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Molecular Structures of Cation⋯π(Arene) Interactions for Alkali Metals with π- and σ-Modalities

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Abstract: The monovalent cations of Na^+, K^+, Rb^+, and Cs^+ derived from the highly electropositive alkali metals represent prototypical charged spheres that are mainly subject to relatively simple electrostatic and solvation (hydration) forces. We now find that the largest of these Rb^+ and Cs^+ are involved in rather strong cation⋯π(arene) interactions when they are suitably disposed with the ambifunctional hexasubstituted benzene C_6E_6. The ether tentacles (E = methoxymethyl) allow these cations to effect η^1-bonding to the benzene center in a manner strongly reminiscent of the classical σ-arene complexes with positively charged electrophiles where $Z^+ = CH_3^+$, Br^+, Cl^+, Et_3Si^+, etc. The somewhat smaller potassium cation is involved in a similar M^+⋯π(arene) interaction that leads to η^2-bonding with the aromatic center in the π-mode previously defined in the well-known series of silver(I)/arene complexes. We can find no evidence for significant Na^+⋯ π(arene) interaction under essentially the same conditions. As such, the σ-structure of the Rb^+ and Cs^+ complexes and π-structure of the K^+ complex are completely integrated into the continuum of σ−π bondings of various types of electrophilic (cationic) acceptors with arene donors that were initially identified by Mulliken as charge-transfer.

Introduction

Attractive electrostatic interactions of simple metal ions such as Na^+ and K^+ with benzene are known from gas-phase studies[1,2] and have been extensively analyzed theoretically.[3−5] However, the wider implications to the condensed phase were more recently inspired by Burley and Petsko,[6] who suggested that intramolecular cationic interactions with (electron-rich) aromatic centers play important roles in protein structures, and by Dougherty et al.[7] who recognized that the cation⋯π interaction constituted a general (noncovalent) binding force.

Although the metal-ion/benzene interactions of 15−40 kcal mol^{-1} in the gas phase may appear promising, most attempts to complex alkali-metal cations (M^+) with simple arenes in solution have failed because such bonding energies are insufficient to offset the penalty incurred in cation desolvation and counterion separation. In the majority of cases, the modest gains from M^+⋯π(arene) interactions are thus unable to compete with the loss of polar M^+⋯hydrophilic interactions. However, there are several notable studies of successful cation⋯π(arene) binding of alkali metals in the (crystalline) solid state. Thus, Michl and co-workers[8] were able to exploit the relatively weak electrostatic interactions extant between $M^+ = K^+$, Rb^+, and Cs^+ with the large (bulky icosahedral) carboranate $X^- = CB_{11}(CH_3)_{12}^-$ to prepare a remarkable series of crystalline salts $(C_6H_6)_2M^+X^-$ in which the alkali metal cations are centrosymmetrically sandwiched between benzene molecules. Alternatively, Dougherty and co-workers[9] synthesized various artificial (macrocyclic) receptors containing multiple aromatic components to characterize different cation⋯π(arene) interactions. A third approach primarily by Gokel and co-workers[10] employed crown (lariat) ethers as primary binding sites for alkali-metal cations, in which the relevant π-interactions occurred to aromatic substituents. The latter approach seems to offer a variety of highly flexible possibilities for studying weak (metal)-cation⋯π(arene) interactions.

Our interest in cation⋯π(arene) interactions has a strong *structural* bias derived from our mechanistic focus on various M^+-assisted aromatic activations.[11] Importantly, the structural

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(1) For early studies, see: (a) Woodlin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 501. (b) Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6133.

(2) (a) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85*, 1814. (b) Guo, B. C.; Purnell, J. W.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1990**, *168*, 155.

(3) (a) Tsuzuki, S.; Yoshida, M.; Uchimaru, T.; Mikami, M. *J. Phys. Chem.* **2001**, *105*, 769. (b) Amicangelo, J. C.; Armentrout, P. B. *J. Phys. Chem.* **2000**, *104*, 11420.

(4) Feller, D.; Dixon, D. A.; Nicholas, J. B. *J. Phys. Chem.* **2000**, *104*, 11414.

(5) (a) Ikuta, S. *J. Mol. Struct.* **2000**, *530*, 201. (b) Pullman, A.; Berthier, G.; Savinelli, R. *J. Mol. Struct.* **2001**, *537*, 163.

(6) Burley, S. K.; Petsko, G. A. *FEBS Lett.* **1986**, *203*, 139.

(7) (a) Shepodd, T. J.; Petti, M. A.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1983. (b) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261*, 1708. (c) Dougherty, D. A. *Science* **1996**, *271*, 163.

(8) (a) King, B. T.; Noll, B. C.; Michl, J. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1001. See also an early study: (b) Atwood, J. L.; Crissinger, K. D.; Rogers, R. D. *J. Organomet. Chem.* **1978**, *155*, 1.

(9) For a review, see: Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303.

(10) (a) Gokel, G. W.; De Wall, S. L.; Meadows, E. S. *Eur. J. Org. Chem.* **2000**, 2967. (b) Meadows, E. S.; De Wall, S. L.; Barbour, L. J.; Gokel, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3092. (c) Although our primary focus is in simple cation⋯π(arene) interactions with ethereal tethers, there are other examples involving sulfur and phosphorus tethers. See, for example: Rabe, G. W.; Liable-Sands, L. M.; Incarvito, C. D.; Lam, K.-C.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 4342. Niemeyer, M.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 7264.

(11) Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **2000**, *65*, 6807.

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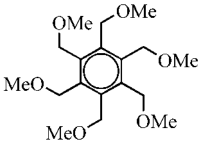
Chart 1



features inherent to weak cation bindings of the alkali metals, where $M^+ = Na^+$, K^+, Rb^+, and Cs^+, pose an especially difficult problem of design and synthesis because they require *minimal* geometrical constraints of adjutant ligand sites for these monovalent cations which basically represent featureless spheres of progressively increasing size.[12] We now report on the polyfunctional arene ligand C_6E_6 with ether groups (E) to serve as intramolecular guides for the delivery of alkali-metal cations to the benzenoid π-center (C_6). The planar projection in Chart 1 shows that C_6E_6 constitutes a "reverse" lariat ether in the sense that it consists of a π-arene nucleus with multiple ethereal substituents rather than a crown ether nucleus with multiple π-aromatic substituents.

