J. Am. Chem. Soc. **1993**, *115*, 9542–9546

Complexation of the Cations of Six Alkalides and an Electride by Mixed Crown Ethers

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Received May 10, 1993[⊗]

Abstract: It is well-known that crown ethers form sandwich complexes with the cations of many metals, but to date, the same crown ether formed both halves of the sandwich. Six new alkalides and an electride have now been synthesized that contain mixed sandwich complexes of alkali metal cations with 18-crown-6 (18C6), 15-crown-5 (15C5), and 12-crown-4 (12C4). The properties of Cs$^+$(18C6)(15C5)Na$^-$ and Cs$^+$(18C6)(15C5)e$^-$ demonstrate the existence of these stoichiometric compounds, but single-crystal X-ray diffraction studies yielded only the crystal systems and cell parameters. The crystal structures of K$^+$(18C6)(12C4)Na$^-$, K$^+$(18C6)(12C4)K$^-$, K$^+$(18C6)(12C4)K$^-$·18C6, Rb$^+$(18C6)(12C4)Na$^-$, and Rb$^+$(18C6)(12C4)Rb$^-$ were determined, thus verifying the thermodynamic stability of the mixed sandwich compounds relative to the "parent" compounds that contain only one type of complexant.

Introduction

Complexed cations sandwiched by crown ethers have been known for a long time, in both ordinary salts[1] and alkalides and electrides.[2,3] However, the complexation of cations by two different crown ether molecules to form mixed sandwich cations has not been previously reported. The formation of mixed sandwich complexes was first indicated in an experiment in which the electride Cs$^+$(18C6)$_2$e$^-$ was added to another electride, Cs$^+$(15C5)$_2$e$^-$, to serve as a temperature reference in ^{133}Cs NMR measurements.[4,5] In this experiment, a new peak appeared at a position that was different from that of either Cs$^+$(18C6)$_2$e$^-$ or Cs$^+$(15C5)$_2$e$^-$. This suggested the formation of a new electride that contained the mixed sandwich complex, Cs$^+$(18C6)(15C5)e$^-$.

When Cs$^+$ is complexed by two 18-crown-6 molecules, the average Cs$^+$–O distances (3.31–3.36 Å) are longer than those in the 1:1 complex in the salt Cs$^+$(18C6)·SCN$^-$(3.15 Å)[6] as well as those in Cs$^+$(15C5)$_2$e$^-$ (3.15 Å).[7] This suggests that the two crown ether molecules in Cs$^+$(18C6)$_2$ make van der Waals contact with each other before they are fully in contact with the Cs$^+$ cation. Examination of space-filling models also demonstrates a "loose fit" for two 18C6 molecules. Similarly, the models of two 15C5 molecules do not fit together snugly when encapsulating a cesium cation. Replacing one 18C6 molecule with a 15C5 molecule could provide a better fit for the cation. Preliminary studies of the existence of Cs$^+$(18C6)(15C5)e$^-$, the synthesis and characterization of the corresponding sodide, Cs$^+$(18C6)(15C5)Na$^-$, and the syntheses and structures of five other mixed sandwich alkalides based on K$^+$(18C6)(12C4) and Rb$^+$(18C6)(12C4) are described in this paper.

Experimental Section

The synthesis of mixed sandwich alkalides and electrides followed the same procedures used for the normal sandwich compounds[2,8] except that two different crown ethers were used in a 1:1 mole ratio. The synthesis cell was cooled during evacuation to prevent loss of the more volatile 15-crown-5 or 12-crown-4. The procedures for the study of properties[9] as well as crystal growth and handling have been described in previous papers.[10,11] The ^{133}Cs and ^{23}Na MAS-NMR spectra were recorded with a Bruker WH180 spectrometer. The X-ray diffractometer used in structure determinations was a Nicolet P3 diffractometer.

