chloride chain, *i.e.* with the *trans*-(III) conformation and with an axially coordinated chloride ligand. As the spectra show only three ^{13}C resonances this chloride must be in rapid exchange between the two axial positions on the NMR timescale; a six-coordinate structure cannot be ruled out, with coordinated nitromethane in the remaining axial position. In aqueous solution an analogous *trans*-(III) structure is likely upon first dissolution of the complex, probably with water replacing the axial chloride, but a minor isomer forms after 24 h (Table 3). This isomer has the same number of resonances as the original species, and only the *trans*-(I) isomer satisfies this requirement. Isomerism from *trans*-(III) to *trans*-(I) forms has been observed previously for nickel(II) complexes of tetramethylcyclam (Moore, Sachinidis & Willey, 1983). By analogy with the nickel(II) complexes, it is likely that in the *trans*-(I) form the Zn atom is five coordinate, with the axial position occupied by a water molecule or chloride ion. In water, the *trans*-(III) form is most probably six coordinate with two axially bonded water molecules.

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Structure of Disodium Methyl Phosphate Hexahydrate

BY W. T. KLOOSTER AND B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, *USA*

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Abstract. $2Na^+.CH_3O_4P^{2-}.6H_2O$, $M_r = 264.09$, monoclinic, Pc, $a = 7.277$ (1), $b = 6.298$ (2), $c = 11.477$ (4) Å, $\beta = 92.44°$, $V = 525.5$ Å^3, $Z = 2$, $D_x = 1.669$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 35.26$ cm^{-1}, $F(000) = 276$, $T = 298$ K, $R = 0.028$ for 781 independent reflections. Three P—O bond lengths are the same (1.513 Å) within experimental error, with the ester P—O bond length significantly longer [1.626 (3) Å]. The Na ions are octahedrally coordinated by water O atoms and have no direct interaction with the phosphate O atoms. Water molecules form three hydrogen bonds with each phosphate O atom, except the ester O atom which at most forms one weak interaction.

Introduction. Because the phosphodiester linkage is important for the structure and electrostatic properties of nucleic acids and phospholipids, we decided to carry out an experimental study of the charge density distribution of this group, using the crystal structure of a suitable salt of dimethyl phosphate as a model system. Although we have recently achieved this objective (Klooster & Craven, unpublished results), our initial efforts to obtain the monosodium salt by hydrolysis of trimethyl phosphate, gave the disodium salt. The composition of the disodium methyl phosphate hexahydrate crystals was determined by the X-ray structure determination which we now report.

Experimental. Hydrolysis of trimethyl phosphate (Aldrich Chemical Company, Inc.) with an equimolar amount of sodium hydroxide in ethanol (McIvor, McCarthy & Grant, 1956), after evaporation to dryness, gave only a few crystals suitable for X-ray study. A crystal 0.5 × 0.2 × 0.2 mm elongated along the c axis, showing the forms {100}, {010} and {001}, was mounted with the c axis close to the φ axis of an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were obtained from 20 centered reflections ($12 < 2\theta < 114°$), Ni-filtered Cu $K\alpha$ radiation. Bragg intensities were measured to $2\theta \leq 120°$, ω–2θ scans,

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Table 1. *Fractional positional parameters and thermal parameters* (Å^2)

