

Solid-State Evidence for π -Complexation of Sodium and Potassium Cations by Carbon–Carbon Triple Bonds

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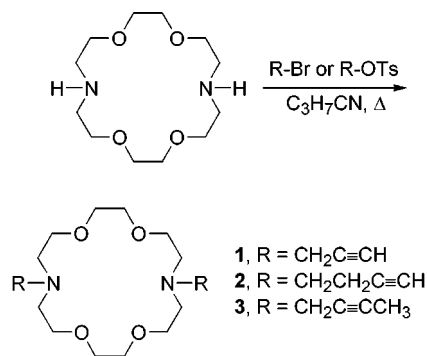
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Alkali metal cation– π interactions of Na^+ and K^+ with benzene, phenol, and indole have inspired much interest, study, and debate. The pioneering efforts of Kebarle and co-workers¹ showed that the enthalpic interaction between benzene and K^+ was significant and similar in magnitude to that between K^+ and a single water molecule. Subsequent studies by Castleman et al.² found similar results for the Na^+ cation. As expected for the more charge-dense Na^+ cation, the enthalpic interactions were stronger than for K^+ . Similar enthalpies were observed for the interaction of Na^+ with benzene, a molecule of water, or a molecule of methanol. Theoretical³ and gas-phase experimental studies⁴ reported by Dunbar and Ryzhov have extended our understanding of these phenomena. A variety of other efforts have been reported, and these studies were summarized by Ma and Dougherty in a 1997 review.⁵ Our successful recent efforts have focused on the complexation of Na^+ and K^+ by the side chains of tryptophan (Trp, W), tyrosine (Tyr, Y), and phenylalanine (Phe, F), namely indole,⁶ phenol,⁷ and benzene.⁸ We now report what is, to our knowledge, the first solid-state structural evidence for alkali metal cation π -complexation by the neutral triple bond of an alkyne.

Structural evidence for metal cation triple bond complexes may be found in the literature dating to 1973. In that year, Beauchamp, Rochon, and Theophanides reported the solid-state structure of $\text{K}[\text{Pt}((\text{C}_2\text{H}_5)_2\text{C}(\text{OH})\text{C}\equiv\text{CC}(\text{OH})(\text{C}_2\text{H}_5)_2)\text{Cl}_3]$.⁹ The key interaction of the alkyne was with Pt; K^+ served as counteranion for the complex anion. Studies after that recorded similar alkyne complexes involving W,¹⁰ Mo,¹¹ Re,¹² and a further but related example of a Pt complex.¹³ Of greater relevance to the present

Scheme 1



work is a series of organometallic “tweezer” compounds that were reported, beginning in 1996.¹⁴ In these structures, a transition metal ion is typically π -bonded directly to two molecules of trimethylsilylacetylene anion: $\text{M}(\text{C}\equiv\text{C}-\text{TMS})_2$. The alkali metal ion complexed to the triple bond is Li^+ , Na^+ , K^+ , or Cs^+ , but most commonly K^+ . A very recent example is a Na^+ -alkyne π -complex of $\text{PhC}\equiv\text{CSm}[\text{N}(\text{TMS})_2]_3$ in which Na^+ is also coordinated by three THF molecules.¹⁵ In every case thus far reported, the triple bond involved in alkyne complexation has been the organometallic salt of a terminal alkyne.

Early studies from our laboratory used diaza-18-crown-6 as the primary cation complexing unit and incorporated propargyl sidearms (compound **1**).¹⁶ Receptor molecules having a single carbon atom between the macrocycle and the double bond, triple bond, or arene failed to exhibit sidearm coordination when either Na^+ or K^+ was ring-bound. In recent work involving the arene donors, extension of the sidearms by an additional carbon was adopted as the strategy.^{6–8} Continuing that successful approach, two new compounds were prepared for the present study, *N,N'*-bis(3-butynyl)-4,13-diaza-18-crown-6, **2**, and *N,N'*-bis(2-butynyl)-4,13-diaza-18-crown-6, **3**. Compounds **2** (89%, oil) and **3** (64%, mp 74–75 °C) were prepared by alkylation (Scheme 1) using the incipient sidearm as either the bromide or tosylate. The KI complex of each was prepared by vapor diffusion crystallization from acetone–hexane: **2**·KI (mp 113–114 °C) and **3**·KI (mp 182–183 °C). In addition, the NaI complex of **2** (**2**·NaI, mp 141–142 °C) was isolated.

Solid-state structures of **2**·KI, **2**·NaI, and **3**·KI are shown in Figure 1. First, and most important, unlike bis(propargyl)-4,13-diaza-18-crown-6, **1**, bis(homopropargyl) compound **2** formed a complex with KI in which the macrocyclic-bound cation was additionally complexed by the sidearm alkynes.

