CATION–π INTERACTIONS IN THE SOLID STATE: CRYSTAL STRUCTURES OF $M^+(BENZENE)_2CB_{11}Me_{12}^-$ (M = Tl, Cs, Rb, K, Na) AND $Li^+(TOLUENE)CB_{11}Me_{12}^-$

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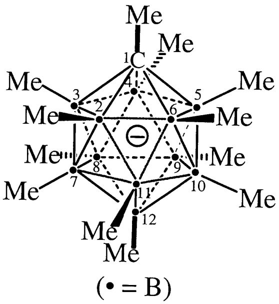
Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday.

In these crystal structures, the relatively weak electrostatic interactions between the bulky $CB_{11}Me_{12}^-$ anion and the title cations permit cation–π interactions in the solid state. In all cases, single-crystal X-ray diffraction analysis reveals η^6-arene–cation interactions within 10% of the expected van der Waals distance. The Tl^+, Cs^+, Rb^+, and K^+ structures are isomorphous, with the benzene molecules sandwiching the cation and four anions equatorially disposed in a nearly square arrangement. Both the cation and the near-square of closest anions are positioned to interact favorably with the local dipoles of benzene. The smaller Na^+ crystallizes in polymeric chains with a nearly tetrahedrally coordinated cation in van der Waals contact with two anions and two benzene molecules in a tilted-sandwich arrangement. The Li^+ structure possesses two motifs, a simple van der Waals sandwich of a toluene molecule and an anion, and chains of half-occupied toluene–Li complexes on inversion centers between anions. The simple van der Waals model is reasonably accurate for the cation–arene distances, only slightly underestimating the separation (2–10% deviation), with worse agreement for the smaller cations.

Key words: Crystal structure determination; Noncovalent interactions; Cation–π interactions; Carborane anions; Boranes; Carboranes; Sandwich complexes; Arenes; Alkali metal cations.

We report single-crystal X-ray analyses of the salts $M^+(\eta^6\text{-benzene})_2$ (M = Tl, Cs, Rb, K, Na) and $Li^+(\eta^6\text{-toluene})$ with the nearly icosahedral weakly coordinating anion $CB_{11}Me_{12}^-$ (**1**$^-$) (ref.[1], Scheme 1). Each structure exhibits significant η^6-arene–cation interactions at van der Waals contact[2]. A review of alkali-metal (except Li) organometallic X-ray structures contains several structures analogous to those presented here, and even predicts the cation–π interaction in salts of carborate anions[3]. This general[4] and biologically important interaction has been recently reviewed[5] and studied in the gas phase[6,7], in solution using aromatic cryptands[8,9], and computationally[10,11]. The physical basis of the cation–π interaction is a combination of dispersion forces, polarization, charge transfer, and electrostatic interactions. However, for a given arene and a series of cations, the electrostatic term dominates the variations in strength[12]. For hydrocarbon arenes, calculations suggest that a geometry with the cation directly above the π system in van der Waals contact is favored[5], placing the cation directly above the most negative portion of the electrostatic surface. Alternatively, at this geometry, the cation is favorably located with respect to the six local sp^2 C–H dipoles. We find the simple van der Waals model to be reasonably accurate for our cation–arene distances, only slightly underestimating the separation (2–10% deviation), with worse agreement for the smaller cations.



SCHEME 1
Structure of $CB_{11}Me_{12}^-$ (**1**$^-$) with atom numbering shown

EXPERIMENTAL

Literature procedures[1] were used to prepare PPh_4**1**$^-$. The salt Cs^+**1**$^-$ was preparerd by ion exchange of PPh_4**1**$^-$ on an Amberlyst XN-1010 column in the H^+ form in methanol, neutralization of the eluent with CsOH, and evaporation to dryness under reduced pressure. Excess CsOH was removed by dissolving the product in Et_2O, filtering, and evaporating to dryness under reduced pressure. Pure Cs^+**1**$^-$ was obtained in quantitative yield. Other salts of anion **1**$^-$ were prepared by a 3 × 3 countercurrent partitioning of an Et_2O solution of Cs^+**1**$^-$ against a 20% aqueous solution of the chloride salt of the desired cation. The Et_2O layer was evaporated to dryness under reduced pressure and metal chloride impurities were removed by the same method as excess CsOH above. Pure salts were obtained in quantitative yield on mg to g scale. The $M^+(benzene)_2$**1**$^-$ (M = Tl, Cs, Rb, K) crystals were grown from 1 : 1 diethyl ether–benzene solutions by overnight ether evaporation in air. Neither these salts nor the solvents were dried before crystallization. Crystals of $Na^+(\eta^6\text{-benzene})_2$**1**$^-$ were grown from the dried salt (180 °C, 7 Pa, 24 h) in anhydrous (distilled from Na/benzophenone) superheated benzene (180 °C) in a sealed tube by cooling. Octahedral crystals initially formed but changed into plates over a few hours and the diffraction data were collected on the plates. Crystals of $Li^+(\eta^6$-toluene)$\mathbf{1}^-$ were grown from the dried salt (180 °C, 7 Pa, 24 h) in anhydrous (distilled from Na/benzophenone) toluene by slow evaporation of toluene under a stream of dried N_2. Attempts to grow crystals of $Li^+\mathbf{1}^-$ incorporating benzene were unsuccessful.