(*a*) Non-hydrogen atoms

The temperature factor has the form $T = \exp[-\sum_i\sum_j h_ih_ja_i^*a_j^*U_{ij}]$ or $T = \exp[-8\pi^2U(\sin\theta/\lambda)^2]$ for O*W*6′. $U_{\rm iso}$ is one-third the trace of the orthogonalized U tensor. E.s.d.'s given in parentheses refer to the least significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$U_{\rm iso}$
P	0.2420	0.2805 (1)	0.5520	0.0094 (5)	0.0172 (5)	0.0162 (5)	0.0004 (4)	−0.0008 (4)	−0.0005 (4)	0.0143
O1	0.0806 (5)	0.2354 (5)	0.6270 (3)	0.0206 (16)	0.0339 (17)	0.0304 (17)	−0.0024 (11)	0.0031 (14)	−0.0006 (12)	0.0283
O2	0.2484 (4)	0.5031 (5)	0.5031 (3)	0.0266 (15)	0.0243 (15)	0.0372 (17)	−0.0006 (12)	−0.0031 (13)	0.0078 (14)	0.0295
O3	0.4238 (4)	0.2124 (5)	0.6093 (3)	0.0171 (16)	0.0272 (16)	0.0306 (17)	0.0041 (11)	−0.0050 (13)	0.0022 (12)	0.0251
O4	0.1963 (5)	0.1194 (5)	0.4439 (3)	0.0222 (15)	0.0355 (18)	0.0273 (16)	−0.0065 (12)	0.0005 (12)	−0.0087 (14)	0.0283
C	0.3145 (8)	0.1050 (9)	0.3498 (5)	0.0333 (28)	0.0528 (33)	0.0289 (24)	0.0003 (24)	0.0046 (20)	−0.0154 (25)	0.0382
Na1	0.7539 (3)	0.7284 (3)	0.4489 (2)	0.0237 (9)	0.0299 (9)	0.0249 (9)	−0.0007 (7)	−0.0001 (8)	−0.0021 (7)	0.0262
Na2	0.7535 (3)	0.3461 (3)	0.2267 (2)	0.0272 (9)	0.0292 (8)	0.0292 (9)	0.0000 (7)	0.0005 (6)	−0.0009 (8)	0.0285
O*W*1	0.9760 (5)	0.5799 (5)	0.3273 (3)	0.0215 (17)	0.0456 (19)	0.0226 (16)	−0.0003 (14)	0.0009 (13)	0.0021 (14)	0.0299
O*W*2	0.5287 (5)	0.7958 (6)	0.5925 (4)	0.0196 (17)	0.0279 (19)	0.0407 (21)	0.0026 (16)	0.0018 (14)	−0.0011 (14)	0.0294
O*W*3	0.9821 (5)	0.7937 (7)	0.6041 (3)	0.0285 (21)	0.0304 (21)	0.0383 (22)	−0.0081 (16)	0.0000 (15)	0.0030 (14)	0.0324
O*W*4	0.5275 (5)	0.5873 (6)	0.3182 (3)	0.0215 (18)	0.0432 (20)	0.0296 (18)	−0.0009 (14)	−0.0015 (14)	0.0016 (14)	0.0315
O*W*5	0.7475 (5)	0.3951 (5)	0.5571 (3)	0.0199 (16)	0.0335 (16)	0.0462 (19)	0.0004 (15)	0.0011 (14)	0.0063 (16)	0.0332
O*W*6	0.8133 (7)	1.0857 (8)	0.3762 (5)	0.0373 (26)	0.0416 (27)	0.0448 (32)	−0.0048 (17)	−0.0084 (20)	0.0135 (21)	0.0415
O*W*6′	0.872 (5)	1.020 (6)	0.326 (3)							0.053 (12)

(*b*) Hydrogen atoms

E.s.d.'s given in parentheses refer to the least significant digit. The temperature factor has the form $T = \exp[-8\pi^2U(\sin\theta/\lambda)^2]$. The numbering of the hydrogen atoms is as follows: the first digit indicates to which oxygen atom it is bound, the second digit indicates which phosphate O atom it forms a hydrogen bond with.

	x	y	z	U
H1	0.275 (12)	0.020 (15)	0.288 (8)	0.078 (25)
H2	0.298 (9)	0.234 (10)	0.294 (6)	0.040 (17)
H3	0.431 (12)	0.096 (12)	0.368 (8)	0.065 (23)
H11	1.045 (9)	0.619 (10)	0.257 (6)	0.048 (18)
H12	1.065 (9)	0.523 (10)	0.380 (6)	0.045 (17)
H22	0.449 (10)	0.731 (11)	0.573 (6)	0.034 (19)
H23	0.482 (10)	0.922 (14)	0.587 (6)	0.054 (21)
H31	1.012 (8)	0.900 (11)	0.605 (5)	0.025 (16)
H32	1.082 (13)	0.722 (11)	0.598 (8)	0.059 (22)
H42	0.452 (13)	0.574 (13)	0.347 (8)	0.062 (28)
H43	0.494 (12)	0.668 (13)	0.240 (8)	0.068 (20)
H51	0.857 (12)	0.347 (14)	0.576 (7)	0.066 (24)
H53	0.655 (13)	0.318 (12)	0.574 (7)	0.059 (20)

