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Dipotassium and Sodium/Potassium Crystalline Picrate Complexes with the Crown Ether 6,7,9,10,12,13,20,21,23,24,26,27-Dodecahydrodibenzo[*b*,*n*]-[1,4,7,10,13,16,19,22]octaoxacyclotetracosin (Dibenzo-24-crown-8)

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Abstract

The crystal structures of the dipotassium and the mixed sodium/potassium picrate complexes with the crown ether dibenzo-24-crown-8 (DB24C8) were solved and found to be nearly identical. (I): NaKpic$_2$(DB24C8), $[NaK(C_6H_2N_3O_7)_2(C_{24}H_{32}O_8)]$, $M_r = 966{\cdot}8$, triclinic, $P\bar{1}$, $a = 8{\cdot}164\,(2)$, $b = 9{\cdot}960\,(2)$, $c = 13{\cdot}368\,(3)$ Å, $\alpha = 103{\cdot}92\,(3)$, $\beta = 108{\cdot}03\,(2)$, $\gamma = 93{\cdot}23\,(2)°$, $V = 993{\cdot}0\,(7)$ Å^3, $Z = 1$, $D_m = 1{\cdot}54$ ($T = 298$ K), $D_x = 1{\cdot}62\,(1)$ g cm^{-3}, $\lambda = $ (Mo $K\alpha$) $0{\cdot}71069$ Å, $\mu = 2{\cdot}37$ cm^{-1}, $F(000) = 500$, $T = 103$ K, $R = 0{\cdot}086$ for 2904 unique reflections. (II): K$_2$pic$_2$(DB24C8), $[K_2(C_6H_2N_3O_7)_2(C_{24}H_{32}O_8)]$, $M_r = 982{\cdot}9$, triclinic, $P\bar{1}$, $a = 8{\cdot}231\,(4)$, $b = 9{\cdot}850\,(2)$, $c = 13{\cdot}346\,(4)$ Å, $\alpha = 103{\cdot}91\,(2)$, $\beta = 106{\cdot}82\,(3)$, $\gamma = 93{\cdot}37\,(2)°$, $V = 995{\cdot}7\,(9)$ Å^3, $Z = 1$, $D_m = 1{\cdot}59$ ($T = 298$ K), $D_x = 1{\cdot}638\,(8)$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}71069$ Å, $\mu = 3{\cdot}30$ cm^{-1}, $F(000) = 508$, $T = 163$ K, $R = 0{\cdot}042$ for 4835 unique reflections. Both structures feature eight-coordinated cations between alternating layers of relatively flat crown ligands and paired picrates. In the mixed-metal system the two cations are disordered between two $P\bar{1}$-related sites; these metal sites have a coordination environment only slightly different from that in the dipotassium

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structure. Na^+ is able to occupy an environment similar to that of K^+ under the conditions of these crystals, a situation not previously observed in the chemistry of crown ethers or macrocylic multidentates.

Introduction

One approach to understanding the highly selective complexation and transport of metal ions by biomolecules has been through the study of metal–crown complexes. These macrocyclic polyethers have been shown to discriminate between similar cations in solution, to mimic the ion transport properties of structurally related antibiotics such as valinomycin (Izatt, Rytting, Nelson, Haymore & Christensen, 1969) and to form stable complexes in which the cation is encapsulated, sandwiched, or otherwise coordinated by the crown. The structures of several solid-state complexes, involving crowns ranging in size from five to ten (—C—C—O—) units, and with one or two benzyl rings fused to the macrocyclic ring, have been analyzed by X-ray diffraction techniques. The type of interaction between cation and (neutral) crown is in general dependent on the size and charge density of the cation, the size and flexibility of the crown, the nucleophilicity of the counterion, and the nature of the solvent. For a recent, complete, review of this field, see Bajaj & Poonia (1988).

Focusing on Na/K discrimination, we have undertaken the synthesis and analysis of several mixed-cation (NaX)(KX)(DB24C8) complexes. Here DB24C8 is the cyclic polyether dibenzo-24-crown-8 (Fig. 1), and X is a chelating organic anion such as 2-hydroxybenzoate (sal), 2,6-dihydroxybenzoate (HOsal), 3,5-dinitrobenzoate (dnb), 2-nitrophenolate (onp), 2,4-dinitrophenolate (dnp), and 2,4,6-trinitrophenolate (pic). X-ray analysis of the first mixed-cation complex synthesized, that in which X = sal, revealed it to be a homogeneous cocrystallization of the metallic complexes $[Na(sal)]_2(DB24C8)$ and $[K(sal)]_2(DB24C8)$ (Momany, Hackert, Sharma, & Poonia, 1987). In that structure, the coordination environments of the two cations differ significantly between the two complexes, primarily in that the conformation of the crown molecule is flat in the di-K complex and distinctly puckered in the di-Na complex. This is consistent with the general observation regarding charge-separated complexes, that the shape of the flexible crown is modified to accommodate the size of the cation. In this article we describe the synthesis and X-ray structures of the mixed-metal Na/K and dipotassium DB24C8 picrate complexes. The results imply that Na and K can occupy virtually identical coordination cavities within the mixed-cation complex [Na(pic)K(pic)](DB24C8).

