Crystal Structure of Phenacylkojate [2-(Hydroxymethyl)-5-phenacyl-4*H*-pyran-4-one] Monohydrate and Comparison with some of its Complexes with Alkali-metal Salts

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The structure of the title compound has been determined by three-dimensional *X*-ray crystal-structure analysis. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 7·883(8), b = 18·781(5), c = 9·649(6) Å, β = 112·99(8)°, Z = 4. The structure was solved by direct methods and refined by full-matrix least-squares to R 0·044 for 1063 independent diffractometer observations.

The crystal structure is held together by a network of hydrogen bonds involving the water molecules and the carbonyl and hydroxy-groups of the phenacylkojate molecules. The phenacylkojate molecules are approximately planar and the water molecules occupy the same positions relative to the ligands as the cation in the alkali-metal complexes. Comparison with known crystal structures of the complexes shows the conformation of the ligand molecule to be similar throughout apart from the position of the hydroxy-group. The results show no simple trend relating anion and cation size to overall crystal structure but some indication is given of the probable arrangements in the other complexes with alkali-metal halides.

ALKALI-METAL halides form complexes with phenacylkojate,[1] (pak), in one of two stoicheiometries [MX(pak)$_2$] or [MX(pak)] depending on the sum of the radii of the anion and cation.[2] Crystal structures have been determined for examples of both cases [3-5] and that of the free ligand was carried out to serve as a base for comparison.

Preliminary *X*-ray photographs showed the crystal to be monoclinic, space group $P2_1/c$, the unit cell containing four (pak),H_2O units. Observations were collected on an automatic diffractometer and the structure was solved by statistical direct methods. Full-matrix least-squares refinement was carried out for all atoms and the final parameters are given in Table 1.

The results were compared with those previously obtained for the complexes [3-5] in an attempt to relate crystal structure to anion and cation radii and to compare the conformation of the ligand in different environments. It was not possible to distinguish unequivocally between directional lone-pair effects and simple electrostatic attraction in complex formation and prediction of the configurations of other complexes is only possible on a qualitative basis.

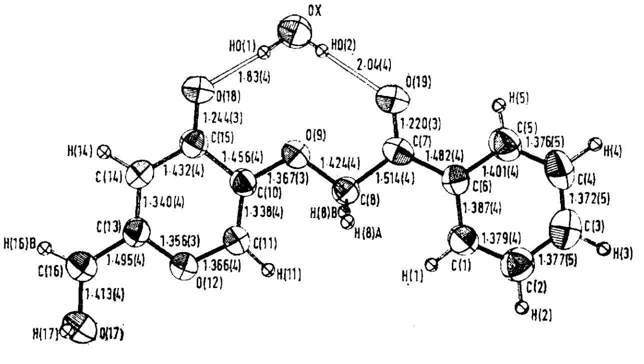

FIGURE 1 The asymmetric unit of (pak),H_2O with 50% probability vibration ellipsoids for non-hydrogen atoms. Hydrogen atoms are shown as small circles. Bond lengths (Å) and standard deviations are shown together with the crystallographic numbering scheme. Note that H(16)A is obscured by C(16) in the projection

The Structure of (pak),H_2O.—The crystal structure consists of chains of pak molecules (see Figure 1 for formula and crystallographic numbering scheme) extending to infinity in the direction of the crystallographic c axis, one molecule being linked to the next by hydrogen bonding through an intermediate water molecule. Adjacent chains are linked along the a axis by interactions between benzene and pyranone rings lying approximately parallel with interplanar spacings of *ca.* 3·5 and 3·6 Å. There are no strong interactions linking the chains along the b axis, the closest approach in this direction being 2·62 Å between the oxygen atom of the water molecule (OX) and H(3) of a neighbouring molecule. A packing diagram showing the overall structure and the hydrogen-bonding arrangement around the water molecule is given in Figure 2.

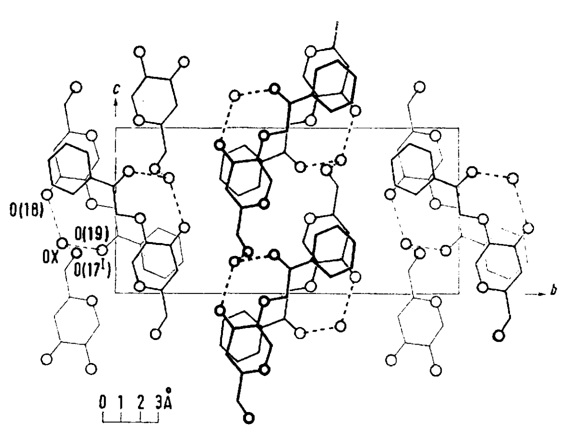

FIGURE 2 The structure of (pak),H_2O projected along the a axis. Hydrogen bonds are shown as broken lines. The Roman numeral superscript I refers to another asymmetric unit at $x,y,z-1$

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[1] C. D. Hurd and R. J. Sims, *J. Amer. Chem. Soc.*, 1949, **71**, 2240.

[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.

