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σ-Donor, π-donor, and anion competition in π-complexation of alkali metal cations

Jiaxin Hu,[a] Leonard J. Barbour[b] and George W. Gokel*[a]

[a] *Division of Bioorganic Chemistry, Bioorganic Chemistry Program, and Department of Molecular Biology & Pharmacology, Washington University School of Medicine, 660 South Euclid Ave., Campus Box 8103, St. Louis, MO 63110, USA. E-mail: ggokel@molecool.wustl.edu*

[b] *Department of Chemistry, University of Missouri, Columbia, MO 65211, USA*

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Removal of or replacement of one of two phenylethyl sidearms on azalariats leads to clear evidence for cation–π interactions with the remaining sidearm.

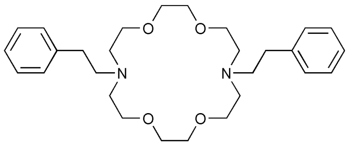
Lariat ethers[1] having arene-terminated sidearms have proved to be an ideal vehicle for assessing various interactions with alkali metal cations.[2–8] Early attempts in our laboratory to obtain evidence for cation–π interactions used diaza-18-crown-6 compounds having benzyl, allyl, or propargyl sidearms. Solid state complexes were obtained but they failed to show the expected cation–π interaction between, for example, benzene and either Na^+ or K^+.[9] The recognition that Nature separates the aromatic residues of histidine, phenylalanine, tryptophan, and tyrosine from nitrogen by two carbons, rather than one, led to an alteration of the receptor system. Receptors derived from 4,13-diaza-18-crown-6 having sidearms of the type CH_2CH_2Ar were prepared and their alkali metal complexes showed clear evidence for M^+–arene π-interactions.[10] This was true when the arene was benzene,[11] phenol,[12] or indole.[13] Indeed, even cation–π complexes involving double[14] and triple[15] bonds were obtained by using this receptor system.

In all of these cases, the counter anion was excluded from the coordination sphere. Hydrogen bonding of a sidearm to the anion was observed in some cases but a concern remained that crystal packing forces might be controlling the complexation phenomenon to the exclusion of, for example, electronic effects. This concern was dispelled for the $CH_2CH_2C_6H_5$ sidearmed receptor by converting the phenyl into a pentafluorophenyl ring. In this case, the $CH_2CH_2C_6F_5$ sidearms turned away from the complex and iodide ion was in contact with the ring bound cation.[11] Another convincing strategy would be to prepare compounds having a single arm to see if, when complexed, the arene would occupy one apex and the counter ion would engage the other. We now report the successful results of those experiments.

Three receptors were prepared for the present studies. Compound **1** has been previously reported.[11] Compound **2** was prepared by the following procedure. Monoalkylation of diaza-18-crown-6 with 2-bromoethylbenzene (CH_3CN, reflux, 20 h) gave *N*-(2-phenylethyl)-4,13-diaza-18-crown-6, which was then heated (CH_3CN, reflux) with $CH_3OCH_2CH_2OMs$ to afford **2** (69%, oil). Compound **3** (55%, oil) was obtained by alkylation of aza-18-crown-6 with 2-bromoethylbenzene (CH_3CN, reflux). Crystals suitable for X-ray crystallography were grown under vapor diffusion conditions (ethanol or ethyl acetate/hexane) as previously described.[10] The complexes were obtained as follows: **2**·KPF_6, mp 111–112 °C, colorless parallelepipeds; **3**·KI, mp 143–144 °C, colorless parallelepipeds; **3**·$KB(PhCl\text{-}p)_4$, mp 182–183 °C, colorless needles.†

The previously described[10] complex **1**·KI is shown in Fig. 1 and serves as a benchmark.

Average distances are as follows: K–O, 2.69 Å; K–N, 3.06 Å and K–arene, 3.43 Å. The iodide counter ion is well outside the coordination sphere of potassium, more than 7 Å away. When one of the phenylethyl sidearms of **1** is replaced by 2-methoxyethyl, compound **2** results. Both the arene and the ether sidearm coordinate K^+. The average distances for **2**·KPF_6 are: $d_{K–O}$, 2.74 Å; $d_{K–N}$, 2.97 Å; $d_{K–OMe}$, 3.08 Å and $d_{K–arene}$, 3.12 Å. The K^+ to macroring donor interactions are similar to those in **1**·KI. The apical oxygen contact is more remote than expected and the arene is 0.3 Å closer. This stronger arene–metal interaction may account for the apparently weak K–OCH_3 contact. Like **1**·KI and related lariat ether complexes, the PF_6^- counter ion does not contact the bound metal ion.