Intensity data were collected on a Siemens SMART CCD diffractometer with graphite monochromated MoKα (λ = 0.71073 Å). Structure solution was by direct methods (Tl^+, Na^+, Li^+) or by isomorphous replacement (Cs^+, Rb^+, K^+) using the SHELXTL package[13]. For all structures, the arenes were modeled as regular hexagons and their hydrogen atoms fixed with standard bond lengths and angles. The hydrogens of anion $\mathbf{1}^-$ were directly located in the Tl^+, Cs^+, Rb^+, and K^+ structures but were modeled as tori of electron density in the Na^+ and Li^+ structures. The carbon atom of the CB_{11} core of the anion $\mathbf{1}^-$ was only located in the Na^+ structure and for one of the crystallographically independent anions in the Li^+ structure. In all other cases, crystallographically imposed disorder prevented definitive assignment of the carbon vertex and the core was modeled as B_{12}. Crystallographic parameters are given in Table I. Compelling evidence for a general reassignment of the *Cmcm* structures to a noncentrosymmetric space group such as $Cmc2_1$ does not exist[14]. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC-114984 (Tl^+), No. CCDC-114983 (Cs^+), No. CCDC-114982 (Rb^+), No. CCDC-114981 (K^+), No. CCDC-114980 (Na^+), and No. CCDC-114979 (Li^+). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2, 1EZ, U.K. (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As often occurs[2], the Tl^+, Cs^+, Rb^+, and K^+ crystals are isomorphous. In these structures, the metal cation is apically η^6-coordinated to two sets of symmetry equivalent, nearly parallel (±3 to 5°), disordered benzene molecules in an essentially linear arrangement (centroid–cation–centroid angle 180 ± 3°) and equatorially coordinated to a single methyl group of each of four anions arranged in a symmetrical trapezoid, nearly square (all angles 90 ± 3°; the methyl-carbon-to-metal distances are given in Table II and compared to the sum of the van der Waals radii). Similar coordination to Cs^+ has been observed[15]. As shown in Fig. 1, the metal is essentially octahedrally coordinated. Both the cations and the anions are favorably oriented with regard to the local dipoles of the benzene molecule. In turn, each anion $\mathbf{1}^-$ is coordinated to four metal cations through four coplanar methyl groups of the icosahedron, (for example, positions 2, 3, 9, and 10) and the anions are in contact with each other. Infinite planes are generated (plane group *cm*), and these are stacked with an axial glide (*c*), as shown in Fig. 2.

For these isomorphous structures, the anion and cation are in close contact. However, for Cs^+, Rb^+, and K^+, the η^6-arene–cation distance increasingly exceeds the van der Waals contact with decreasing cation size (Fig. 3).