Because C_6E_6 is comprised of a benzenoid ring having short links to six ethereal oxygens, it statistically provides a reasonable probability for M^+ to be (weakly) coordinated to at least a pair of ether groups and thus be brought to within the target sphere where the $M^+\cdots\pi$(arene) interactions can then take place.[13] In this study, we also paid particular attention to suitable low-coordinating anions for complexation and cocrystallization of C_6E_6 with the alkali metal salts for X-ray crystallographic analysis.

Results

I. Synthesis and Conformational Structure of the Ethereal Arene Ligand. Hexakis(methoxymethyl)benzene C_6E_6 was prepared in high yields by the multiple brominations of hexamethylbenzene followed by exhaustive treatment with sodium methoxide.[14,15] Crystallization from ethanol solution yielded colorless monoclinic crystals containing two crystallographic (nonequivalent) centrosymmetric units with identical geometries but different crystal environments. X-ray crystallographic analysis shows that C_6E_6 exists in the stable conformation **A** with the six ethereal substituents (E = methoxymethyl) turned alternately above and below the benzene plane.[16] Such a molecular conformation minimizes intramolecular repulsions of the α-hydrogens, as is typical for hexa(alkyl)-substituted benzenes such as hexaethylbenzene.[17] Importantly, the three oxygens on each C_6 face do not impede access to the benzene ring because they are situated 3.2−3.5 Å away from its main (C_3) symmetry axis (Figure 1). The crystal structure of C_6E_6 is additionally stabilized by "unconventional" hydrogen bonds [i.e., $C-H\cdots O$ with $H\cdots O$ 2.5−2.6 Å[18] and $C-H\cdots C(Ar)$ with $H\cdots C$ 2.93 Å[19]] owing to the enhanced acidity of the terminal methoxy groups and the heightened electron-donor ability of the hexa(alkyl)benzene ring.[20] The latter is also manifested in the unique charge-transfer complex of C_6E_6 and carbon disulfide obtained by mere crystallization from a concentrated solution. The structural diagram of the [1:1] complex in Figure 2 shows the intimate inner-sphere separation (3.08 Å) of sulfur from the mean aromatic plane which is 0.4 Å closer than that expected from the sum of the van der Waals radii.[21] It is noteworthy that the structure/conformation of C_6E_6 in this charge-transfer crystal is the same as that present in the pure crystal (Figure 1).

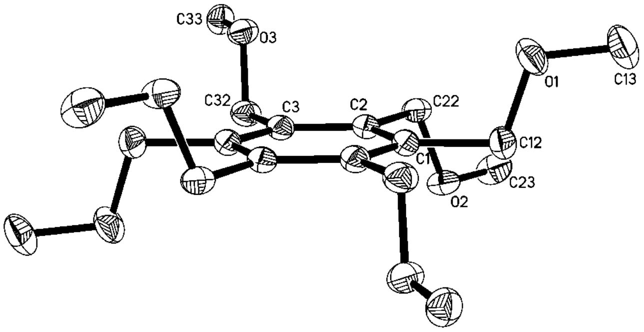


Figure 1. The ORTEP view of hexakis(methoxymethyl)benzene C_6E_6 showing alternate orientations of the ether substituents. Hydrogen atoms are removed for clarity. Thermal ellipsoids are shown within 50% probability level.

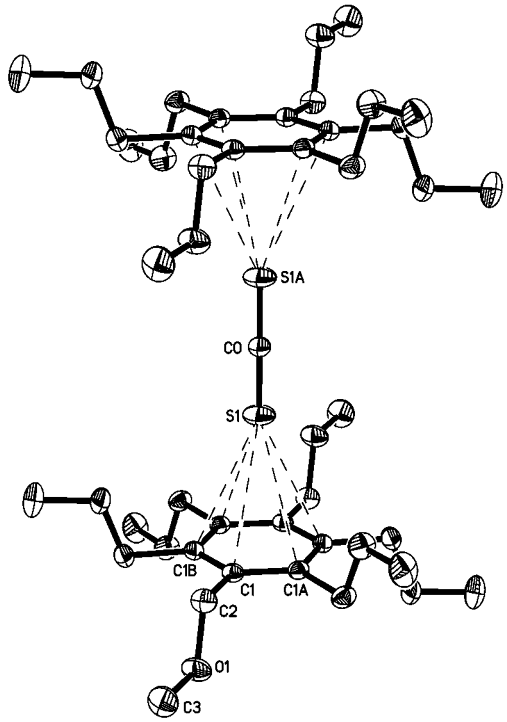


Figure 2. The ORTEP view of the sandwich structure of the inner-sphere complex of hexakis(methoxymethyl)benzene with carbon disulfide. Hydrogen atoms are omitted for clarity.

II. Crystallization of Weak Cation⋯π(Arene) Complexes with Alkali Metals. The weak bonding of alkali-metal cations to C_6E_6 is readily apparent from conformational considerations arising from a given ethereal oxygen which is separated too far

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(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 123−125.

(13) Here, we are concerned that coordination to the ether adjutant serves merely to "gather in" the alkali-metal cation, but not so strongly as to be a dominant force by itself (as in crown ethers).

(14) Compare: (a) Backer, H. J. *Rev. Trav. Chem.* **1935**, *54*, 745, 833. (b) Závada, J.; Pánková, M.; Holý, P.; Tichý, M. *Synthesis* **1994**, 1132.

(15) Hardy, A. D. U.; MacNicol, D. D.; Wilson, D. R. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1011.

(16) The torsion angles in $C_6-CH_2-O-CH_3$ lie in the range 171.5−177.3(2)°.

(17) Barnes, J. C.; Chudek, J. A.; Hunter, G.; Blake, A. J.; Dyson, P. J.; Johnson, B. F. G.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **1995**, *91*, 2149.

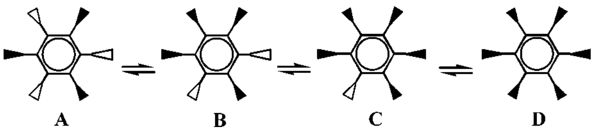
(18) (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. (b) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.

(19) (a) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669. See also: (b) Lindeman, S. V.; Kosynkin, D.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13268.

(20) See: Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 8985.