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

The existence of the hydrogen bonds has been confirmed by the location on the difference map, and subsequent refinement, of the hydrogen atoms involved. Each water molecule is hydrogen bonded through its hydrogen atoms to the two carbonyl oxygen atoms of one pak molecule (see Figure 1) and one of its lone pairs interacts with the hydroxy-hydrogen atoms of another pak molecule. The hydrogen bond distances are normal for O · · · O hydrogen bonds and the angle subtended at the hydrogen atoms is close to 180° in each case (see Table 2). The second lone pair on the oxygen atom does not take part in formal hydrogen bonding, the next closest contact being to H(4) of a neighbouring pak molecule. Though the hydrogen lies close to the lone pair the O · · · H separation of 2·48 Å is too long for anything but weak interaction. Table 2 gives bond lengths and angles in the hydrogen-bond system. The i.r. spectrum shows a broad band at 3265 cm^{-1}, characteristic of the presence of water, and a sharper band at 3470 cm^{-1} due to the hydroxy-group of the pak molecule.

The bond lengths (Figure 1 and Table 2) are as expected except for the rather short C–C distances in the benzene ring. Bond angles for non-hydrogen atoms (Figure 3) are mainly normal with a few significant deviations from the trigonal or tetrahedral angles. The most important of these is the angle subtended at O(9) which is 7·5° greater than the tetrahedral angle but still significantly less than 120°. Other deviations occur at C(15), C(16), C(7), and C(10) (see later).

TABLE 1

Fractional co-ordinates ($\times 10^4$) and isotropic vibration parameters ($U_{iso} \times 10^3$), with standard deviations in parentheses

	x/a	y/b	z/c	U_{iso}		y/b	x/a	z/c	U_{iso}
C(1)	0384(5)	1246(2)	3912(4)	*	O(18)	5244(3)	−1988(1)	5922(2)	*
C(2)	−0652(5)	1853(2)	3377(4)	*	O(19)	1659(3)	−0388(1)	2563(2)	*
C(3)	−1591(5)	1951(2)	1852(5)	*	OX	4173(4)	−1551(1)	2966(3)	*
C(4)	−1544(5)	1434(2)	0863(4)	*	H(1)	0997(32)	1186(12)	4949(27)	30(8)
C(5)	−0538(5)	0822(2)	1384(4)	*	H(2)	−0759(39)	2200(16)	4103(31)	71(11)
C(6)	0466(4)	0721(2)	2929(3)	*	H(3)	−2363(45)	2376(18)	1541(35)	86(12)
C(7)	1581(4)	0065(2)	3441(3)	*	H(4)	−2339(43)	1479(16)	−0219(34)	71(11)
C(8)	2669(5)	−0027(2)	5115(3)	*	H(5)	−0509(48)	0450(18)	0779(37)	95(13)
O(9)	3570(3)	−0700(1)	5359(2)	*	H(8)A	1802(33)	0005(13)	5710(27)	40(8)
C(10)	4570(4)	−0890(2)	6821(3)	*	H(8)B	3651(35)	0365(14)	5496(27)	50(9)
C(11)	4816(5)	−0478(2)	8016(3)	*	H(11)	4297(34)	0011(14)	7996(25)	35(8)
O(12)	5840(3)	−0691(1)	9456(2)	*	H(14)	6943(34)	−2259(14)	8773(27)	42(9)
C(13)	6602(4)	−1350(2)	9689(3)	*	H(16)A	9063(45)	−1293(15)	11515(33)	77(11)
C(14)	6372(5)	−1794(2)	8543(4)	*	H(16)B	7854(40)	−1998(15)	11541(30)	60(10)
C(15)	5389(4)	−1596(2)	7002(3)	*	H(17)	6277(47)	−1388(19)	12364(38)	98(14)
C(16)	7739(5)	−1495(2)	11312(4)	*	HO(1)	4484(46)	−1682(18)	3969(41)	91(13)
O(17)	7107(4)	−1149(1)	12320(3)	*	HO(2)	3404(50)	−1231(20)	2870(40)	98(14)

* Anisotropic vibration parameters ($U_{ij} \times 10^4$ Å^2) in the expression: $2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	549(24)	554(25)	466(24)	−2(20)	169(20)	−5(19)
C(2)	637(27)	550(25)	703(27)	9(21)	242(23)	−34(22)
C(3)	586(28)	634(29)	799(32)	55(24)	220(25)	136(23)
C(4)	658(28)	843(33)	488(27)	92(23)	90(22)	173(21)
C(5)	620(26)	718(28)	468(24)	14(21)	215(20)	46(21)
C(6)	428(23)	458(21)	428(22)	−18(17)	186(18)	60(17)
C(7)	504(23)	508(22)	411(22)	−74(19)	198(18)	−35(18)
C(8)	522(23)	437(23)	440(22)	34(18)	232(19)	28(16)
O(9)	688(17)	515(15)	403(14)	106(12)	223(13)	28(11)
C(10)	469(22)	435(21)	372(21)	−14(17)	164(18)	17(16)
C(11)	627(25)	502(25)	402(21)	83(20)	185(19)	39(18)
O(12)	694(17)	471(15)	408(14)	90(12)	154(12)	−16(11)
C(13)	490(23)	399(23)	463(22)	11(18)	168(18)	28(17)
C(14)	598(25)	382(22)	503(23)	72(18)	190(20)	−7(18)
C(15)	521(23)	437(23)	460(23)	−30(18)	187(18)	10(17)
C(16)	634(27)	545(26)	450(23)	9(21)	180(19)	−10(18)
O(17)	883(20)	738(18)	423(15)	84(16)	218(14)	−13(12)
O(18)	922(20)	574(16)	447(14)	119(14)	229(14)	−85(12)
O(19)	787(19)	641(18)	498(15)	61(14)	207(14)	−97(12)
OX	1046(22)	798(19)	566(18)	213(18)	400(16)	22(14)

