

The Interaction of Alkali Metal Cations with Aromatic Molecules in Complexes of the Type $M[AlMe_3X] \cdot \text{aromatic}$, $M[Al_2Me_6X] \cdot \text{aromatic}$, and Related

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Abstract. The crystal structures of 13 compounds of the form $M[Al_2Me_6X] \cdot \text{aromatic}$ and related have been examined in order to learn about the $M^+ \dots \text{aromatic}$ approach. Four types of interactions have been discerned: (1) metal \dots aromatic, (2) metal \dots aromatic \dots metal, (3) aromatic \dots metal \dots aromatic, and (4) no metal \dots aromatic contact. It was found that the closest $K^+ \dots C(\text{aromatic})$ and $Cs^+ \dots C(\text{aromatic})$ separations are essentially equal after a correction for the difference in metal radii. The strength of the $K^+ \dots \text{aromatic}$ attraction was found to be sufficient to move the K^+ ion 0.3 Å out of the plane of the crown ether in two complexes of dibenzo-18-crown-6.

Key words: alkali metal ions, metal-aromatic interactions, crystal structure, aluminum alkyls.

1. Introduction

Over the past several years we have carried out numerous studies on $M[Al_2Me_6X]$ (M = alkali metal or tetraalkylammonium cation, X = anion) in the presence of aromatic solvents. Much attention has been focused on the novel solution behavior (the liquid clathrate effect) [1]. In an effort to understand the basis for the phenomena observed in solution, many X-ray structural analyses have been carried out on $M[Al_2Me_6X]$ and related complexes. Since these substances have all been crystallized from aromatic solvents, several of the lattices have been found to contain aromatic molecules [2–12]. This presents an unusually good opportunity to study the interaction of alkali metal ions with aromatic systems since such 'ionic' materials are not normally found in nonpolar solvents. In previous contributions we have dwelt on the geometry of the anion and on the manner in which it fits with ideas about the solution behavior. Herein, the topic is the role of the aromatic molecules in the solid-state structures. It will be shown that there are cases in which aromatic molecules interact with the M^+ cations and there are those in which the aromatics simply pack in the lattice. Instances of the former will be divided into three types of association.

2. Results and Discussion

The presence of solvent molecules in lattices of target molecules is a well-known occurrence. An explanation based on more effective packing is commonly offered. Indeed, one of the first $M[Al_2Me_6X]$ species to be characterized structurally, $K[Al_2Me_6F]$, was found to contain

Table I. Summary of $K^+ \dots$ aromatic interactions

| Compound | Interaction type | K...C(aromatic) Distance, (Å) | | Ref. |
|--|--------------------------------|-------------------------------|---------|------|
| | | Range | Average | |
| [K · DB-18-C-6] [AlMe ₃ NO ₂] · 0.5C ₆ H ₆ | 3 | > 3.9 | | [6] |
| K[GaMe ₃ NCS] · 0.5C ₆ H ₆ | 3 | > 3.9 | | [7] |
| K[Al ₄ Me ₁₂ SO ₄] · 0.5C ₆ H ₄ Me ₂ - <i>p</i> | 2 | 3.45(2)–3.58(2) | 3.51 | [2] |
| K[Al ₂ Me ₆ F] · C ₆ H ₆ | 3 | > 3.9 | | [13] |
| K[AlMe ₃ NO ₃] · C ₆ H ₆ | 1 | 3.29(1)–3.46(1) | 3.36 | [4] |
| K[Al ₇ O ₆ Me ₁₆] · C ₆ H ₆ | 1 | 3.27(1)–3.39(2) | 3.33 | [8] |
| [K · DB-18-C-6] [Al ₂ Me ₆ O ₂] · 1.5C ₆ H ₆ ^a | 2 and 3 | 3.35(3)–3.46(3) ^b | 3.42 | d |
| K[Al ₃ Me ₉ SeMe] · 2C ₆ H ₆ | 2 extended ^c | 3.33–3.47 | | [5] |
| [K · DB-18-C-6] [Al ₂ Me ₆ Cl] · 2C ₆ H ₆ | 1 and 3 | 3.29(2)–3.50(3) ^b | 3.39 | [6] |
| [K · DB-18-C-6] [GaMe ₃ NCS] · 2.5C ₆ H ₆ | 1 and 3 | 3.48(1)–3.72(1) ^b | 3.59 | |

^a DB-18-C-6 represents the crown ether dibenzo-18-crown-6.