(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Chart 2



(in the most stable conformer **A** in Chart 2) from any neighboring ether to allow multiple coordination (as in crown-ether complexations).[22] As a result, numerous and varied attempts to isolate the desired mixed complexes with alkali-metal salts merely led to the phase separation of either pure component C_6E_6 or M^+X^- (see Experimental Section). Because the problem was undoubtedly exacerbated by the stronger electrostatic forces inherent to simple alkali-metal salts, we investigated a series with the large tetraphenylborate counteranion. Potassium tetraphenylborate did not yield suitable crystals with C_6E_6, and the rubidium and cesium salts yielded mixed crystals of composition $C_6E_6[M^+BPh_4^-]$ in which the alkali-metal cations were coordinated with only the tetraphenylborate moiety.[23] However, sodium tetraphenylborate afforded the [1:1] target complex $[C_6E_6Na^+]BPh_4^-$ by careful evaporation of an equimolar solution in ethanol, presumably allowed by the weaker interionic forces than those present in the potassium, rubidium, and cesium analogues.[24] For the latter, we were able to isolate crystalline complexes of the desired structure $[C_6E_6M^+]X^-$ using hexafluoroantimonate salts ($X = SbF_6^-$) from a mixed solvent (CH_3CN/CH_3OH) containing C_6E_6 and $M^+SbF_6^-$ prepared in situ from potassium bromide, rubidium, and cesium iodides with silver hexafluoroantimonate (see Experimental Section for details).

III. Cation Bindings of Alkali Metals to C_6E_6. The conformational mobility of C_6E_6 in solution involves the successive rotation of methoxymethyl substituents to transform the stable alternating conformer **A** to the least-stable all-syn conformer **D**, as schematically depicted in Chart 2.

The intermediate conformers **B** and **C** have two and four (nonequivalent) coordination sites, each containing a pair of neighboring *syn*-methoxymethyl groups.[25] Indeed, the following molecular structures of the Na^+, K^+, Rb^+, and Cs^+ complexes derive from these C_6E_6 conformers.

A. Sodium Ion Complex of C_6E_6. The sodium ion complex of C_6E_6 is a tetrahydrate, in which the centrosymmetric dicationic cluster $[H_2ONa^+(\mu^2\text{-}H_2O)_2Na^+OH_2]$ is encapsulated by two molecules of C_6E_6, as shown in Figure 3. The C_6E_6 moiety exists in conformation **D** with all six methoxy groups turned toward the sodium cations.[26] The general architecture of the $C_6E_6Na^+$ complex is determined largely by three factors: (1) sodium cations which are coordinated by a pair of *ortho*-ether groups, (2) the radius of a single sodium cation which is insufficient to fill out the cavity over the benzene ring of C_6E_6, and (3) the ionic radius of Na^+ which is not large enough to allow a single cation to coordinate two molecules of C_6E_6 without severe interligand repulsion. As a result, not one but two sodium cations are fitted into the molecular cavity with the aid of two bridging aqua ligands at the interionic $Na^+\cdots Na^+$ distance of 3.43 Å. This disodium dihydrate unit links a pair of C_6E_6 donors through two additional (terminal) water molecules to maintain an overall unhindered sandwich structure − keeping the distance of 7.24 Å between parallel benzene rings. Thus, as a whole, the sodium moiety generally has a (elongated) globular structure with a hydrophilic nucleus and hydrophobic surface. Although the sodium cations in this interesting structure are well insulated from their tetraphenylborate counteranions, the diminished electrostatics are not sufficient to promote a measurable cation···π(arene) interaction (vide infra).

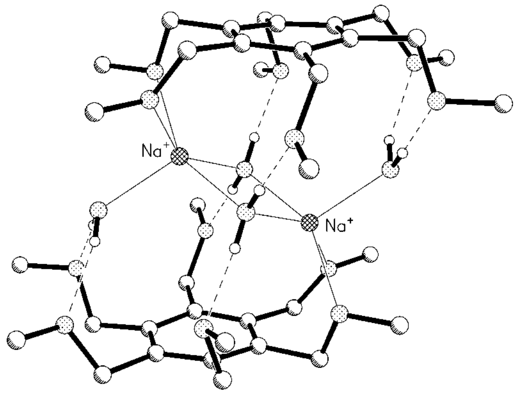


Figure 3. Structure of the Na^+ complex of C_6E_6. Coordination bonds $Na^+\cdots O$ are shown by single lines, and the hydrogen bonds $O-H\cdots O$ are shown by dashed lines.[26b] Aliphatic hydrogens and BPh_4^- counterions are omitted for clarity.

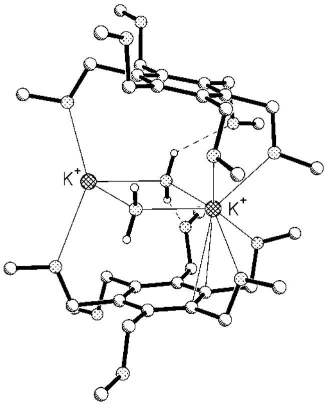


Figure 4. Structure of the K^+ complex of C_6E_6. Coordination bonds $K^+\cdots O$ and the shortest contacts $K^+\cdots C(Ar)$ are shown by single lines. Hydrogen bonds $O-H\cdots O$ are shown by dashed lines.[26b] Aliphatic hydrogens and $[SbF_6]^-$ counterions are omitted for clarity.

B. Potassium Ion Complex of C_6E_6. The crystal of the potassium complex $C_6E_6K^+$ in Figure 4[26b] is somewhat reminiscent of the sodium complex in that the sandwich structure

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(22) More than one ether group is likely to be needed for gathering in the alkali-metal cation. See ref 13.

(23) These mixed crystals (see Experimental Section) consist of alternating layers of C_6E_6 and $M^+BPh_4^-$. Compare: Hoffman, K.; Weiss, E. *J. Organomet. Chem.* **1974**, *67*, 221.

(24) For the crystallographic study relating to the origin of the different properties of $Na^+BPh_4^-$ as compared with its K^+, Rb^+, and Cs^+ analogues, see: Arnott, S.; Abrahams, S. C. *Acta Crystallogr.* **1958**, *11*, 449.

(25) (a) Molecular mechanics calculations indicate the relative stabilities of these conformers to decrease monotonically in the order 0, +2.8, +5.5, and +7.7 kcal/mol for conformers **A** through **D**, respectively. (b) We take the conformational mobility of C_6E_6 to be analogous (except for possible hydrogen bonding) to that of the similar hexaethylbenzene ligand examined by Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073.

(26) (a) This highly hindered conformation arises from dominant coordinations of all six ethers of C_6E_6 with the Na^+/water cluster − two ethereal oxygens being involved in hydrogen bonds with terminal aqua ligands ($H\cdots O$ of 1.91 and 2.01 Å), two ethers making hydrogen bonds with bridging aqua ligands ($H\cdots O$ of 1.89 and 1.96 Å), and the remaining two ethers being directly coordinated to the sodium cation ($Na^+\cdots O$ of 2.337 and 2.369 Å). (b) The molecular structure is shown in the figure as a stick/ball representation for reasons of clarity, and the corresponding more elaborated (but visually overcrowded) ORTEP diagram is presented in the Supporting Information.