Experimental

Crystal preparation

To prepare the mixed-metal Na/K complex, Na^+pic^-, K^+pic^- and DB24C8 (0·1 mmol) were mixed in a 1:1:1 ratio; for the dipotassium complex, the mixture contained K^+pic^- and DB24C8 (0·1 mmol) in a 2:1 molar ratio. The compounds were dissolved by warming in 5 mL of a 1:1 acetone–isopropanol mixture. Each beaker was left open at 298 K until the acetone was expelled and solid complex crystallized (90–120 min). Yellow crystalline products obtained from the two reaction mixtures were characterized by micromelting point study, infrared spectroscopy and elemental analysis, and shown to be $NaK(pic)_2(DB24C8)$ (m.p. 458-460 K) and $K_2(pic)_2(DB24C8)$ (m.p. 433 K), respectively.

Data collection

Data were collected from a crystal of the NaK complex measuring approximately. 0·1 × 0·2 × 0·4 mm. Reflections were measured on a Syntex $P2_1$ automated four-circle diffractometer using graphite-monochromated Mo$K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation. The device was equipped with the Syntex LT-1 low-temperature flow system, maintained at 103 K. Lattice constants were determined by a least-squares refinement of 15 strong reflections (θ range 2·3–16·9°). The computed density for $Z = 1$ at the reduced temperature is 1·62 g cm^{-3}. The observed density at room temperature, measured in a CsBr concentration gradient, is 1·54 g cm^{-3}.

Intensity data were collected by a variable-speed ω method in which each peak was scanned symmetrically over a centered range of 1° in ω. Backgrounds were counted at 1° on each side of the peak for a total amount of time equal to the scan time. Four standard reflections ($101,1\bar{1}\bar{2},1\bar{1}0,\bar{2}\bar{2}1$) were used to monitor crystal and instrument stability and their intensities were remeasured every 100 reflections. Of 4562 unique reflections collected between 2θ values of 4 and 55° ($0{\cdot}0491 \le \sin\theta/\lambda \le 0{\cdot}6497$ Å^{-1}; $0 \le h \le 10$, $-12 \le k \le 12$, $-15 \le l \le 17$), 2904 were considered observed [$I > 2{\cdot}5\sigma(I)$] and used in the solution of the structure. A parabolic decay correction was applied, though the decay was less than 5% (Henslee & Davis, 1975). The intensities were also corrected for absorption using the technique of de Meulenaer & Tompa (1965) (transmission-factor range 0·956–0·975) and Lp effects.

Data for the dipotassium complex were collected on the same diffractometer system, with lattice-constant determination and all other parameters the same except the following. The K_2-complex crystal measured approximately 0·2 × 0·4 × 0·7 mm and was maintained at 163 K during data collection. At this temperature its calculated density was 1·638 g cm^{-3} ($Z = 1$). At room temperature the density measured by flotation in a CCl$_4$/ethyl iodide gradient was 1·59 g cm^{-3}. 4835 reflections were considered observed [$I > 3\sigma(I)$] from a total of 5597 unique reflections collected between 2θ values of 4·3 and 60° ($0·0528 \leq \sin\theta/\lambda \leq 0·7035$ Å^{-1}; $0 \leq h \leq 11$, $-13 \leq k \leq 13$, $-18 \leq l \leq 16$). Absorption, Lp and decay corrections were applied as with the NaK crystal (transmission-factor range 0·838–0·944).

Although the two sets of lattice constants are very similar (corresponding parameters agree to within 1·5%), different choices of the reduced cell are dictated by the slight differences that do exist; this served initially to obscure the similarity between the two systems. The reduced cell of (I) is described by $a = 8·164$ (2), $b = 9·960$ (2), $c = 13·333$ (2), $\alpha = 74·00$ (2), $\beta = 72·42$ (1), $\gamma = 86·77$ (2)°. The transformation applied to the reduced cell of (I) to give the nonreduced cell is given by: $\mathbf{a} \rightarrow -\mathbf{a}$, $\mathbf{b} \rightarrow \mathbf{b}$, $\mathbf{c} \rightarrow \mathbf{a} - \mathbf{c}$. In order to facilitate the comparison between the structures, we have elected to use a nonreduced cell for the NaK system that closely resembles the K$_2$ system's reduced cell.