TABLE I
Crystallographic parameters

Empirical formula	$C_{30}H_{68}B_{16.50}Li_{1.50}$	$C_{25}H_{48}B_{11}Na$	$C_{25}H_{48}B_{11}K$	$C_{25}H_{48}B_{11}Rb$	$C_{25}H_{48}B_{11}Cs$	$C_{25}H_{48}B_{11}Tl$
Formula mass	615.60	490.53	506.64	553.01	600.45	671.92
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/c$	$Pmc2_1$	$Cmcm$	$Cmcm$	$Cmcm$	$Cmcm$
a (Å)	8.9918(2)	9.83610(10)	18.1212(12)	18.217	18.237(2)	18.3261(3)
b (Å)	39.5106(8)	9.2475(2)	18.6810(12)	18.9257(3)	19.352(2)	19.0629(2)
c (Å)	11.9507(2)	17.3552(3)	17.9675(11)	18.0733(3)	18.205(3)	17.6864(3)
α (°)	90	90	90	90	90	90
β (°)	108.1180(10)	90	90	90	90	90
γ (°)	90	90	90	90	90	90
Volume (Å^3)	4035.23(14)	1578.62(5)	6082.4(7)	6231.02(14)	6425.0(15)	6178.72(16)
Z	4	2	8	8	8	8
ρ_{calc} (g cm^{-3})	1.013	1.032	1.107	1.179	1.242	1.445
μ (mm^{-1})	0.049	0.064	0.189	1.604	1.167	5.242
Transmission coeff.	0.9975 and 0.9877	0.99 and 0.99	0.9850 and 0.9489	0.7294 and 0.7294	0.9770 and 0.6400	0.5318 and 0.1276
T (K)	159(2)	161(2)	160(2)	160(2)	170(2)	160(2)
λ (Å)	0.71073 MoKα	0.71073 MoKα	0.71073 MoKα	0.71073 MoKα	0.71073 MoKα	0.71073 MoKα
Reflections collected	20026	12185	9305	27986	18443	23685
Unique reflections	5285 $R_{int} = 0.093$	4098 $R_{int} = 0.0384$	1772 $R_{int} = 0.1072$	1140 $R_{int} = 0.0431$	3929 $R_{int} = 0.0677$	3972 $R_{int} = 0.0720$
Refl. observed	3226	3323	994	921	2927	3351
R index[a] ($I > 2\sigma(I)$)	$R_1 = 0.1128$	$R_1 = 0.0625$	$R_1 = 0.0727$	$R_1 = 0.0489$	$R_1 = 0.0456$	$R_1 = 0.0312$
R indices[a] (all data)	$R_1 = 0.1733$ $wR_2 = 0.2471$	$R_1 = 0.0833$ $wR_2 = 0.1746$	$R_1 = 0.1368$ $wR_2 = 0.1965$	$R_1 = 0.0625$ $wR_2 = 0.1364$	$R_1 = 0.0730$ $wR_2 = 0.1063$	$R_1 = 0.0395$ $wR_2 = 0.0702$
Weighting coeffs[b]	$a = 0.0269$ $b = 6.6779$	$a = 0.0786$ $b = 0.5462$	$a = 0.0603$ $b = 0.8212$	$a = 0.0528$ $b = 7.3558$	$a = 0.0469$ $b = 0.8028$	$a = 0.0149$ $b = 7.7699$
Goodness-of-fit[c], F^2	1.098	1.114	1.082	1.203	1.036	1.202

[a] $R_1 = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|)$; $wR_2 = (\Sigma|w(w(F_o^2 - F_c^2)^2|)/(\Sigma|w(F_o^2)^2|)$; [b] $w^{-1} = [s^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; [c] GooF = S = $(\Sigma[w(F_o^2 - F_o^2)^2]/(M - N))^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

ingly exceeds the van der Waals contact with decreasing cation size (Fig. 3). This is explained by assuming that anion–cation interactions are the dominant packing force and referring to Fig. 4. Large cations keep the anions separated, allowing the benzene molecules to approach the cation more closely. Smaller cations allow the anions to come together, preventing close approach by benzene. Tl^+ is in van der Waals contact with the benzenes

TABLE II
Important Distances

Cation	Distance, Å					
	Measured M-arene centroid	Other measured M-arene centroid	Calculated M-benzene centroid	Measured M-methyl carbon	Expected van der Waals M-methyl carbon[2]	Measured M-anion centroid
Tl^+	3.08[a,*]	3.03[19,c,†]		3.59, 3.48, 3.54, 3.39	3.64	6.65, 6.60, 6.59, 6.63
Cs^+	3.28[a,*]	3.58[20,‡] 3.29[21,†]		3.60, 3.59, 3.60, 3.47	3.81	6.67, 6.55, 6.66, 6.74
Rb^+	3.19[a,*]			3.51, 3.49, 3.49, 3.34	3.66	6.59, 6.53, 6.55, 6.62
K^+	3.14[a,*]	3.38[22,*] 3.38, 3.08[9,c,**]	2.84[23]	3.43, 3.41, 3.30, 3.43	3.52	6.54, 6.48, 6.48, 6.54
Na^+	2.69, 2.71[b,*]	2.73[17,‡]	2.24,[23] 2.4 to 2.6[12] 2.37[11]	2.70	3.16	5.96
Li^+	simple 2.39 inversion 2.45[d,‡]	2.01, 1.90[24,c,*] 1.94[25,*]	1.92[23]	simple 2.36, 2.33, 2.35 inversion 2.40, 2.26, 2.24	2.90	3.75, 3.74