Results and Discussion

Unit Cell Parameters of Cs$^+$(18C6)(15C5)Na$^-$ (I) and Cs$^+$(18C6)(15C5)e$^-$ (II) and Some Properties of the Sodide. Considerable effort went into the preparation and characterization of these two salts, since mixtures that contained the complexed cations Cs$^+$(18C6)$_2$, Cs$^+$(18C6)(15C5), and Cs$^+$(15C5)$_2$ occurred readily. Sandwich complexes of this type form in a number of solvents, and the exchange rates are generally fast on the NMR time scale.[12,13] By slow recrystallization it was possible to obtain polycrystalline samples that appeared to be homogeneous and whose properties indicated the presence of primarily the mixed sandwich compound. The ^{23}Na and ^{133}Cs MAS-NMR spectra confirmed the presence of Na$^-$ and complexed Cs$^+$ in all three compounds, Cs$^+$(18C6)$_2$Na$^-$, Cs$^+$(18C6)(15C5)Na$^-$ (I), and Cs$^+$(15C5)$_2$Na$^-$. The ^{23}Na chemical shift of −61 ppm for the compound I is diagnostic for Na$^-$.[14-16] The ^{133}Cs chemical shifts of the two "parent" compounds (−61 ppm for the former and +24 ppm for the latter) are characteristic for these complexed cations in crystalline alkalides, as shown in Table I, as well as for Cs$^+$(18C6)$_2$ in solution.[17] The ^{133}Cs chemical shift, −8 ppm, in the mixed sandwich compound lies between those of the two

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[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1993.

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0002-7863/93/1515-9542$04.00/0

Table I. Characteristic ^{133}Cs NMR Chemical Shifts of the Complexed Cations in Different Alkalides

compd	chem shift, ppm[a]
$Cs^+(18C6)_2Na^-$	−61
$Cs^+(18C6)_2K^-$	−58
$Cs^+(18C6)_2Rb^-$	−57
$Cs^+(18C6)(15C5)Na^-$	−8
$Cs^+(15C5)_2Na^-$	+24
$Cs^+(15C5)_2K^-$	+24
$Cs^+(15C5)_2Rb^-$	+29

[a] Chemical shifts are referenced to Cs^+ in infinitely dilute aqueous solution.

homocomplexant compounds. Rapid precipitation of samples that contained both crown ethers gave two or three peaks at the positions indicated above. Thus, the NMR spectra provide clear evidence for the formation of predominantly one type of mixed sandwich sodide.

The properties of $Cs^+(18C6)(15C5)e^-$ will be described in detail in a separate paper. Here we simply note that the ^{133}Cs NMR chemical shift and its temperature dependence are very different from those of $Cs^+(18C6)_2e^-$ and $Cs^+(15C5)_2e^-$, as are the electrical conductivity, the magnetic susceptibility, and the EPR behavior. Thus, there can be no doubt that a mixed electride is formed, even though disorder prevented the determination of its crystal structure (see below).

Crystallization of the sodide, I, from the mixed solvent system $MeNH_2$–Me_2O–Et_2O yielded well-formed reddish crystals. Black crystals with hexagonal symmetry were obtained by crystallizing the electride, II, from Me_2O–Me_3N mixtures. Attempts to determine the crystal structures with crystals obtained from several syntheses were unsuccessful. The diffraction power of typical mixed sandwich crystals was much lower than those of regular sandwich crystals of comparable size. Rotation photographs showed not only lower brightness of the spots but also some bright and dark areas within the outline of the crystal (when the crystal was sufficiently large). This indicated the presence of a mosaic structure in the crystal. In spite of these difficulties, it was possible to index the crystals as monoclinic for the sodide and hexagonal for the electride. The cell parameters are compared with those of the "parent" compounds in Table II.

Inspection of the cell parameters clearly shows that I and **II** are different from the "parent" compounds that have only one type of crown ether. In fact, **II** even belongs to a crystal system different from that of either of the single-complexant electrides. Although the diffraction data alone cannot confirm the presence of a single compound, they are consistent with the evidence from a variety of experiments that mixed sandwich compounds are thermodynamically more stable than those prepared from either 18C6 or 15C5 alone, even though the disorder is severe enough to prevent determination of the complete crystal structure. For the electride, the large size of the unit cell also mitigates against a complete structure determination.