Structure solution

The structure of the mixed-metal complex was solved first. Our inability to obtain a solution in a series of early passes employing the *MULTAN* direct-methods programs (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) led to a detailed study of the Patterson map.

Coordinates and intensities of the 100 highest Patterson peaks, as determined by the program *SHELX76* (Sheldrick, 1976), were input to the *FRODO* (Jones, 1978) molecular-graphics program and displayed on an Evans & Sutherland graphics screen. The layered distribution of maxima in the Patterson map implied that the molecules themselves were arranged in a stratiform manner. Also evident was a strong set of vectors related by approximate twelvefold symmetry, arising from the two six-membered rings. Based on the orientations and separations of these features in the Patterson map, we deduced a set of possible relative positions of the benzyl and phenolic groups. One of these, supplied to *MULTAN* as a partial structure, resulted in a reasonable, although incomplete structure solution. Difference electron density maps then revealed the remaining non-H atoms, and isotropic least-squares refinement [minimizing $\sum(F_o - F_c)^2$ with unit weights] in space group $P\bar{1}$ converged with $R = 0·145$ where $R = \sum|F_o - F_c|/\sum|F_o|$. Scattering factors taken from Cromer & Mann (1968).

A crucial question in the mixed complex concerned the distribution of the two different metal cations in an essentially centrosymmetric structure. Attempts were made to refine the two metal sites independently in space group $P1$. Since least-squares refinement of the complete structure in $P1$ was mathematically ill-conditioned, various subsets of the structure were alternately held fixed while refinement proceeded with the remaining atoms. No significant deviation from centrosymmetry appeared in these trials. Difference Fourier maps resulted in equally strong, though slightly elongated, peaks at both positions of the missing metal cations. No peak splitting could be seen at the cation or, in F_o Fourier maps, at the loci of any coordinating oxygens. As a further test, the occupancies of the two metal sites were found to refine to values corresponding to one half each of the two different alkali cations at each site, regardless of whether they were initially set to values corresponding to sodium or to potassium. At this point the stoichiometry of the metal ions in crystals of the same batch was assayed by atomic absorption chromatography and confirmed to be 1:1. Furthermore, precession photographs of the major zones revealed no evidence of weak reflections at intermediate reciprocal-lattice points as would be expected if a superlattice were present in the Na/K crystal. These tests, plus the lack of peak splitting, and equal occupancies, force the conclusion that the

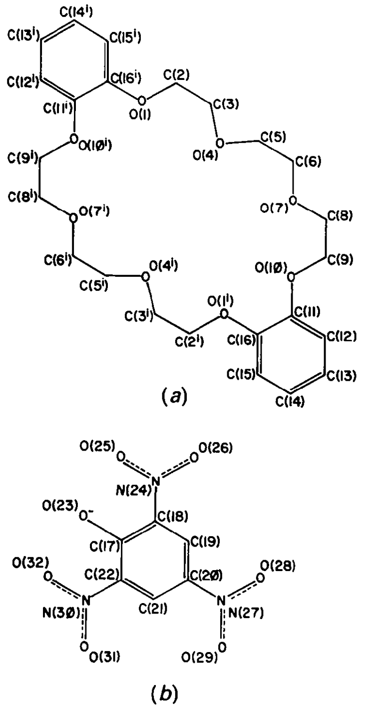

Fig. 1. (*a*) Diagram of the crown molecule showing the atom-numbering scheme. Superscripts are used to designate symmetry-related atoms (see also Tables 2–4). (*b*) Atom-numbering scheme for the picrate anion.

Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for non*-H *atoms*

U_{eq} is the trace of the orthogonalized U_{ij} tensor.

