

# Synthesis and X-ray Structural Analysis of a Unique Co-crystallization Complex of [NaSal]<sub>2</sub>DB24C8 and [KSal]<sub>2</sub>DB24C8

CORY MOMANY and MARVIN L. HACKERT

Chemistry Department and Clayton Foundation Biochemical Institute, University of Texas, Austin, TX 78712, U.S.A.

JYOTSNA SHARMA and NARINDER S. POONIA

Research Oasis, 68, Vishnupuri Proper, Indore 452 001, India

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**Abstract.** Sodium salicylate (NaSal where Sal = 2-hydroxybenzoate), when mixed with dibenzo-24-crown-8 (DB24C8) yields a bimetallic complex [NaSal]<sub>2</sub>DB24C8 in most polar organic media, while potassium salicylate (KSal) under similar conditions shows a tendency to yield 1:1 or 2:1 complexes depending upon medium or synthesis. However, the presence of both NaSal and KSal together results in a unique mixed cation complex of composition NaKSal<sub>2</sub>DB24C8. This product melts sharply (190–92°C) without decomposition, displays IR spectral characteristics comparable to those of [Na(Sal)]<sub>2</sub>DB24C8, and is stable in aqueous media as shown by the detectable cation effect on the UV absorption bands of Sal and DB24C8. Single crystal X-ray analysis of NaK(Sal)<sub>2</sub>DB24C8 reveals that the system represents a co-crystallization complex of individual (KSal)<sub>2</sub>DB24C8 and (NaSal)<sub>2</sub>DB24C8 molecules. The crystals are monoclinic,  $P2_1/c$ ,  $a = 19.976(2)$  Å,  $b = 9.031(1)$  Å,  $c = 25.541(5)$  Å,  $\beta = 122.065(9)^\circ$ ,  $V = 3904.6(9)$  Å<sup>3</sup>,  $T = 298$  K,  $Z = 2 + 2$ ,  $\text{CuK}\alpha$   $\lambda = 1.5418$  Å, and  $2\theta$  ( $2.5^\circ$ – $100^\circ$ ). Final  $R$  factor for the 3012 observed reflections ( $F > 3\sigma$ ) is 0.092. Both the Na<sub>2</sub>- and K<sub>2</sub>-molecules possess crystallographic centers of symmetry with one metal and its associated anion on each side of the crown ring. However, the conformations of the crowns are very different in the two molecules, with the K<sub>2</sub>-crown being nearly planar and the Na<sub>2</sub>-crown being quite puckered. Four oxygen atoms from the DB24C8 (K $\cdots$ O, 2.680–2.908 Å) and three carboxyl oxygen atoms (K $\cdots$ O, 2.472–2.708 Å) from separate salicylate ions coordinate with each potassium. Three oxygens from the crown (Na $\cdots$ O, 2.536–2.65 Å) and three carboxyl oxygens (Na $\cdots$ O, 2.31–2.563 Å) coordinate with each sodium. The salicylate ions lie on opposite sides and nearly perpendicular ( $77.2^\circ$ , Na<sub>2</sub>-molecule;  $82.7^\circ$  K<sub>2</sub>-molecule) to each crown but coordinate to both of the metal ions within a molecule. The K $\cdots$ K $\cdots$ K $\cdots$  and Na $\cdots$ Na $\cdots$ Na $\cdots$  distances in the respective molecules are 3.95 and 3.34 Å.

**Key words:** Co-crystallization complex, dibenzo-24-crown-8, potassium, salicylate, sodium, X-ray diffraction.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82044 (18 pages).

## 1. Introduction

The ions, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, participate in many biological reactions [1]. In most organisms, K<sup>+</sup> and Mg<sup>2+</sup> are selectively taken up, while there are some botanical species that prefer Na<sup>+</sup> over K<sup>+</sup> [2]. This discrimination between pairs of cations is controlled and guided by the anionic, solvating, and complexing species involved in the natural processes. To define the relevant chemical principles controlling the biological functions of these cations, we have undertaken a chemical approach using X-ray crystallography to study the anion *vs.* solvent and ligand *vs.* anion and/or solvent preferences of each individual alkali (M<sup>+</sup>) and alkaline earth (M<sup>2+</sup>) cations (general abbreviation, M<sup>Z+</sup>) [3,4].

Until recently, our main effort has been to understand conditions that ensure a chemical diversity between similar cations, such as  $\text{Na}^+$  and  $\text{K}^+$ , through the use of appropriate anionic species and the electrically neutral ligands [5–9]. Our findings to date are that the diversity between  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  is as much a function of the charge density difference between the cations concerned as it is a function of the degree of charge localization (cation pairing) of the counteranion. Superimposed on both effects is the solvation effect.

Now our emphasis is upon forcing different cations to behave chemically alike. In this paper we illustrate that  $\text{Na}^+$  and  $\text{K}^+$  can be forced to accept common chemical environments despite that under normal conditions [4, 6] with crowns as ligands,  $\text{Na}^+$  is anionophilic while  $\text{K}^+$  is ligandphilic. We have succeeded in synthesizing a unique crystalline compound  $\text{NaK}(\text{Sal})_2\text{DB24C8}$  that has been shown by X-ray analysis to be a co-crystallization complex of  $[\text{NaSal}]_2\text{DB24C8}$  and  $[\text{KSal}]_2\text{DB24C8}$  with two molecules of each constituting a common unit cell.

