Alkali-metal Complexes of Phenacyl Kojate (5-Phenacyloxy-2-hydroxymethyl-4*H*-pyran-4-one)

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Complexes of the type MX,(phenacyl kojate) have been prepared where MX = CsBr, NH_4Br, RbI, CsI, NH_4I, NaNCS, KNCS, RbNCS, and CsNCS. When MX = NaCl, KCl, RbCl, CsCl, NH_4Cl, NaBr, KBr, RbBr, NaI, and KI, complexes of the type MX_2,2(phenacyl kojate) are formed.

NUMEROUS examples of cationic complexes of alkali metals are known in which the ligand, uni- or multidentate, replaces the solvation of the metal leaving the ligated metal with an overall positive charge.[1] Recently, much interest has centred on the complexation of alkali metals by naturally occurring [2] and synthetic macrocyclic [3,4] ligands, stimulated by the biological implications of such systems.[5] Studies on open-chain, multidentate ligands have so far been limited to polyethers.[6,7] Alkali-metal compounds have also been reported in which, through the formation of either an intramolecular hydrogen bond (*e.g.* the potassium salt of monensic acid [8]) or an intermolecular hydrogen bond (*e.g.* the complex formed from isonitrosoacetophenone and potassium *o*-nitrophenolate [9]), the number of donor atoms available to the metal from the anion is increased to provide it with an electron-rich environment.

5-Hydroxy-2-hydroxymethyl-4*H*-pyran-4-one [kojic acid, (I)] is an antibiotic substance produced in an aerobic process by a variety of micro-organisms and from a wide range of carbon sources.[10] Alkali-metal complexes of (I) have been observed in reactions with potassium alcoholates and acetate,[11] and it is possible that these are of the acid-salt type, the complexation being facilitated by the formation of a hydrogen bond between the anion and (I).

The reaction of phenacyl bromide and (I) in ethanol, in the presence of potassium hydroxide, gave 5-phenacyloxy-2-hydroxymethyl-4*H*-pyran-4-one [phenacyl kojate, (II)].[12] When the reaction was carried out in methanol, in the presence of sodium methoxide, crystals of a product analysing as NaBr,2(II) were obtained.[12] This suggests that (II) might act as a non-cyclic multidentate ligand, and we have now shown that the complex may be prepared by the reaction of (II) and NaBr in methanol. This reaction has been extended to include M = K, Rb, Cs, or NH_4, and the effect of changing the anion (Cl, Br, I, or NCS) on the complex formation tion has been investigated. The formation of alkali-metal complexes with the non-cyclic ligand (II) is discussed, and the compounds isolated, in reactions open to the atmosphere, are listed in Table 1, together with their chemical analyses.

RESULTS

The reaction of compound (II) with alkali-metal chlorides, bromides, and iodides in methanol gave complexes of stoicheiometry MX,(II) for CsBr, CsI, and RbI, and MX,2(II) for the remaining halides. The complex with RbBr was monohydrated and two crystalline species were iso-

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lated for NaI,2(II), one trihydrated and the other anhydrous. Sodium, potassium, rubidium, and caesium thiocyanates gave KNCS,(II). NH_4Cl gave a 1 : 2 complex, NH_4Br and NH_4I gave 1 : 1 complexes, and under atmospheric conditions (II),H_2O was isolated from the reaction of (II) with NH_4NCS and with lithium salts. The discrete nature of the complexes was established by i.r. spectroscopy and by *X*-ray diffraction.[13,14] The complexes were found to dissociate in aqueous solution to give (II),H_2O and the alkali-metal salt.

TABLE 1

	M.p.	% Found			% Required			M [a]
		C	H	N	C	H	N	(*X*-Ray)
(II) [b]	144·5—145	64·2	4·4		64·6	4·6		258 (260)
(II),H_2O	144—145	59·8	4·2		60·4	5·0		276 (278)
NaCl,2(II) [b]	158—158·5							565 (578)
NaBr,2(II) [b]	197—197·5							625 (623)
NaI,2(II)	193—195d	50·4	3·2		50·1	3·6		
NaI,2(II),3H_2O	193—195d (t.p. 120°)	46·8	3·8		46·4	4·1		726·5 (723)
NaNCS,(II)	222—225d	52·8	3·7	4·1	52·8	3·5	4·1	
KCl,2(II)	204—206d	56·3	3·7		56·6	4·1		
KBr,2(II)	208—210d	52·4	3·7		52·6	3·8		635 (639)
KI,2(II)	>205d	49·2	3·6		49·1	3·5		689 (686)
KNCS,(II)	197—200d	50·5	3·4	3·1	50·4	3·4	3·9	
RbCl,2(II)	201—203d	52·4	3·7		52·5	3·8		
RbBr,2(II),H_2O	195—198d	47·8	3·5		47·8	3·7		705 (703)
RbI,(II)	150—153	35·6	2·5		35·6	2·6		465 (472)
RbNCS,(II)	174—178d	44·8	3·1	3·5	44·7	3·0	3·5	
CsCl,2(II)	179—181	48·9	3·4		48·8	3·5		693 (688)
CsBr,(II)	168—171d	35·0	2·2		35·5	2·5		454·5 (471)
CsI,(II)	196—199d	32·9	2·5		32·3	2·3		511 (520)
CsNCS,(II)	150—152	40·0	2·6	3·0	39·9	2·7	3·1	451 (466)
NH_4Cl,2(II)	175—178d	57·9	5·1	2·1	58·6	4·9	2·4	
NH_4Br,(II)	185—188d	46·5	4·4	3·9	46·9	4·5	3·9	
NH_4I,(II)	200—205d	41·5	3·9	3·1	41·5	3·9	3·5	