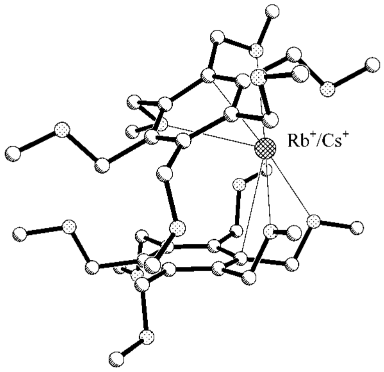


Figure 5. Structure of the Rb^+ complex of C_6E_6 (isostructural to the Cs^+ complex). Coordination bonds $Rb^+(Cs^+)\cdots O$ and the shortest contacts $Rb^+(Cs^+)\cdots C$ are shown by single lines.[26b] The coordinated $[SbF_6]^-$ counterion was omitted for clarity.

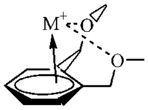
consisting of two C_6E_6 moieties intercalates a di(potassium)-di(aqua) cluster $[K^+(\mu^2\text{-}H_2O)_2K^+]$, in which the cations are more distant from one another ($K^+\cdots K^+$ of 4.10 Å) owing to the larger ionic radius.[27] Interestingly, this large diatomic moiety can no longer be accommodated within the molecular cavity of C_6E_6, and only a single potassium ion remains efficiently coordinated to a pair of *ortho*-ether groups with $K^+\cdots O$ distances of 2.55−3.07 Å. (The other potassium ion is pushed outside the cavity and thus exposed to short ionic contacts with two disordered SbF_6^- counterions.) As a result, the molecules of C_6E_6 enjoy only partial conformational relief, and two noncoordinated ether groups are turned outward to describe an overall **B** conformation of C_6E_6 (see Chart 2). Furthermore, owing to the larger ionic radius, the potassium cation is able to directly link two pairs of *ortho*-ether groups (without water mediators) to bring the two encapsulating C_6E_6 units closer together (6.86 Å) than they are in the sodium complex. Most importantly, the two-site coordination of K^+ to C_6E_6 represents the desired “hinge” to place the cationic center within the benzenoid locus.

C. Rubidium (and Cesium) Ion Complex of C_6E_6. The Rb^+ and Cs^+ ion complexes of C_6E_6 are isomorphous and isostructural and thus share the same overall molecular shape with the 2-fold crystallographic symmetry depicted in Figure 5.[26b] Significantly, the molecular cavity of C_6E_6 is insufficient to accommodate a pair of these large cations, and a single cation coordinates *ortho*-ether groups of two molecules of C_6E_6 at $Rb^+\cdots O$ distances of 2.80−3.08 Å or $Cs^+\cdots O$ distances of 2.91−3.17 Å. A pair of encapsulating C_6E_6 have the same **B** conformation as in the potassium complex, but in the absence of a second cation the ligands fall much closer to each other, with dihedral angles of 35° and 38° and center-to-center distances of 5.67 and 5.73 Å for the Rb^+ and Cs^+ analogues, respectively. [Note that the greater ionic radii of Rb^+ and Cs^+ also result in the expansion of their coordination sphere(s) to include a SbF_6^- counterion.]

Discussion

The molecular structures of the sodium, potassium, rubidium, and cesium complexes of the hexakis-methoxymethyl derivative of benzene C_6E_6, as presented in Figures 3−5, provide considerable insight into the nature of the $M^+\cdots\pi$(arene) bonding if due consideration is paid to the weak interactions inherent to alkali-metal cations (M^+). Thus, this benzenoid donor depends on the ethereal tentacles (E) which serve an adjutant role to initially gather in the cations via coordination to a pair of neighboring syn substituents present in either conformer **B** or conformer **D** (Chart 2). As such, the $M^+\cdots\pi$(arene) interactions are constrained by the molecular “hinge” represented by the $E{-}M^+{-}E$ coordination depicted in Chart 3.

Chart 3



From Chart 3 we identify four independent factors to gauge the principle $M^+\cdots\pi$(arene) interactions, viz., (a) the M^+ separation from the benzene plane, (b) distortion from local symmetry in the $C_6E_6M^+SbF_6^-$ crystal structures, (c) the selective distortion of the benzene plane, and (d) the angular distortion of the ethereal coordination.

A. $M^+\cdots\pi$(Arene) Separation. In practice, the structural criterion to distinguish between a *nonbonding* (equilibrium) separation and a *bonding* (direct) interaction between donor/acceptor dyads is simply based on the distance which separates them,[28] and usually a distance shorter than the sum of their van der Waals radii is considered (prima facie) evidence for chemical attraction. However, the structural analysis for alkali-metal cations is somewhat ambiguous because a clear definition of a van der Waals radius suffers from their localized unit charge (with a consequent large electrostatic potential), and the cations are always sterically shielded by their ligand sphere from any contacts other than coordination bonding. As such, alkali-metal cations rarely form (readily definable) van der Waals contacts in the condensed phase, and pertinent experimental evidence to deduce reliable radii is generally lacking. Accordingly, let us first consider a direct criterion for the cation$\cdots\pi$(arene) contacts simply based on a combination of M^+ ionic radii (derived from alkali-metal structures in ionic crystals)[29] and the van der Waals radius of carbon.[21] These intermolecular contacts for Na^+ through Cs^+ are listed in Table 1 (column 2) together with the interaction distances (column 3) recently obtained from high-level theoretical calculations.[3−5,30] Finally, Table 1 lists in column 4 the $M^+\cdots$benzene (toluene) separation in some recent crystal structures[8a] designed to answer this question in the absence of polar coordinating groups and minimal electrostatic (counterion) interactions.[31]

Taken all together, the three sources of the intermolecular $M^+\cdots\pi$(arene) interactions (as listed in Table 1) are in surprisingly good agreement, especially if one considers the critical consideration of the systematic discrepancies. We can see that the $M^+\cdots\pi$(arene) interactions are consistent within 0.2 Å. Referred to these estimates, the $Na^+\cdots\pi$(arene) separation in the C_6E_6 complex as listed in column 5 exceeds the upper limit by 0.1 Å. In the potassium complex, the cation−π separation is shorter than the lower limit by 0.06 Å. Likewise, rubidium

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(27) The crystal structure of the potassium complex $C_6E_6K^+SbF_6^-$ consists of two identical but symmetrically independent units that are disordered around 2-fold axes of symmetry.