## 2. Experimental Section

### 2.1. CHEMICAL STUDIES

$\text{NaSal}$  and  $\text{KSal}$  were prepared by mixing equivalent amounts of the caustic alkali of interest (0.05 mol) with  $\text{HSal}$  in 50% aq. ethanol ( $\sim 20$  ml). The isolated  $\text{MSal}$  was recrystallized from a minimum amount of absolute ethanol and dried *in vacuo* for 24 h at  $100^\circ\text{C}$ .

To synthesize the metal-crown complexes, reaction mixtures of  $\text{NaSal}$  or  $\text{KSal}$  with  $\text{DB24C8}$  (in 1 : 1 and 2 : 1 ratios) as well as of  $\text{NaSal}$ ,  $\text{KSal}$ , and  $\text{DB24C8}$  (in a 1 : 1 : 1 ratio) were prepared in a diverse selection of dried organic media (methyl cyanide, acetone, methanol, ethanol, isopropanol, and *n*-butanol). The reactants (0.3 mM with respect to  $\text{DB24C8}$ ) were dissolved upon warming the solvent ( $\sim 4$  ml) and immediately sealed to prevent entrance of moisture. Crystallization of the product was first attempted by keeping the reaction mixture at room temperature (up to 6 h) and then continued in a refrigerator overnight if necessary. Alternatively, the experiments were repeated by initially dissolving the reactants in acetone (the most efficient solvent which only weakly solvates). After expelling the acetone, the residue was recrystallized from a still less polar medium (acetonitrile, isopropanol, and/or *n*-butanol).

The solid product obtained from either procedure was subjected to a solid-to-melt phase change study using a hot stage microscope (Franz Kustner KG Bredu HMK, 71/3732). IR spectra of the reactants in  $\text{KBr}$  discs were obtained using a Perkin-Elmer Spectrometer (Model 377), and microanalysis for Na and K was done on a Shimadzu Atomic Absorption Spectrophotometer (Model AA-640-13). UV spectral studies on  $\text{MSal}$  and the  $(\text{MSal})_2\text{DB24C8}$  complexes in methanol and water were performed using a Varian recording spectrophotometer (Model UV-VIS 634).

### 2.2. STRUCTURAL ANALYSIS OF $\text{NaK}(\text{Sal})_2\text{DB24C8}$

Data collection was conducted at room temperature (298K) on a Syntex four circle goniostat equipped with a Picker X-ray generator and a KRISSEL CONTROL automation package. Intensity data were obtained using a modified  $\omega$ -scan mode. The profile of each reflection was scanned for 13 steps over a range of  $0.78^\circ$  in  $\omega$ . Backgrounds were counted for 10 sec on each side of the peak. A crystal of dimensions  $0.3\text{ mm} \times 0.2\text{ mm} \times 0.3\text{ mm}$  was used in data collection. Lattice constants were determined by a least squares refinement of 20 reflections. Three standard reflections were measured every 4 h to monitor crystal and instrument

stability. Intensities were corrected for crystal decay (min. 1.00, max. 1.16) and absorption corrections (min. 1.03, max. 1.39) were applied using an empirical  $\psi$  scan approach. Intensities were further corrected for Lorentz and polarization effects. Of 4021 independent reflections collected between  $2\theta$  values of  $2^\circ$  and  $100^\circ$  ( $\lambda = 1.5418 \text{ \AA}$ ), 3012 were considered observed ( $F > 3\sigma$ ). Most nonhydrogen atom positions were determined by the direct methods program MULTAN [10]. The remaining nonhydrogen atoms were located in difference electron-density maps. To confirm that the  $\text{K}^+$  and  $\text{Na}^+$  positions were assigned correctly by MULTAN, and that mixed complexes did not exist, a difference electron density map was computed based on the positions of all the nonmetal atoms (excluding hydrogens). Two peaks of differing size were observed with the  $\text{K}^+$  position assigned by Multan corresponding to the larger peak. Isotropic refinement converged at  $R = 0.167$ . Anisotropic refinement converged at  $R = 0.109$ . Addition of calculated hydrogen positions (not refined) yielded a final  $R$  factor of 0.092 for  $R = \Sigma |F_o - F_c| / \Sigma |F_o|$ . The density measured at room temperature in a gradient of dichloromethane and bromobenzene was  $1.34 \text{ g/cm}^3$  while the calculated density for  $Z = 2 + 2$  was  $1.332 \text{ g/cm}^3$ .

### 3. Results

To prevent ambiguity in the following text, the pure metal complexes such as [NaSal]<sub>2</sub>DB24C8 and [KSal]<sub>2</sub>DB24C8 are abbreviated as Na<sub>2</sub>-complex and K<sub>2</sub>-complex, respectively, while the individual molecules of [NaSal]<sub>2</sub>DB24C8 and [KSal]<sub>2</sub>DB24C8 in the NaK(Sal)<sub>2</sub>DB24C8 co-crystallization complex are abbreviated as Na<sub>2</sub>-molecule and K<sub>2</sub>-molecule, respectively. Table I summarizes the essential chemistry of the MSal-DB24C8 systems.