Structures of Three Alkalides That Contain the K^+(18C6)(12C4) Mixed Sandwich Cation. One might logically assume that we carried out a directed search for other mixed sandwich alkalides and electrides after the discovery of the Cs^+(18C6)(15C5) compounds. However, the discovery of mixed sandwich alkalides from 18-crown-6 and 12-crown-4 was actually the result of a mistake! During an experiment, several polycrystalline samples, which were grouped together and labeled as the known sodide, $K^+(18C6)Na^-$, were combined in a crystal-growing apparatus that contained a mixed solvent, Me_2O–Et_2O, in an attempt to grow single crystals of $K^+(18C6)Na^-$. At the end of the slow cooling period, some green crystals were harvested, one of them was mounted on the X-ray diffractometer, and reflection data were collected. The structure, however, turned out to be the new mixed sandwich compound, $K^+(18C6)(12C4)Na^-$(**III**). Obviously, one or more of the sample tubes used in this experiment contained $K^+(12C4)_2Na^-$, which is a known compound that had been synthesized earlier.[18]

$K^+(18C6)(12C4)Na^-$ was then deliberately synthesized by combining stoichiometric amounts of 18-crown-6, 12-crown-4, K, and Na in a cell under an inert atmosphere. The routine synthesis procedures were used with $MeNH_2$ as the primary solvent and Et_2O as the cosolvent. These crystals are shiny green, which is unusual for alkalides. Both "parent" compounds, $K^+(18C6)Na^-\cdot 2MeNH_2$ and $K^+(12C4)_2Na^-$, are golden or reddish.

Two observations indicate that the new compound is thermodynamically more stable than either of the single-component sodides, $K^+(18C6)Na^-$ or $K^+(12C4)_2Na^-$. First, $K^+(12C4)_2Na^-$ can exist without decomplexing only in more polar solvents such as Me_2O or $MeNH_2$. When a cosolvent such as Et_2O or Me_3N is added to the solution in an attempt to precipitate the sodide, metal particles are precipitated, indicating partial decomplexation. Second, $K^+(18C6)Na^-$ crystallizes with two solvent molecules ($MeNH_2$), one on each side of the 18-crown-6 ring plane, and K^+ at the center of the ring.[19] When the crystals were subjected to high-vacuum pumping to remove excess solvent, the solvent molecules in the structure were also removed, the structure was destroyed, and only a powder pattern was observed by X-ray diffraction. Apparently, the complexed K^+(18C6) cation in the crystal requires solvent molecules for stabilization in order to provide the preferred coordination of K^+. No examples are known of the sandwiched complex ion $K^+(18C6)_2$.

Another mixed sandwich alkalide, $K^+(18C6)(12C4)K^-$(**IV**) (reddish in color), was synthesized and crystallized by using stoichiometric amounts of potassium metal (2 mol), 18-crown-6, and 12-crown-4. The third alkalide of the 18-crown-6 and 12-crown-4 family is $K^+(18C6)(12C4)K^-\cdot 18C6$ (**V**). It was obtained in an experiment that used an excess of crown ethers in an attempt to synthesize the mixed sandwich electride, $K^+(18C6)(12C4)e^-$. Instead of an electride, golden crystals were formed and the compound was found to be the alkalide (**V**) with an uncomplexed 18-crown-6 molecule in the structure.

A major problem in the determination of the structures of mixed sandwich alkalides and electrides is that all have some degree of disorder so that structure refinements are troublesome. As indicated above, the structures of the mixed sandwich compounds $Cs^+(18C6)(15C5)Na^-$ and $Cs^+(18C6)(15C5)e^-$ have not been solved. The structures of alkalides that contain K^+ and the mixed sandwich of 18-crown-6 and 12-crown-4 have shown different degrees of disorder, and in some structures there were a few atoms refined in the last stage of refinement as "nonpositive definite". This difficulty could be overcome by allowing a few non-H atoms to be refined isotropically.

