Crystal Structure of a Hydrated Complex of Sodium Iodide with Phenacylkojate [2-(Hydroxymethyl)-5-phenacyl-4*H*-pyran-4-one]

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The structure of the title complex has been determined by three-dimensional *X*-ray crystal-structure analysis. Crystals are orthorhombic, space group $P2_12_12_1$, with unit-cell dimensions a = 12·215(7), b = 33·424(11), and c = 7·004 Å, Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0·067 for 843 independent diffractometer observations. The two independent molecules of phenacylkojate have different environments, one co-ordinating to the sodium ion and the other hydrogen bonding to a water molecule. The environment about the sodium ion is approximately octahedral with Na^+–O distances in the range 2·30—2·58 Å; three equatorial positions are occupied by oxygen atoms from one molecule, one apex by the hydroxy-group from another, and the two remaining (*cis*) positions by water molecules. Extensive hydrogen bonding between the hydroxy-groups, water molecules, and the iodide ion as well as the Na^+–O co-ordination hold the polymeric structure together. Hydrogen-bond distances are in the range 2·76—2·85 for O ··· O and 3·48—3·55 Å for O ··· I^- contacts.

ALKALI-METAL halides form complexes with phenacylkojate[1] [pak, 2-(hydroxymethyl)-5-phenacyl-4*H*-pyran-4-one] in one of two stoicheiometries, [MX(pak)$_2$] or [MX(pak)], depending on the sum of the radii of the anion and cation.[2] The crystal structure of an example of each has been determined, [KI(pak)$_2$] representing the 1 : 2 (ref. 3) and [CsNCS(pak)] the 1 : 1 complexes.[4] While a complex [NaI(pak)$_2$] has been crystallized which

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[1] C. D. Hurd and R. J. Sims, *J. Amer. Chem. Soc.*, 1949, **71**, 2441.

[2] D. E. Fenton, *J.C.S. Dalton*, 1973, 1380.

[3] D. L. Hughes, S. E. V. Phillips, and M. R. Truter, *J.C.S. Dalton*, 1974, 907.

[4] S. E. V. Phillips and M. R. Truter, *J.C.S. Dalton*, 1974, 2517.

appears similar to the other monoclinic 1 : 2 complexes, a hydrated form, [NaI(pak)$_2$],nH$_2$O, can also be prepared. Elemental analysis and the molecular weight from preliminary X-ray measurements suggested that n was 3 so that there were eleven oxygen atoms as potential donor atoms for each sodium cation. While the i.r. spectrum indicated that there was hydrogen bonding it did not distinguish between co-ordinated and lattice water. We now describe a crystal-structure analysis undertaken to establish the environment of the sodium ion.

The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in the unit cell. Observations were collected on an automatic diffractometer and the structure was solved by conventional Patterson and Fourier methods. The formula was established as of the dihydrate, $n = 2$. Full-matrix least-squares refinement was carried out for all non-hydrogen atoms and the final parameters for all atoms are given in Table 1. The crystallographic numbering scheme is shown in Figures 1 and 2.

TABLE 1

Fractional co-ordinates ($\times 10^4$) and isotropic vibration parameters ($U_{\text{iso}} \times 10^3$ Å^2), with standard deviations in parentheses, unless the parameter was not refined