[a] Calculated values in parentheses. [b] Ref. 12.

The i.r. spectrum of compound (I) showed bands at 1658 cm^{-1} [ν(C=O)] and at 1628, 1608, and 1570 cm^{-1} which were attributed to the ν(C=C) in the γ-pyranone.[10] The broad bands in the OH region showed evidence of strong inter- and intra-molecular hydrogen bonding (3270, 3170, 3095 cm^{-1}). Phenacyl bromide has ν(C=O) at 1690 cm^{-1} and this is unchanged in (II). Compound (II) gives two crystalline forms, needles [which are (II),H_2O] and plates which are anhydrous (II). The plates have ν(OH) at 3495 cm^{-1} and bands at 1690, 1640, 1615, and 1595 cm^{-1}; the needles have ν(OH) at 3485s and 3235br and further bands at 1690, 1640, 1608, and 1595 cm^{-1}. The spectra differ in the region 1300—800 cm^{-1}. The i.r. spectra of the 2 : 1 complexes resemble those of the plates; and the 1 : 1 complexes are closer to those of the needles, most especially in the 1600 cm^{-1} region. The use of i.r. spectra for alkali-metal complexes is often made difficult by the possible creation of artefacts. For example, the presence of sodium in KBr discs causes alterations in the spectra of D-glucose, and this has been attributed to the formation of NaBr,2(D-glucose).[15] A similar effect has been observed with benzo-15-crown-5.[16] However, for (II) and (II,H_2O) the spectra as Nujol mulls and KBr discs were the same, and different from the spectra of the complexes.

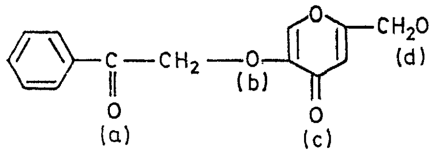
The ammonium halide complexes prepared exhibit the same trends as the caesium complexes, in stoicheiometry and ν(OH) (see Table 2). No complex was isolated for NH_4NCS. It is possible that this may be caused by the competition of the ligand and water for the deliquescent salt.

In KI,2(II) crystal structure analysis has shown each potassium ion to be co-ordinated by eight oxygen atoms.[13] This is the number of oxygen atoms frequently observed for potassium.[1,17] The co-ordinating oxygen atoms are the two ketonic (a,c) and the ethereal (b) oxygens from each of two molecules of (II), and the two hydroxyl oxygens (d) from adjacent (II) molecules. The pyranone ring oxygen is not involved in co-ordination, and the alcohol

TABLE 2

Infrared spectra ν(OH) frequencies cm^{-1}

	Cl	Br	I	NCS
Na	3310	3350	3370	3345
K	3255	3280	3325	3245
Rb	3240	3290	3350	3290
Cs	3225	3290	3335	3275
NH_4	3220	3260	3340, 3150	
(II)	3490			
(II),H_2O	3470, 3265bd			



(II)

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groups lie between a potassium cation and an iodide ion and appear hydrogen-bonded to the iodide.

DISCUSSION

The isolation of complexes of the alkali metals with neutral ligands has led to attempts to correlate complex formation with various physico-chemical properties of the metals and their salts. Pedersen proposed,[18] in general terms, that solid complexes of the cyclic polyethers with alkali-metal salts were formed if the lattice energies of the components were not too high, and the complexing power of the ligand was strong enough.