In order to obtain better refinement, we used the data reduction and correction programs of Blessing[20] to process the raw reflection data before structure refinement. The structure refinement program used was either SDP[21] or TEXSAN.[22] In all structures, the positional and thermal parameters of some (in **III** and **V**) or all (in **IV**) hydrogen atoms were not refined. They were allowed to ride on the carbon atoms to which they belong. As described in the literature, the potassium cation complexed by 18-crown-6 can be in two different positions.[23,24] One is at the center of the plane defined by the six oxygens of the 18-crown-6 ring, and another is out of this plane. Both cases occur in alkalide structures.

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Table II. Cell Parameters of Sodides and Electrides That Contain the Cesium Cation Complexed by 18-Crown-6 and/or 15-Crown-5

compd	space group (or symmetry)	a, Å	b, Å	c, Å	β, deg	V, Å^3
$Cs^+(18C6)_2Na^-$	mono $C2/c$	13.581	15.684	17.429	93.16	3706.8
$Cs^+(18C6)(15C5)Na^-$	mono	12.8565	19.7471	13.4322	93.66	3382.3
$Cs^+(15C5)_2Na^-$	tri $P\bar{1}$	8.661	9.010	10.315		792.1
$Cs^+(18C6)_2e^-$	mono $C2/c$	13.075	15.840	17.359	92.30	3592.3
$Cs^+(18C6)(15C5)e^-$	hex	33.108	33.108	16.2656	120	15440
$Cs^+(15C5)_2e^-$	tri $P\bar{1}$	8.597	8.886	9.941		733.1

Table III. Crystallographic and Refinement Data for $K^+(18C6)(12C4)Na^-$ (III), $K^+(18C6)(12C4)K^-$ (IV), $K^+(18C6)(12C4)K^-\cdot 18C6$ (V), $Rb^+(18C6)(12C4)Na^-$ (VI), and $Rb^+(18C6)(12C4)Rb^-$ (VII)

	III	IV	V	VI	VII
space group	*Pnma*	*Pnma*	$P2_1/c$	*Pnma*	*Pnma*
cell params					
a, Å	13.735(5)	13.795(26)	15.857(8)	13.989(5)	14.063(10)
b, Å	13.679(5)	14.090(24)	21.059(13)	13.677(14)	14.167(10)
c, Å	16.885(7)	17.059(15)	14.535(7)	16.683(5)	17.030(10)
β, deg			88.898(40)		
Z	4	4	4	4	4
temp, K	210	210	210	180	180
no. of reflctns used in refinmt with $F_o^2 > 3\sigma(F_o^2)$	1102	886(2σ)	2280	2060	1135
no. of variables	211	147	441	147	147
R	0.059	0.037	0.055	0.072	0.059
R_w	0.047	0.039	0.063	0.050	0.031
high peak in final diff map, e/Å^3	0.25	0.15	0.39	0.66	0.48

Table IV. Positional and Thermal Parameters for $K^+(18C6)(12C4)Na^-$

atom[a]	x	y	z	B(eq), Å^2
K	0.3937(1)	0.2500	0.3461(1)	3.78(8)
Na	0.1075(3)	0.7500	0.3607(2)	9.2(3)
O1	0.5717(3)	0.2500	0.4411(3)	4.5(3)
O4	0.5031(3)	0.0676(3)	0.3843(3)	5.3(2)
O7	0.4254(3)	0.0780(4)	0.2334(3)	6.3(3)
O10	0.3477(4)	0.2500	0.1738(4)	7.0(4)
O11	0.2159(3)	0.3523(3)	0.3411(2)	6.1(2)
O14	0.3009(3)	0.3535(4)	0.4933(3)	7.8(3)
C2	0.5696(5)	0.1625(6)	0.4872(4)	6.2(4)
C3	0.5828(5)	0.0782(6)	0.4337(5)	6.5(5)
C5	0.5177(7)	−0.0069(6)	0.3266(5)	7.0(5)
C6	0.4322(7)	−0.0113(7)	0.2744(6)	7.8(6)
C8	0.3474(7)	0.0772(8)	0.1795(6)	9.1(6)
C9	0.3578(6)	0.162(1)	0.1289(5)	9.6(7)
C12A	0.1655	0.1053	0.3962	11(1)[b]
C12B	0.2098	0.4394	0.4062	22(4)[b]
C13A	0.2225	0.3975	0.4887	10(1)[b]
C13B	0.2395	0.0643	0.4366	3.9(7)[b]
C15A	0.2967	0.2738	0.5661	8(1)[b]
C15B	0.2475	0.1731	0.5485	8(1)[b]
C16A	0.1420	0.2806	0.2974	3.8(6)[b]
C16B	0.1346	0.1839	0.3436	6.1(8)[b]