[a] Distance between the cation and the centroid of all components of the disordered benzene molecules. [b] Distance between the cation and the centroids of all components of two the crystallographically different sets of disordered benzene molecules. [c] Calculated from the average M^+-ring C distance assuming a standard benzene geometry. [d] Distance between the cations and the aromatic centroids for the crystallographically different cation-toluene pairs, respectively. † Mesitylene, ‡ Toluene, * Benzene, ** 1,3-Calix[4]-bis-crown-6.

and does not fit this trend, but its bonding to benzene is probably stronger due to the potential for covalent interaction between the benzene occupied orbitals and the low-lying vacant 6p orbitals of this metal ion.

The coordination of the Tl^+, Cs^+, Rb^+, and K^+ cations to two benzene[6,7] molecules is consistent with gas phase results. The binding energy of K^+ to the first molecule of benzene is 80.4 kJ/mol, the second molecule of benzene binding with an energy of 78.7 kJ/mol, and the third and fourth binding with an energy of only 60.7 and 52.7 kJ/mol, respectively. The

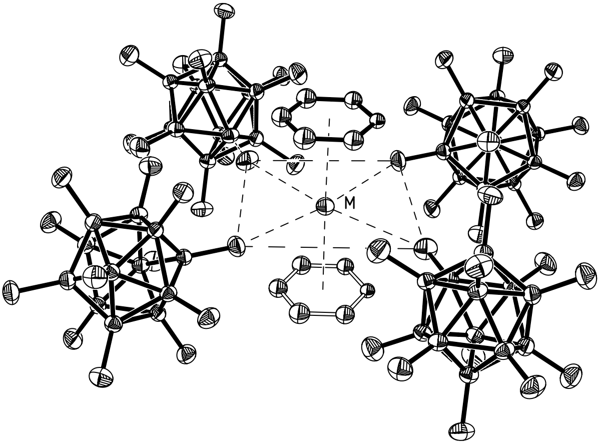


FIG. 1

View of cation coordination in the isomorphous (*Cmcm*) $M^+(\eta^6\text{-benzene})_2\mathbf{1}^-$ structures (M = Tl, Cs, Rb, K). This representation is taken from the Tl^+ data. Thermal ellipsoids are at 50% and the other isomorphous structures have similar thermal parameters. Hydrogen atoms are omitted for clarity

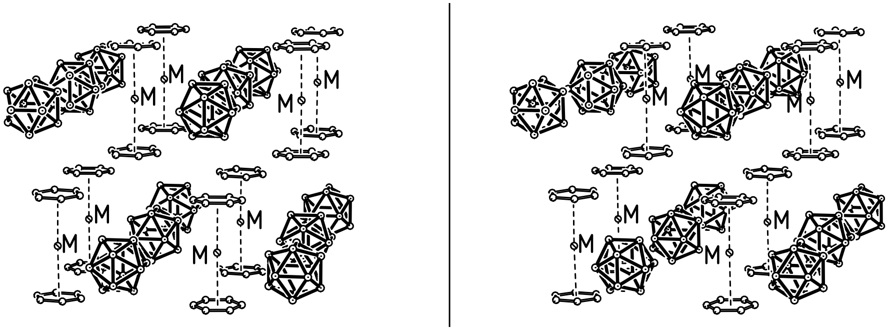


FIG. 2

Stereoview of the crystal packing in the isomorphous (*Cmcm*) $M^+(\eta^6\text{-benzene})_2\mathbf{1}^-$ structures (M = Tl, Cs, Rb, K). Hydrogen atoms are omitted for clarity coordination of Tl^+, Cs^+, and Rb^+ with benzene in the presence of water and diethyl ether is also not surprising: gas phase affinity experiments show that the interaction with water is weaker than the interaction with benzene.