#### 3.1. SYNTHESIS OF COMPLEXES

Potassium salicylate (KSal) tends to yield a solid bimetallic K<sub>2</sub>-complex (m.p. 145–160°C), as well as a monometallic K-complex (m.p. 245–265°C) depending on the solvent medium. However, the complexes cannot be synthesized in a pure state under any condition because the K-crown interaction is relatively weak (see UV results below). On the other hand, sodium salicylate (NaSal) displays a stronger Na $\cdots$ O (crown) interaction and yields an isolatable bimetallic Na<sub>2</sub>-complex (m.p. 215–225°C) from most media including the highly crown-deactivating (crown-solvating) methyl alcohol. The mono-metallic Na-complex cannot be synthesized under any conditions as NaSal does not undergo ion pair loosening in the organic media that is needed for encapsulation of the two cations by the large crown ring. Interestingly, the two impure K<sub>2</sub>- and K-complexes as well as the Na<sub>2</sub>-complex can be independently synthesized from the crown-deactivating methanol (which bridges the crown ring), but not the mixed cation complex NaK(Sal)<sub>2</sub>DB24C8 for which NaSal, KSal, and DB24C8 recrystallize uncomplexed.

#### 3.2. THERMAL BEHAVIOR

The temperature of the solid-to-melt phase change of the mixed metal complex NaK(Sal)<sub>2</sub>DB24C8 (190–192°C) lies between that of the Na<sub>2</sub>-complex (215–220°C) and the K<sub>2</sub>-complex (145–160°C) and is the most sharply defined of the three complexes. In agreement with the observation that NaSal pairs bond more strongly than KSal, complexes of  $\text{K}^+$  do not regenerate KSal on melting or on heating the melt, but the Na<sub>2</sub>-complex

Table I. Essential chemistry of the MSal-DB24C8 systems

Reaction mixture (proportion)	Favourable synthesis medium <sup>a</sup>	Stoichiometry of complex isolated (melting behaviour) <sup>b,c</sup>	UV spectral features in water (methanol)	Comments
NaSal: DB24C8 (2:1)	Me, Et, Ip, Bu, Ac, An	2:1 (215–255° m, 260° rc, 300° nm)	210, 218, 277–292 nm (206, 221, 277–295 nm)	In methanol both carboxylate and the ethereal bands show a red shift compared to that in water.
NaSal: DB24C8 (1:1)	Ac- <i>Ip</i>	2:1 (as above)		Bimetallic complex isolates even from a 1:1 reaction mixture.
KSaI: DB24C8 (2:1)	Me, Ip, Ac, Ac- <i>Ip</i>	C <sub>1</sub> , 2:1 (150–160° m) C <sub>2</sub> , 1:1 (245–265° m)		Isolation of the pure products was not possible; from Ethanol, n-Butanol and Acetonitrile, the products are even gummy due to poor complexation. From methanol, both complexes separate out as a mixture.
KSaI: DB24C8 (1:1)	Ac- <i>Ip</i>	C <sub>1</sub> , 2:1 (150–160° m) C <sub>2</sub> , 1:1 (245–265° m)		Ac- <i>Ip</i> proved to be a favourable medium for a 1:1 reaction mixture. The product obtained however is 2:1, even from a 1:1 reaction mixture.
NaSal: KSaI: DB24C8 (1:1:1)	Et, Bu, Ac, An, Ac- <i>Ip</i>	1:1:1 (190–192° m)	210, 217, 276–293 nm (206, 221, 276–294 nm)	Intriguingly, the salts and the crown recrystallize uncomplexed from methanol.
NaSal: KSaI: DB24C8 (1:2:1)	Ac- <i>Ip</i>	1:1:1 (190–192° m)		
NaSal: KSaI: DB24C8 (2:1:1)	Ac- <i>Ip</i>	1:1:1 (190–192° m)		Mixed cation complex is synthesized more favourably than the Na <sub>2</sub> <sup>+</sup> , K <sub>2</sub> <sup>+</sup> , and K-complexes.

<sup>a</sup> Solvent notations are: Me, Methanol; Et, Ethanol; Ip, Isopropanol; Bu, n-Butanol; Ac, Acetone; An, Acetonitrile; Ac-*Ip*, Isopropanol after expulsion of acetone. Italics indicates the most favourable medium for synthesis.

<sup>b</sup> Notations for melting behaviour are: m, melting; nm, non-melting; rc, recrystallization from the melt.

<sup>c</sup> C<sub>1</sub> and C<sub>2</sub> denote the first and second crops, respectively.

regenerates NaSal from the melt at 260°C. However, the mixed cation complex does not generate NaSal on melting or on heating the melt, suggesting an intriguing stabilization effect on the melt in the presence of both NaSal and KSal.

### 3.3. INFRARED SPECTRAL RESULTS

The 960 cm<sup>-1</sup> peak of DB24C8 ( $\nu$ C $\cdots$ O) [11], the 982 cm<sup>-1</sup> peak of NaSal ( $\nu$ Na $\cdots$ O<sup>-</sup>/Na $\cdots$ O) [12], and the 950 cm<sup>-1</sup> peak of KSal ( $\nu$ K $\cdots$ O<sup>-</sup>/K $\cdots$ O) were affected the most on the formation of NaK(Sal)<sub>2</sub>DB24C8 and yielded a collective band centered around ~940 cm<sup>-1</sup>. This was accompanied for the complex by the appearance of various new peaks at 605, 758, 775, ~1050, ~1130, and 1220 cm<sup>-1</sup> which for the Na(Sal)<sub>2</sub>DB24C8 complex appear at 590, 750, not observed, 1055, 1110–1140 (doublet) and 1210 cm<sup>-1</sup>, respectively.