Panel a (top) shows the structure of **2**·KI in the typical lariat ether complex conformation. The sidearms coordinate the ring-bound cation from opposite sides. The $\text{K}\cdots\text{N}$ (2.967 Å) and $\text{K}\cdots\text{O}$ (2.723, 2.866 Å) distances are typical. The symmetrical triple bond carbons are 3.102 and 3.174 Å from K^+ , and the C–K–C angle is 21.65°. Potassium is eight-coordinate in this complex, and iodide ion is excluded from the solvation sphere ($\text{K}\cdots\text{I}$ distance, 5.900 Å).

The corresponding NaI complex (**2**·NaI) is shown in panel b. Like the KI complex of **2**, the sidearms are part of the coordination

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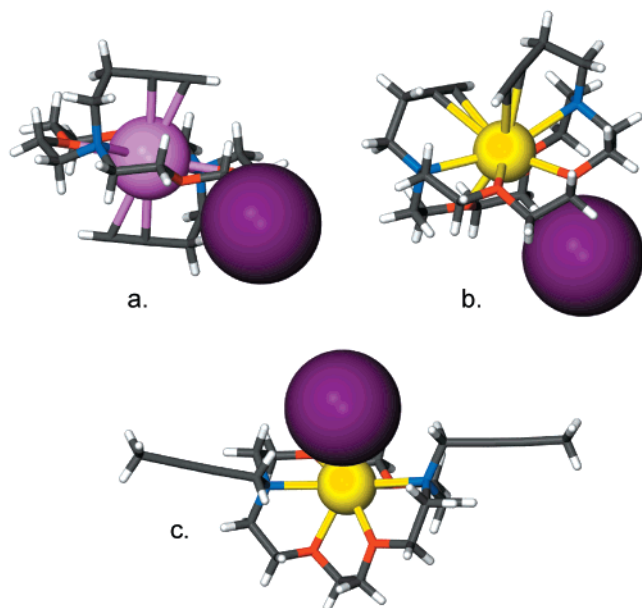


Figure 1. Solid-state structures of **2**·KI (panel a, top left) **2**·NaI (panel b), and **3**·KI (panel c, bottom).

sphere. Comparable distances for **2**·NaI are shorter than those observed for **2**·KI, as expected, owing to the smaller size of Na^+ . The $\text{Na}\cdots\text{O}$ distances are 2.499, 2.529, 2.570, and 2.568 Å. The weaker interaction of Na^+ with macrocyclic nitrogen than with oxygen is apparent in the 2.916 and 2.822 Å distances. The interaction of the alkyne carbons with Na^+ on one sidearm may be described as a triangle having sides of 3.078 and 3.093 Å with an angle of 22° between them. The second sidearm interactions are nearly identical (3.000 Å, 3.112 Å, 22.07°). Again, iodide is too distant (5.995, 6.018 Å) from Na^+ to interact.

The most striking feature of **2**·NaI is that the sidearms coordinate the ring-bound cation from the same, rather than the opposite, side. We have observed similar behavior in Na^+ and K^+ lariat ether complexes having $\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_2\text{CH}_2\text{OCH}_3$ sidearms.¹⁷ Potassium cation is near the mean plane of the

macrocyclic donors in *E*-**2**·KI but substantially out of the plane in *Z*-**2**·NaI. This is expected on the basis of the shorter donor-ion distances but also affords a steric constraint favoring the sidearm interaction from the same side of the ring.

The success of $\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ sidearms as donors in **2**·KI stands in marked contrast to the lack of participation by $\text{CH}_2\text{C}\equiv\text{CH}$ (propargyl) sidearms in the corresponding complex **1**·KI.¹⁶ On the basis of our recent work with arene-terminated sidearms,¹⁸ we felt that the triple bond position rather than the sidearm length was the critical issue. Even so, it seemed possible that a four-carbon sidearm having an internal triple bond might also afford a π -complex. Compound **3** is the isomer of **2** and was prepared to test this possibility. Panel c of Figure 1 shows the solid-state structure of **3**·KI. Notably, the sidearms are extended rather than folded back toward the macrocycle and its bound cation. The $\text{K}\cdots\text{N}$ (2.987 Å) and $\text{K}\cdots\text{O}$ (2.790, 2.814 Å) distances are similar to the corresponding value observed in **2**·KI. The nearer sidearm triple bond carbon is >5 Å from K^+ . The K^+ ion is seven-coordinate by virtue of the macrocyclic donors and iodide, which is only 3.403 Å from the cation. Note that this is about half the $\text{K}\cdots\text{I}$ distance observed in **2**·KI.

In summary, we report here the first solid-state evidence for a stabilizing interaction between an alkali metal and a neutral carbon-carbon triple bond (*E*-**2**·KI, *Z*-**2**·NaI). The triple bond must be appropriately positioned on the sidearm, or competition with the counteranion will be lost (**3**·KI). The shorter contacts between the macrocyclic donors and Na^+ alter the sidearm geometry from *anti* to *syn* in *Z*-**2**·NaI. These results show that interactions between triple bonds and alkali metals may occur broadly, although they have not heretofore been documented in the solid state.

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