	x/a	y/b	z/c	U_{iso}
I	2012(2)	1248(1)	1258(4)	*
Na	1093(12)	3994(4)	0626(20)	35(5)
C(1)	4608(33)	2973(12)	−1519(70)	50(14)
C(2)	5123(33)	2594(13)	−1578(72)	58(15)
C(3)	4563(31)	2259(11)	−1414(74)	41(12)
C(4)	3409(30)	2270(11)	−1133(70)	50(13)
C(5)	2904(31)	2639(10)	−1060(58)	38(10)
C(6)	3502(26)	2995(10)	−1188(68)	27(10)
C(7)	2997(31)	3387(9)	−0894(49)	24(10)
C(8)	3662(22)	3769(11)	−0965(50)	27(9)
O(9)	2966(23)	4079(7)	−0314(29)	34(7)
C(10)	3439(27)	4444(10)	0051(43)	17(10)
C(11)	4443(32)	4555(12)	−0483(50)	42(13)
O(12)	4898(19)	4918(8)	−0041(32)	29(8)
C(13)	4222(24)	5222(9)	0658(43)	7(9)
C(14)	3186(26)	5121(9)	1135(55)	25(9)
C(15)	2712(27)	4744(9)	0859(50)	25(11)
C(16)	4852(26)	5595(10)	0974(51)	23(10)
O(17)	4182(18)	5863(7)	2047(28)	25(8)
O(18)	1768(17)	4640(6)	1237(37)	29(6)
O(19)	1996(21)	3408(6)	−0696(29)	33(7)
C′(1)	6699(27)	4315(10)	3857(61)	40(11)
C′(2)	7477(25)	4629(10)	3808(61)	37(10)
C′(3)	7169(32)	5019(12)	4395(50)	51(13)
C′(4)	6123(31)	5085(12)	4747(56)	38(13)
C′(5)	5355(31)	4818(12)	4739(51)	35(12)
C′(6)	5586(25)	4425(9)	4253(46)	12(10)
C′(7)	4813(30)	4108(11)	4139(57)	38(12)
C′(8)	5080(28)	3705(13)	3726(65)	53(11)
O′(9)	4153(19)	3464(7)	3682(48)	46(8)
C′(10)	4256(26)	3051(10)	3695(72)	22(10)
C′(11)	5176(29)	2860(11)	3485(63)	40(12)
O′(12)	5327(18)	2445(7)	3487(38)	26(7)
C′(13)	4372(32)	2218(12)	3701(86)	52(13)
C′(14)	3412(27)	2373(11)	3994(58)	32(11)
C′(15)	3289(28)	2802(11)	3836(73)	40(11)
C′(16)	4630(30)	1768(11)	3936(65)	49(12)
O′(17)	3844(19)	1542(7)	4787(29)	31(7)
O′(18)	2372(17)	2982(7)	3885(43)	43(7)
O′(19)	3836(20)	4188(7)	4477(32)	32(8)
OX(1)	1834(20)	3785(8)	3930(39)	47(8)
OX(2)	−0642(15)	3848(6)	1697(27)	26(7)
HO(11)	1518(244)	3549(86)	3238(426)	57
HO(12)	2437(221)	3970(78)	4480(373)	57
H′(17)	3163(233)	1382(65)	3655(375)	57
H(1)	5109	3255	−1627	63
H(2)	6014	2577	−1781	63
H(3)	5007	1971	−1622	63
H(4)	2915	1989	−0900	63
H(5)	2007	2658	−0898	63
H(8)A	3995	3841	−2375	63
H(8)B	4394	3752	−0025	63
H(11)	4986	4342	−1222	63
H(14)	2675	5360	1730	63
H(16)A	5114	5721	−0431	63
H(16)B	5648	5527	1680	63
H′(1)	6932	4002	3735	63
H′(2)	8295	4559	3257	63
H′(3)	7834	5237	4475	63
H′(4)	5864	5406	5070	63
H′(5)	4503	4886	5114	63
H′(8)A	5676	3573	4809	63
H′(8)B	5533	3668	2376	63
H′(11)	5947	3046	3306	63
H′(14)	2704	2187	4382	63
H′(16)A	5377	1741	4830	63
H′(16)B	4850	1639	2570	63

* Anisotropic vibration parameters ($U_{ij} \times 10^3$ Å^2) in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}k^2b^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + U_{33}l^2c^{*2})]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
I	38(1)	49(1)	45(1)	−3(2)	3(3)	−1(3)

A hydrogen atom H(n) is attached to C(n); for methylene carbon atoms there is a further distinction A and B. H(8)A and H(16)A lie below the plane of the paper in Figure 1, while H′(8)A and H′(16)A lie above the plane of the paper in Figure 2 so that the 'A' atoms are on the same side of both molecules and the same as those in the crystalline hydrate of pak.[5]

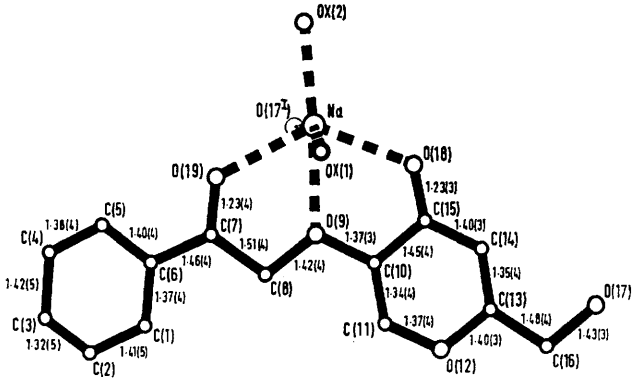

FIGURE 1 View of molecule (1) with the sodium ion and its co-ordination shell. Bond lengths (Å) with standard deviations in parentheses are shown. Roman numeral superscripts here and elsewhere refer to the following asymmetric units: I $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$; II $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; III $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; IV $-\frac{1}{2} + x, \frac{1}{2} - y, -z$; V $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; VI $x, y, -1 + z$