[a] O1, O4, O7, O10, C2, C3, C5, C6, C8, and C9 belong to 18-crown-6. O11, O14, C12A, C12B, C13A, C13B, C15A, C15B, C16A, and C16B belong to 12-crown-4. [b] The positions of these atoms were not refined and the multiplicities of the atoms are as follows: C12A, 0.65; C12B, 0.35; C13A, 0.525; C13B, 0.475; others, 0.50.

In $K^+(18C6)Na^-\cdot 2MeNH_2$,[19] K^+ is located exactly in the oxygen ring plane with one $MeNH_2$ molecule on each side of the plane. In the cases of mixed (18C6)(12C4) complexed alkalides, K^+ is about 1 Å out of the plane of the six oxygens of 18-crown-6.

(a) Structure of $K^+(18C6)(12C4)Na^-$ (III). The crystal structure data are listed in Table III along with those of other structures, and the positional and thermal parameters are shown in Table IV. Bond distances, bond angles, and other crystallographic data for this compound and others to follow are included in the supplementary material. Figures 1 and 2 show the single-molecule drawing and the ORTEP stereo packing diagram, respectively, for $K^+(18C6)(12C4)Na^-$.

During the refinement it was found that the carbon atoms on 12-crown-4 have large temperature factors (near 20 Å^2 for B). This was caused primarily by the mirror symmetry of the space group (*Pnma*). The 12-crown-4 molecule does not usually possess mirror symmetry. The oxygens of the 12-crown-4 molecule were refined well with normal temperature factors, indicating that they are well described by the mirror symmetry. On the other hand, the carbon atoms had to be divided into two configurations which are mirror images of each other. These carbons were thus refined with disorder, and except for that of one atom (C12B), the temperature factors were much lower. Refinement with another space group ($Pna2_1$) with lower symmetry did not give improvement.

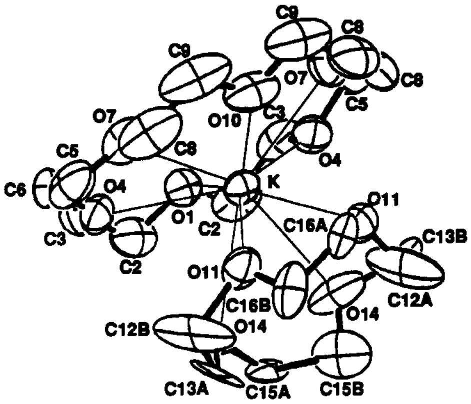

Figure 1. Single-molecule drawing for $K^+(18C6)(12C4)Na^-$.

The K^+ ion is 1.15 Å out of the least-squares plane of the six 18-crown-6 oxygen atoms and 2.19 Å out of the plane of the four 12-crown-4 oxygens. The K^+–O distances in III are rather uniform for the oxygens of 18-crown-6 (2.925–3.058 Å) but are distributed for the oxygens of 12-crown-4 (2.815, 3.131 Å). The bond distances and angles for atoms of 18-crown-6 are well within the normal values, but those of 12-crown-4 deviate substantially from normal, probably due to the disorder.

In contrast to those of the 18-crown-6 configuration, in which the oxygens and carbons alternate on both sides of the least-squares plane of the six oxygens, the carbons of 12-crown-4 are all on one side of the plane of the four oxygens, away from the K^+ ion.

(b) Structure of $K^+(18C6)(12C4)K^-$ (IV). This compound, $K^+(18C6)(12C4)K^-$, is isostructural with III. Its crystal structure data are listed in Table III.