(28) Pauling, L. *Nature of the Chemical Bond*; Cornell: Ithaca, NY, 1960.

(29) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(30) Although these separations may be questionable for the weaker (long-distance) bonding interactions, alternative choices are lacking in view of the limited experimental data available.

(31) The values in column 4 come with the caveat that they may not be free of systematic errors (and thus may not provide statistically valid comparisons) owing to the separate observations reported by King et al.[8a]

Table 1. Interatomic Separation $M^+\cdots C(Ar)$ (Å) Based on Theoretical and Experimental Data

contact	sum of ionic and van der Waals radii	ab initio calculations	experimental $[M^+Bz_2]$ complexes	this work	expected from only $O\cdots M^+$ coordination
$Na^+\cdots C(Ar)$	2.86	2.80	3.04	**3.153/3.240**	3.22
$K^+\cdots C(Ar)$	3.22	3.24	3.38[a]	**3.156/3.185** (3.560/3.621)[b] **3.208/3.244**[c] (3.504/3.603)[b,c]	3.43
$Rb^+\cdots C(Ar)$	3.36	3.41	3.48	**3.339** (3.687/3.731)[d]	3.57
$Cs^+\cdots C(Ar)$	3.51	3.67	3.56	**3.444** (3.794/3.817)[d]	3.65

[a] Bis-toluene complex. [b] Distances in parentheses refer to the opposite (nonbonded) ligand C_6E_6 (see text). [c] Second symmetrically independent unit. [d] In parentheses − distances to *ortho*-carbon atoms.

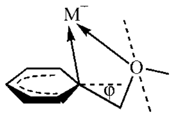
and cesium ion···π interactions are shorter by only 0.02 and 0.07 Å, respectively. Unfortunately, the margins are not sufficient to draw definitive conclusions, and the short $M^+\cdots\pi$(arene) distances in Table 1 alone do not clearly signify a bonding contact. In other words, the various measures of M^+ separation are not adequate for distinguishing the efficacy of Na^+ from that of K^+ or Rb^+/Cs^+ in cation···π(arene) interactions, and we therefore conclude that some other structural criterion must be invoked, as follows.

B. M^+ Disorder from Local Symmetry. In the potassium complex $C_6E_6K^+$, it is unclear why K^+ is disordered over two positions[27] so that the $K^+(\mu\text{-}H_2O)_2K^+$ cluster has a lower symmetry than its ligand environment. [Note that the shell of the complex consisting of two molecules of C_6E_6 has a 2-fold symmetry coincident with crystallographic symmetry.] Rotational disorder of SbF_6^- counterions cannot account for such a disorder because the centers of gravity of the anions obey the 2-fold symmetry with good precision. In both alternative positions, the potassium cation (K1) is equally coordinated by two pairs of ethereal oxygens from both C_6E_6 units. There is no obvious reason it cannot occupy a position on the 2-fold axis − yet it misses it by 0.8−0.9 Å. A careful consideration of all intramolecular contacts, however, reveals the oscillation of the potassium cation between two benzenoid rings so as to make significantly shorter $K^+\cdots C$ contacts of 3.156−3.244 Å with one of them relative to the other (3.504−3.621 Å), as listed in Table 1. If no (or even a repulsive) interaction exists between K^+ and the benzenoid rings, it is expected to remain equidistant. Such an observed oscillation of K^+ is possible only if short-range attractive interactions exist, like the sharply distance-dependent polarization forces recently predicted by Tsuzuki et al.[3a] In other words, the potassium cation prefers to be well-bonded to a single benzenoid ring rather than weakly bonded to two.[32]

The highly symmetrical η^2-coordination of the potassium cation with the benzenoid ring is similar to that recently described for silver(I) complexes to arene ligands.[33] Interestingly, this coordination mode collapses to a η^1-coordination in the Rb^+ and Cs^+ complexes, in apparent conflict with the local symmetry of the coordinated ether groups. Thus, the alkali cation connected to carbon C3 with the $Rb^+\cdots C$ distance of 3.34 Å is almost equally distant from both of its neighbors C2 at 3.73 Å and C4 at 3.69 Å. However, the corresponding ethereal links $Rb^+\cdots O2$ and $Rb^+\cdots O4$ are significantly less equivalent (3.39 and 3.08 Å, respectively). Further, the ethereal oxygen O2 is conformationally turned away from the Rb^+ and instead takes part in an intermolecular hydrogen bond with a neighboring (water) molecule. The preferential η^1-coordination of Rb^+ and Cs^+ can thus be attributed to dominant (intrinsic) cation···π-(arene) interactions of Rb^+ and Cs^+ rather than an artifact of ionic coordination with the ether adjutants.

C. Selective Distortion of Benzenoid Planarity. A close scrutiny of the benzenoid geometry in the rubidium and cesium complexes in Table 2 reveals a small but experimentally significant distortion from planarity. In particular, the methylene carbon C31 connected to the ipso center C3 deviates from the coordination plane by 0.09 Å or $\varphi = 3.5°$ in the Rb^+ complex, and by 0.12 Å or $\varphi = 4.4°$ in the Cs^+ complex, both in a direction *opposite* to the coordinating metal centers, as illustrated in Chart 4.

Chart 4



Such a selective distortion points to an incipient η^1-coordination of Rb^+ and Cs^+ to the benzenoid center, as in a weak σ-complex.[34] Indeed, we infer from recent theoretical calculations[3a] that a positively charged ion poised over the ipso carbon will induce polarization in the benzene plane and result in bending at this center[35] in the order $Rb^+/Cs^+ > K^+ > Na^+$. Moreover, the alternating bond-length distributions within the benzenoid chromophore [i.e., elongated $C_{ipso}-C_{ortho}$ distances of 1.408(3) Å, shortened $C_{ortho}-C_{meta}$ distances of 1.401(3) Å, and somewhat elongated $C_{meta}-C_{para}$ distances of 1.406(3) Å in the Rb^+ complex] would be in excellent agreement with a

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(32) Moreover, two molecules of C_6E_6 cannot approach one another more closely owing to steric hindrance (vide supra).

(33) Compare: Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707.

(34) (a) Such a possibility was first (theoretically) considered as the analogue of *σ-protonated* arenes (i.e., arenium cations) by Kebarle and co-workers,[2a] but rejected owing to computational limitations (see the legend to their Figure 6). (b) For a classic (X-ray) structure of an arene σ-complex, see: Rathore, R.; Hecht, J.; Kochi, J. K. *J. Am. Chem. Soc.* **1998**, *120*, 13278.