Co-ordination and Overall Structure.—The two independent molecules of pak in the structure have different environments, one co-ordinating to the cation as in [KI(pak)$_2$] (ref. 3) and [CsNCS(pak)] (ref. 4) and the other hydrogen bonding to a water molecule in a similar way to that found in (pak),H$_2$O.[5] The sodium ion is co-ordinated by O(9), O(18), and O(19) of molecule (1), its six-fold co-ordination shell being completed by two molecules and O(17) from a pak molecule related by symmetry to molecule (1) (see Figure 1). The co-ordination distances (see Table 2) are normal for six-co-ordinate sodium, having a range 2·30—2·58 Å. The

[5] S. E. V. Phillips and M. R. Truter, following paper.

co-ordination geometry can reasonably be described in terms of a distorted octahedron, the distortion being imposed by the fixed relative position of O(9), O(18), and O(19). Table 2 shows the angles subtended at the sodium ion and Table 3 the equation of the weighted mean plane through the sodium and O(9), O(8), O(19), and OX(2), and that of the pak molecule (1) as a whole. The sodium ion lies only 0·09(1) Å from the weighted mean plane of its associated pak molecule; values reported in other complexes of sodium with chelating ligands[6] for the distance of the sodium from the plane of the rest of the chelate ring vary from zero to *ca.* 1·5 Å.

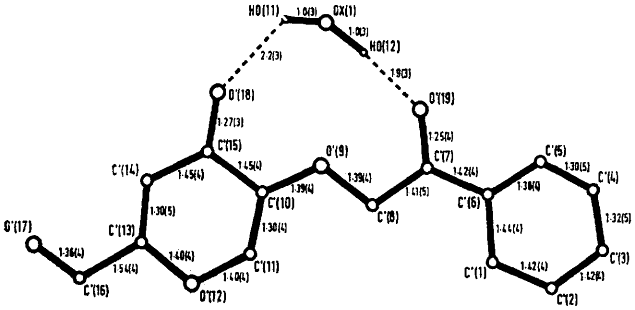

FIGURE 2 View of molecule (2) with its associated water molecule. Bond lengths (Å) are shown with standard deviations in parentheses. Poor refinement resulted in the unrealistic position of HO(11); see also Table 2

TABLE 2

Interatomic distances (Å) and angles (°) in the structure

(*a*) Sodium co-ordination

Na–O(9)	2·40(3)	Na–O(17$^{\mathrm{I}}$)	2·57(2)
Na–O(18)	2·35(2)	Na–OX(1)	2·58(3)
Na–O(19)	2·43(2)	Na–OX(2)	2·30(2)

(*b*) A–Na–B–angles

A B	O(9)	O(18)	O(19)	O(17$^{\mathrm{I}}$)	OX(1)	OX(2)
O(9)		67	64	81	87	174
O(18)			131	93	88	117
O(19)				81	88	112
O(17$^{\mathrm{I}}$)					166	104
OX(1)						88

(*c*) Hydrogen-bonded contacts and bonds involving hydrogen

OX(1) ··· O′(18)	2·76(3)	OX(2) ··· I$^{\mathrm{IV}}$	3·55(2)
OX(1) ··· O′(19)	2·82(3)	HO(11) ··· O′(18)	2·2(3)
OX(1) ··· O(17$^{\mathrm{II}}$)	2·77(3)	HO(12) ··· O′(19)	1·9(3)
OX(2) ··· O′(17$^{\mathrm{III}}$)	2·85(3)	H′(17) ··· I	2·2(3)
O′(17) ··· I	3·48(2)	H′(17)–O′(17)	1·3(3)

(*d*) Bond angles involving hydrogen

HO(11)–OX(1)–HO(12)	157(26)	C′(16)–O′(17)–H′(17)	115(11)
OX(1)–HO(11) ··· O′(18)	113(22)	O′(17)–H′(17) ··· I	165(16)
OX(1)–HO(12) ··· O′(19)	153(22)		

Roman numeral superscripts refer to other asymmetric units as defined in the legend to Figure 1. OX(1) and OX(2) are water molecule atoms.