Thiourea (tu) complexes of the alkali-metal bromides and iodides (MX,4tu) have been isolated and their structures shown to be similar.[19] A calculation, on the assumption that the binding is predominantly electrostatic and that the Madelung constants for the complexes are similar, gave a lattice energy of the order 180 kcal mol^{-1}, and, as the calculated contribution from the thiourea was *ca.* 17 kcal mol^{-1}, only those alkali-metal salts with lattice energy less than 160 kcal mol^{-1} could gain by forming 1 : 4 complexes with thiourea.[20]

Diacetamide complexes of the alkali metals have been isolated and formation criteria proposed.[21] Complex formation was found to occur if the percentage ionic character of the alkali-metal salt present was less than 63% (*i.e.* equivalent to less than two units difference in electronegativity) and if the cation : anion radius ratio was less than 0·78. The structures of the NaBr,2-(diacetamide) [22] and KI,2(diacetamide) [23] complexes have been determined and are interpreted as consisting of chemically interacting ion pairs clathrated within a matrix of oriented ligand dipoles. The ligand is chelated to the alkali-metal cation.

The isolation of complexes having (II) as a ligand does not appear to be governed either by the lattice energy of MX or by the relative electronegativities of M^+ and X^-.

The complexes are found to fall into two stoicheiometric groups. For the halides a lattice energy division may be made, as, if the lattice energy of the alkali-metal salt is greater than 150 kcal mol^{-1} a 1 : 1 complex is formed (see Tables 1 and 3). This, however, cannot be used as a general criterion as no lithium complexes were isolated, and no alkali-metal thiocyanate complexes were isolated with 1 : 2 stoicheiometry.

If the general criterion is taken as the sum of the cationic and anionic radii a value greater than 3·60 Å leads to 1 : 1 complexes, for the alkali metals and NH_4I. NH_4Br, however, does not obey this postulate. The size of the cation or anion alone does not appear to impose stoicheiometric restriction, as shown by the 1 : 2 complexes with RbCl, CsCl, NaI, and KI.

TABLE 3

Lattice energies [a] (kcal mol^{-1}) and ionic radii [b]

		Li	Na	K	Rb	Cs	NH_4
	r/Å	0·60	0·95	1·33	1·48	1·69	1·48
Cl	1·81	201	186	169	163	155	158
Br	1·95	191	177	161	156	149	152
I	2·16	178	164	151	147	140	144
NCS	[2·74 [c]]	183	163	149			145

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A small cation with its large electric field will attract both the dipolar solvent molecules and the potential complexor, whereas the larger cations will neither be heavily solvated, nor will they attract the complexor as readily. Therefore, in a situation where, as we have, lithium has access to solvent molecules, water molecules, and potential donor molecules, it is possible that it will retain its solvation sheath, especially if the spatial availability of the donor atoms is restricted by the steric requirements of the ligand.

The ligand (II) offers several possible ligating situations, and these can give rise to chelation, as in KI,2(II), or to bridging. It is possible that in the 1 : 1 complexes (II) is shared between metal ions or that a dimeric molecule exists as has been found for the cyclic polyether complex (temf)CsNCS.* [24] In this, as in the binuclear complex, (dibenzo-24-crown-8)-2KNCS,† [25] the thiocyanate group bridges the two metal atoms. The facility of the larger anions to form bridges could aid the existence of such systems for the 1 : 1 complexes. It is also possible that if a matrix of (II), resembling that of diacetamide in its complexes, is a feature common to the 1 : 2 complexes, then the presence of the combined bulk of the larger cations and anions could dislocate the packing arrangement and not allow the 1 : 2 situation. The hydrogen bonding between the alcoholic hydroxyl group and the anion may also be disrupted and a potential stabilising factor therefore removed.

The disruption of hydrogen bonding in the systems is indicated by the trends in ν(OH) (Table 2). For the halide ions the decreased capacity for hydrogen bonding

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* temf = (7*R*,9*R*,18*S*,20*S*)-6,7,9,10,17,18,20,21-Octahydro-7,9,18,20-tetramethyldibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin.

† Dibenzo-24-crown-8 = 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosin.

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to the halide ion in the bromides and iodines is reflected in the shift of this band to higher values for iodide than bromide than chloride.

EXPERIMENTAL

I.r. spectra were measured as Nujol mulls or KBr discs using a Perkin-Elmer 457 spectrometer. M.p.s (uncorrected) were measured using a hot-stage microscope. Microanalyses were carried out by the University College Microanalytical Laboratory.

Phenacyl kojate,bis(phenacyl kojate)sodium bromide, and bis(phenacyl kojate)sodium chloride were prepared by the methods of Hurd and Sims.[12]

The synthetic method was the same for all of the complexation reactions attempted. The ligand and the alkali-metal salt were warmed together in AnalaR methanol and set aside to cool. The crystals which appeared were separated and investigated. The mother liquor was then set aside to evaporate and either further crystals of the complex or of (II),H_2O were recovered. The reactions were carried out using various combinations of stoicheiometry but only those complexes listed in Table 1 were isolated.

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