TABLE 2

(*a*) O · · · O hydrogen-bond distances (Å)

OX · · · O(17^I)	2·726(3)	OX · · · O(19)	2·872(3)
OX · · · O(18)	2·765(3)		

(*b*) Bond lengths (Å) involving hydrogen atoms

O(17)–H(17)	0·81(3)	C(4)–H(4)	0·99(3)
OX–HO(1)	0·93(4)	C(5)–H(5)	0·92(3)
OX–HO(2)	0·83(4)	C(8)–H(8)A	1·05(2)
OX · · · H(17^I)	1·98(3)	C(8)–H(8)B	1·03(3)
O(18) · · · HO(1)	1·83(4)	C(11)–H(11)	1·00(2)
O(19) · · · HO(2)	2·04(4)	C(14)–H(14)	0·97(3)
C(1)–H(1)	0·93(2)	C(16)–H(16)A	1·05(3)
C(2)–H(2)	0·98(3)	C(16)–H(16)B	0·97(3)
C(3)–H(3)	0·98(3)		

(*c*) Bond angles (°) involving hydrogen atoms

HO(1)–OX–HO(2)	101(3)	C(16)–O(17)–H(17)	107(3)
OX–HO(1) · · · O(18)	175(3)	C(10)–C(11)–H(11)	126(1)
OX–HO(2) · · · O(19)	175(4)	O(12)–C(11)–H(11)	111(1)
OX · · · H(17^I)–O(17^I)	153(4)		

All other bond angles involving hydrogen atoms are not significantly different from the expected trigonal or tetrahedral angles. The Roman numeral superscript I refers to the next asymmetric unit along the *c* axis (see legend to Figure 2).

The molecule is approximately planar, except for O(17), and the weighted mean plane of all non-hydrogen atoms in the molecule except O(17) is given in Table 3. O(17) Lies **−0·569(3)** and the oxygen atom of the associated water molecule **0·727(3)** Å from the plane. Mean planes through the two six-membered rings (Table 3) show each to be approximately, but not rigorously, planar. Though the deviations of the atoms from the planes are small they are larger, compared with the apparent standard deviations, than might be expected for accurately planar groups. This suggests that systematic errors may be present, causing the least-squares standard deviations to be optimistically low. A similar effect is evident in the torsion angles around the benzene ring which deviate from 0° by as much as 2·1° while the standard deviations are 0·6°. Torsion angles for the non-hydrogen atoms of the molecule all approximate to 0 or ±180°, except those involving O(17). The angle O(12)–C(13)–C(16)–O(17) is 31·7(4)° and shows the hydroxy-group to be well out of the plane of the pyranone ring in a position facilitating the formation of the hydrogen bond to the neighbouring water molecule.

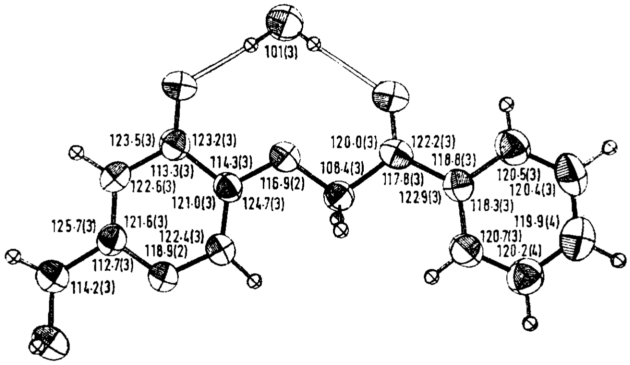

FIGURE 3 The asymmetric unit of (pak),H_2O showing bond angles and standard deviations

TABLE 3

Mean planes through the pak molecule. The equations refer to an equal orthogonal system of axes parallel to the crystallographic *a*, *b*, and *c** axes. Deviations (Å) of the atoms from these planes are shown in square brackets; atoms designated in italics were used to define the planes

Plane (1)

$$0{\cdot}898x' + 0{\cdot}436y' - 0{\cdot}065z' + 0{\cdot}2158 = 0$$

[*C(1) −0·04, C(2) −0·07, C(3) −0·05, C(4) −0·05, C(5) −0·04, C(6) −0·02, C(7) 0·03, C(8) 0·06, O(9) 0·05, C(10) 0·02, C(11) 0·06, O(12) 0·04, C(13) −0·05, C(14) −0·12, C(15) −0·05, C(16) −0·01, O(18) −0·04, O(19) 0·06,* O(17) −0·57, H(17) 1·37, OX 0·73]

Plane (2)

$$0{\cdot}893x' + 0{\cdot}446y' - 0{\cdot}064z' + 0{\cdot}226 = 0$$

[*C(1) 0·001, C(2) −0·011, C(3) 0·011, C(4) 0·000, C(5) −0·009, C(6) 0·005,* C(7) 0·040, C(8) 0·070, O(19) 0·062]

Plane (3)

$$0{\cdot}924x' + 0{\cdot}377y' - 0{\cdot}059z' + 0{\cdot}025 = 0$$

[*C(10) −0·005, C(11) −0·013, O(12) 0·006, C(13) 0·002, C(14) −0·021, C(15) 0·020,* C(16) 0·078, O(17) −0·541, H(17) −1·33, O(18) 0·068, O(9) −0·014, C(8) −0·097]

Standard deviations are: carbon ±0·004, oxygen ±0·003, and hydrogen ±0·04 Å.