	NaK complex				K_2 complex			
	x	y	z	U_{eq}	x	y	z	U_{eq}
M^+	3715 (2)	6245 (2)	0411 (1)	44 (2)	3646·6 (5)	6196·3 (4)	0451·7 (3)	22·4 (3)
O(1)	−2711 (5)	4029 (4)	−2324 (3)	37 (3)	−2653 (2)	4015 (1)	−2338 (1)	33 (1)
C(2)	−1704 (7)	5254 (5)	−2332 (4)	34 (5)	−1686 (2)	5267 (2)	−2349 (1)	22 (1)
C(3)	−0531 (8)	5807 (6)	−1161 (5)	39 (5)	−0514 (2)	5824 (2)	−1183 (1)	24 (1)
O(4)	1002 (5)	6685 (4)	−1041 (3)	40 (3)	0981 (2)	6711 (1)	−1079 (1)	24 (1)
C(5)	0742 (7)	8091 (6)	−1054 (4)	39 (5)	0759 (2)	8150 (2)	−1047 (2)	24 (1)
C(6)	2511 (7)	8888 (6)	−0805 (5)	39 (5)	2518 (2)	8950 (2)	−0778 (2)	26 (1)
O(7)	3715 (5)	8829 (4)	0226 (3)	35 (3)	3667 (2)	8885 (1)	0241 (1)	24 (1)
C(8)	3537 (8)	9827 (6)	1137 (4)	38 (5)	3505 (2)	9912 (2)	1149 (2)	25 (1)
C(9)	4762 (8)	9608 (6)	2171 (4)	37 (5)	4669 (3)	9694 (2)	2177 (2)	25 (1)
O(10)	4191 (5)	8246 (4)	2230 (3)	38 (3)	4066 (2)	8330 (1)	2254 (1)	24 (1)
C(11)	4703 (6)	8000 (5)	3242 (4)	31 (3)	4628 (2)	8038 (2)	3241 (1)	20 (1)
C(12)	5953 (7)	8855 (5)	4174 (4)	34 (5)	5898 (2)	8870 (2)	4143 (1)	23 (1)
C(13)	6328 (7)	8494 (6)	5158 (4)	39 (5)	6310 (2)	8481 (2)	5116 (1)	24 (1)
C(14)	5459 (7)	7320 (6)	5224 (4)	39 (5)	5453 (2)	7275 (2)	5184 (1)	26 (1)
C(15)	4231 (7)	6445 (6)	4293 (4)	36 (5)	4196 (2)	6412 (2)	4271 (1)	24 (1)
C(16)	3863 (6)	6772 (5)	3303 (4)	31 (4)	3808 (2)	6771 (2)	3296 (1)	20 (1)
C(17)	7753 (7)	6308 (6)	2059 (4)	37 (5)	7847 (2)	6403 (2)	2131 (1)	29 (1)
C(18)	7396 (7)	5526 (6)	2779 (4)	35 (5)	7473 (2)	5589 (2)	2836 (1)	22 (1)
C(19)	8233 (6)	5863 (5)	3888 (4)	32 (5)	8290 (2)	5909 (2)	3939 (1)	24 (1)
C(20)	9496 (7)	7015 (6)	4383 (4)	35 (5)	9565 (2)	7054 (2)	4430 (1)	23 (1)
C(21)	9978 (7)	7814 (6)	3778 (4)	35 (5)	10078 (2)	7868 (2)	3828 (1)	23 (1)
C(22)	9151 (6)	7462 (5)	2673 (4)	32 (4)	9280 (2)	7524 (2)	2728 (1)	21 (1)
O(23)	6950 (6)	6073 (5)	1070 (3)	59 (5)	7059 (2)	6207 (2)	1152 (1)	27 (1)
N(24)	6084 (6)	4286 (5)	2333 (4)	41 (5)	6158 (2)	4355 (2)	2387 (1)	25 (1)
O(25)	5184 (6)	3986 (5)	1360 (4)	54 (5)	5211 (2)	4103 (2)	1442 (1)	31 (1)
O(26)	5940 (6)	3577 (5)	2933 (4)	57 (5)	6038 (2)	3595 (2)	2972 (1)	39 (1)
N(27)	10307 (6)	7416 (5)	5569 (4)	39 (4)	10347 (2)	7440 (2)	5603 (1)	28 (1)
O(28)	9832 (6)	6702 (4)	6088 (3)	48 (4)	9830 (2)	6730 (2)	6121 (1)	36 (1)
O(29)	11403 (7)	8456 (5)	5991 (3)	58 (5)	11478 (2)	8461 (2)	6025 (1)	37 (1)
N(30)	9776 (6)	8328 (5)	2079 (4)	39 (4)	9905 (2)	8387 (2)	2134 (1)	23 (1)
O(31)	10465 (7)	9510 (5)	2568 (4)	60 (6)	10559 (2)	9612 (1)	2621 (1)	35 (1)
O(32)	9595 (7)	7835 (5)	1130 (4)	69 (5)	9794 (2)	7861 (2)	1186 (1)	38 (1)

metal ions are randomly distributed between the two sites. As discussed in Marsh (1986), we consider the structure to be centrosymmetric with the metals disordered. The distribution and statistics of the normalized structure-factor moduli were consistent with a centrosymmetric structure ($\langle E \rangle$ = 0·792). The addition of the hydrogens and the final cycles of least-squares refinement were carried out in $P\bar{1}$ and led to an R value of 0·082 for observed and 0·114 for all reflections, S = 2·96 and final Δ/σ = 0·46. The final difference electron density map contained extrema of ± 0·7 e Å^{-3}.