with ω-scan width $(0.8 + 0.15\tan\theta)^\circ$, scan speed 0.9 to 6.7° min^{-1}, $-8 \le h \le 8$, $0 \le k \le 7$, $-12 \le l \le 12$, for a total of 1791 reflections. Three monitor reflections (002, 400, $0\bar{2}2$), measured every 2000 s, varied in intensity by < 7% during the data collection for reflection 400, and < 2% for the other two. The intensities were scaled on the basis of the changes in monitor intensities, and an absorption correction was also applied (Busing & Levy, 1957). Correction factors were in the range 1.78 to 2.60. Averaging gave 781 independent reflections with $R_{\rm int}(F_o) = 0.011$. There were only five reflections having $F_o < 3\sigma_{\rm cs}(F_o)$. Several reflections $h0l$ with l odd, which should be absent for *Pc* were observed to have weak, but significant intensities ($< 32\sigma_{\rm cs}$). However, these were attributed to multiple reflection effects, as a result of the ψ scans we performed.

The structure was determined by direct methods (*MITHRIL*; Gilmore, 1983) assuming space group *Pc*. A full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters with the program *FLS* (Shiono, 1971; a modified version of *ORFLS*) gave $R = 0.041$. The function minimized was $\sum w\Delta^2$ with $\Delta = |F_o| - |F_c|$. In this refinement the P atom x and z parameters were fixed in order to define the origin of the unit cell. Atomic scattering factors were from Cromer & Waber (1974) for C, O, P and from Stewart, Davidson & Simpson (1965) for H. A difference Fourier revealed all H atoms, except at O*W*6. One apparent H atom was found bonded to O*W*6, but on refinement, its isotropic displacement parameter became negative. It was assumed that O*W*6 was disordered and partially occupied the site O*W*6′ which we had assigned as an H atom. Refinement gave site factors 0.94 (2) for O*W*6 and 0.16 (2) for O*W*6′. Since the sum of unconstrained site factors (1.10) exceeds unity, we believe that the O*W*6′ site is occupied approximately 95% by an H atom bonded to O*W*6, and 5% by a water O atom. The shortest intermolecular distance involving O*W*6′ is 2.74 (4) Å with the phosphoester atom O4.

The final results are $R = 0.028$, $wR = 0.039$, $S = 1.92$, with $\sigma^2 = \sigma_{\rm cs}^2 + (0.02F_o)^2$, 183 variables. Last cycle gave $(\Delta/\sigma)_{\rm max} = 0.07$. A final difference Fourier map gave maxima of -0.14 and 0.15 e Å^{-3}. Atomic parameters are listed in Table 1, distances and angles in Table 2.* The atomic nomenclature is shown in Fig. 1 and the crystal structure is shown in Fig. 2.

Discussion. In the methyl phosphate anion (Fig. 1) the methyl C atom is *trans* with respect to O1. The phosphoester P—O4 bond length of 1.626 (3) Å is significantly longer than the other three P—O bond lengths which are the same within experimental error and have an average value of 1.513 Å. These are similar to the distances observed in the crystal structures of disodium DL-α-glycerolphosphate hexa-

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* Lists of structure factors, bond lengths and angles involving H atoms, torsion angles, and hydrogen-bond geometries have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54165 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic and intermolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

P—O1	1.512 (3)	P—O4	1.626 (3)
P—O2	1.512 (3)	O4—C	1.412 (7)
P—O3	1.514 (3)		
O1—P—O2	115.0 (2)	O2—P—O4	107.7 (2)
O1—P—O3	112.6 (2)	O3—P—O4	107.5 (2)
O1—P—O4	100.3 (2)	P—O4—C	120.8 (3)
O2—P—O3	112.6 (2)		

	Na1	Na2
Na—O*W*1	2.372 (4)	2.442 (4)
Na—O*W*2	2.411 (4)	2.373 (4)
Na—O*W*3	2.418 (4)	2.392 (4)
Na—O*W*4	2.355 (4)	2.502 (4)
Na—O*W*5	2.440 (4)	2.538 (4)
Na—O*W*6	2.445 (5)	2.400 (5)
Na—O*W*6′	2.49 (4)	2.49 (4)
O*W*1—Na—O*W*2	166.3 (2)	163.5 (2)
O*W*1—Na—O*W*3	92.1 (1)	92.1 (1)
O*W*1—Na—O*W*4	87.3 (1)	82.5 (1)
O*W*1—Na—O*W*5	89.3 (1)	88.0 (1)
O*W*1—Na—O*W*6	91.6 (2)	88.7 (2)
O*W*2—Na—O*W*3	86.1 (1)	87.5 (2)
O*W*2—Na—O*W*4	91.4 (1)	93.1 (1)
O*W*2—Na—O*W*5	77.0 (1)	75.8 (1)
O*W*2—Na—O*W*6	101.9 (2)	107.8 (2)
O*W*3—Na—O*W*4	166.8 (2)	163.0 (2)
O*W*3—Na—O*W*5	78.4 (1)	77.0 (1)
O*W*3—Na—O*W*6	88.2 (2)	93.4 (2)
O*W*4—Na—O*W*5	88.4 (1)	86.7 (1)
O*W*4—Na—O*W*6	105.0 (2)	102.5 (2)
O*W*5—Na—O*W*6	166.6 (2)	169.7 (2)