The weighted mean and statistical standard deviation for the benzene ring C–C bonds was **1·383(4)** Å with a statistical standard deviation in each bond length of 0·01 Å. This suggests that the least-squares standard deviations are too low or that the ring is not regularly hexagonal. The low mean value does not agree well with the observed values for benzene of 1·397 (Raman [6]) and 1·392 Å (*X*-ray [7]), and a mean of 1·394 Å found in a survey of bond lengths for various aromatic compounds.[8] The inference is that some systematic error may be present, probably in the form of a librational effect. Inspection of the thermal-ellipsoid plots of the benzene-ring carbon atoms (Figure 1) shows that C(6) vibrates approximately isotropically and with a rather low root-mean-square amplitude. The oscillations of the other ring atoms tend to be very anisotropic and the amplitudes of the motions are greatest for the atoms farthest from C(6). A libration correction was carried out, assuming that rigid-body motion of the benzene ring was occurring about C(6) as a pivot. The two rigid-body vibration tensors of Cruickshank [9] were calculated and the bond-length corrections obtained by the method of Busing and Levy.[10] The results showed the rigid-body model to be a reasonable, but not perfect, description of the thermal motion of the atoms, the most important rigid-body rotational oscillation being the ' rock ' about the C(3) · · · C(6) axis. The corrected bond lengths showed a weighted mean of **1·393(5)** Å, a value in agreement with those from other studies for phenyl rings.

Pak and Its Complexes.—The four structures reported here and elsewhere [3-5] provide six independent determinations of the geometry of the pak molecule. Tables 4 and 5 list the bonds and angles for non-hydrogen atoms in the molecules and show a weighted mean and statistical standard deviation for each set of six measurements of the same value.

Bond lengths for which the spread of values is large are limited to the benzene rings, C(6)–C(7), and C(7)–C(8). The librational effect observed for (pak),H_2O persists throughout the series and the weighted mean of all 36 ring C–C bond lengths is 1·380(4) Å, a value short by 0·015 Å of the generally accepted value. Bond lengths are otherwise generally as expected except for the difference in length of the two carbonyl C=O bonds. While C(7)–O(19) has a mean bond length normal for a ketonic carbonyl, that for C(15)–O(18) is longer by 0·024 Å. Electron donation from the two C=C bonds may be responsible but this is not indicated by the C–C bond lengths.

Mean bond angles are again largely as expected, most of the deviations from the trigonal or tetrahedral angles

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[6] B. P. Stoicheff, *Canad. J. Phys.*, 1954, **32**, 339.

[7] E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc.*, 1958, **A247**, 1.

[8] *Chem. Soc. Special Publ.*, No. 18, 1965.

[9] D. W. J. Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

[10] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

being readily explained on steric grounds. A space-filling model showed ' crowding ' of the hydrogen atoms on C(1) and C(8), and particularly on C(11). The only hydrogen atom in the (pak),H_2O structure which deviates significantly from its expected position is H(11), such that the angle C(10)–C(11)–H(11) is 126(1)°. This indicates that H(11) is forced out of position by H(8)A and H(8)B and this repulsion causes a slight deformation of the molecule in a way tending to bring O(18) and O(19) closer together. This effect is evident in the bond angles observed along the chain joining the two rings and it may be enhanced by the co-ordinated metal ion or hydrogen-bonded water molecule. That the angle C(8)–O(9)–C(10), mean 117·0(3)°, deviates by almost 8° from the tetrahedral angle, is due to purely steric effects. The angle observed is the result of the hybridization state of O(9) being midway between (*a*) sp^3 and (*b*) $sp^2 + \pi$ forms. Simple perturbation theory favours form (*b*) but, in practice, the best description of the system is some intermediate between the two forms.[11]

TABLE 4

Bond lengths and standard deviations (Å) for different determinations of pak. The weighted mean and statistical standard deviation is quoted for each bond length