TABLE 3

Weighted mean planes for the structure. The equations refer to an equal axial system parallel to the crystallographic axes. Deviations (Å) of the atoms from these planes are shown in square brackets; atoms designated in italics were used to define the plane

Plane (1)

$$-0{\cdot}3364X + 0{\cdot}2725Y - 0{\cdot}9014Z - 2{\cdot}7398 = 0$$

[*Na 0·05, O(9) −0·05, O(18) −0·02, O(19) −0·02, OX(2) −0·04,* OX(1) −2·53, O(17$^{\mathrm{I}}$) 2·56]

Plane (2)

$$-0{\cdot}1726X + 0{\cdot}1776Y - 0{\cdot}9688Z - 1{\cdot}8080 = 0$$

[*C(1) 0·02, C(2) −0·28, C(3) −0·47, C(4) −0·41, C(5) −0·13, C(6) 0·04, C(7) 0·18, C(8) 0·31, O(9) 0·20, C(10) 0·07, C(11) 0·29, O(12) 0·11, C(13) −0·04, C(14) −0·21, C(15) −0·15,* C(16) −0·17, O(18) −0·27, O(19) 0·27, Na −0·09, O(17) −0·60]

Plane (3)

$$-0{\cdot}0632X + 0{\cdot}0769Y + 0{\cdot}9950Z + 2{\cdot}2314 = 0$$

[*C′(1) 0·14, C′(2) 0·19, C′(3) −0·09, C′(4) −0·24, C′(5) −0·25, C′(6) −0·03, C′(7) 0·03, C′(8) 0·20, O′(9) 0·24, C′(10) 0·11, C′(11) 0·14, O′(12) 0·02, C′(13) −0·12, C′(14) −0·21, C′(15) 0·02, C′(16) −0·41, O′(18) 0·11, O′(19) −0·11,* Na 2·74, O′(17) −1·01, H′(17) −0·2]

The other molecule of pak, molecule (2) with primed atom designations, has no contact with the sodium ion but, as shown in Figure 2, is hydrogen bonded to one of the co-ordinating water molecules [OX(1)] which lies 0·32(3) Å from the molecular mean plane.

The overall structure, shown in the packing diagram (Figure 3), is held together by Na^{+}–O contacts, parallel stacking of benzene and pyranone rings, and an extensive network of hydrogen bonds. The benzene ring of molecule (1) lies approximately parallel to the pyranone rings of two molecules of type (2), C′(10)—(15) and C′(10$^{\mathrm{VI}}$)—(15$^{\mathrm{VI}}$), at distances of *ca.* 3·5 and 3·4 Å respectively, the interactions helping to bind the structure together in the direction of the crystallographic *c* axis. The hydrogen-bonding system is complex and involves all the hydroxy-groups and the iodide ion. The oxygen [OX(1)] of the water molecule hydrogen bonded to molecule (2) and co-ordinated to the sodium ion is also hydrogen bonded to the O(17) atom co-ordinated to the next sodium ion along in the *c* direction, forming chains of the type: Na–O(17) ··· OX(1)–Na–O(17) ···, *etc.* (see Table 2 for distances and angles). The oxygen [OX(2)] of the other water molecule is hydrogen bonded through its hydrogen atoms to the iodide ion and the hydroxy-group of molecule (2), one of its lone pairs contacting the sodium ion and the other having no specific interactions. The hydroxy-group of molecule (2) is also hydrogen bonded to an iodide ion one cell further along in *c*, forming chains of the type: ··· I^{-} ··· OX(2) ··· O(17) ··· I^{-} ···, *etc.* (see Table 2). The linking of the structure along the *a* and *b* directions is effected by hydrogen bonding through the iodide ion and the Na^{+} ··· O(17) contacts.

