalized structure factor amplitudes were computed, and the phases were found by the *MULTAN* program (Germain, Main & Woolfson, 1971).

The atomic parameters of 9α-chlorocortisol were refined by block-diagonal least-squares calculations. After four cycles of anisotropic refinement, a difference map showed the locations of 22 of the 29 hydrogen atoms, and a second difference map did not reveal any additional atoms. The missing hydrogens included all of the hydroxyl hydrogens. Missing hydrogens bonded to carbon atoms were placed at their geometrically expected positions by assuming tetrahedral and trigonal planar geometry at carbon atoms with sp^3 and sp^2 hydridization respectively. The parameters for all the atoms including the hydrogens were then refined for two final cycles using data for which $\sin\theta/\lambda>0{\cdot}15$. Reflections (171 during the final cycle) for which $|F_c|/|F_o|$ was less than 0·7 were also excluded from the refinement. Weights were chosen such that $\langle w\Delta^2\rangle$ would be independent of $|F_o|$ where $w^{-1}=\{1+[(|F_o|-b)/a]^2\}$ and the constants a and b were taken to be 7e and 5e respectively. The R index was defined as $\sum(||F_o|-|F_c||)/\sum|F_o|$, and its final value was 6·5% for the 1277 reflections having $I>3\sigma$ and 8·0% for all data. The final refined positional and thermal parameters are given in Table 1.*

Discussion. The crystallographically observed conformation of 9α-chlorocortisol (9α-chloro-11β,17α,21-trihydroxy-4-pregnene-3,20-dione) is shown in Fig. 1. This figure also illustrates the atomic numbering and the non-hydrogen thermal vibration ellipsoids scaled to 50% probability. The interatomic distances and bond angles involving the nonhydrogen atoms are

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30528 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.