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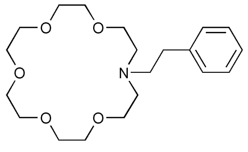

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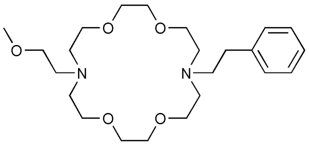

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When only one sidearm is present, it seems reasonable that the vacant apical position will be occupied by another donor. Solvent or adventitious moisture are candidates to play this role but the counter ion is clearly the most available. In **3**·KI, the sidearm arene occupies one apex of the complex and the other position is filled by iodide anion. The average distances for **3**·KI are: K–O, 2.79 Å; K–N, 3.05 Å; and K–arene, 3.13 Å. The K–I distance is 3.67 Å. Assuming radii for K^+ and I^- of 1.51 and 2.2

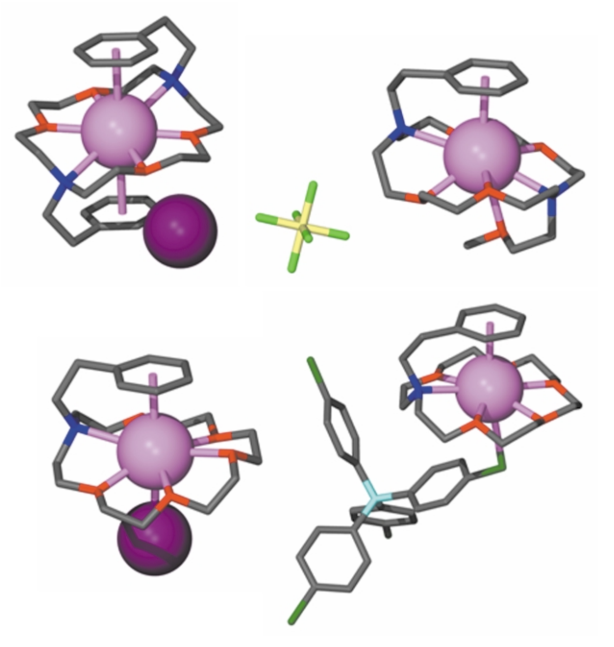

Fig. 1 Top, left: **1**·KI, right: **2**·KPF_6. Bottom, left: **3**·KI, right: **3**·$KB(C_6H_4Cl)_4$.

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Å, respectively, the minimum K–I distance should be 3.71 Å. Using 1.8 Å as the half-thickness of a benzene ring,[16] the minimum K–arene distance should be 3.3 Å. Because the K–arene contact (3.13 Å) is so short, the other K$^+$–donor distances are slightly longer than expected in this complex.

Almost identical distances are observed for the **3**·KB(C_6H_4Cl-*p*)$_4$ complex. The average distances in this case are: $d_{K–O}$, 2.77 Å; $d_{K–N}$, 3.02 Å and $\mathrm{d}_{K–arene}$, 3.00 Å. The $d_{K–Cl}$ contact is 3.28 Å. Bond distances in this complex are generally as expected. The remarkable feature is the extremely short K$^+$–arene contact. Although both complexes of **3** have nearly linear (~160–180°) arene–K–halogen arrays, the closer K–arene distance in **3**·KB(C_6H_4Cl)$_4$ suggests greater reliance on the π-interaction than on covalent or ionic halide. The longer (~0.1 Å) K–arene distance in **3**·KI compared to **3**·KB(C_6H_4Cl)$_4$ suggests that the charged halide is the better donor.

We present here three novel lariat ether complexes that exhibit clear cation–π interactions between K$^+$ and a benzene ring. By varying the identity of, or removing completely, the second sidearm, the π-interaction is shown to result from stereoelectronic effects rather than from crystal packing forces.

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Notes and references

† *Crystal data*: for **2**·KPF_6: $C_{23}H_{40}F_6KN_2O_5P$, a = 8.989(3), b = 22.393(7), c = 14.259(5) Å, β = 98.813(6)°, monoclinic, space group $P2_1/n$. For **3**·KI: $C_{20}H_{33}IKNO_5$, a = 15.2796(14), b = 10.8811(10), c = 14.0760(13) Å, β = 93.035(2)°, monoclinic, space group $P2_1/c$. For **3**·KB(PhCl-*p*)$_4$: $C_{44}H_{49}BCl_4KNO_5$, a = 16.0216(17), b = 13.3313(14), c = 20.516(2) Å, β = 91.629(2)° , monoclinic, space group $P2_1/n$. CCDC reference numbers 189371–189373. See http://www.rsc.org/suppdata/cc/b2/b204338f/ for crystallographic data in CIF or other electronic format.

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