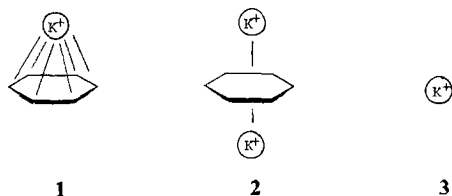
^b Range and average are only given for rings associated by type **1** interactions.

^c The crystal is composed of layers of cations and anions. In the cation layer each K^+ ion is surrounded effectively by four C₆H₆ molecules.

^d See J. L. Atwood and S. K. Seale, *J. Organomet. Chem.* **114**, 107 (1976).

a molecule of benzene per cation-anion pair [2]. Now, however, a sufficiently large number of crystal structures of compounds related to liquid clathrates have been investigated, and patterns can be discerned. The discussion will first center on the interaction of K^+ with aromatic systems, then move to Cs^+ , and finally draw on comparisons between the two ions.

A perusal of the ten structures listed in Table I affords the observation of three distinct types of $K^+ \dots$ aromatic interactions, **1**, **2**, and **3**, the latter of which represents no direct contact at all.



The Type **1** interactions involve a rather symmetric disposition of the K^+ ion over the ring (or vice versa). In the four examples given in Table I [3–6] the ranges of distances from closest $K \dots C$ to farthest differ by only 0.1 to 0.2 Å. (No orbital overlap of any consequence exists between the metal ion and the aromatic ring.) Typical examples are given in Figure 1. The average $K \dots C(\text{aromatic})$ approach is *ca.* 3.4 Å.

In Type **2** interactions, the aromatic molecule serves to 'insulate' potassium ions one from another. This certainly is a favorable electrostatic situation, and is a cornerstone of the current understanding of liquid clathrate behavior in general. The examples shown in Figure 2 [7, 8] demonstrate that the potassium ions are *not* disposed directly over the center of the aromatic ring as in Type **1** situations. It would seem that this is a packing effect, since the $K^+ \dots K^+$ separation is not greatly increased over that of a symmetrical $K \dots$ aromatic $\dots K$ arrangement. (In each of the two examples the aromatic lies on a crystallographic center of inversion.)