Again the refinement was carried out by disordering the carbon atoms of 12-crown-4 and refining them isotropically. The

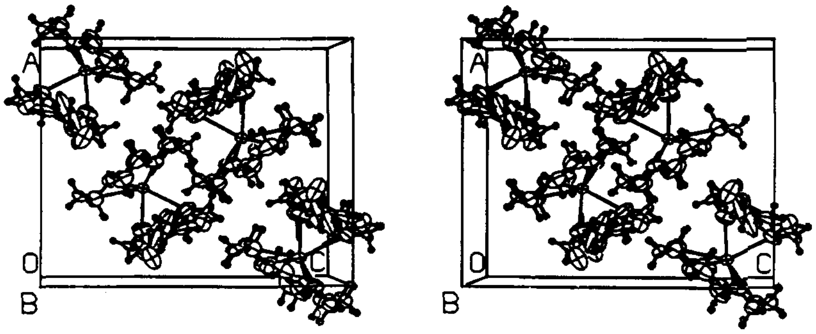

Figure 2. ORTEP stereo packing diagram for $K^+(18C6)(12C4)Na^-$.

complexed cation is very similar to that in compound III. The cation K^+ is 1.13 Å out of the 18-crown-6 oxygen plane, with oxygens and carbons of the 18-crown-6 ring alternately above and below the plane. All carbon atoms of 12-crown-4 are on the other side of the oxygen plane at distances that range from 0.44 to 1.14 Å from the plane. The K^+–O distances vary from 2.93 to 3.06 Å for oxygens of 18-crown-6 and are 2.82 and 3.13 Å for the oxygens of 12-crown-4. The bond distances and angles are normal for those in 18-crown-6 but deviate from normal values for those in 12-crown-4.

(c) Structure of $K^+(18C6)(12C4)K^-\cdot 18C6$ (V). This compound was the first alkalide observed that has a "free" crown ether molecule in the structure. The crystal structure data for this compound are listed in Table III, its positional and thermal parameters are shown in Table V, and Figure 3 shows the ORTEP packing diagram. This structure was refined well, and only the eight carbon atoms of 12-crown-4 have relatively high temperature factors (B from 10.0 to 14.4 Å^2). C21 and C26 were refined isotropically to avoid the "nonpositive definite" status. K^+–O bond distances range from 2.80 to 3.17 Å. Bond distances for C–C or C–O bonds range from 1.27 to 1.52 Å, and bond angles for C–C–O and C–O–C, from 107.0 to 127.0°.

The potassium cation is 1.28 Å out of the plane of the six 18-crown-6 oxygen atoms and 2.13 Å out of the plane of the four 12-crown-4 oxygens. These two planes are almost parallel to one another (dihedral angle 6.8°). The complexed cation $K^+(18C6)(12C4)$ is very similar to those in the other two compounds (III and IV). The "free" crown ether molecule is located between the large cations and anions and has its regular shape with oxygens and carbons alternating in and out of the least-squares plane of the oxygens.

Structures of Two Alkalides That Contain the $Rb^+(18C6)(12C4)$ Mixed Sandwich Cation. Since rubidium is very similar to potassium, it was natural to investigate the Rb–18C6–12C4 system along with the K–18C6–12C4 system. Two alkalides were synthesized that contain mixed sandwich complexes of Rb^+, and their crystal structures were determined.

(a) Structures of $Rb^+(18C6)(12C4)Na^-$ (VI) and $Rb^+(18C6)(12C4)Rb^-$ (VII). These two compounds are isostructural with the corresponding potassium compounds (III and IV). Compound VI is bright green. Table III gives the crystallographic data. The structural features of these compounds are almost identical to those of III and IV, except that the cation Rb^+ is 1.24 (VI) and 1.20 (VII) Å from the oxygen atom ring plane of 18-crown-6 and 2.30 Å from that of the 12-crown-4 ring, distances slightly larger than those in the potassium compounds.

Summary

While we do not have the structural or thermodynamic data needed to compare the stability of the mixed 18-crown-6–15-crown-5 cesium cation with those of the two "parent" sandwich complexes, we have been able to obtain structural information on the 18-crown-6–12-crown-4 potassium and rubidium alkalides.