	(pak),H_2O	[Cs(NCS)(pak)]	[KI(pak)$_2$] Molecule (1)	[KI(pak)$_2$] Molecule (2)	[NaI(pak)$_2$],2H_2O Molecule (1)	[NaI(pak$_2$)],2H_2O Molecule (2)	Weighted means
C(1)–C(2)	1·379(4)	1·382(17)	1·397(29)	1·425(27)	1·414(51)	1·416(38)	1·389(7)
C(2)–C(3)	1·377(5)	1·413(18)	1·379(31)	1·345(28)	1·317(47)	1·418(43)	1·379(11)
C(3)–C(4)	1·372(5)	1·340(16)	1·310(29)	1·316(28)	1·424(47)	1·320(49)	1·356(13)
C(4)–C(5)	1·376(5)	1·355(15)	1·358(27)	1·389(28)	1·381(41)	1·296(47)	1·368(9)
C(5)–C(6)	1·401(4)	1·382(14)	1·386(24)	1·421(26)	1·397(39)	1·383(44)	1·397(4)
C(6)–C(1)	1·387(4)	1·381(13)	1·364(23)	1·363(25)	1·374(45)	1·436(38)	1·384(7)
C(6)–C(7)	1·482(4)	1·519(13)	1·428(22)	1·523(24)	1·463(40)	1·423(41)	1·482(13)
C(7)–C(8)	1·514(4)	1·505(14)	1·532(23)	1·540(24)	1·515(42)	1·413(53)	1·513(11)
C(8)–O(9)	1·424(4)	1·434(12)	1·419(19)	1·398(19)	1·416(35)	1·390(38)	1·420(5)
O(9)–C(10)	1·367(3)	1·369(11)	1·377(18)	1·358(18)	1·374(34)	1·387(35)	1·369(3)
C(10)–C(11)	1·338(4)	1·333(13)	1·362(21)	1·328(23)	1·335(42)	1·302(41)	1·337(5)
C(10)–C(15)	1·456(4)	1·453(13)	1·455(22)	1·461(22)	1·454(38)	1·448(42)	1·455(1)
C(11)–O(12)	1·366(4)	1·368(12)	1·368(19)	1·375(21)	1·371(41)	1·399(37)	1·370(3)
O(12)–C(13)	1·356(3)	1·360(11)	1·354(18)	1·363(18)	1·397(34)	1·400(39)	1·361(5)
C(13)–C(14)	1·340(4)	1·330(13)	1·311(22)	1·300(22)	1·352(39)	1·299(46)	1·330(7)
C(14)–C(15)	1·432(4)	1·439(14)	1·451(22)	1·452(23)	1·401(34)	1·448(40)	1·436(5)
C(13)–C(16)	1·495(4)	1·500(15)	1·485(24)	1·485(25)	1·481(39)	1·544(44)	1·496(6)
C(16)–O(17)	1·413(4)	1·416(14)	1·413(20)	1·420(21)	1·427(34)	1·360(39)	1·412(6)
C(15)–O(18)	1·244(3)	1·216(10)	1·220(19)	1·217(19)	1·234(33)	1·271(34)	1·236(7)
C(7)–O(19)	1·220(3)	1·206(10)	1·218(18)	1·186(19)	1·232(41)	1·247(35)	1·216(6)

TABLE 5

Bond angles and standard deviations (°) for different determinations of pak. The weighted mean and statistical standard deviation is quoted for each bond angle

	(pak),H_2O	[Cs(NCS)-(pak)]	[KI(pak)$_2$] Molecule (1)	[KI(pak)$_2$] Molecule (2)	[NaI(pak)$_2$],2H_2O Molecule (1)	[NaI(pak)$_2$],2H_2O Molecule (2)	Weighted means
C(1)–C(2)–C(3)	120·2(4)	120·0(11)	118·3(24)	119·5(22)	121·9(40)	119·8(33)	120·0(3)
C(2)–C(3)–C(4)	119·9(4)	119·4(12)	120·7(24)	121·0(23)	120·2(40)	117·6(39)	119·9(3)
C(3)–C(4)–C(5)	120·4(3)	121·2(12)	121·6(24)	124·9(23)	118·1(37)	125·8(43)	121·1(8)
C(4)–C(5)–C(6)	120·5(3)	120·7(10)	120·0(20)	113·8(20)	121·6(35)	120·5(38)	120·0(9)
C(5)–C(6)–C(1)	118·3(3)	119·9(10)	118·9(16)	122·9(19)	118·7(35)	118·9(31)	119·1(6)
C(6)–C(1)–C(2)	120·7(3)	118·8(12)	119·7(20)	117·9(19)	119·3(40)	116·8(30)	119·8(5)
C(1)–C(6)–C(7)	122·9(3)	122·0(9)	123·4(16)	119·5(18)	119·1(35)	115·2(31)	121·9(9)
C(5)–C(6)–C(7)	118·8(3)	118·1(9)	117·8(16)	117·6(18)	122·1(32)	125·8(33)	119·0(8)
C(6)–C(7)–C(8)	117·8(3)	118·0(8)	117·7(15)	117·7(16)	121·7(33)	124·7(34)	118·3(7)
C(6)–C(7)–O(19)	122·2(3)	120·5(9)	123·0(16)	120·2(17)	119·0(31)	117·6(33)	121·4(6)
C(8)–C(7)–O(19)	120·0(3)	121·5(9)	119·2(15)	122·1(16)	119·2(30)	117·7(34)	120·2(5)
C(7)–C(8)–O(9)	108·4(3)	108·6(8)	107·7(14)	107·5(14)	106·6(24)	111·6(31)	108·3(4)
C(8)–O(9)–O(10)	116·9(2)	116·6(7)	117·0(13)	116·4(13)	117·2(29)	120·2(29)	117·0(3)
O(9)–C(10)–C(11)	124·7(3)	124·1(9)	124·6(14)	125·1(15)	125·5(35)	124·6(32)	124·7(1)
O(9)–C(10)–C(15)	114·3(3)	114·8(8)	113·2(14)	114·0(14)	115·4(31)	119·9(31)	114·6(6)
C(11)–C(10)–C(15)	121·0(3)	121·1(9)	122·0(15)	120·9(16)	118·6(33)	115·5(32)	120·7(6)
C(10)–C(11)–O(12)	122·4(3)	122·8(9)	121·4(15)	124·2(17)	123·8(36)	126·9(34)	122·8(5)
C(11)–O(12)–C(13)	118·9(2)	118·4(7)	118·6(14)	116·5(14)	118·8(28)	115·3(28)	118·4(4)
O(12)–C(13)–C(14)	121·6(3)	121·6(9)	122·4(17)	122·6(16)	117·4(29)	123·6(37)	121·6(5)
O(12)–C(13)–C(16)	112·7(3)	110·0(8)	108·5(15)	109·5(15)	110·9(27)	111·7(32)	111·3(7)
C(14)–C(13)–C(16)	125·7(3)	128·3(10)	128·8(16)	127·8(16)	131·2(32)	123·8(40)	126·9(8)
C(13)–C(14)–C(15)	122·6(3)	123·1(10)	124·0(16)	124·2(16)	125·2(33)	118·6(35)	122·9(5)
C(14)–C(15)–C(10)	113·3(3)	112·9(8)	111·3(15)	111·4(15)	115·0(31)	119·3(31)	113·2(7)
C(14)–C(15)–O(18)	123·5(3)	124·2(9)	125·1(16)	126·6(16)	127·7(36)	123·9(33)	124·3(5)
C(10)–C(15)–O(18)	123·2(3)	122·9(9)	123·6(16)	121·8(16)	117·4(31)	116·7(31)	122·4(8)
C(13)–C(16)–O(17)	114·2(3)	111·8(9)	110·0(15)	112·9(16)	108·0(27)	116·4(34)	113·0(9)