The subsequent structure solution of the dipotassium complex was relatively straightforward. A partial solution was provided directly by *MULTAN*. Remaining non-H positions were determined from difference electron density maps. Isotropic refinement of non-H positions resulted in R = 0·095, and anisotropic refinement converged at R = 0·062. H-atom loci were determined by difference electron density maps. Further refinement of positional and thermal parameters resulted in R = 0·042 for observed and 0·046 for all reflections for this complex, S = 3·46 and final Δ/σ = 0·015. The final electron density map contained extrema of ±0·5 e Å^{-3}.

Results

The numbering schemes for the atoms of the crown and for the picrate anion are given in Fig. 1. Table 1* presents the coordinates for all atoms in their respective cells (NaK nonreduced), isotropic thermal parameters, and the distances between the loci of corresponding atoms in the two structures (errors in least-squares superposition), tabulated as 'deviation'. As an indicator of the similarity of the two structures, all of the atomic deviations are under 0·2 Å.

In both structures, coplanar pairs of picrates, oriented with their oxyanions apposed, alternate with nearly flat crowns to form stacks along the **a** axis of the crystal (Fig. 2). The entire crown is roughly planar, with the planes of the two benzyl rings only

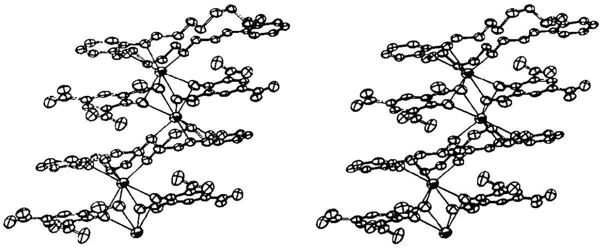

Fig. 2. Stereo *ORTEP* drawing of two unit cells, adjacent in the **x** direction, of the NaK complex.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53746 (63 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Metal–oxygen coordination lengths* (Å) *for* NaK(DB24C8)pic$_2$ *and* K$_2$(DB24C8)pic$_2$

	NaK complex	K$_2$ complex
Crown		
M^+—O(1′)	2·982 (5)	2·911 (2)
M^+—O(4)	2·593 (4)	2·699 (2)
M^+—O(7)	2·644 (4)	2·730 (2)
M^+—O(10)	2·652 (4)	2·707 (2)
Picrates		
M^+—O(23)	2·543 (5)	2·689 (2)
M^+—O(25)	2·965 (5)	2·880 (2)
M^+—O(23′)	2·557 (5)	2·684 (2)
M^+—O(25′)	2·764 (6)	2·900 (2)

Table 3. *Bond lengths* (Å) *for non*-H *atoms*

	NaK complex	K$_2$ complex
O(1)—C(2)	1·436 (7)	1·434 (2)
C(2)—C(3)	1·506 (7)	1·520 (2)
C(3)—O(4)	1·429 (7)	1·419 (3)
O(4)—C(5)	1·432 (7)	1·432 (2)
C(5)—C(6)	1·508 (8)	1·509 (3)
C(6)—O(7)	1·441 (6)	1·433 (2)
O(7)—C(8)	1·427 (7)	1·425 (2)
C(8)—C(9)	1·507 (8)	1·502 (3)
C(9)—O(10)	1·438 (7)	1·441 (3)
O(10)—C(11)	1·373 (7)	1·371 (2)
C(11)—C(12)	1·387 (6)	1·383 (2)
C(12)—C(13)	1·394 (9)	1·395 (3)
C(13)—C(14)	1·369 (9)	1·382 (3)
C(14)—C(15)	1·386 (6)	1·395 (2)
C(15)—C(16)	1·386 (8)	1·384 (3)
C(16)—C(11)	1·400 (8)	1·411 (3)
C(16)—O(1′)	1·373 (5)	1·368 (2)
C(17)—C(18)	1·458 (9)	1·457 (3)
C(18)—C(19)	1·373 (7)	1·377 (3)
C(19)—C(20)	1·377 (7)	1·380 (2)
C(20)—C(21)	1·383 (9)	1·393 (3)
C(21)—C(22)	1·367 (7)	1·371 (2)
C(22)—C(17)	1·455 (7)	1·458 (2)
O(23)—C(17)	1·237 (6)	1·242 (2)
N(24)—C(18)	1·459 (7)	1·459 (2)
O(25)—N(24)	1·240 (6)	1·231 (2)
O(26)—N(24)	1·215 (8)	1·224 (3)
N(27)—C(20)	1·459 (7)	1·453 (2)
O(28)—N(27)	1·229 (8)	1·230 (3)
O(29)—N(27)	1·222 (6)	1·228 (2)
N(30)—C(22)	1·472 (8)	1·458 (3)
O(31)—N(30)	1·207 (6)	1·230 (2)
O(32)—N(30)	1·204 (7)	1·221 (2)