Table V. Positional and Thermal Parameters for $K^+(18C6)(12C4)K^-\cdot 18C6$

atom[a]	*x*	*y*	*z*	*B*(eq), Å^2
K	0.7421(2)	0.8037(1)	0.1583(2)	3.62(6)
K2	0.2423(3)	0.6308(2)	–0.0050(3)	9.2(1)
O1	0.8504(5)	0.8595(3)	0.3074(5)	4.3(2)
O4	0.6729(5)	0.8643(3)	0.3443(5)	4.3(2)
O7	0.5600(4)	0.7977(3)	0.2351(5)	4.4(2)
O10	0.6264(5)	0.6842(3)	0.1624(5)	4.3(2)
O13	0.8003(4)	0.6701(3)	0.1230(5)	4.0(2)
O16	0.9087(5)	0.7487(3)	0.2239(5)	4.1(2)
O19	0.7071(5)	0.9315(4)	0.1219(5)	5.7(2)
O22	0.8669(5)	0.8827(3)	0.0676(6)	5.9(2)
O25	0.8029(5)	0.7949(4)	–0.0491(6)	6.8(3)
O28	0.6371(6)	0.8369(4)	0.0057(5)	6.7(3)
O101	0.3756(5)	0.9106(3)	0.0558(5)	4.5(2)
O104	0.5309(4)	1.0097(3)	–0.1840(5)	4.4(2)
O107	0.4421(5)	0.8977(3)	–0.1273(5)	4.2(2)
O201	0.8871(5)	1.0983(3)	0.0738(5)	5.1(2)
O204	0.9169(5)	1.0729(4)	–0.1203(5)	5.5(2)
O207	0.9891(5)	0.9538(4)	–0.1893(5)	5.4(2)
C2	0.8135(7)	0.8888(5)	0.3868(8)	5.0(4)
C3	0.7278(7)	0.9155(5)	0.3625(8)	5.4(4)
C5	0.5880(8)	0.8855(5)	0.3292(8)	5.5(4)
C6	0.5357(8)	0.8273(5)	0.3174(8)	5.1(4)
C8	0.5078(7)	0.7438(5)	0.2178(8)	4.6(4)
C9	0.5453(7)	0.7099(5)	0.1377(8)	5.3(4)
C11	0.6586(8)	0.6407(5)	0.0963(8)	5.2(4)
C12	0.7420(7)	0.6191(5)	0.1277(8)	4.3(3)
C14	0.8841(7)	0.6526(5)	0.1429(7)	3.9(3)
C15	0.9375(7)	0.7110(5)	0.1483(8)	4.7(3)
C17	0.9628(7)	0.8010(5)	0.2413(8)	5.6(4)
C18	0.9300(7)	0.8335(5)	0.3285(8)	5.0(4)
C20	0.7778(8)	0.9690(6)	0.113(1)	10.0(5)
C21	0.8492(9)	0.9462(6)	0.079(1)	8.1(4)[b]
C23	0.899(1)	0.8711(8)	–0.0189(8)	10.7(6)
C24	0.861(1)	0.8348(7)	–0.0795(9)	14.4(6)
C26	0.7311(9)	0.7940(7)	–0.106(1)	8.0(4)[b]
C27	0.6554(9)	0.817(1)	–0.076(1)	14.4(7)
C29	0.604(1)	0.8995(6)	0.020(1)	13.9(6)
C30	0.6429(9)	0.9432(7)	0.0624(9)	9.6(5)
C102	0.6184(8)	1.0998(6)	–0.1510(8)	5.3(4)
C103	0.6111(7)	1.0368(6)	–0.2007(8)	4.8(4)
C105	0.5157(8)	0.9565(5)	–0.2429(8)	4.8(3)
C106	0.4335(8)	0.9264(5)	–0.2135(7)	4.9(4)
C108	0.3691(7)	0.8675(5)	–0.0940(8)	4.6(3)
C109	0.3768(8)	0.8526(5)	0.0050(8)	5.9(4)
C202	0.8719(8)	1.1411(5)	0.0017(9)	6.5(4)
C203	0.8471(7)	1.1074(6)	–0.0847(8)	5.7(4)
C205	0.8907(8)	1.0401(6)	–0.2005(9)	6.5(4)
C206	0.9687(9)	1.0085(6)	–0.2431(9)	6.7(4)
C208	1.0627(8)	0.9238(6)	–0.2232(8)	6.0(4)
C209	1.0918(7)	0.8723(5)	–0.1594(8)	5.6(4)