(35) In qualitative valence-bond terminology (see: Hubig, S. M.; Lindeman, S. V.; Kochi, J. K. *Coord. Chem. Rev.* **2000**, *200*, 831), this bending is associated with increased electron density selectively at the ipso carbon, that is,

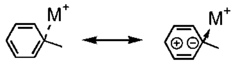
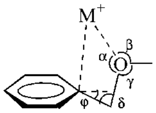


Table 2. Distortions of the Bond Angles in Ether Groups of C_6E_6 as a Result of Coordination to Alkali Metal Ions



angular parameter	Na^+ complex	K^+ complex[a]	Rb^+ complex[b]	Cs^+ complex[b]	uncomplexed **I**
α	123.0	103.5/105.0	110.7	111.2	
	110.7	116.9/118.3	121.4/108.4	122.2/109.6	
β	124.2	132.1/130.2	137.0	136.3	
	122.4	131.3/129.3	128.1/117.1	127.6/117.8	
$(\beta - \alpha)/2$	0.6	14.3/12.6	13.1	12.5	
	5.9	7.2/5.5	3.3/4.3	2.7/4.1	
γ	112.3	113.5/112.7	111.0	110.8	av 110.0
	111.5	110.0/111.4	110.5/111.6	110.2/111.2	
$360 - (\alpha + \beta + \gamma)$[c]	0.5	11.0/12.1	1.3	1.7	
	15.4	1.8/1.0	0.0/22.9	0.0/19.4	
δ	108.8	106.2/106.8	111.3	111.1	av 109.0
	108.5	107.3/107.6	106.9/107.6	107.4/107.5	
φ	0	0	3.5	4.4	0

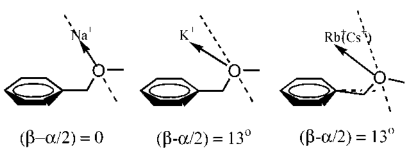
[a] The values (in two lines) correspond to two symmetrically independent complex units. [b] The values in the first line correspond to the *ipso*-ether group, and in the second line to the *ortho*-ether groups. [c] This parameter describes the deviation of the coordination geometry of oxygens from planarity.

σ-complex to Rb^+ or Cs^+ if only the differences exceeded the experimental uncertainties.[11]

D. Angular M^+ Coordination to Ethereal Ligands. The coordination geometry of alkali-metal cations is very flexible owing to their spherical symmetry (i.e., M^+ generally lacks any specific coordination polyhedra). By contrast, the coordination geometry of ethereal oxygens is much more strictly determined because they always coordinate cations along the direction of the maximum electron density of their lone pairs.[37] Ideally, the coordinated cations are positioned within the C−O−C plane of the ether group so that both $M^+\cdots O-C$ bond angles are equal. The calculated $M^+\cdots\pi$(arene) separations resulting from ideal $M^+\cdots O$(ether) coordinations in $C_6E_6M^+$ for Na^+ through Cs^+ are listed in Table 1 (column 6). It is particularly noteworthy that the experimental values for the larger cations K^+, Rb^+, and Cs^+ lie roughly 0.2 Å closer to the arene plane than that dictated by a pure (undistorted) ethereal coordination.

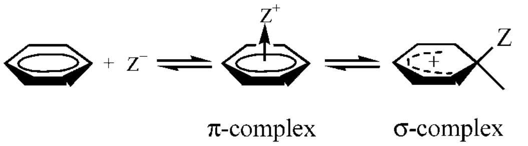
The relevant distortions of ethereal coordination to M^+ are expressed by the angular parameters listed in Table 2. From the comparison of the endo and exo angles of the $M^+\cdots O-C$ coordination (designated as α and β, respectively, in the structural scheme depicted in Table 2), we can see that the position of M^+ *always deviates toward the benzene ring* relative to the bisecting plane of the C−O−C group − so that β is always wider than α. Chart 5 shows the magnitude of the distortion $(\beta - \alpha)/2$ to be less than 0.6° for Na^+ but increases to almost 15° for K^+, Rb^+, and Cs^+.

Chart 5



Summary and Conclusions

X-ray crystallographic studies of the [1:1] complexes of $M^+ = Na^+$, K^+, Rb^+, and Cs^+ show that the ambifunctional hexakis(methoxymethyl)benzene C_6E_6 captures alkali-metal cations via a pair of ether tentacles (E) and loosely positions them over the benzene ring − thus providing favorable steric conditions for the target $M^+\cdots\pi$(arene) interactions, as illustrated in Chart 3. In this manner, the sodium cation maintains its position, but we are unable to detect any structural evidence (based on either bond distances, bond angles, or molecular deformations) to indicate significant $Na^+\cdots\pi$(arene) interaction. Although the potassium cation is similarly placed, there is unmistakable structural evidence (based on bond angle deformation in Chart 4 and cation disorder) that K^+ gravitates toward the benzene center in a π-bonding mode with η^2-coordination to a pair of ring carbons that is similar to that in the well-known silver(I) complexes with arenes.[33] It is particularly noteworthy that $M^+\cdots\pi$(arene) interactions are even more intense in the isomorphous and isostructural Rb^+ and Cs^+ complexes − to such an extent that both cations are essentially η^1-bonded to a single (ipso) ring carbon. Such a juxtaposition of Rb^+/Cs^+ with the aromatic center is highly reminiscent of a variety of σ-complexes that follow the collapse of the preequilibrium π-complex,[11,36,38] for example:



(1)

Particularly diagnostic of the reversible $\pi-\sigma$ transformations in eq 1 is the deformation of the planar benzenoid ring to accommodate the now tetrahedral (ipso) carbon. The transition from η^2-coordination in the potassium π-complex to η^1-coordination in the Rb^+ and Cs^+ σ-complexes is consistent with cation$\cdots\pi$(arene) interactions that increase in the order $K < Rb^+ = Cs^+$ because the formation of σ-complexes requires

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(36) We believe that the structural criteria discussed herein have general applicability to cation$\cdots\pi$ interactions, and we hope to develop these in further studies.

(37) Ion-dipole character of these interactions requires all dipoles of the CH_2-O-CH_2 moieties to be directed toward the complexed cation. For a detailed analysis, see: Burden, I. J.; Coxon, A. C.; Stoddard, J. F.; Wheatley, C. M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 220.

(38) (a) Vasilyev, A.; Lindeman, S. V.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **2001**, 909; *New J. Chem.* **2002**, *26*, 582. (b) Rosokha, S. V.; Kochi, J. K. *J. Org. Chem.* **2002**, *67*, 1727.