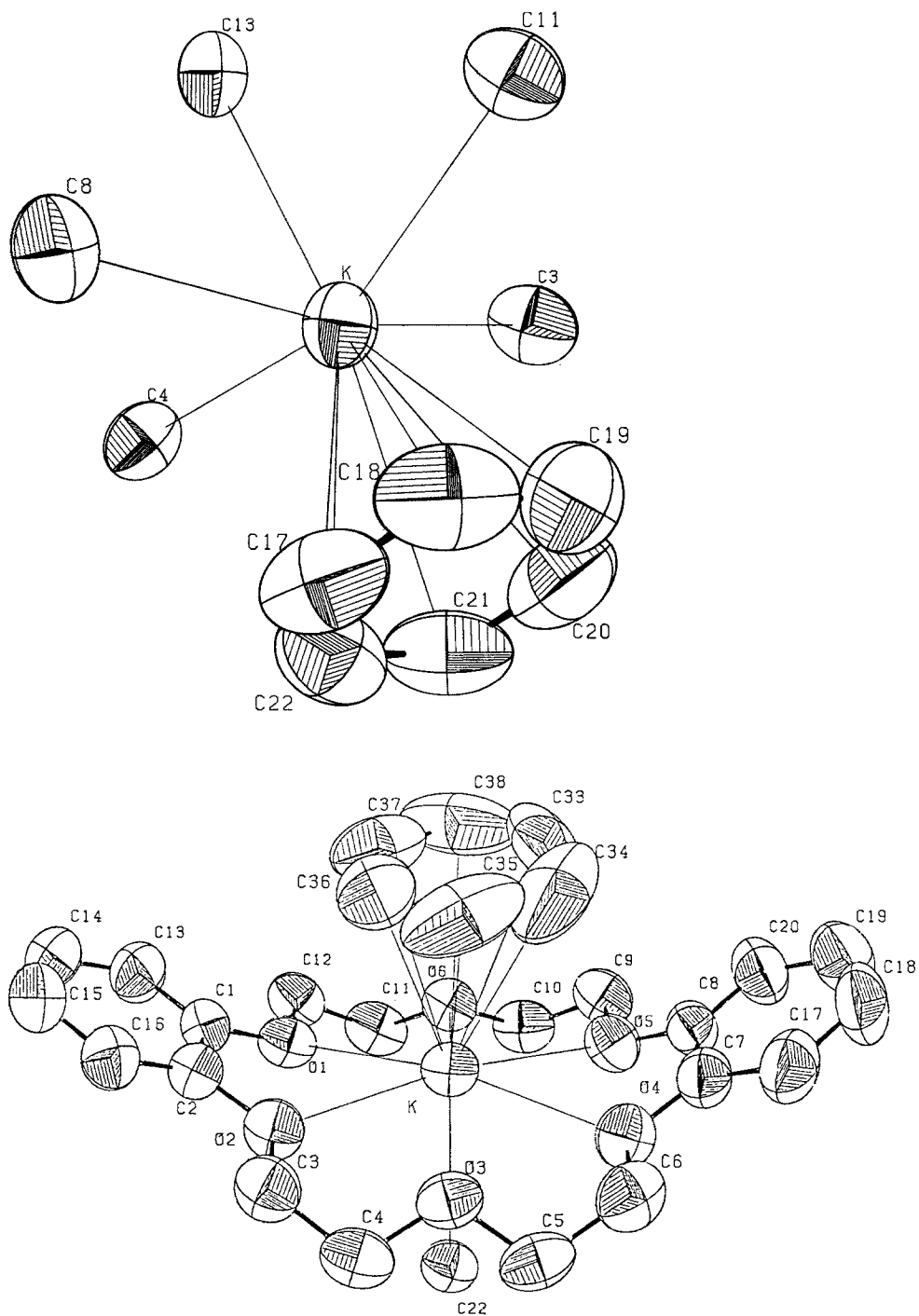


Fig. 1. (a) Example of a Type I interaction of a potassium ion with a benzene ring in the structure of $K[Al_7O_6Me_{16}] \cdot C_6H_6$. (b) Type I interaction of a potassium ion which is encased in a crown ether in $[K \cdot DB-18-C-6] [Al_2Me_6Cl] \cdot 2C_6H_6$. Reprinted with permission from [5].