### 3.4. UV SPECTRAL RESULTS

Solution studies on MSal and MSal-DB24C8 complexes, redissolved in methanol, revealed comparative MSal ion-pairing and M<sup>+</sup> $\cdots$ O (crown) complexation for Na<sup>+</sup> and K<sup>+</sup>. Of the MSal salts, NaSal is detectably more strongly paired (even in water) compared to KSal so that the carboxylate absorption appears towards the red end (294 nm compared to 293 nm for K<sup>+</sup>Sal<sup>-</sup>) and the comparatively electronically 'depleted' phenyl absorbs towards the blue end (228 nm as compared to 229 nm for KSal). It is worth noting that UV-effects arising out of the differences in the M<sup>+</sup> $\cdots$ O or M<sup>+</sup> $\cdots$ O<sup>-</sup> bond strengths are usually very small. The uncomplexed DB24C8 displays an absorption of the ethereal ring at 270 nm and of the phenyl at a rather higher energy (218 nm). A crown-phenyl is electronically more depleted by the neutral 'catechol oxygen' than the Sal-phenyl (to which the electron supplying carboxylate is attached).

The crown on complexation with metal ions shows a red shift of the ethereal absorption while the carboxylate absorption of Sal displays a blue shift due to the consequent ion pair loosening. The two shifts are more pronounced for the Na<sub>2</sub>-complex than the NaK-complex; the carboxylate band for the Na<sub>2</sub>-complex shows up at the highest energy (292 nm) while the uncomplexed NaSal appears at the lowest energy (294 nm). A correlation between stronger Na<sup>+</sup> $\cdots$ O (crown) interaction in solution and a comparatively easy isolation of the solid [NaSal]<sub>2</sub>DB24C8 complex is noteworthy.

### 3.5. CRYSTALLOGRAPHIC RESULTS

Crystallographic parameters are listed in Table IIA. The positional parameters and standard deviations for all non-hydrogen atoms are given in Table IIB. Structure factors and other crystallographic data are provided as supplementary material. The numbering schemes, bond distances, bond angles, and standard deviations for the dipotassium complex and for the disodium complex are shown in Figures 1 and 2, respectively. Atoms related by the centers of symmetry are designated by primes. Figures 3 and 4 are stereo ORTEP drawings of the dipotassium and disodium complexes, respectively, while Figure 5 is a stereo drawing illustrating the packing in the *P*2<sub>1</sub>/*c* unit cell.

Structural analysis reveals the complex NaK(Sal)<sub>2</sub>DB24C8 to be a co-crystallization product of [NaSal]<sub>2</sub>DB24C8 and [KSal]<sub>2</sub>DB24C8 molecules with a unit cell consisting of two centrosymmetric molecules of each. The crown of the K<sub>2</sub>-molecule is planar to within

Table IIA. Crystallographic parameters

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$a = 19.976(2) \text{ \AA}$
$b = 9.031(1) \text{ \AA}$
$c = 25.541(5) \text{ \AA}$
$\beta = 122.065(9)^\circ$
$V = 3904.6 \text{ \AA}^3$
$D_c = 1.332 \text{ g/cm}^3$
$D_o = 1.34 \text{ g/cm}^3$
Space group $P2_1/c$
$Z = 2 + 2$
$F(000) = 1618$
$\text{Cu}K\alpha\lambda = 1.5418 \text{ \AA}$

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Table IIB. Atomic coordinates in fractions of cell edges (standard deviations)

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Atom	$x/a (\sigma)$	$y/b (\sigma)$	$z/c (\sigma)$	Atom	$x/a (\sigma)$	$y/b (\sigma)$	$z/c (\sigma)$
K <sup>+</sup>	-0.0055(1)	-0.0241(3)	0.5744(1)	Na <sup>+</sup>	0.5063(2)	0.0953(4)	0.4468(1)
O(1A)	-0.0217(4)	-0.2545(7)	0.6340(3)	O(1B)	0.4747(3)	0.01677(7)	0.3401(3)
C(2A)	0.0251(5)	-0.388(1)	0.6493(5)	C(2B)	0.4235(6)	0.292(1)	0.3119(5)
C(3A)	0.0401(6)	-0.409(1)	0.5978(5)	C(3B)	0.3646(6)	0.291(1)	0.3294(5)
O(4A)	0.0855(4)	-0.2937(7)	0.5967(3)	O(4B)	0.4059(4)	0.3067(8)	0.3945(3)
C(5A)	0.0971(6)	-0.307(1)	0.5463(5)	C(5B)	0.3488(8)	0.300(2)	0.4127(7)
C(6A)	0.1581(6)	-0.195(1)	0.5554(5)	C(6B)	0.385(1)	0.348(2)	0.4757(7)
O(7A)	0.1433(4)	-0.1643(8)	0.4953(3)	O(7B)	0.4420(5)	0.254(1)	0.5154(4)
C(8A)	0.2082(7)	-0.083(1)	0.4999(5)	C(8B)	0.4705(9)	0.296(1)	0.5748(7)
C(9A)	0.1908(6)	-0.052(1)	0.4367(5)	C(9B)	0.4283(8)	0.231(1)	0.6031(6)
O(10A)	0.1257(4)	0.0500(7)	0.4079(3)	O(10B)	0.4504(4)	0.0729(8)	0.6151(4)
C(11A)	0.1101(5)	0.111(1)	0.3540(4)	C(11B)	0.4273(6)	-0.005(1)	0.6484(5)
C(12A)	0.0523(5)	0.224(1)	0.3303(4)	C(12B)	0.4698(5)	-0.138(1)	0.6734(4)
C(13A)	0.0323(6)	0.294(1)	0.2757(5)	C(13B)	0.4566(6)	-0.227(1)	0.7113(5)
C(14A)	0.0689(7)	0.254(1)	0.2449(5)	C(14B)	0.3980(9)	-0.189(2)	0.7216(7)
C(15A)	0.1261(7)	0.148(1)	0.2677(5)	C(15B)	0.3544(8)	-0.064(2)	0.6958(8)
C(16A)	0.1461(6)	0.075(1)	0.3217(5)	C(16B)	0.3683(7)	0.028(2)	0.6585(6)
C(17A)	-0.1821(5)	-0.291(1)	0.4124(5)	C(17B)	0.3037(5)	-0.229(1)	0.3733(4)
C(18A)	-0.2358(6)	-0.351(1)	0.3536(6)	C(18B)	0.2516(5)	-0.338(1)	0.3706(5)
C(19A)	-0.2911(7)	-0.451(1)	0.3508(7)	C(19B)	0.1973(7)	-0.397(1)	0.3135(7)
C(20A)	-0.2916(7)	-0.489(1)	0.4026(9)	C(20B)	0.1909(8)	-0.351(2)	0.2602(7)
C(21A)	-0.2383(8)	-0.430(1)	0.4602(7)	C(21B)	0.2398(7)	-0.241(2)	0.2623(5)
C(22A)	-0.1832(6)	-0.330(1)	0.4645(5)	C(22B)	0.2952(5)	-0.183(1)	0.3193(5)
C(23A)	-0.1197(6)	-0.183(1)	0.4174(5)	C(23B)	0.3639(6)	-0.164(1)	0.4335(5)
O(24A)	-0.0706(3)	-0.1311(6)	0.4694(3)	O(24B)	0.4089(4)	-0.0644(8)	0.4356(3)
O(25A)	-0.1210(4)	-0.1547(8)	0.3688(3)	O(25B)	0.3685(4)	-0.2147(8)	0.4821(4)
O(26A)	-0.2360(4)	-0.3149(9)	0.3039(3)	O(26B)	0.2576(4)	-0.3861(7)	0.4230(4)