hydrate (McAlister & Sundaralingam,1980) and trisodium D-2-phosphoglycerate hexahydrate (Lis, 1985). However, the O—C bond length 1.412 (7) Å is somewhat shorter than in these related structures [1.430 (4) Å]. The methyl C—H bond lengths and angles are normal. The water molecule O—H bond lengths range from 0.66 to 1.05 Å, and H—O—H angles range from 101 to 118°.

Both Na atoms are octahedrally coordinated by water O atoms, there being no direct interaction of Na with phosphate O atoms. In this respect the structure is the same as disodium DL-α-glycerolphosphate hexahydrate (McAlister & Sundaralingam, 1980). Na—O*W* distances are in the range 2.36 to 2.54 Å (Table 2). The octahedra which surround Na1 and Na2 share a face and these double octahedra are joined by edge sharing to form chains along **c**. This is very similar to the arrangement of octahedra in disodium monohydrogenphosphate heptahydrate (Baur & Khan, 1970) as shown in Fig. 3. The chains are further crosslinked by corner sharing involving the disordered water O*W*6. The resulting sheets of octahedra, extending parallel to (010), have holes. These accommodate the phosphate anions. All water O atoms, except possibly O*W*6, act as O—H donors in two hydrogen bonds with phosphate O1, O2 or O3. These O atoms each accept three hydrogen bonds. In contrast, the ester O4 atom is not hydrogen bonded, except possibly for a very weak interaction with O*W*6 (Fig. 1).

Garbassi, Giarda & Fagherazzi (1972) have reported the structure of diammonium methyl phosphate dihydrate $2NH_4^+.(CH_3O)O_3P^{2-}.2H_2O$ determined from Weissenberg X-ray data. Although there appears to be an extensive hydrogen-bonding system in this structure, details are lacking because the H atoms could not be located.

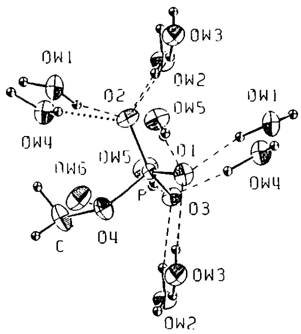

Fig. 1. The crystal environment of the methyl phosphate anion, showing the atomic nomenclature. Thermal ellipsoids (Johnson, 1976) are shown at the 50% probability level. Note the three hydrogen bonds at O2 and the longer distance H42···O2, 2.41 Å (dotted).

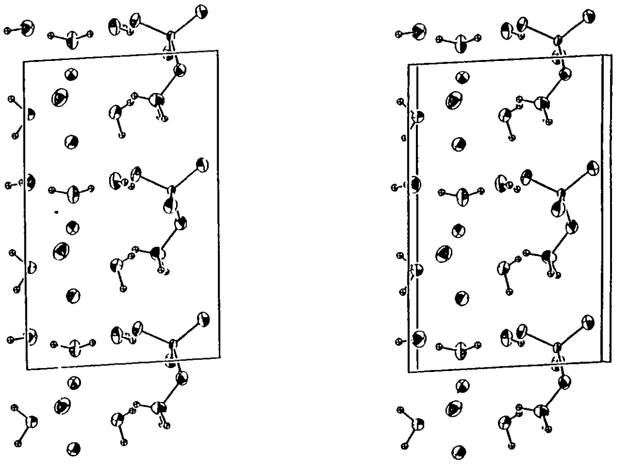

Fig. 2. Stereo diagram of the view down the *b* axis, with *c* from left to right. Thermal ellipsoids as in Fig. 1.