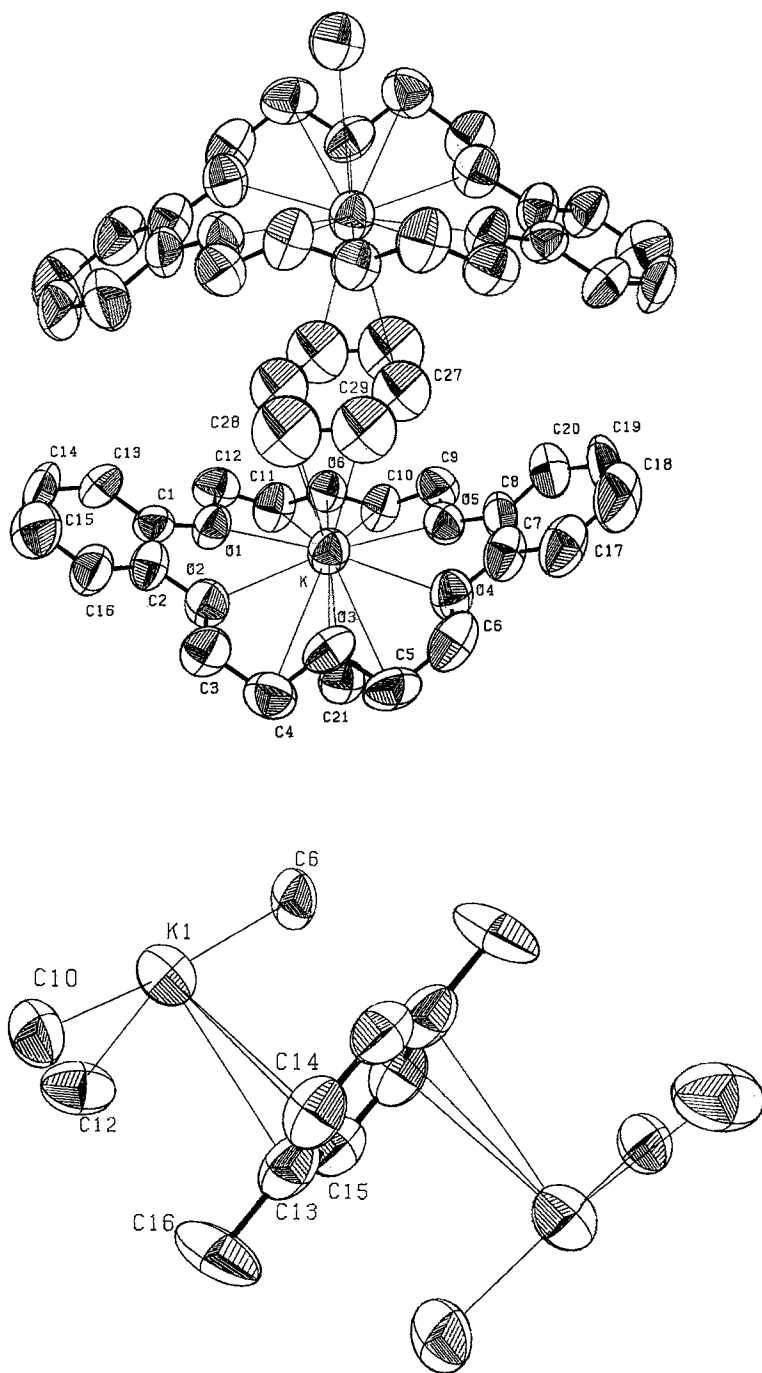


Fig. 2. Type 2 interaction in (a) $[K \cdot DB-18-C-6] [Al_2Me_6O_2] \cdot 1.5C_6H_6$ and (b) $K[Al_4Me_{12}SO_4] \cdot 0.5C_6H_4Me_2 - p$.

All of the aromatic molecules in $K[Al_2Me_6F] \cdot C_6H_6$ [2] and $K[GaMe_3NCS] \cdot 0.5C_6H_6$ [6] are positioned far distant from the potassium ions in the lattice. This is also true of a portion of the aromatics in three of the other crystal structures [5,6,8]. In these cases two packing situations can be discerned. With $K[GaMe_3NCS] \cdot 0.5C_6H_6$, the benzene molecules occupy sites which are distributed throughout the lattice such that the solvent molecules are simply packed in amongst the cations and anions. In $[K \cdot DB-18-C-6][Al_2Me_6O_2] \cdot 1.5C_6H_6$, however, the Type 3 C_6H_6 molecules form essentially a larger at $ca. z \approx \frac{1}{2}$ which runs throughout the crystal. This is illustrated in the stereoview given as Figure 3.