The trend in M–benzene distances for the Cs^+, Rb^+, and K^+ structures predicts a η^6-arene–Na^+ distance of 2.95 Å, about 0.5 Å greater than the expected van der Waals contact (Fig. 3). Perhaps because of this, the Na^+ crystal does not adopt the same geometry, but rather crystallizes in the non-centrosymmetric space group[16] $Pmc2_1$ (Fig. 5), with the smaller Na^+ nearly tetrahedrally coordinated, in van der Waals contact with two methyl groups, one from each of two anions, and two benzene molecules in a tilted-sandwich arrangement. In turn, each anion is coordinated to two Na^+

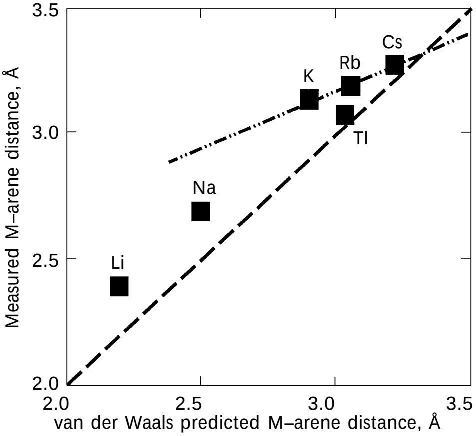


FIG. 3

Measured M–arene centroid distances against the expected van der Waals distances. The dashed line is the van der Waals prediction and the dashed-dotted line is the least-squares linear fit for the isomorphous alkali metal $M^+(\eta^6\text{-benzene})_2\mathbf{1}^-$ structures (M = Cs, Rb, K)

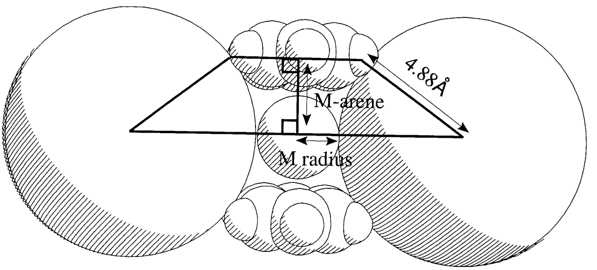


FIG. 4

Projection of the cation coordination in the four isomorphous *Cmcm* $M^+(\eta^6\text{-benzene})_2\ \mathbf{1}^-$ structures (M = Tl, Cs, Rb, K) through the plane defined by the trapezoid diagonal and the line connecting the arene centroids, with the anions $\mathbf{1}^-$ represented by spheres proportional to their van der Waals radii cations through two methyls of the lower belt of the carborane (positions 7 and 9), forming polymeric chains (Fig. 6). Interestingly, this arrangement has been observed before with the $Al(SiMe_3)_4$ anion[17].

The structure of the lithium salt contains two independent motifs (Fig. 7). In one motif, the Li^+ ion (Fig. 8) is tetrahedrally coordinated to the aromatic portion of a toluene molecule and three methyl groups (positions

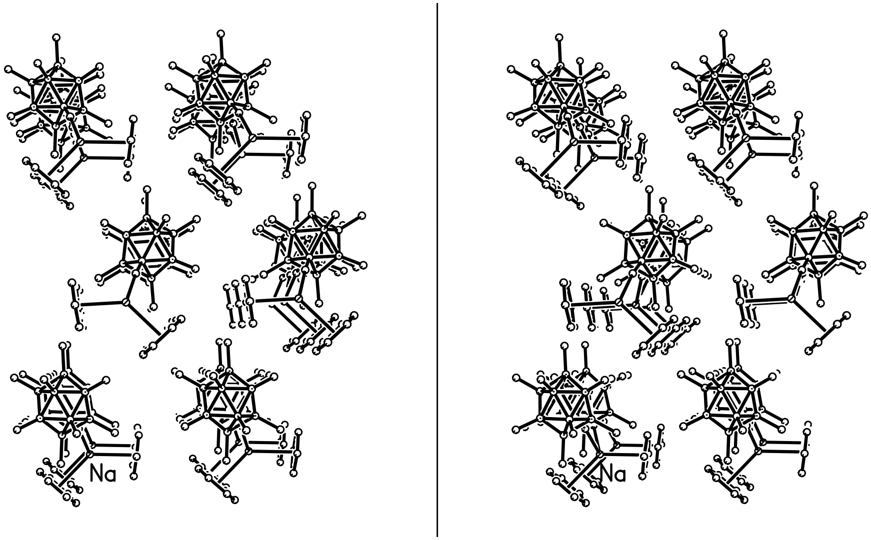


FIG. 5
Stereoview of the crystal packing in the $Na^+(\eta^6\text{-benzene})_2\mathbf{1}^-$ structure. Hydrogen atoms are omitted for clarity