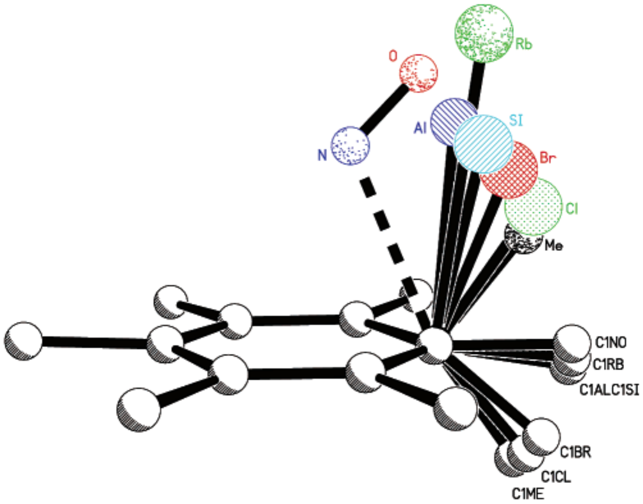

Figure 6. Continuous variation of $\sigma-\pi$ structures established by X-ray crystallographic analyses of cation$\cdots\pi$(arene) interactions involving various (cationic) electrophiles with hexamethyl (and related) benzenes as indicated in eq 1.

significant electron redistribution.[35] Indeed, the continuous transition of $\pi-\sigma$ structures (all determined by X-ray crystallography) is illustrated in Figure 6 by the concomitant variation of both ipso angles (i.e., from the benzene plane to Z^+ and to the substituent E) with electrophiles of different acceptor strengths in the approximate order $CH_3^+ > Cl^+ > Br^+ > Et_3Si^+ > Ar_3Al \approx Rb^+/Cs^+ > NO^+$.[11] [Note that arene bonding to the last (weakest) electrophile NO^+ is best discussed as π because the ipso angle is nil.[20]]

These structural data lead to the inescapable conclusion that alkali-metal cations can participate in important and specific $M^+\cdots\pi$(arene) interactions, especially in the order $Cs^+ \approx Rb^+ > K^+ > Na^+$ which is notably reversed from that observed in the gas phase and predicted by the most recent theoretical computations.[39] However, they are in better agreement with an earlier Monte Carlo simulation of benzene complexes of alkali-metal cations in aqueous media that give the $M^+\cdots\pi$(arene) affinities in the order $Na^+ \ll Rb^+ < K^+$.[7b]

Because the alkali-metal cations in this study experience both hydrophilic and hydrophobic forces, we believe that our conclusions are more relevant to the actual conditions of the $M^+\cdots\pi$(arene) coordination in biological systems and other condensed phases where the alkali-metal cations cannot be entirely free of the solvent shell and from ion-pairing forces. From this perspective, the pronounced $K^+\cdots\pi$(arene) interactions versus the undetectable $Na^+\cdots\pi$(arene) interactions under almost identical conditions are especially pertinent to further studies of cation$\cdots\pi$ interactions more generally.[43]

Experimental Section

Materials. Salts of Alkali Metal Ions. Potassium bromide (KBr), triflate (KO_3SCF_3), and perchlorate ($KClO_4$), rubidium iodide (RbI) and acetate (RbO_2CCH_3), and cesium iodide (CsI) were from Aldrich and used for crystallizations without further purification. Tetraphenylborates of sodium, potassium, rubidium, and cesium ($NaBPh_4$, $KBPh_4$, $RbBPh_4$, and $CsBPh_4$) were also from Aldrich. Rubidium and cesium tetrachloroaluminates ($RbAlCl_4$ and $CsAlCl_4$) were prepared as solutions in CS_2 according to the following procedure: 0.012 mol of CsCl or RbCl (Aldrich) were placed in 10 mL of dry CS_2 under an argon atmosphere. After addition of 0.005 mol of $AlCl_3$ (Aldrich) and vigorous stirring during 3 h, the salt was partially dissolved, and the resulting solution was used for crystallizations. Potassium, rubidium, and cesium hexafluoroantimonates ($KSbF_6$, $RbSbF_6$, and $CsSbF_6$) were prepared by ion exchange between KBr (RbI, CsI) and $AgSbF_6$ (Aldrich) as follows: 1 mmol of RbI was dissolved in 10 mL of dry methanol under heating and stirring, 1 mmol of $AgSbF_6$ was dissolved in 5 mL of dry acetonitrile, and the solutions were mixed under an argon atmosphere and then separated from the precipitate. (A similar procedure was used for potassium and cesium salts.) The dry hexafluoroantimonate salts were isolated by removal of the solvent in vacuo. Potassium hexafluoroarsenate was obtained similarly from KBr and $AgAsF_6$ (Aldrich).

Solvents. Reagent-grade ethanol, dimethylformamide, benzene, ethyl acetate, and tetrahydrofuran from Merck were used without additional purification. Acetonitrile (Merck) was refluxed for 30 min with an equal volume of aqueous $KMnO_4$ (10 g L^{-1}) and Li_2CO_3 (10 g L^{-1}). After separation, it was refluxed for 12 h over CaH_2 under an argon atmosphere. Methanol (Merck) was similarly purified by refluxing over CaH_2 during 12 h. Carbon disulfide (Merck) was stirred with an equal volume of aqueous $KMnO_4$ (5 g L^{-1}) for 3 h and then stirred twice with 50 g of metallic mercury for 6 h. This was followed by distillation with an equal volume of aqueous mercury sulfate (2.5 g L^{-1}) for 4 h. It was finally dried over 50 g of $CaCl_2$ for 10 h and then distilled from P_2O_5 and CaH_2 under an argon atmosphere. All of the solvents after the final distillation from CaH_2 were stored in Schlenk flasks under an argon atmosphere. Hexakis(methoxymethyl)benzene, C_6E_6, was synthesized using literature procedures.[14,15] Hexamethylbenzene, dibromine, 1,2-dibromoethane, and sodium metal were from Aldrich.