Hydrogen Bonds.—The existence of three of the six hydrogen bonds was confirmed by the location of the hydrogen atoms on the difference map, the presence of the other three being assumed from interatomic distances and angles subtended at the oxygen atoms. The hydrogen-bond distances are given in Table 2 together with some distances and angles involving the hydroxy-hydrogen atom. The confirmation of the O ··· I hydrogen bond supports the suggestion[3] of the existence of such bonds in [KI(pak)$_2$] at distances of 3·39 and 3·43 Å. The i.r. spectrum is consistent with these results, showing evidence of hydrogen bonding with broad peaks at 3270 and 3390 and a shoulder at 3200 cm^{-1}.

The pak Ligands.—Bond lengths (Figures 1 and 2) and

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[6] M. R. Truter, *Structure and Bonding*, 1973, **16**, 71.

angles (Figures 4 and 5) for both ligands are as expected and none differs significantly from the corresponding value found for the free ligand.[5] The weighted mean C–C distances in the rings are 1·384(15) [molecule (1)] and 1·383(23) Å [molecule (2)]. These values are rather low and may reflect systematic errors due to rotational vibrations of the type encountered in the free ligand structure,[5] while the large spread is partly due to poor refinement.

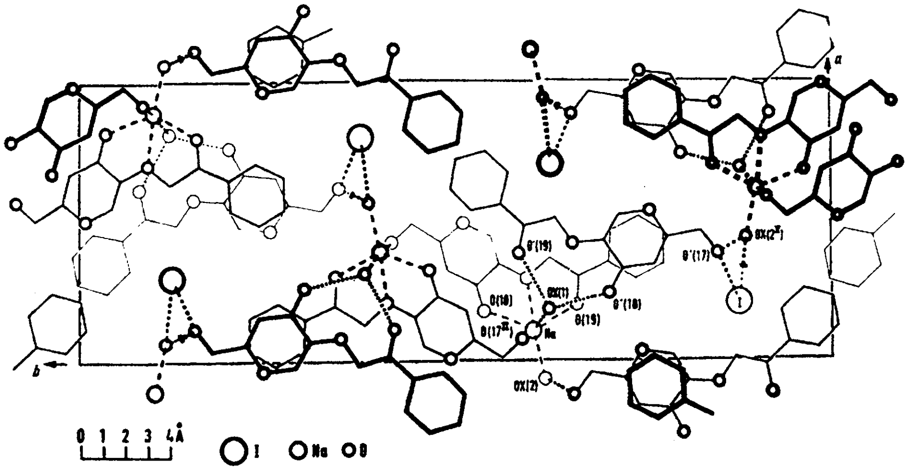

FIGURE 3 The structure of [NaI(pak)$_2$],2H$_2$O projected along the *c* axis. Na$^+$–O Co-ordination is shown by broken lines and hydrogen-bonded contacts by dotted lines. Hydrogen bonds of the type O(17^{II}) · · · OX(1) have been omitted for clarity; O(17^{II}) eclipses O(17^{I}) in this projection. Roman numeral superscripts are as defined in the legend to Figure 1

Both ligand molecules are roughly planar, the hydroxy-oxygen atoms tending to be out of the plane (Table 3).

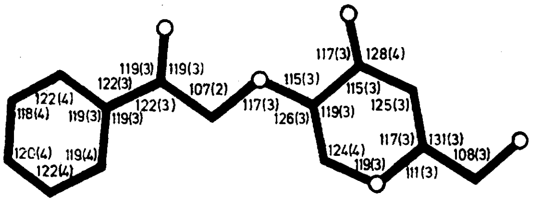

FIGURE 4 Bond angles (°) and standard deviations for molecule (1)

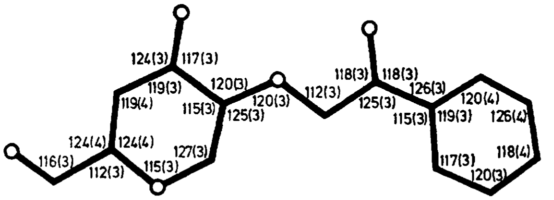

FIGURE 5 Bond angles (°) and standard deviations for molecule (2)

The benzene and pyranone rings are rigorously planar in both pak molecules. The departure from planarity for each molecule takes the form of a slight arching along the long axis, though this effect is less marked than in the other complexes reported.[3,4] Torsion angles for non-hydrogen atoms are all in the region of 0 or ±180°, a few differing from the values by $>3\sigma$, notably the angles about the C(13)–C(16) bond in each molecule (Table 4).