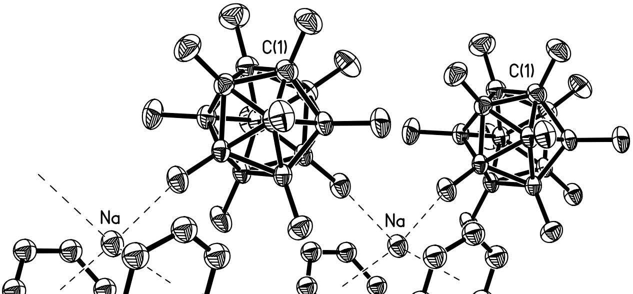


FIG. 6
View of the cation coordination in the $Na^+(\eta^6\text{-benzene})_2\mathbf{1}^-$ structure. Thermal ellipsoids are at 50% and hydrogen atoms are omitted for clarity

7, 8, and 12) with no other significant interactions. This Li^+–cluster centroid distance (3.747 Å) is much less than the formal van der Waals distance expected if the anion **1**$^-$ were a rigid sphere, 5.38 Å. Examination of the distances between the three Li^+ coordinated methyl carbons reveals that the methyl groups have been pushed apart, slightly engulfing the cation. The triangular face of the icosahedron of methyl groups that is coordinated to the cation has edges (C–C distances) 0.07 Å longer than the average (3.47 Å) of the other edges that would be equivalent in perfect C_{5v} symmetry of the skeleton of the isolated anion. This distortion of the anion is not observed in any of the other salts. The distances between the Li^+ cation and the carbons of the three coordinated methyl groups (average 2.34 Å) are significantly less than the sum of the van der Waals radius of $–CH_3$ and the ionic radius of Li^+ (2.90 Å). Both this failure of the van der Waals model

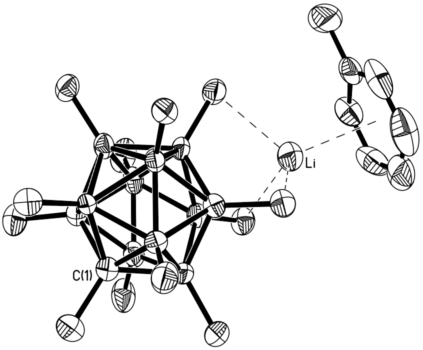


FIG. 7
View of the simple cation coordination in the $Li^+(\eta^6\text{-toluene})\mathbf{1}^-$ structure. Thermal ellipsoids are at 50% and hydrogen atoms are omitted for clarity

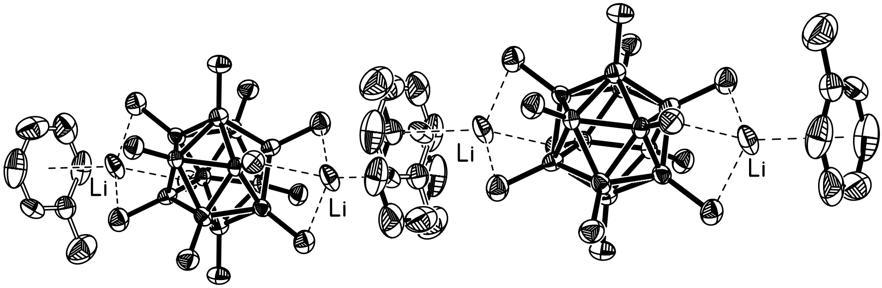


FIG. 8
View of the cation coordination on inversion centers in the $Li^+(\eta^6\text{-toluene})\mathbf{1}^-$ structure. All Li^+ and toluene components are half occupied. These chains are infinite, but here only one component of the terminal toluenes is indicated. Thermal ellipsoids are at 50% and hydrogen atoms are omitted for clarity

and this distortion of the anion undoubtedly reflect the very strong electrostatic attraction of the small Li^+ cation to its counterion, and illustrate the limits of a rigid and constant van der Waals radius of what is really an irregular icosahedron. The Li^+ cation is the only one of those examined that is small enough to feel the unevenness of the nearly spherical shape of **1**$^-$ and is tightly pinned against three of its methyl groups.