Table 6 lists torsion angles for non-hydrogen atoms in each molecule, together with those involving H(17), where the hydrogen atom was located. Angles deviating from 0 or ±180° by >3σ are indicated. Most torsion

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[11] M. R. Truter and M. Mercer, *J.C.S. Dalton*, 1973, 2215.

angles for non-hydrogen atoms approximate to 0 or ±180°, the most notable exceptions being those about C(13)–C(16). Examination of the model shows that rotation about this bond should be free but values for O(12)–C(13)–C(16)–O(17) between 20 and −20° are unlikely because of the position of O(12). The angle deviates from 0 or ±180° in five of the six molecules, sometimes by large amounts (−31·7° for the free ligand), and its value probably depends chiefly on the crystal packing. Deviations for other angles are small and all the molecules are roughly planar. The planarity is imposed by steric effects and interactions between the various π-electron systems, *i.e.* the benzene ring, the two carbonyl groups, the C=C double bonds, and the π lone pair on O(9).

TABLE 6

Torsion angles and standard deviations (°) for different determinations of pak

	(pak),H_2O	[Cs(NCS)(pak)]	[KI(pak)$_2$] Molecule (1)	[KI(pak)$_2$] Molecule (2)	[NaI(pak)$_2$], $2H_2O$ Molecule (1)	[NaI(pak)$_2$], $2H_2O$ Molecule (2)
C(1)–C(2)–C(3)–C(4)	2·1(6) *	−0·2(22)	4·2(38)	0·6(35)	−1·2(68)	−8·2(54)
C(2)–C(3)–C(4)–C(5)	−1·1(6)	1·3(22)	1·2(38)	−1·3(38)	0·7(63)	5·3(62)
C(3)–C(4)–C(5)–C(6)	−0·6(6)	−1·2(21)	−5·0(35)	2·6(34)	−2·3(59)	−2·9(65)
C(4)–C(5)–C(6)–C(1)	1·3(5)	0·0(19)	3·3(29)	−3·5(30)	4·3(59)	3·3(54)
C(5)–C(6)–C(1)–C(2)	−0·4(5)	1·0(19)	2·1(28)	3·1(30)	−4·7(60)	−6·2(49)
C(6)–C(1)–C(2)–C(3)	−1·3(6)	−0·9(21)	−5·8(34)	−1·5(31)	3·3(68)	8·6(51)
C(2)–C(1)–C(6)–C(7)	179·0(3) *	−176·5(12)	−177·2(19)	179·6(18)	172·5(37)	175·1(32)
C(4)–C(5)–C(6)–C(7)	−178·0(3) *	176·6(11) *	−177·5(19)	180·0(18)	−172·8(36)	−178·2(3·7)
C(1)–C(6)–C(7)–O(19)	−179·0(3) *	174·5(11) *	−179·0(17)	−178·0(18)	176·3(35)	179·7(31)
C(5)–C(6)–C(7)–O(19)	0·3(5)	−3·0(17)	1·8(26)	−1·3(27)	−6·6(54)	1·1(55)
C(1)–C(6)–C(7)–C(8)	179·4(3)	−4·1(16)	−2·2(25)	3·7(25)	0·6(54)	1·8(53)
C(5)–C(6)–C(7)–C(8)	0·0(5)	178·4(11)	178·5(16)	−179·6(17)	177·7(34)	−176·8(37)
C(6)–C(7)–C(8)–O(9)	177·7(3) *	179·3(9)	−179·2(14)	−178·4(14)	−170·4(30) *	−179·1(33)
C(7)–C(8)–O(9)–C(10)	−177·6(3) *	−179·1(9)	−171·2(13) *	−174·9(13) *	169·5(27) *	−166·2(33) *
C(8)–O(9)–C(10)–C(11)	−2·8(4) *	11·4(15) *	−5·25(22)	−4·5(23)	13·3(48)	−9·8(58)
C(8)–O(9)–C(10)–C(15)	177·3(3) *	−169·8(9) *	170·5(14) *	176·8(14)	−175·4(28)	174·0(35)
O(9)–C(10)–C(11)–O(12)	−179·5(3)	177·1(10)	−178·8(14)	179·3(15)	−178·0(31)	−180·0(34)
O(9)–C(10)–C(15)–C(14)	−177·8(3) *	−178·5(9)	179·5(13)	179·6(14)	−176·9(28)	−175·4(34)
O(9)–C(10)–C(15)–O(18)	2·0(5) *	1·1(16)	−1·8(24)	−4·7(23)	3·9(44)	2·0(55)
C(10)–C(11)–O(12)–C(13)	−1·6(5) *	1·5(16)	−2·4(23)	−0·1(25)	−13·6(50)	1·3(56)
C(10)–C(15)–C(14)–C(13)	−4·0(5) *	1·1(16)	0·6(24)	2·7(24)	2·2(50)	−10·8(58)
C(11)–O(12)–C(13)–C(14)	0·0(4)	0·0(16)	−1·8(24)	3·8(23)	9·9(43)	−3·9(58)
C(11)–O(12)–C(13)–C(16)	177·8(3) *	−178·5(10)	−176·1(14)	−179·7(15)	−177·7(28)	−173·0(32)
O(12)–C(13)–C(14)–C(15)	3·0(5) *	−1·4(18)	2·6(27)	−5·3(27)	−4·8(49)	8·6(64)
O(12)–C(13)–C(16)–O(17)	31·7(4) *	−176·3(10) *	−177·6(13)	−173·0(14) *	−168·1(24) *	158·2(32) *
C(13)–C(14)–C(15)–C(10)	−4·0(5) *	1·1(16)	0·6(24)	2·7(24)	2·2(50)	−10·8(58)
C(13)–C(14)–C(15)–O(18)	176·2(3) *	−178·5(12)	−178·1(18)	−172·7(18) *	−178·6(33)	172·0(40)
C(14)–C(15)–C(10)–C(11)	2·4(5) *	0·4(16)	−4·7(23)	0·9(23)	−4·8(47)	8·1(56)
C(14)–C(13)–C(16)–C(17)	−150·6(3) *	5·2(19)	8·6(26) *	3·3(27)	3·0(48)	−10·8(62)
C(13)–C(16)–O(17)–H(17)	81·5(27) *	−87(7) *				91(13) *