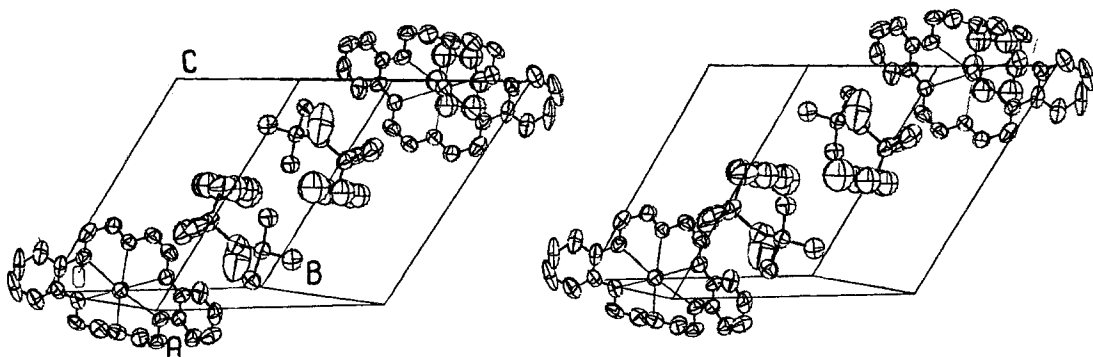


Fig. 3. Stereoview of the packing in $[K \cdot DB-18-C-6][Al_2Me_6O_2] \cdot 1.5C_6H_6$ illustrating the layer of benzene molecules at $z \approx \frac{1}{2}$.

Even more interesting unit cell packing situations are seen with Cs^+ structures. A summary is presented as Table II.

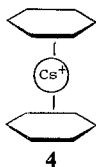
Table II. Summary of Cs^+ ...aromatic interactions

| Compound | Interaction type | $Cs \dots C(\text{aromatic})$ Distance, (Å) | | Ref. |
|---|----------------------|---|---------|------|
| | | Range | Average | |
| $Cs[AlMe_2I_2] \cdot C_6H_4Me_2 - p$ | 4^a | 3.75(3)–3.90(3) | 3.84 | [10] |
| $Cs[Al_2Me_6N_3] \cdot 2C_6H_4Me_2 - p$ | 4 | 3.561(8)–3.696(7) | 3.64 | [9] |
| $Cs[Al_7O_6Me_{16}] \cdot 3C_6H_5Me$ | 1^b | 3.65(4)–3.93(3) | 3.80 | [4] |

^a **4** extended which could be viewed as **2** extended.

^b **1** or badly distorted **4**.

The new interaction is Type **4** in which the metal is 'sandwiched' between aromatic molecules. An example of an isolated **4** is presented in Figure 4, the environment of the cation



in $Cs[Al_2Me_6N_3] \cdot 2C_6H_4Me_2 - p$ [9]. The cesium ion lies on a crystallographic mirror plane which also passes through both *p*-xylene molecules. A complete account of this and chemically related structures will appear subsequently in the *Journal*.