The i.r. spectrum is consistent with the presence of two different pak molecules. It could not be used to predict this because, except in the region >3000 cm^{-1}, the spectra of the uncomplexed phenacylkojate and of the alkali-metal salt complexes scarcely differ;[2] in particular, all show one carbonyl stretching band at 1680 cm^{-1}. For the hydrated sodium iodide complex, however, this band is split into one at 1690 and one at 1673 cm^{-1}; a band at 825 cm^{-1} is found only for this complex.

TABLE 4

Torsion angles (°) in the pak molecules having values significantly different from 0 or ±180°

C(6)–C(7)–C(8)–O(9)	−170(3)
C(7)–C(8)–O(9)–C(10)	170(3)
O(12)–C(13)–C(16)–O(17)	−168(2)
C'(7)–C'(8)–O'(9)–C'(10)	−166(3)
O'(12)–C'(13)–C'(16)–O'(17)	158(3)

Positive angle corresponds to clockwise rotation of the nearest to eclipse the furthest bond.

DISCUSSION

The other complexes reported for alkali-metal salts with phenacylkojate have 1 : 1 or 1 : 2 stoicheiometry;[2] this hydrated form is unique to sodium iodide. Six-co-ordination of sodium could be achieved by triple chelation from two (pak) molecules, and indeed may be in the anhydrous complex [NaI(pak)$_2$] which has similar symmetry and morphology to the other complexes. The present structure provides an example of the preference of sodium for water as a ligand and possibly also of the preference for an irregular rather than a symmetrical co-ordination.

EXPERIMENTAL

The complex [NaI(pak)$_2$],2H$_2$O [m.p. 193—195 °C (decomp.)] was prepared by dissolving the correct molar proportions of NaI and pak in warm ethanol–methanol (60 : 40%). Fine needle crystals were formed on slow cooling and evaporation, and two samples for data collection were obtained by cutting short sections from longer crystals with a scalpel. Crystal (1) had dimensions $0{\cdot}009 \times 0{\cdot}009 \times 0{\cdot}035$ cm and was mounted on a glass fibre about its *c* axis and crystal (2) had dimensions $0{\cdot}012 \times 0{\cdot}009 \times 0{\cdot}022$ cm and was mounted about its *a* axis. Data were collected on a Stöe STADI 2 two-circle automatic diffractometer up to the (*hk*8) layer for crystal (1) and for the (0*kl*) layer for crystal (2). Accurate unit-cell dimensions were refined by least-squares from the 2θ values of 40 indexed powder lines from powder photograph taken with a Guinier camera by use of Cu-K_α radiation.

Crystal Data.—$(C_{14}H_{12}O_5)_2NaI,2H_2O$, $M = 706{\cdot}4$, Orthorhombic, $a = 12{\cdot}215(7)$, $b = 33{\cdot}424(11)$, $c = 7{\cdot}004(2)$ Å, $U = 2859(2)$ Å^3, $D_m = 1{\cdot}69$, $Z = 4$, $D_c = 1{\cdot}64$, $F(000) = 1424$. Space group $P2_12_12_1$. Mo-K_α radiation, monochromated; $\lambda(\text{Cu-}K_\alpha) = 1{\cdot}5405$ Å, $\lambda(\text{Mo-}K_\alpha) = 0{\cdot}70927$ Å (1 Å $= 10^{-10}$ m). Single-crystal diffraction intensities measured by counter, $\mu(\text{Mo-}K_\alpha) = 12{\cdot}18$ cm^{-1}.

Intensities were collected for the (*hkl*) octant in layers up to a maximum 2θ of 50° for crystal (1), several reflections of the type (0*kl*) not measurable in this setting being collected as part of the zero layer for crystal (2). ω Step scans were carried out with steps of 0·01° at a rate of one step s^{-1}. The zero-layer scans had a range 99 steps but the scan range was increased for the upper layers in such a way as to account for the spot-shape distortion caused by the Weissenberg geometry. Backgrounds were counted for 20 s at the ends of each scan and a standard reflection was chosen for each layer and measured after every 50 reflections. The total number of unique reflections collected was 2863. Lorentz and polarization factors (*LP*) were applied and standard deviations calculated from the formula $\sigma^2(F) = \sigma^2(I)/(4.I.LP)$, where $\sigma^2(I) =$ total count + (0·25 background) × (scan time/background time)^2. Reflections were considered unobserved if the intensity (I) was <20 counts or $<3\sigma(I)$. Reflections measured in the second setting only were scaled approximately to those of the first setting, by use of several strong reflections measured in both settings. All interlayer scale factors were then taken to be unity for the purpose of structure solution. The total number of observed unique reflections was 843.