Table 4. *Bond angles* (°) *for non*-H *atoms*

	NaK complex	K$_2$ complex
C(16′)—O(1)—C(2)	117·8 (4)	118·0 (1)
O(1)—C(2)—C(3)	103·3 (5)	103·6 (2)
C(2)—C(3)—O(4)	113·0 (5)	113·4 (2)
C(3)—O(4)—C(5)	114·1 (4)	115·1 (1)
O(4)—C(5)—C(6)	106·6 (5)	106·9 (2)
C(5)—C(6)—O(7)	112·1 (5)	113·1 (2)
C(6)—O(7)—C(8)	112·9 (4)	113·4 (1)
O(7)—C(8)—C(9)	108·5 (5)	109·3 (2)
C(8)—C(9)—O(10)	107·2 (4)	107·2 (1)
C(9)—O(10)—C(11)	117·1 (3)	118·0 (1)
O(10)—C(11)—C(16)	115·3 (4)	114·9 (1)
O(10)—C(11)—C(12)	125·5 (5)	125·2 (2)
C(16)—C(11)—C(12)	119·2 (5)	119·9 (2)
C(11)—C(12)—C(13)	119·6 (5)	119·7 (2)
C(12)—C(13)—C(14)	121·0 (5)	120·5 (1)
C(13)—C(14)—C(15)	119·8 (6)	120·2 (2)
C(14)—C(15)—C(16)	120·1 (5)	119·7 (2)
C(15)—C(16)—C(11)	120·3 (4)	119·9 (1)
C(15)—C(16)—O(1′)	125·3 (5)	125·1 (2)
C(11)—C(16)—O(1′)	114·4 (5)	114·9 (2)
C(17)—C(18)—C(19)	124·4 (5)	124·0 (1)
C(18)—C(19)—C(20)	119·5 (6)	119·7 (2)
C(19)—C(20)—C(21)	121·2 (5)	121·3 (2)
C(20)—C(21)—C(22)	118·9 (5)	118·6 (2)
C(21)—C(22)—C(17)	125·4 (5)	124·9 (2)
C(22)—C(17)—C(18)	110·6 (4)	111·2 (1)
O(23)—C(17)—C(22)	123·8 (6)	122·9 (2)
O(23)—C(17)—C(18)	125·6 (5)	125·8 (2)
N(24)—C(18)—C(17)	120·3 (4)	120·2 (1)
N(24)—C(18)—C(19)	115·3 (5)	115·8 (2)
O(25)—N(24)—C(18)	119·5 (5)	119·9 (2)
O(26)—N(24)—C(18)	118·6 (4)	118·1 (1)
O(25)—N(24)—O(26)	121·9 (5)	122·0 (2)
N(27)—C(20)—C(19)	119·2 (6)	119·5 (2)
N(27)—C(20)—C(21)	119·6 (4)	119·2 (1)
O(28)—N(27)—C(20)	118·2 (4)	118·0 (1)
O(28)—N(27)—O(29)	123·8 (4)	123·6 (2)
N(30)—C(22)—C(21)	115·8 (4)	116·3 (1)
N(30)—C(22)—C(17)	118·9 (4)	118·7 (1)
O(31)—N(30)—C(22)	118·5 (5)	118·2 (2)
O(31)—N(30)—O(32)	122·4 (6)	122·7 (2)

0·59 (4) Å apart, closely resembling both the K-complex crown within the NaK(sal)$_2$DB24C8 structure (Momany *et al.*, 1987), and the uncomplexed crystalline crown (Hanson, Hughes & Truter, 1976). The crown exhibits a distinctly two-lobed structure, where the two halves coordinate separately and in opposite directions.