* These angles differ from 0 or ±180° by $>3\ \sigma$.

Hydrogen Bonding.—A common feature of the structures is the part played by hydrogen bonding in holding the crystal structure together. The hydroxy-group of the pak molecule is always involved as the hydrogen-atom donor and as acceptor in the case of [NaI(pak)$_2$],$2H_2O$, molecule (2). The i.r. spectra of the complexes show the persistence of hydrogen bonding throughout the rest of the series.[2] A derivative of pak containing a methoxy- in place of the hydroxy-group did not form crystalline complexes with alkali-metal halides,[12] indicating that the hydrogen-bonding capacity is indispensable in the formation of such complexes. No good spectra of any of the complexes have so far been obtained in solution probably because they dissociate in polar solvents.

Co-ordination to Alkali-metal Cations.—The carbonyl and chain-ether oxygen atoms of the pak molecule are favourably arranged for triple chelation to metal cations and all the structures show this effect. The role of the hydroxy-group is two-fold in that it serves to complete the co-ordination sphere of the cation by occupying the gaps left by the two-dimensional chelating ligands and it links neighbouring cations together through the pak molecule. O(12) Is located in an inaccessible position and does not become involved in co-ordination or hydrogen bonding. Other gaps in the cation co-ordination shell are filled by anions, [Cs(NCS)(pak)], or water molecules, [NaI(pak)$_2$],$2H_2O$. The overall effect, together with hydrogen bonding, is to produce polymeric complexes existing in the solid state only.

It is not clear whether the co-ordination geometries are best explained on the basis of simple electrostatic or directional lone-pair effects. In order to find the expected geometries based on a charged-sphere model the dimensions of the molecule in (pak),H_2O were assumed. Given the M^+–O distance expected, the deviation of the metal ion, M^+, from the plane of the three equidistant oxygen atoms O(9), O(18), and O(19) may be calculated by simple geometry. Table 7 shows the observed and calculated values for the deviations

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[12] D. E. Fenton, unpublished results, 1973.

for each of the complexes taking the mean M^+–O distance from ref. 13. There is no calculated value for the Na^+ case, since this ion is too small to contact all the oxygen atoms simultaneously. While the observed deviation for Na^+ is small, as might be expected, and the two values for K^+ are in good agreement with those calculated, values for the Cs^+ complex do not follow the trend and this is reflected in the long Cs^+–O(9) contact [3·322(7) Å].[4]

TABLE 7

Observed and calculated values for the deviation (Å) of the cation from the plane defined by O(9), O(18), and O(19)

	Calc.	Obs.
Na^+		0·054(14)
K^+	1·05	1·181(4), 0·983(4)
Cs^+	1·94	0·330(1)

An investigation into the positions and directions of the oxygen lone-pairs does not provide a consistent explanation either. While the carbonyl lone-pairs lie in the plane of the molecule, the observed bond angle at O(9) suggests its lone pairs lie in the plane and at 90° to it, respectively, with some contribution from the tetrahedral form. The Na^+ and Cs^+ ions lie close to the lone pairs in their complexes but the geometry of K^+ complex is not adequately explained. Angles subtended at co-ordinating oxygens (Table 8) tend to support the lone-pair argument. The conclusion must be that both electrostatic and lone-pair effects play a part in determining the co-ordination geometry. The tendency for the alkali-metal cation to have a preferred co-ordination number has a marked effect, and all three cations have their normal complements of nearest neighbours. Packing considerations must also be important, the ease of packing planar molecules with interacting π-electron systems, the position of the hydroxy-group and the three chelating oxygens being the major factors. The different stoicheiometries are probably caused by such packing effects and the size of the cavities left when the layered structure of pak molecules is built up.

