Solid state evidence for π-complexation of sodium cation by carbon–carbon double bonds

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Solid state evidence shows that neutral double bonds, attached to flexible sidearms of a lariat ether, serve as intramolecular π-donors for a ring-bound Na+ cation.

The interactions of metal and organic cations with olefins and arenes have been the subject of considerable interest and study beginning more than a quarter century ago. As early as the late 1960s, pioneers in crystallography reported the structures of complexes between silver and olefins. Ganis and Dunitz, for example, reported the structure of a complex between cyclodecene and silver(I).[1] Almost simultaneously, the silver-bullvalene structure was reported.[2] A number of other Ag+···olefin complexes have been reported since.[3] Alkali metal–π interactions have also been documented for some time. Two early solid state structures of K+–arene contacts deserve note. One is the structure of KBPh4 in which K+ is nestled in the space created by adjacent arenes in the anion.[4] The other involves a neutral benzene molecule in contact with a crown-ether-bound K+. In the latter case, the interaction is apparent from the fact that the adjacent arene pulls the cation out of the crown ether plane.[5] Numerous solid state structures have appeared that are suggestive of alkali metal ion coordination with benzene[6] or other aromatic compounds present within the structure,[7] or within the crystal lattice.[8]

By 1981, Kebarle and coworkers[9] demonstrated the interaction of K+ with benzene in the gas phase. The magnitude of the enthalpic stabilization was remarkable; similar in magnitude to that provided K+ by a molecule of water. Similar results were found for the interaction of Na+ with benzene by Castleman Jr. and coworkers.[10] Additional computational[11] and experimental studies,[12] reported by Dunbar, Ryzhov and coworkers, have extended our understanding of these phenomena. The interaction of various cations with arenes has been summarized[13] and more recently reviewed by us for alkali metal–arene interactions.[14] In addition, we have recently reported the use of lariat ethers to demonstrate the complexation of Na+ and/or K+ by indole,[15] phenol[16] and benzene.[17]

Several recent studies have demonstrated alkali metal interactions with olefins. Silver and sodium complexes of a Z-stilbene-derived crown showed clear evidence for olefin–cation contacts within the macroring.[18] Although the major focus of this work was Ag+ complexation, Na+–C distances of ~2.8 Å were reported. Our approach in the search for Na+ and K+ to olefin interactions was to use a crown ether as the basic complexing unit. The unsaturated unit was placed on a flexible sidearm that could position itself to augment binding if appropriate. Earlier studies using this strategy involved aza-18-crown-6[19] (2) and diaza-18-crown-6[20] (3) in which the sidearm(s) was allyl. In neither case was sidearm participation confirmed. A recent report showed that N-allylaza-15-crown-5, 1, when complexing Ag+ ion, formed a coordination polymer involving the ring bound cation and an adjacent double bond.[21] We now report a sodium crown ether complex (4·NaPF6) in which the flexible sidearms are capable of serving as axial donors for a ring-bound cation or of turning completely away from the macroring.
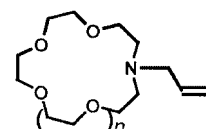
1, n = 1, R = CH2CH=CH2
2, n = 2, R = CH2CH=CH2
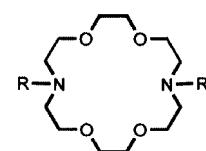
3, R = CH2CH=CH2
4, R = CH2CH2CH=CH2
5, R = CH2CH=CHCH3

Two new crown ethers were prepared for the present study: N,N'-bis(but-3-enyl)-4,13-diaza-18-crown-6, 4, and N,N'-bis-(but-2-enyl)-4,13-diaza-18-crown-6, 5. Both were prepared by heating 4,13-diaza-18-crown-6 in CH3CN with Na2CO3 and the alkenyl bromide corresponding to the desired sidearm. Compound 4 was obtained in 67% as a colorless oil. The NaPF6 salt, i.e. 4·NaPF6, mp 116–117 °C, was obtained by crystallization from acetone–diethyl ether. Compound 5 was isolated (45%) as a white powder, mp 56–57 °C (after crystallization from acetone:hexane).