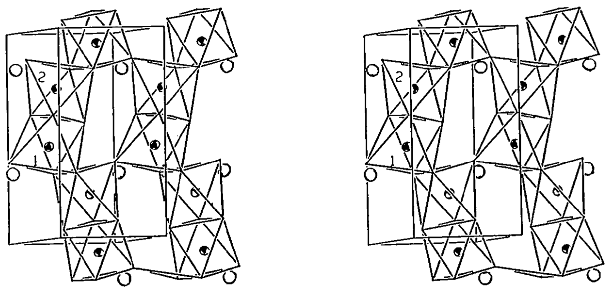

Fig. 3. Stereo diagram of the octahedrally coordinated sodium atoms (indicated by 1 and 2). The minor sites (O*W*6′) for the water oxygen O*W*6 are represented by the open circles. The O*W*6···O*W*6′ distance is 0.84 (4) Å. The view is 20° rotated from *a**, with *c* from left to right.

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Structure of a New Type of Copper Carboxylate Complex: $[Cu(C_{14}H_8O_3)(C_{10}H_8N_2)]_2.C_3H_7N.H_2O$

BY SHI-XIONG LIU

Institute of Structural Chemistry, Fuzhou University, Fuzhou, Fujian 350002, *People's Republic of China*

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Abstract. Bis[4,4′-Bipyridyl-μ-(9-hydroxy-9*H*-fluorene-9-carboxylato-*O*,μ-*O*′)copper] dimethylformamide monohydrate, $C_{48}H_{32}Cu_2N_4O_7.C_3H_7N.H_2O$, $M_r = 979{\cdot}01$, monoclinic, $P2_1/n$, $a = 10{\cdot}404\,(4)$, $b = 16{\cdot}454\,(5)$, $c = 13{\cdot}539\,(5)$ Å, $\beta = 103{\cdot}99\,(3)°$, $V = 2249$ Å^3, $Z = 2$, $D_x = 1{\cdot}45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}48$ cm^{-1}, $F(000) = 1008$, $T = 296$ K, $R = 0{\cdot}068$ for 2707 observed reflections. Each Cu atom has a square pyramidal configuration; these two CuN_2O_3 square pyramids are combined by sharing an O—O edge, forming a binuclear unit. All binuclear units are connected through N atoms of the 4,4′-bipyridyl ligands, resulting in an infinite network structure.

Introduction. Copper(II) carboxylate complexes have been studied extensively (Doedens, 1976); most of them as the familiar binuclear molecule $[Cu(RCOO)_2L_2]_2$ with the quadruply bridged copper carboxylate structure (Hanic, Štempelová & Hanicová, 1964; Borel & Leclaire, 1976). However, some copper(II) complexes of an α-hydroxylated acid have a mononuclear structure (Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti, 1968; Ahlgrén & Hämäläinen, 1975; Ahlgrén, Hämäläinen & Pajunen, 1977; Ahlgrén & Hämäläinen, 1977). Recently, we have successfully synthesized a series of binuclear copper(II) complexes of an α-hydroxylated acid, which have Cu_2O_2 core. As a first part of our systematic investigation, the crystal structure of the title compound is reported.

Experimental. Dark-green prismatic crystals were grown from DMF solution. Cell dimensions and crystal-orientation matrix determined on an AFC5R diffractometer by a least-squares treatment of the setting angles of 20 reflections in the range $10 < \theta < 15°$. Crystal dimensions 0·12 × 0·18 × 0·48 mm; intensities of reflections with indices h 0 to 12, k 0 to 20, l −16 to 16 with $2\theta < 52°$ measured; ω–2θ scans; ω-scan width $(1{\cdot}732 + 0{\cdot}400\tan\theta)°$, graphite-monochromatized Mo $K\alpha$ radiation. Intensities of three reflections measured every 150 reflections showed no evidence of crystal decay. 4904 reflections measured, 4609 unique, $R_{\rm int} = 0{\cdot}015$. 2707 with $I > 3\sigma(I)$ were used in structure solution and refinement. Data corrected for Lorentz and polarization factors and absorption effects [*DIFABS* (Walker & Stuart, 1983), max. and min. transmission factors 1·040 and 0·863; Gaussian integration: grid 6 × 6 × 6 (Coppens, Leiserowitz & Rabinovich, 1965)]. Space group $P2_1/n$ uniquely determined from systematic absences.

The crystal structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares calculations with anisotropic thermal parameters for most non-H atoms and with isotropic thermal parameters for non-H atoms of the DMF and

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