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Lariat Effect visualized through the Bathochromic Shift of Counter Anion Absorption

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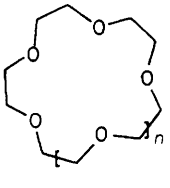
The bathochromic shift of the absorption band of the counter anion, extracted into the organic phase with a macrocyclic ligand from aqueous metal picrate solutions, has been shown to be a convenient measure for evaluating the geometry of cation–ligand complexes in solution.

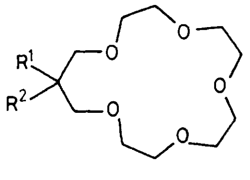
Lariat ethers, possessing an extra donor group on a side arm of a crown ether, are believed to show enhanced cation binding abilities, as compared with the reference crown ethers, by further ligation of the side arm.[1—4] Indeed, an *X*-ray crystallographic study has demonstrated participation of the extra binding site in an isolated crystalline complex of a nitrogen-pivot lariat ether, *N*-(2-methoxyethyl)-monoaza-18-crown-6, with potassium iodide.[2b] However, in the solution phase, no direct evidence supporting involvement of the side arm has been presented. We reveal now the role of the side arm as an effective binding site in lariat ethers by observing the behaviour of the counter anion upon complexation in the solution phase, and further propose a convenient, and potentially general, method for evaluating the geometry of cation–ligand complexation.

When a cation accommodated in a crown cavity is further ligated by the side arm of a lariat ether from an open face of the complex, several chemical and physical properties of the donating side arm as well as the 'lariated' cation must change considerably. Simultaneously the counter anion is also subject to significant influence. The most drastic change is the enforced elongation of the cation–anion distance by insertion of the side arm between the ions. This insertion, although it stabilizes the cation by ligation with the extra donor, reduces the stabilization of the counter anion owing to reduction in coulombic interaction, which may readily be detected spectroscopically. We therefore investigated the spectroscopic change of absorption band of the counter anion extracted into the organic phase in the solvent extraction of aqueous metal picrates with some crown ethers, related lariat ethers, and cryptands. In solvent extraction, only the ion pair complexed with the ligand may exist in the organic phase, which has advantages over the ligand titration of metal picrates dissolved in a homogeneous solution.[5]

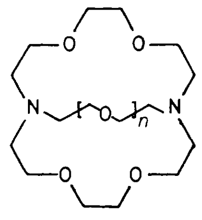
Aqueous solutions of alkali and heavy metal picrates were extracted with dichloromethane solutions of 15-crown-5 (**1**), 16-crown-5 (**2**),[6] lariat ethers (**3**)—(**5**),[1] 18-crown-5 (**6**), and cryptands (**7**) and (**8**). The organic phase separated after equilibration at 25 °C was analysed spectrophotometrically, resulting in a variety of positions of the major absorption maxima of the picrate ion, which are characteristic of the counter anion and ligand employed; the results are shown in Table 1. An interesting observation in the crown-5 series is that, for all cations employed, the absorption maximum red-shifts gradually on going from 15-crown-5 (**1**) to the double-armed lariat ether $(O_2)_2$–16-crown-5 (**4**) through 16-crown-5 (**2**) and O_2–16-crown-5 (**3**).† Significantly, with the double-armed lariat ether (**4**), all the picrates gave the same ultimate absorption maximum at 375 nm irrespective of counter cation, and the single-armed lariat ether (**3**) also afforded very similar values around 372—375 nm. On the



(**1**) n = 1
(**6**) n = 2



(**2**) $R^1 = R^2 = H$
(**3**) $R^1 = Me$, $R^2 = MeOCH_2CH_2OCH_2$
(**4**) $R^1 = R^2 = MeOCH_2CH_2OCH_2$
(**5**) $R^1 = R^2 = n-C_8H_{17}OCH_2$



(**7**) n = 1
(**8**) n = 2

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† The extractabilities for potassium and thallium picrates did not follow this order, for which facile formation of 1:2 sandwich complexes of these cations with 15-crown-5 may be responsible.

other hand, bis(octoxymethyl)-16-crown-5 (**5**), which may be regarded as a 'dummy' lariat ether lacking an effective donor atom at an appropriate position of the side arm, did not function as a lariat ether, and merely led to almost identical absorption maxima as the simple 16-crown-5 (**2**). Thus, the anomalous bathochromic shifts for the lariat ethers (**4**) and (**5**) are concluded to originate not from the steric hindrance of long side chain(s) but from a genuine lariat effect of the donating side arm. The ultimate value observed for the double-armed lariat ether (**4**) importantly coincides exactly with that for the three-dimensional ligand cryptands (**7**) and (**8**). This indicates that both lariat ether and cryptand render the anion of each metal picrate well-separated from the counter cation to yield the same ultimate absorption maxima.

The above two extreme situations, which we observed for the two-dimensional 15-crown-5 and the three-dimensional lariat ethers or cryptands, may be compared directly with the behaviour of metal salts dissolved in polar aprotic solvents of different polarities. Less polar solvents with low dielectric constants give a contact ion pair, while more polar solvents highly stabilize the cation by dense solvation leaving the counter anion at a remote position outside the solvent cage in a less solvated state. Sodium picrate, for instance, exhibited an absorption band for the contact ion pair at 350 nm in tetrahydrofuran and a band for dissociated, or solvent-separated, picrate ion at 377 nm in dimethyl sulphoxide or dimethylformamide. The latter band is very similar in shape and wavelength to that observed for the picrates complexed with lariat ethers and cryptands, indicating a similar environment around the picrate ion in both cases.

The absorption shifts caused by 16-crown-5 and 18-crown-6 are also interesting and significant. As compared with 15-crown-5, 16-crown-5 showed a large bathochromic shift particularly for the size-fitted cations, Na^+ and Ag^+. This result supports our previous proposal[6] that the enlarged crown cavity of 16-crown-5 is much more suitable in size and donor-orientation for these cations than 15-crown-5 and therefore these cations 'nest' in 16-crown-5 but 'perch' on 15-crown-5. However, the further bathochromic shift up to 367 nm of sodium picrate caused by 18-crown-6 needs another rationale; the encapsulating complexation of the small cation is inferred to be operative to some extent. We may conclude that the bathochromic shift of counter anion absorption is a convenient and versatile measure for evaluating the geometry of cation–ligand interaction in the solution phase.

Table 1. Absorption maxima in nm of metal picrates extracted into dichloromethane with various ligands.[a]

	Cation					
Ligand	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+
15-Crown-5 (**1**)	358	367	364	362	358	365
16-Crown-5 (**2**)	362	363	365	362	363	363
O_2–16-Crown-5 (**3**)	373	374	375	375	372	374
$(O_2)_2$–16-Crown-5 (**4**)	375	375	375	375	375	375
$(OctO)_2$–16-Crown-5 (**5**)	362	365	367	364	362	365
18-Crown-6 (**6**)	367	369	368	369	368	373
[2.2.1]Cryptand (**7**)	375	375	375	375	375	375
[2.2.2]Cryptand (**8**)	375	375	375	376	375	376

[a] Extraction experiments were conducted at 25.0 ± 0.1 °C with a dichloromethane solution (10 ml) of the ligand (0.3 mM) and an aqueous solution (10 ml) of metal picrate (3.0 mM).

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