Between each pair of alternating crown and anion layers is a metal ion, coordinated by four crown oxygens and two pairs of picrate oxygens. The coordination distances are presented in Table 2. The average cation—oxygen distance is notably shorter in the Na/K *versus* the di-K complex [2·71 (1) *versus* 2·775 (6) Å] in spite of the general similarity of the two structures. Each pair of picrates coordinates, through the same set of four oxygens, to two metal ions, one above and one below. While picrate oxygens [O(23), O(23′), O(25), O(25′)] are doubly coordinated, each crown oxygen coordinates to one metal only; four of the crown oxygens coordinate above the crown, the other four below. Each half DB24C8 crown, coordinating as a unit, thus performs a role similar to that of the whole BZ15C5 (benzo-15-crown-5) crown in the Cs(pic)(BZ15C5) and Ba(pic)$_2$(BZ15C5) structures (Venkatasubramanian, Joshi, Poonia, Montfort, Ernst & Hackert, 1985; Venkatasubramanian, Poonia, Clinger, Ernst & Hackert, 1984). Bond lengths for both complexes are presented in Table 3, and bond angles are given in Table 4.

Discussion

Among the crystal structures of sodium and potassium crown complexes now published there is a tendency for sodium (ionic radius 0·97 Å) to be in contact with its counterion (anion-paired) while the larger potassium cation is more likely to be coordinated only by the neutral ligand (charge-separated). This is representative of the trend evident for the first four alkali metals, in which decreasing charge density correlates with decreasing anionphilicity. K$^+$ (ionic radius 1·33 Å) crystallizes in both anion-paired and charge-separated environments, but seems to prefer the latter when the crown is either small enough for two crown molecules to coordinate the cation in a 'sandwich', as with BZ15C5 (Mallinson & Truter, 1972; Xu, Clinger, Hackert & Poonia, 1985), or large enough to encapsulate the cation, as in the case of DB30C10 (Bush & Truter, 1972). At the intermediate crown size represented by DB24C8, anion pairing is observed in all cases, usually with the crown encircling two cations and counterions coordinating in the axial directions. For these reasons DB24C8 was a logical choice to try to create a mixed Na/K complex in which the two metal ions occupy similar coordination environments.

The first reported structure of a mixed-metal Na/K crown complex appeared in Momany *et al.* (1987), featuring DB24C8 and the anion salicylate. In that structure, although cocrystallized, each metal cation complexed separately with its own crown and anions, thus affording a good opportunity to compare Na/K differential complexation tendencies. The stoichiometry in those subcomplexes is $(M^+\mathrm{sal}^-)_2$DB24C8, with two metal ions encircled by the neutral ligand and the axial directions occupied by two salicylates. Each K^+ ion is coordinated by four crown oxygens and three salicylate oxygens. The Na^+ ions also coordinate to three salicylate oxygens. However, in contrast with K^+, Na^+ ions pull their encircling crown into a tighter, sigmoidal conformation, coordinating more closely to three of the crown oxygens [average value 2·58 (2) Å] to the exclusion of the fourth crown oxygen [distance 3·03 (1) Å]. Sodium's six coordination distances average 2·51 (2) Å while potassium's seven distances average 2·72 (2) Å. The mode of binding is anion-paired in both subcomplexes. The shorter coordination sphere of sodium forces its crown into a puckered conformation while the crown conformation observed for the potassium complex is flat. Thus, in that structure, the two metal ions mold distinct coordination environments from the same compounds, thereby expressing their respective complexation 'preferences'.

The present structures have the same $(M^+X^-)_2$DB24C8 stoichiometry, and are similarly ion-paired, but, by placing the metal ions between stacked layers of crowns and counterions, create a single type of cation site and a single crown conformation. In the case of dipotassium complex (II), it is not surprising that the crown conformation closely resembles that of the $K_2(\mathrm{sal})_2$DB24C8 complex. The stacking of picrates with the benzyl groups of DB24C8, which has been observed previously (Hughes & Wingfield, 1977), also confers stability to this arrangement. What is surprising is that, even when half of the potassium cations are replaced by sodium (structure I), the crown remains in the 'potassium' conformation. Evidently the ligand/anion matrix, with the interacting π-orbitals of its stacked benzyl and phenyl rings, is sufficiently stable to accommodate either cation without distortion of the $P\bar{1}$ lattice.