The other motif consists of chains of half-occupied η^6-toluene–Li^+ complexes on inversion centers between anions (Fig. 9). The η^6-toluene–Li^+ distance is slightly greater (2.45 Å) than in the simple motif (2.39 Å), presumably because the cation is dispersed between anions. However, the distance between the Li^+ cation and the methyl carbons (average 2.29 Å) is still significantly less than the van der Waals prediction (2.90 Å). This Li^+ cation is also tightly pinned against three methyl groups.

The very tight ion pairing ("engulfing") of Li^+ by the anion **1**$^-$ may be related to some of the unusual properties[1,18] of this ionic compound, such as its volatility and high solubility in benzene, which are not observed for other salts of anion **1**$^-$. Even the driest saturated solutions of Li^+**1**$^-$ in benzene studied exhibited easily detectable electric conductivity (specific conductance = $1.8 \cdot 10^{-3}$ S/m), possibly due to species such as $Li^+(\eta^6$-ben-

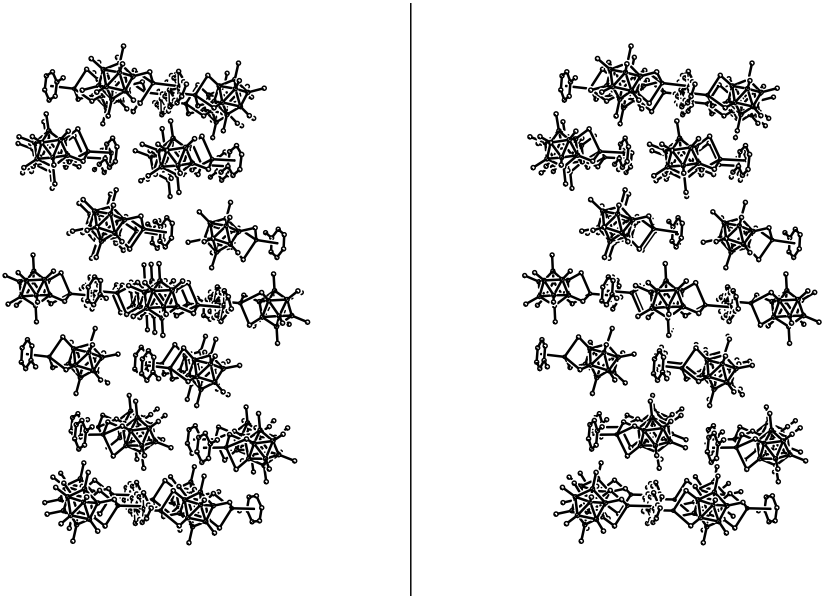


FIG. 9

Stereoview of the crystal packing in the $Li^+(\eta^6$–toluene)**1**$^-$ structure. Hydrogen atoms are omitted for clarity zene)$_n$Li(**1**)$_2^-$, and this needs to be examined further. Traces of water increase the conductivity dramatically and clearly facilitate the dissociation of ion pairs or aggregates.

Other examples of η^6-arene–alkali metal cation distances are provided in Table II and are consistent with our observations. The *ab initio* gas-phase bond length for several η^6-benzene–cation complexes has been calculated by several groups (Table II). As previously noted[2], the calculated values underestimate the actual distances, here by 0.3–0.4 Å. Obviously, the details of these condensed-phase structures cannot be explained merely by considering the interaction of an isolated cation with an arene.

CONCLUSIONS

Coordination of closed-shell monovalent cations with arenes occurs in the solid state in the presence of the weakly coordinating counterion **1**$^-$. The preferred coordination is η^6 and sandwich structures are favored.

In the four isomorphous structures with Tl^+, Cs^+, Rb^+, and K^+, the arene position is such that the electrostatic interactions with both the cation and the four neighboring anions are favorable. The coordination distances are slightly longer than the expected van der Waals contacts, especially for the smaller cations. Understandably, calculated geometries of gas-phase η^6-benzene–cation complexes do not agree quantitatively with these condensed-phase measurements. The coordination sphere of the cation is completed by four methyl groups, one from each of four anions **1**$^-$, and is thus octahedral overall.

The Na+ cation appears to be too small to accommodate this arrangement and has a tetrahedral coordination sphere with two benzene rings and two methyl groups, one from each of two anions 1– (a tilted double-decker sandwich).

The Li^+ cation also has a tetrahedral arrangement, with one toluene ring (open-faced sandwich) and three methyl groups from a single anion **1**$^-$. The Li^+ cation penetrates somewhat into the protective methyl sheath of the anion by pushing methyl groups aside.

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