TABLE 8

Angles (°) subtended at co-ordinating oxygen atoms

		K^+			OX	OX(1)
M	Na^+	Molecule (1)	Molecule (2)	Cs^+	(pak),H_2O	[NaI(pak)$_2$],2H_2O
C(8)–O(9)–M	125	115	119	123	124	108
C(10)–O(9)–M	117	113	115	120	117	105
C(15)–O(18)–M	123	117	120	131, 137	125	89
C(7)–O(19)–M	123	120	123	138	131	88
C(16)–O(17)–M	135	111	109	111	126	96

EXPERIMENTAL

Crystals (m.p. 144—145 °C) of (pak),H_2O were prepared by dissolving pak in a little warm methanol containing a few drops of water and allowing the solution to cool slowly. The crystal chosen for data collection was a short needle with dimensions 0·015 × 0·015 × 0·050 cm. The crystal was set on a rigid mount * on a Picker four-circle automatic diffractometer and accurate cell dimensions were obtained by least-squares refinement of the 2θ settings of 16 manually centred reflections.

Crystal Data.—$C_{14}H_{12}O_5,H_2O$, $M = 278·2$, Monoclinic, $a = 7·883(8)$, $b = 18·781(5)$, $c = 9·649(6)$ Å, $\beta = 112·99(8)°$, $U = 1306(1)$ Å^3, $D_m = 1·41$ (flotation), $Z = 4$, $D_c = 1·41$, $F(000) = 584$. Space group $P2_1/c$. Mo-K_α radiation, Zr filtered; λ(Mo-$K_{\alpha1}$) = 0·70927 Å (1 Å = 10^{-10} m). Single-crystal diffraction intensities, measured by counter, μ(Mo-K_α) = 1·20 cm^{-1}.

Intensities were collected in shells of reciprocal space for the (hkl) and (hkl) octants to a maximum 2θ of 45°. Scanning was carried out at 2° min^{-1} from 0·5° below the Mo-$K_{\alpha1}$ to 0·5° above the Mo-$K_{\alpha2}$ peak and backgrounds were counted for 10 s at the ends of each scan. Three standard reflections, (024), $(42\bar{3})$, and (161) were measured at intervals of *ca.* 50 reflections. The total number of unique reflections collected was 1664. Lorentz and polarization factors (LP) were applied and the standard deviations were calculated as in ref. 5. Reflections were considered unobserved if the intensity (I) was <15 counts or $<3\sigma(I)$.

Structure Determination.—The K-curve method was used to calculate E values for all reflections but only those with $E > 1·5$ were used in the structure solution. Sign determination was carried out for the 129 E values $>1·8$ using Σ_2 relationships. A multisolution method was used with three origin-defining and four arbitrarily assigned starting reflections. The best set was used to attempt to assign the rest of the E values $>1·5$. Of the 212 E values, 209 were assigned with 97% probability and these were used to calculate an E map. All non-hydrogen atoms were visible in this map and these were refined anisotropically for four cycles of block-diagonal least-squares with observed reflections only and a weighting scheme derived from counting statistics. The R factor fell from 0·62 to 0·12. A difference map calculated at this point showed all the hydrogen atoms except H(17) and these were refined with fixed B_{iso} values of 6·0 Å^2 for two further cycles. A second difference map showed the position of the missing hydrogen atom.

One plane was found to be in bad agreement owing to a faulty measurement by the diffractometer and it was removed from the data set, leaving 1063 observed reflections. A second-order polynomial weighting scheme was calculated and used to refine all parameters, including co-ordinates and B_{iso} for hydrogen atoms, for several cycles of full-matrix least-squares with the program NUCLS.[14] It was necessary to refine co-ordinates and temperature factors in alternate cycles owing to the large number of parameters. The refinement converged to R 0·044 and R' 0·045, the highest peak remaining on the difference map

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* On a support designed by R. H. B. Mais and P. G. Owston, Imperial Chemical Industries Ltd.

[13] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962.

being 0·19 eÅ^{-3}. The final weighting scheme took the form: $w = w(\text{counting})/(2{\cdot}147 - 0{\cdot}2594|F_o| + 0{\cdot}01268\,F_o^2)$. Bond lengths and angles with errors were calculated, by the program ORFFE,[14] from the variance–covariance matrix of the final cycle of refinement of atomic co-ordinates. Scattering-factor curves were taken from ref. 15 for hydrogen and ref. 16 for carbon and oxygen atoms. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 21274 (7 pp., 1 microfiche).*

Computing.—The refinement of unit-cell parameters, data reduction, sign determination by direct methods. Fourier syntheses, block-diagonal least-squares refinement, calculation of planes through various groups of atoms, torsion angles, and interatomic distances were computed on an IBM 1130[17] at Rothamsted Experimental Station. The determination of the orientation matrix for the Picker diffractometer was carried out by use of the program GONIO on an IBM 1130 at the I.C.I. Corporate Laboratory, Runcorn, Cheshire. Full-matrix least-squares refinement and calculation of bond lengths and angles with standard deviations from the full correlation matrix[14] were carried out on an IBM 360/65X at University College, London. Thermal-ellipsoid plots with the program ORTEP[18] were carried out on an ICL 4/70 at Rothamsted Experimental Station.

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

[14] IBM 360 programs: 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.

[15] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[16] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[17] *X*-Ray ARC programs for IBM 1130; see ref. 13 of ref. 3.

[18] Thermal ellipsoid program ORTEP by C. K. Johnson.