[a] O1, O4, O7, O10, O13, O16, C2, C3, C5, C6, C8, C9, C11, C12, C14, C15, C17, and C18 belong to the 18-crown-6 which complexed the K^+ ion. O19, O22, O25, O28, C20, C21, C23, C24, C26, C27, C29, and C30 belong to 12-crown-4. O101, O104, O107, O201, O204, O207, C102, C103, C105, C106, C108, C109, C202, C203, C205, C206, C208, and C209 belong to the free 18-crown-6. [b] Refined isotropically.

The 12-crown-4 oxygens pull the central potassium cation from the center of the ring of 18-crown-6 to a position that is about

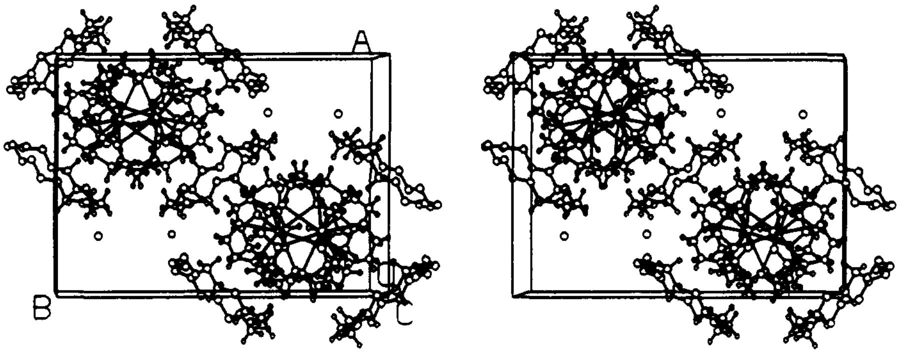

Figure 3. ORTEP stereo packing diagram for $K^+(18C6)(12C4)K^-\cdot 18C6$. Some hydrogen atoms of the free 18-crown-6 are not shown.

1 Å from the plane. Thus, axial ligands such as $MeNH_2$ are no longer needed to provide additional coordination for the K^+ cation. The exposure of the K^+ cation observed in the structure of $K^+(12C4)_2Na^-$ due to size mismatching of K^+ and 12-crown-4 is dramatically reduced by replacing one 12-crown-4 molecule with an 18-crown-6 molecule. This increases the stability of the compounds.

Mixed crown ether sandwich complexed cations represent a new type of coordination compound in host–guest chemistry. Thermodynamic studies on these new complexes should yield more information on the host–guest phenomenon. Unfortunately there are no suitable reversible electrodes for alkali metals other than sodium[25,26] so that one cannot use electrochemistry to measure the thermodynamics of formation of these mixed sandwich alkalides and electrides. Studies of ordinary salts in the presence of two different crown ethers should provide further information about the relative stabilities of the mixed sandwich complexes compared with complexes that contain only a single type of crown ether.

Acknowledgment. This research was supported in part by NSF Solid State Chemistry Grants DMR 87-14751 and DMR 90-17292 and by the Michigan State University Center for Fundamental Materials Research. The X-ray diffractometer used was purchased under NSF Grant CHE-84-03823. We are grateful to Dr. Donald Ward for assistance with the structure determinations, to Dr. Steven Dawes for preliminary studies of mixed sandwich complexes, and to Michael Wagner and Kerry Reidy for additional studies on $Cs^+(18C6)(15C5)e^-$(to be published).

Supplementary Material Available: Tables of bond distances and angles, positional and thermal parameters, general temperature factor expressions, torsion angles, and least-squares planes for compounds **III–VII** and a single-molecule drawing of **V** (30 pages); tables of structure factors for compounds **III–VII** (74 pages).

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