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The symmetry related atoms of the dipotassium complex can be generated by (-X, -Y, 1-Z) and the disodium complex atoms by (1-X, -Y, 1-Z).

0.04 Å and accommodates two K<sup>+</sup> ions through interactions between four oxygens of each half of the crown (K<sup>+</sup>⋯O, 2.680(9) to 2.908(7) Å). A Sal from each axial side chelates a cation through its carboxyl oxygens (K<sup>+</sup>⋯O<sup>-</sup>, 2.708(8) and 2.685(7) Å) with O(24A) also bridging a second cation through a rather short contact (K<sup>+</sup>⋯O<sup>-</sup>, 2.472(6) Å). Thus, each cation avoids solvation by interaction through one or two contacts with Sal. The 'catechol' oxygens, unlike the observation for most M<sup>Z+</sup>-crown complexes [4, 13], establish the shortest

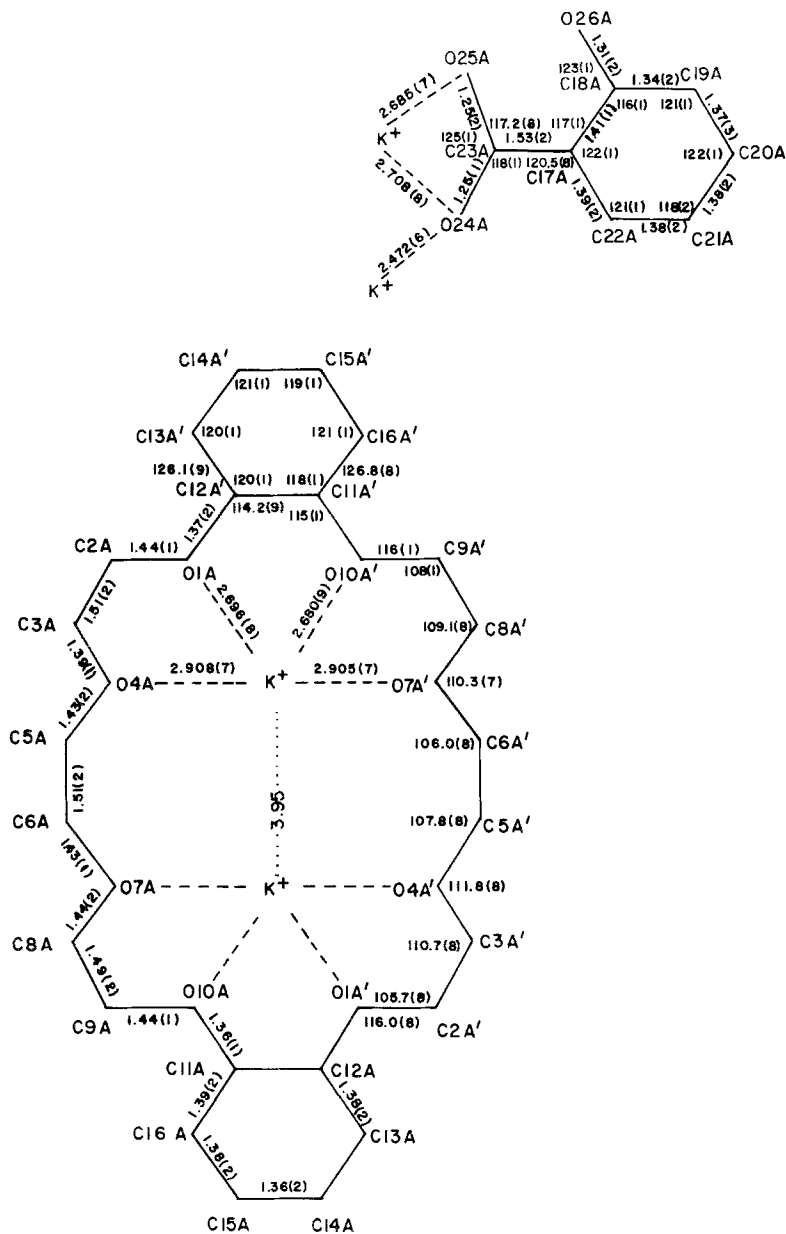


Fig. 1. Diagram of the dipotassium complex showing the atom designations, the bond distances (Å), and angles (°) with the standard deviations of the last digit in parentheses. The center of symmetry lies at (0, 0, 0.5).