This interpretation is supported and extended by the results of post-'final' refinements (in $P\bar{1}$) in which the two half-occupancy metal-ion sites were separated. The $K_{0\cdot5}$ and $Na_{0\cdot5}$ were manually displaced from the position of M^+ in Table 1, each by 0·1 Å, in opposite directions. Initial separations in each of the six axial directions resulted in the same final positions for the K^+ [0·366 (1), 0·619 (1), 0·0425 (8)] and the Na^+ [0·384 (3), 0·637 (2), 0·037 (2)]. This structure, with the cation sites separated by 0·26 (3) Å, has an *R* value of 0·075. This supports the idea that, in each unit cell, the metal ions might occupy slightly different microenvironments within the centrosymmetrically related coordination cavities.

Additional support for slightly different K^+ and Na^+ sites is seen in the effects on the coordination lengths obtained. It was found that this K^+ site possesses crown coordination lengths of 2·93 (1), 2·60 (1), 2·70 (1) and 2·66 (1) Å, while the corresponding distances from the Na^+ site are 3·13 (2), 2·58 (2), 2·50 (2) and 2·65 (2) Å. As in the NaK-salicylate-DB24C8 cocrystal, Na^+ appears to interact strongly with only three of the four crown oxygens. Furthermore, the coordination distances to the picrate oxygens from the two half-cation sites have average values of 2·71 (2) and 2·59 (3) for K^+ *versus* Na^+, reflecting again the respective coordination 'preferences' of the two cation species.

It thus appears that sodium is content to occupy the potassium-like crown cavity by shifting slightly so as to adjust its coordination lengths to a more sodium-like arrangement. Additional minor variations in the crown oxygen positions might also be expected in such a disordered lattice, further contributing to the relatively high *R* value associated with the mixed-metal complex.

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Structure of the Adipate Complex $[Na_2(C_6H_9O_4)_2(C_6H_{10}O_4)].2H_2O$ from Neutron Diffraction at 220 and 295 K

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Abstract

The crystal structure of sodium hydrogen adipate–adipic acid (2/1) dihydrate, $[Na_2(C_6H_9O_4)_2(C_6H_{10}O_4)].2H_2O$, $M_r = 518{\cdot}4$, has been determined from neutron diffraction data collected at 220 and 295 K. Crystals are monoclinic, space group $C2/m$, with $Z = 2$. At 295 K, $a = 9{\cdot}378\ (2)$, $b = 13{\cdot}379\ (5)$, $c = 10{\cdot}247\ (3)$ Å, $\beta = 95{\cdot}93\ (3)°$, $V = 1278{\cdot}8\ (7)$ Å^3, $D_n = 1{\cdot}346$, $D_m = 1{\cdot}348\ (1)$ g cm^{-3} (in dibromomethane/bromobutane), $\lambda = 1{\cdot}1588\ (2)$ Å, $\mu = 2{\cdot}186$ cm^{-1}, $F(000) = 176{\cdot}4$ fm, $R(F^2) = 0{\cdot}108$ for all 1995 nonequivalent reflections with $\sin\theta/\lambda < 0{\cdot}71$ Å^{-1}. The crystal structure is similar at 220 K except for reduced nuclear mean-square displacements. Hydrogen adipate subunits (called *A*) are linked end-to-end in infinite chains by very short O···O (2·44 Å) hydrogen bonds where the H nuclei are on centers of symmetry within the experimental error. The Na cation is octahedrally coordinated by O atoms from molecules *A* and also by non-ionized adipic acid molecules (called *B*). The *B* molecules have large mean-square nuclear displacements which are described in terms of anharmonicity and disorder.

Introduction

The present study was undertaken in order to determine the charge density distribution in the crystal structure of a salt of a simple carboxylic acid. An earlier candidate for such a study was lithium hydrogen adipate (He & Craven, 1984), but the crystals were unsuitable because the X-ray intensities were considered to be affected by excessive extinction. We turned to the sodium salt, but the crystals were again unsuitable for a charge density study because, as described below, some of the atoms in the structure have large mean-square displacements and are disordered. Nevertheless, the structure has some unusual features which we have investigated using neutron diffraction.

Although it would appear to be straightforward to obtain crystals of sodium adipate or sodium hydrogen adipate from aqueous solution by addition of sodium hydroxide or sodium carbonate to adipic acid, our repeated efforts to do so were unsuccessful. The product was instead a crystalline hydrated complex of adipic acid with sodium hydrogen adipate. The crystal structure (Fig. 1) was first determined from X-ray diffraction (Gao, Clancy & Craven, 1986), but the chemical nature of the structure remained uncertain because it depended critically

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