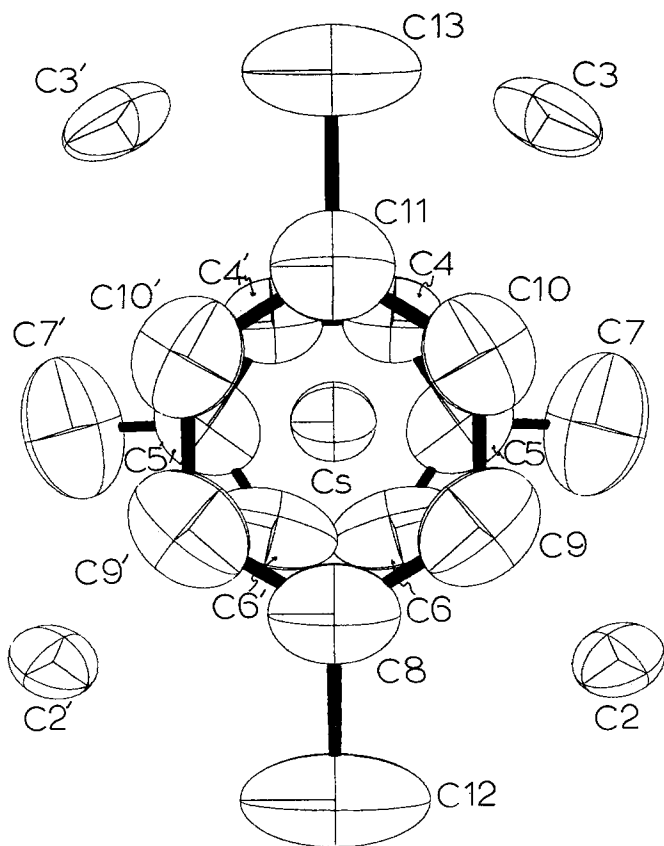


Fig. 4. Cation environment in $\text{Cs}[\text{Al}_2\text{Me}_6\text{N}_3] \cdot 2\text{C}_6\text{H}_4\text{Me}_2 - p$ illustrating the manner in which the cesium ion is sandwiched between the two *p*-xylene molecules.

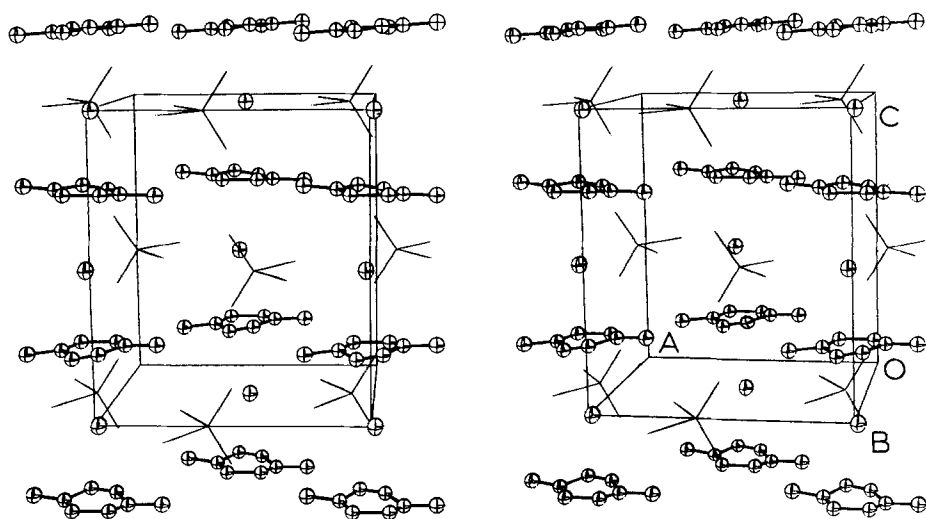


Fig. 5. Stereoview of the unit cell packing in $\text{Cs}[\text{AlMe}_2\text{I}_2] \cdot \text{C}_6\text{H}_4\text{Me}_2 - p$ taken from [10].

Already in the literature is an example of an extended Type 4 interaction, $\text{Cs}[\text{AlMe}_2\text{I}_2] \cdot \text{C}_6\text{H}_4\text{Me}_2 - p$ [10], and a stereoview is shown in Figure 5. The crystal consists of layers of *p*-xylene molecules which sandwich layers of cations and anions. The superficial resemblance to graphite intercalates is striking [11].

The third example of Cs^+ ion packing is a unique extension of **1**. The cesium ion in $\text{Cs}[\text{Al}_7\text{O}_6\text{Me}_{16}] \cdot 3\text{C}_6\text{H}_5\text{Me}$ lies on a crystallographic three-fold axis and has three toluene molecules associated with it (Figure 6) [4]. Each toluene is essentially symmetrically disposed