The solid state structure of 4·NaPF6 is shown in Fig. 1: from the side and above the macroring plane (upper panel) and a top view (lower panel). Both illustrations are shown in the tube representation although the cation is shown as an appropriately-sized sphere in the bottom view. The foremost observation is that the sidearm double bonds participate as axial donors that are equidistant (i.e., the sidearms are symmetric about an axis through the cation) from the cation and above and below the macroring plane. This is of critical importance because the sidearms are flexible and may easily turn away from the macroring. The sidearm ethylene groups are in a gauche arrangement. The interaction between Na+ and the double bond carbons forms a triangle, C(3)–Na–C(4), in which C(4) is the terminal sidechain atom. The distances are 3.150 and 3.103 Å, respectively, and the angle between them (Na+ is at the apex) is 24.28°.

The macrocycle of 4·NaPF6 is in the expected D_{3d} conformation. The Na+···O distances are typical [2.521(2) and 2.545(2) Å] as are the longer Na+···N distances [2.893 and 2.893 Å]. The closest fluorine atom in the hexafluorophosphate group is ~5.5 Å from Na+.

An interesting feature of 4·NaPF6 is that sidearm coordination occurs from opposite sides of the macrocycle. In early studies of lariat ether complexation involving two armed structures, we found that N,N'-bis(2-methoxyethyl)-4,13-diaza-18-crown-6 formed complexes with both Na+ and K+. When Na+ was bound in the macroring, the sidearms coordinated from the same side (i.e. in a syn arrangement). In contrast, ring-bound
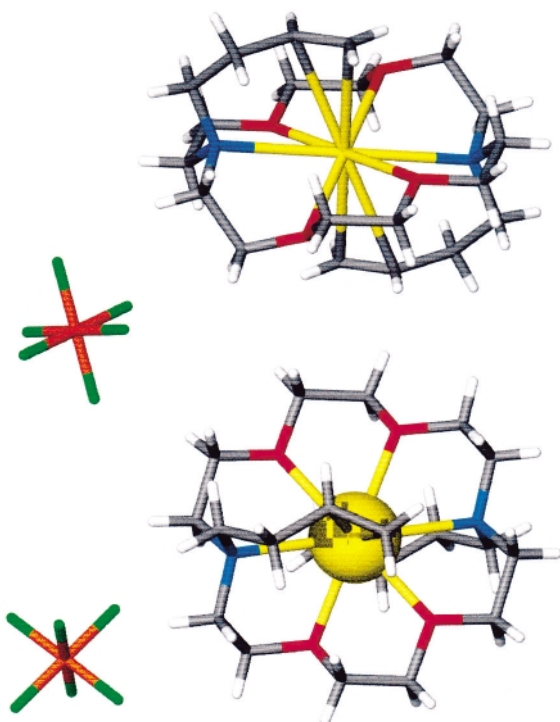
Fig. 1 Solid state structure of **4**·NaPF$_6$ in side (upper panel) and top views.

K$^+$ was coordinated from opposite (*anti*) sides.[19] When the sidearm donor was smaller hydroxy rather than methoxy, the sidearms were *syn* coordinated whether the complexed cation was either Na$^+$ or K$^+$. The *anti* orientation of the sidearms in the present case may result from the larger steric demand of the alkenyl donor groups.

Compound **5** was prepared in the hope that a complex would be isolated in which the ring-bound cation was coordinated by the anion rather than the inappropriately-positioned sidearms. This type of 'control' experiment proved successful for the benzene-sidearmed analogs[17] and in the triple bond case.[23] Thus far, however, we have been unable to obtain crystals of any complex of **5** that are suitable for analysis.

We present here the first evidence for coordination of an alkali metal cation by a natural double bond residue that is not sterically constrained. The lariat ether system is advantageous because the double bond donor group is attached to a flexible sidearm. The sidearm donor may compete with the anion if it is energetically favorable.

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