crown contacts with the cation. The bonding mode suggests that the crown molecule does not experience any conformational strain. The K<sup>+</sup>...K<sup>+</sup> distance is fairly long (3.95 Å).

In the Na<sub>2</sub>-molecule, only three of the four oxygens from half the crown molecule interact with each cation (Na<sup>+</sup>...O, 2.536 to 2.650 Å); the fourth oxygen is not within bonding distance (Na<sup>+</sup>...O(7B'), 3.03 Å and Na<sup>+</sup>...O(7B'), 3.30 Å). Again unlike noted earlier for M<sup>Z+</sup>-crown complexes [4, 13], one of the 'catechol' oxygens establishes the shortest contact

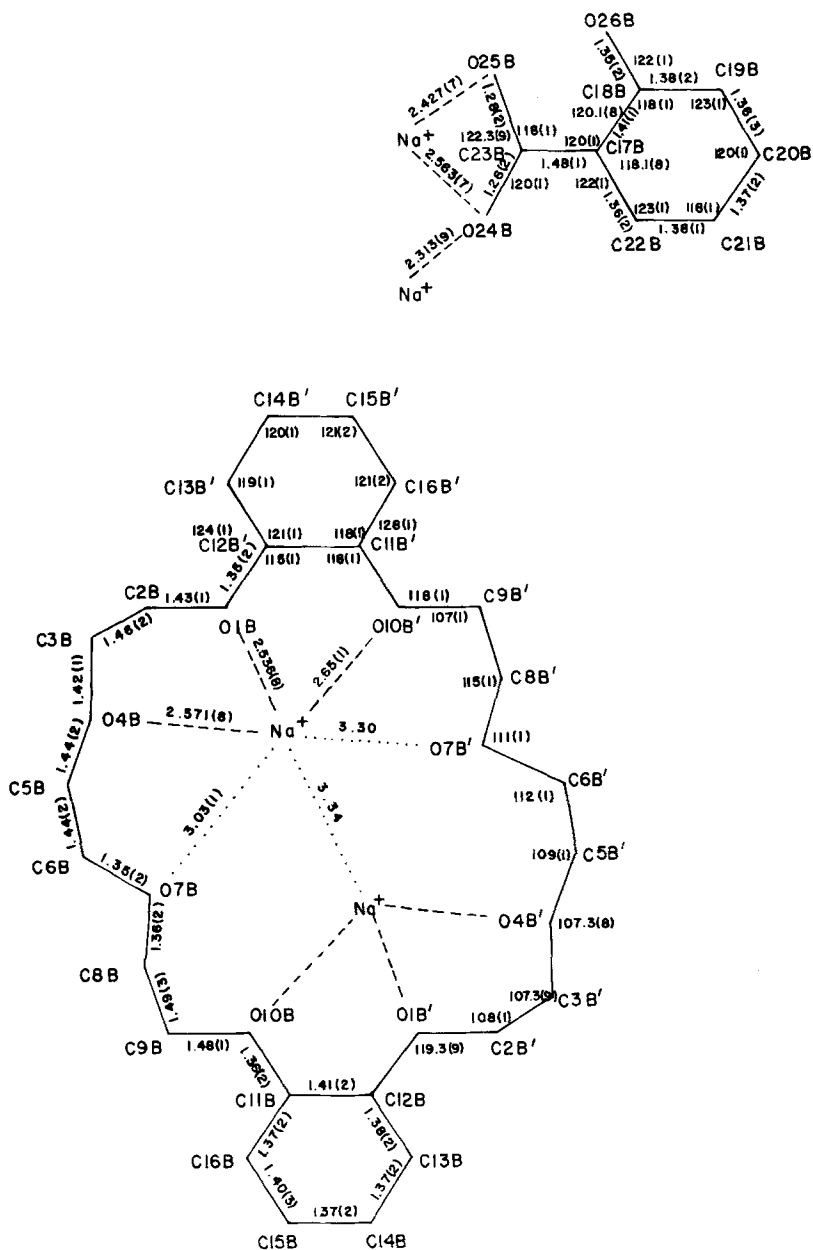


Fig. 2. Diagram of the disodium complex showing the atom designations, the bond distances (Å), and the angles (°) with the standard deviations of the last digit in parentheses. The center of symmetry lies at (0.5, 0, 0.5).