Structure Determination.—Calculation of the three Harker sections of the Patterson synthesis at $x = \frac{1}{2}$, $y = \frac{1}{2}$, $z = \frac{1}{2}$ respectively readily yielded the position of the iodide ion. Structure factors were calculated by use of the heavy-atom position and a Fourier synthesis was computed for all planes where $F_c > 0{\cdot}5F_o$. This map failed to show the structure but some evidence was found for the position of the sodium ion and this was included in the model and a second Fourier synthesis computed. Comparison of the two maps indicated the positions of all non-hydrogen atoms. Attempts to refine the structure by block-diagonal least-squares were unsuccessful as the refinement would not converge; full-matrix methods were necessary. Two cycles of full-matrix least-squares, refining all non-hydrogen atoms isotropically, reduced R from 0·22 to 0·095, with a weighting scheme derived from counting statistics and observed planes only. Refinement was continued using a first-order polynomial-weighting scheme calculated to produce constant values of $\langle W\Delta^2\rangle$, and refinement of scale factors for each layer independently gave R 0·078. Many of the isotropic temperature factors refined to unrealistically low values, particularly C(13) for which B_{iso} was *ca.* 0·6 Å^2; the cause was found to be thirty or more high-order planes with $|F_o|$ values consistently higher than $|F_c|$. It appeared that these planes should have been considered unobserved but had somehow been measured with values higher than the unobserved threshold. A partial solution to this problem was to exclude certain planes from the least-squares refinement, but not from the R-factor totals, according to the following criteria: (*a*) all planes for which $F_c < \frac{1}{2}F_o$, and (*b*) all planes with $\sin\theta/\lambda > 0{\cdot}4$ for which $F_c < \frac{2}{3}F_o$. This only improved the temperature factors a little as did anisotropic refinement of the iodide ion. A difference-Fourier map showed signs of hydrogen atom positions and the 22 hydrogen atoms bonded to carbon atoms were inserted at calculated positions. Three of the six hydroxy-atoms were located and their co-ordinates refined with fixed isotropic temperature factors. The three remaining hydrogen atoms could not be located on the final difference map and there was no sign of the third water molecule. A new weighting scheme was calculated and refinement continued until it converged to R 0·067 and weighted factor, R', 0·054, for the 843 observed planes, the largest (change-to-error) in the final cycle being 0·6 for the x co-ordinate of HO(12). The final weighting scheme for the planes accepted for the refinement took the form $W = W(\text{counting})/(-3{\cdot}877 + 0{\cdot}9113|F_o|)$. No attempt was made to determine the absolute configuration because of the lack of accurate data and absence of chirality in the pak molecule. Bond lengths and angles with errors were calculated by the program ORFFE [7] from the variance–covariance matrix of the final cycle of refinement. Scattering-factor curves were taken from ref. 8 for hydrogen, from ref. 9 for carbon and oxygen, and sodium ion, and from ref. 10 for iodide ion. Anomalous scattering corrections were applied for I$^-$, the values of $\Delta f'$ and $\Delta f''$ being taken from ref. 11. Measured and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21273 (6 pp., 1 microfiche).*

Computing.—Refinement of unit-cell dimensions, data reduction, Patterson and Fourier syntheses, initial full-matrix least-squares refinement, calculation of planes through various groups of atoms, torsion angles, and interatomic distances were computed on an IBM 1130.[12] Final full-matrix least-squares and calculation of bond lengths and angles with standard deviations from a full correlation matrix [7] were carried out on an ICL 4/70 computer at Rothamsted Experimental Station.

We thank Dr. D. E. Fenton for the crystals, Dr. G. H. W. Milburn for the use of the diffractometer, various authors [7,12] for the use of their programs, the Royal Society for some of the apparatus, and the S.R.C. for a Maintenance Award (to S. E. V. P.).

[4/2322 *Received, 7th November,* 1974]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, **1974**, Index issue.

[7] ICL 4/70 program: full-matrix least-squares program NUCLS by R. J. Doedens and J. A. Ibers; interatomic distances and errors program ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy.

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[12] *X*-Ray ARC: IBM 1130 program system; for details see ref. 13 of ref. 3.