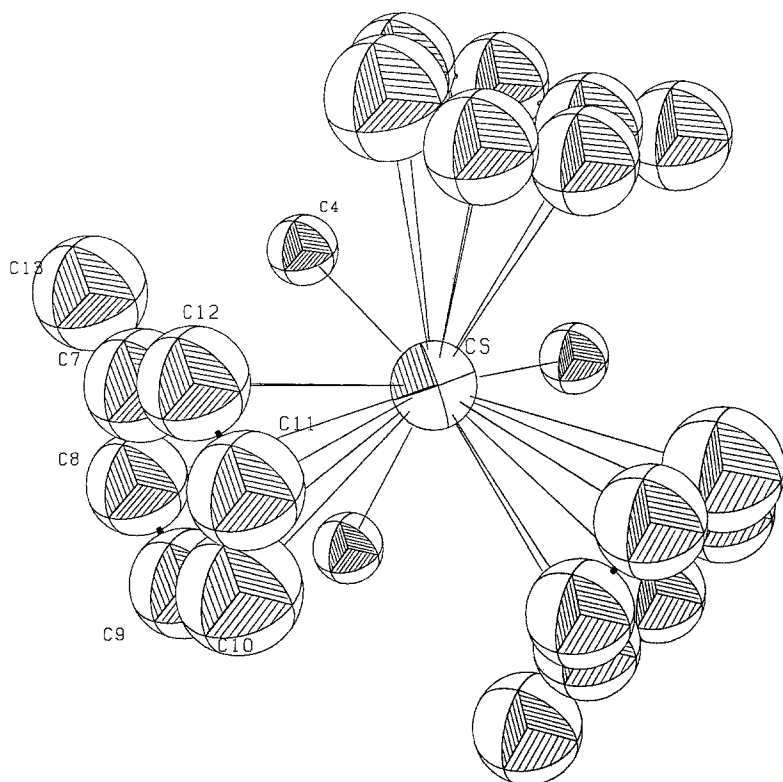


Fig. 6. Cesium environment in $\text{Cs}[\text{Al}_7\text{O}_6\text{Me}_{16}] \cdot 3\text{C}_6\text{H}_5\text{Me}$. The Cs^+ resides on a crystallographic threefold axis.

with respect to the cation, although the range of $\text{Cs} \dots \text{C}(\text{aromatic})$ contacts shows a difference, shortest to longest, of *ca.* 0.3 Å. Not surprisingly, the closest $\text{Cs} \dots \text{C}(\text{aromatic})$ average, 3.64 Å, is found for the discrete Type 4 interaction.

Cesium and potassium may be compared in a number of ways. Potassium is 0.32 Å smaller than cesium in metallic radius, and should interact a bit more strongly with the aromatics than does cesium. This is *not* reflected in the observed $\text{M}^+ \dots \text{C}$ separations. The closest $\text{K} \dots \text{C}$ average, 3.33 Å in $\text{K}[\text{Al}_7\text{O}_6\text{Me}_{16}] \cdot \text{C}_6\text{H}_6$, agrees almost exactly with the 3.64 Å average in $\text{Cs}[\text{Al}_2\text{Me}_6\text{N}_3] \cdot 2\text{C}_6\text{H}_4\text{Me}_2 - p$ after the correction for radii. If the thirteen-structure sample is large enough to be representative, it can be said that the larger size of Cs^+ affords space for interactions with more aromatic molecules than does K^+ .

The discourse above has showed that there are a number of interesting structures associated with the presence of alkali metal cations and aromatic molecules. We believe these can be

factored into four essential geometries, 1–4. But what of the interaction $M^+ \dots$ aromatic itself? There are two manifestations of this attraction. First, it is clear that the cation did not simply crystallize rather symmetrically above the aromatic by chance. Of the thirteen example structures in-hand, ten show the preferential orientation. Second, a hint of the strength of the interaction may be discerned. In $[K \cdot DB-18-C-6] [AlMe_3NO_3] \cdot 0.5C_6H_6$ [12] a Type 3 structure, the potassium ion resides in the plane of the six crown ether oxygen atoms to within 0.01 Å. On the other hand, the potassium ion resides out of the crown ether plane by 0.28 and 0.38 Å and *toward* the aromatic for the Type 2 and Type 1 interaction in $[K \cdot DB-18-C-6] [Al_2Me_6O_2] \cdot 1.5C_6H_6$ and $[K \cdot DB-18-C-6] [Al_2Me_6Cl] \cdot 2C_6H_6$, respectively. It is tempting to ascribe this distinction to an attraction of the aromatic for the potassium ion. Further studies currently in progress may well substantiate this idea.

Acknowledgements

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