( $\text{Na}^+ \cdots \text{O}(1\text{B}), 2.536 \text{ \AA}$ ). The crown ring undergoes a diagonal stretching (Figure 2) and the molecule appears puckered (Figure 4). The  $\text{Na}^+ \cdots \text{Na}^+$  distance is long (3.34 Å). The Sal moieties interact with  $\text{Na}^+$  ions in a similar manner to that with the  $\text{K}^+$  ions ( $\text{Na}^+ \cdots \text{O}^-$ , 2.563 and 2.927 Å; bridge, 2.313 Å) with solvation of the metals again prevented by the two axial Sals. Compared to an earlier known  $\text{Na}_2$ -complex,  $[\text{Na}(\text{Onp})]_2\text{DB24C8}$  (Onp = 2-nitrophenolate) [14], there is a small variation ( $\sim 5^\circ$ ) in the angles around the centrally



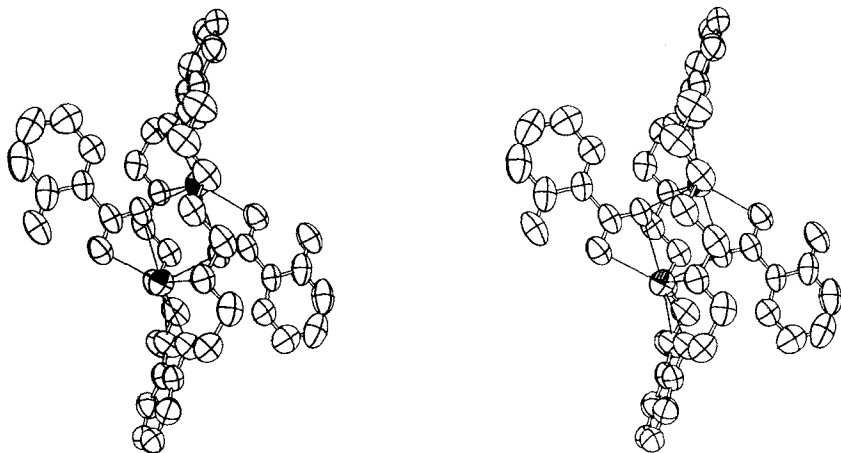


Fig. 3. Stereo ORTEP view of the dipotassium complex.

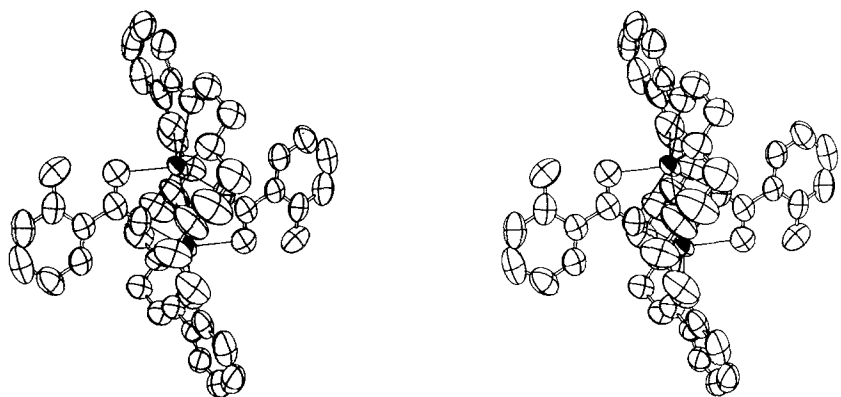


Fig. 4. Stereo ORTEP view of the disodium complex.

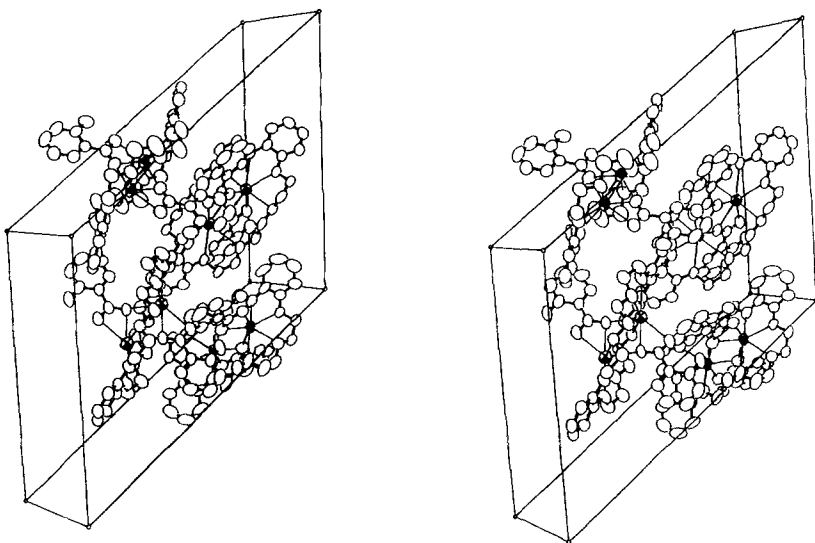


Fig. 5. A stereo ORTEP drawing of the  $P2_1/c$  unit cell. The origin of the box is located at (0.5, 0, -0.25).

located atoms of the crown. The temperature factors for atoms around C(6B) and C(8B) were high as observed in the Onp structure.

The Sal moieties for the  $K_2$ -molecule as well as the  $Na_2$ -molecule lie roughly perpendicular to the plane of the crown ring (82.7 and 77.2°, respectively). The Sal hydroxyls in  $NaK(Sal)_2DB24C8$  may hydrogen bond with their related carboxyl oxygens (for  $KSal$ : O(25A)—O(26A), 2.465 Å; and for  $NaSal$ : O(25B)—O(26B), 2.456 Å); but the hydrogen atoms were not searched for due to the relatively high *R* factor.