Preparation of the Complexes of Alkali Metal Salts with Hexa(methoxymethyl)benzene (C_6E_6). The typical procedure for the preparation of the complexes between alkali metal ions and C_6E_6 was the slow (during few days) evaporation of 1−4 mL of the equimolar mixture of C_6E_6 and the appropriate salt (0.005−0.012 mol/L) in three different solvents (acetonitrile, methanol, and ethanol) at room temperature. The resulting crystals were analyzed by X-ray crystallography. Tetraphenylborate salts were additionally cocrystallized with C_6E_6 from dimethylformamide and from mixed (1:1) dimethylformamide/benzene by slow cooling of the hot (oversaturated) solutions. Attempts were made to cocrystallize the tetrachloroaluminate salts with C_6E_6 from the 0.005 mol/L CS_2 solution left for few days at −20 °C under an argon atmosphere. Numerous attempts were made to cocrystallize potassium hexafluoroarsenate with C_6E_6 by slow evaporation from acetonitrile, methanol, ethyl acetate, and tetrahydrofuran solutions by

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(39) (a) We recognize that the somewhat abbreviated ether tether E may introduce some bias in the placement of M^+ over the benzene ring of C_6E_6.[40] However one views such a restriction, the angular/molecular distortions and crystal disorder provide unmistakable signals for $M^+\cdots\pi$(arene) interaction to increase in the order $Na^+ < K^+ < Rb^+/Cs^+$. (b) Theoretical studies may underestimate the importance of polarizability (especially in the heavy cations) that lead to increased charge-transfer forces, as established by Hubig et al. in ref 35. For the role of such charge-transfer interactions in arene binding, see: Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 8985. Compare also: Mo, Y.; Subramanian, G.; Ferguson, P. M. *J. Am. Chem. Soc.* **2002**, *124*, 4832. Lee, K. Y.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1011.

(40) (a) For example, various high level theoretical calculations[2a,5a,41] of different arene/electrophile interactions reveal only small energy differences between overcenter and overrim configurations. (b) Heretofore, all theoretical calculations of $M^+\cdots\pi$(arene) interactions have focused almost solely on the overcenter configuration − see refs 3−5 and 42.

(41) (a) Hashimoto, S.; Ikuta, S. *J. Mol. Struct.* **1999**, *468*, 85. (b) Grozema, F. C.; Zijlstra, R. W. J.; Swart, M.; Van Duijhen, P. *Int. J. Quantum Chem.* **1999**, *75*, 709. (c) Mebel, A. M.; Lin, H. L.; Lin, S. H. *Int. J. Quantum Chem.* **1999**, *72*, 307. (d) Ammal, S. S. C.; Ananthavel, S. P.; Venuvanalingam, P.; Hegde, M. S. *J. Phys. Chem. A* **1998**, *102*, 532. (e) Matsuzawa, A.; Osamura, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1531. (f) Milano, G.; Guerra, G.; Cavallo, L. *Eur. J. Inorg. Chem.* **1998**, 1513.

(42) (a) Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 4177. (b) Nicholas, J. B.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 1394. (c) Armentrout, P. B.; Rodgers, M. T. *J. Phys. Chem. A* **2000**, *104*, 2238. (d) Feller, D. *Chem. Phys. Lett.* **2000**, *322*, 543.

(43) In particular, the marked difference between Na^+ and K^+ relates to the effectiveness of their complexation equilibria (and transport) in various biological systems, as discussed in refs 7, 9, and 10.

Table 3. Crystallographic Parameters and Refinement Data for the Structures Determined

compound	C_6E_6	$C_6E_6{\bullet}CS_2$	$[Rb^+BPh_4^-]{\bullet}C_6E_6$	$[(C_6E_6)_2Na_2(H_2O)_4]^{2+}{\bullet}2BPh_4^-$	$[(C_6E_6)_2K_2(H_2O)_2]^{2+}{\bullet}2SbF_6^-$	$[(C_6E_6)_2Rb]^+{\bullet}SbF_6^-$	$[(C_6E_6)_2Cs]^+{\bullet}SbF_6^-$
formula	$C_{18}H_{30}O_6$	$C_{19}H_{30}O_6S_2$	$C_{42}H_{50}BO_6Rb$	$C_{84}H_{108}B_2Na_2O_{16}$	$C_{36}H_{64}F_{12}K_2O_{14}Sb_2$	$C_{36}H_{60}F_6O_{12}RbSb$	$C_{36}H_{60}CsF_6O_{12}Sb$
MW	342.42	418.55	747.10	1441.30	1270.58	1006.06	1053.50
space group	*P*2$_1$/*n*	*R*-3	*Cmc*2$_1$	*P*2$_1$/*c*	*P*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	14.9925(6)	14.441(1)	15.9795(6)	10.7648(2)	23.773(1)	15.612(2)	15.437(1)
b (Å)	8.8042(3)	14.441(1)	8.3049(3)	14.0314(2)	12.184(1)	15.020(2)	15.067(1)
c (Å)	15.7850(6)	9.2652(6)	28.772(1)	26.9792(2)	19.996(1)	18.653(3)	18.855(1)
α (deg)	90	90	90	90	90	90	90
β (deg)	116.338(1)	90	90	100.490(3)	114.51(1)	93.065(3)	92.761(1)
γ (deg)	90	120	90	90	90	90	90
V (Å^3)	1867.3(1)	1673.4(2)	3817.8(2)	4007.0(1)	5269.8(6)	4367.6(9)	4380.2(4)
Z	4	3	4	2	4	4	4
D_c (g cm^{-3})	1.218	1.246	1.300	1.195	1.601	1.530	1.598
N [total]	24 519	5103	27 389	49 203	47 975	30 682	17 013
N [nonequiv]	8538	1630	4780	18 057	13 702	9812	5634
R_{int}	0.019	0.012	0.036	0.027	0.047	0.025	0.038
$N [I > 2\sigma(I)]$	6607	1456	3847	13 188	8271	7376	4260
R1	0.0403	0.0305	0.0386	0.0483	0.0793	0.0394	0.0637
wR2	0.1055	0.0881	0.0935	0.1114	0.2075	0.1003	0.1761

slow evaporation at room temperature. Crystals of the complexes between potassium, rubidium, and cesium hexafluoroantimonates and C_6E_6 were obtained by slow evaporation of the equimolar 0.07 mol/L solutions from 1:4 mixtures of acetonitrile/methanol.

X-ray Crystallography. The intensity data for all of the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å) at −150 °C. The structures were solved by direct methods[44] and refined by full matrix least-squares procedure[45] with IBM Pentium and SGI O_2 computers − see Table 3 for the principal details. Semiempirical absorption correction was applied using SADABS program.[46] Positions of hydrogen atoms in aqua ligands were found objectively from difference Fourier series and refined isotropically. [The X-ray structure details of various compounds are on deposit and can be obtained from the Cambridge Crystallographic Data Center, U.K.]

Acknowledgment. We thank R. Rathore for the synthesis of the sodium complex and for many helpful suggestions. We also thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

Supporting Information Available: ORTEP diagrams of the complex molecules − Figures S1−S3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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