#### 4. Discussion

Earlier findings using conventional bi- and tridentate ligands have shown that a decrease in the solubility of a solid  $M^{Z+}$ -complex is dependent on both the  $M^{Z+}$ -ligand bond strength and the pairing strength of the metal-ligand with its counteranion. For a given metal-ligand system in a given solvating medium, favored pairing of the counteranion decreases solubility, but beyond a certain limit it disrupts the metal-ligand bonds to insolubilize the lone  $M^{Z+}$ -salt (as usually observed for the picrate ion with the low charge density cations,  $K^+$  to  $Cs^+$ , and for *o*-nitrophenolate with the larger  $M^{2+}$  ions  $Ca^{2+}$  and  $Ba^{2+}$ ). The strong  $Na$ -Sal and  $Na$ -DB24C8 interactions in solution as shown by the UV spectral results, and the facilitated synthesis of the  $Na_2$ -complex from solution, compared to the analogous  $K^+$ -systems, is in line with this conclusion.

Our aim in synthesizing a mixed cation complex was to see if, with the help of an appropriate anion, the anion-paired  $Na^+$  and  $K^+$  ions could be introduced into the common cavity of a suitably large crown, DB24C8. The role of the anion with regard to the possibility of synthesizing such a complex was found to be dominating. Thus, for salicylate anion, the  $Na_2$  and the  $NaK$ -complexes form stable crystal lattices, while for 2,6-dihydroxybenzoate (HOSal), it is the  $K_2$ -complex and not the  $Na_2$ -complex that can be synthesized (work in progress). The  $NaK(Sal)_2DB24C8$  is the first and only system of the desired composition that we have succeeded in synthesizing. X-ray structural analysis, however, reveals that the system is a cocrystallization product of pure bimetallic products,  $[NaSal]_2DB24C8$  and  $[KSal]_2DB24C8$ . Such a system has not been reported so far and is unique in that both  $Na^+$  and  $K^+$  have been introduced into a common unit cell sufficiently ordered to permit diffraction analysis.

The salicylate anion holds the two different cations through a common bonding mode, but being fairly different in size,  $Na^+$  and  $K^+$  cause widely different conformational changes in the cavity of the crown and thus might make it difficult for both ions to be accommodated simultaneously. The difference in the ion-dipole forces for the  $Na\cdots O$  and  $K\cdots O$  bonds with the crown is understandably also responsible for the diversity.

Control of the anion on the bonding modes of the cation with the crown is obvious from a comparison of the structures of the  $K_2$ -molecule (Figure 1) with  $[K(NCS)]_2DB24C8$  [15] and that of the  $Na_2$ -molecule (Figure 2) with  $[Na(Onp)]_2DB24C8$  complexes which were also synthesized by one of us (N.S.P.). For salicylate as counteranion in the  $K_2$ -molecule,  $K^+$  is satisfied through interaction with only the four oxygens belonging to precisely half the crown molecule (Figure 1). While for NCS in  $[K(NCS)]_2DB24C8$  [15], the ion needs to be stabilized also by the two additional bridging oxygens of the donor ring as well as the  $\pi$ -electron cloud of the phenyl moieties belonging to adjacent complex molecules in the lattice. For Sal in the  $Na_2$ -molecule,  $Na$  interacts with only three oxygens belonging to the two different loops of the ring involved and a diagonal stretching of the donor ring (Figure 2) takes place while for Onp in  $[Na(Onp)]_2DB24C8$  [14] either cation picks up all the three oxygens

from the same loop of the donor ring leading to a two-fold symmetry of the molecule and a major twisting of the ring.

A point in common for all the four bimetallic systems discussed above, whether mixed metal or pure metal, is that the anion must bridge the two cations to keep them bound in the cavity of the crown. The 1 : 1 analogues, which can also be synthesized more favorably for K<sup>+</sup> through a variation in the solvating media [5], presumably are those where such a hold of the anion fails to exist and indeed this can (and should) happen for the relatively less anionphilic K<sup>+</sup> [6]. The anion adjusts also the intermetallic distance in the system. Thus, the distances between Na ions for Sal and Onp [14], are 3.34 and 3.38 Å, respectively, and those between the K<sup>+</sup> ions for Sal and NCS [15], are 3.95 and 3.41 Å, respectively. Obviously, different anions help obviate coulombic repulsion between the two Na<sup>+</sup> or the two K<sup>+</sup> ions at different intermetallic distances depending on the degree of electrostatic stabilization they provide to the cation through bridging.

The Sal anion in the present complex chelates Na<sup>+</sup> as well as K<sup>+</sup> through the two carboxylate oxygens forming a four-membered ring (rather than a five-membered ring through a carboxylate oxygen and a hydroxyl oxygen). This is common for the carboxylate anion towards small (Li [16] or Mg [17]) as well as large (Ca [18] or Sr [19]) s-block cations. It is also worth mentioning that the complex Tl(Sal)(1,10-phenanthroline) [20], where the cation (Tl) is closely related to Na<sup>+</sup> and K<sup>+</sup> with regard to its chemistry, undergoes dimerization in the crystal lattice, and Sal thus not only chelates Tl<sup>+</sup> through a four-membered ring of the carboxyl oxygens but also bridges the other Tl<sup>+</sup> ion as it does towards Na<sup>+</sup> or K<sup>+</sup> in the present complex.

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