Photocontrol of Complexation of Neutral and Cationic Species by *p-tert*-Butylcalix[4]arene Tetraethyl Ester

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A number of sodium salt complexes of *p-tert*-butylcalix[4]arene tetraethyl ester (**1**) were isolated both with and without upper-rim encapsulated acetonitrile or methanol. Upon dissolution in $CDCl_3$, **1** remained largely complexed to the sodium cation but ca. 90 % of the upper-rim bound solvent was released, reflecting the relative values of the binding constants for complexation of the two guest species. Selective decomplexation of lower-rim bound sodium cations could be successfully achieved using low-pressure light sources, triggering the immediate expulsion of the upper-rim bound solvent. The extent of decomplexation at both rims is controlled both by the oxidation of the counter-anionic species at the lower rim and by the fate of the photoproducts generated. The calixarene host molecule, **1**, remains intact during the decomplexation process.

Introduction

Calixarenes are a widely studied class of macrocyclic ligands, obtained from the base-catalysed condensation reaction between *para*-substituted phenols and formaldehyde. The general structure of a calixarene is shown in Figure 1. Functionalisation at the lower rim of parent calixarenes (Figure 1, R = H) has led to a variety of derivatives, which have found use in a number of industrial and analytical applications.[1–3] We have been interested in the calix[4]arene esters in particular as their well-defined hydrophobic region, defined by the upper-rim aromatic moieties and lower-rim hydrophilic regions, allows for complexation of both neutral and cationic guests, respectively.[4–7] There have been a limited number of studies carried out on calixarene complexes, which bind guests at the upper and lower rims simultaneously. In one such study, Pochini et al. have shown that a conformationally mobile calixarene host did not show significant upper-rim complexation of a guest whereas its sodium complex, which is more rigid, strongly interacts with the same guest.[8] Stibor et al. investigated the factors influencing the stability of inclusion complexes of calix[4]arene derivatives with neutral molecules, specifically acetonitrile (MeCN). *p-tert*-Butylcalix[4]arene tetraethyl ester (**1**) (Figure 1: R = $CH_2COOCH_2CH_3$) was included in this study, and Stibor found that the presence of a sodium cation at the lower rim of the calixarene significantly enhanced the binding of neutral guests at the upper rim.[9] Stibor's work correlates well with thermodynamic studies in solution of compound **1** with a series of alkali metal salts in MeCN, MeOH, and benzonitrile carried out by other groups. This latter work had concluded that MeCN was seen to produce an "allosteric effect", whereby the interaction of MeCN with the hydrophobic cavity of **1** preorganises the hydrophilic cavity to interact with cations, and the authors had noted the increased stability of sodium complexes of **1** in MeCN.[10–15]

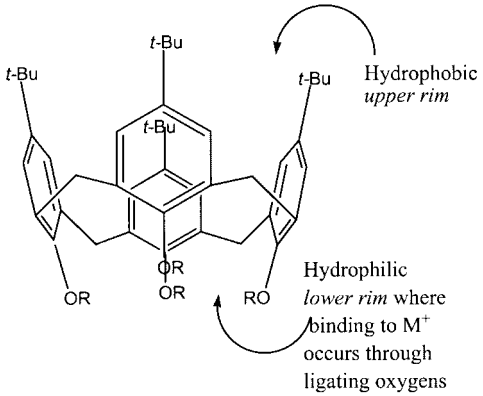

Figure 1. Structural formula of calixarene **1** indicating how it can bind guests.

Our main interest lies in the controlled decomplexation of alkali metal complexes of calixarene esters, specifically the sodium complexes. We have previously reported photodecomplexation studies on sodium iodide and tetraphen-

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ylborate complexes of calixarenes in $CDCl_3$, including those of compound **1**,[16,17] and found the % decomplexation to be anion-dependent. Moreover, the decomplexation reaction did not appear to involve a structural change in the calixarene macrocycle. Most photoresponsive macrocyclic systems in the literature employ an *all or nothing* reaction, whereby complexation is controlled by a photoisomerisable moiety within the macrocycle. For example, Shinkai and his colleagues synthesised an azobenzene-containing crown ether, the *cis* form of which bound K^+, Rb^+, and Cs^+, whereas the *trans* isomer preferentially bound Li^+ and Na^+.[18] Our previous work had shown that decomplexation could be controlled to a pre-determined level for the complexes studied and hence was comparable to an analogue control mechanism or analogue switch. This work also showed that for complexes isolated from acetonitrile, rather than chloroform, the overall % decomplexation of the complexes was reduced by up to 20%.[17] The difference in % decomplexation was thought to be due to the inclusion of MeCN in the upper rim of the complexes, exerting a stabilising or allosteric effect on complexation of sodium at the lower rim.

While our previous work had noted both the anion dependency as well as the dependency on solvent inclusion on the extent of photodecomplexation of complexes of **1**, the exact reasons for either dependency were not fully understood. The present study details photodecomplexation studies on a range of sodium complexes of **1**, prepared with several different counter anions, which were isolated from a number of solvents. Our previous studies had also indicated that photodecomplexation of NaI-**1** and $NaBPh_4$-**1** only occurred in chloroform and not in methanol or acetonitrile. The photoreactivity of the complexes in the nonpolar solvent was though to be related to the existence of ion pairs in this solvent, which would allow for efficient energy transfer from the calixarene macrocycle to the associated counter anion. The role of the photolysis solvent in the decomplexation process was therefore also investigated in this study.

Results and Discussion

NMR Studies on NaX-1 and NaX-1·MeCN Complexes

The sodium salt complexes of **1**, NaX-**1** (X = iodide, thiocyanate, perchlorate, periodate, and tetraphenylborate) were isolated from a series of solvents. While it has been reported that calix[4]arenes tightly bind chloroform, benzene, toluene, xylene, anisole and acetonitrile,[19–23] the limited stability of the sodium complexes in some of these solvents precluded their use.[24] Microanalysis of the isolated complexes indicated that for each of the NaI, NaSCN, $NaIO_4$ and $NaBPh_4$ complexes isolated from MeCN, a solvent molecule was also present and these complexes are henceforth denoted as NaX-**1**·MeCN (X = I^-, SCN^-, BPh_4^-, IO_4^-). The integration of the ^1H NMR signals confirmed that the ratio of NaX-**1**:MeCN was 1:1 in all samples. However, the ^1H NMR signal of the methyl group in MeCN was moved upfield relative to free MeCN in $CDCl_3$. Solid-state studies have shown that an interaction between the calixarene and MeCN occurs possibly via a CH_3-π interaction where the methyl group of the MeCN is orientated toward the hydrophobic upper cavity resulting in a significant shielding effect on the MeCN alkyl hydrogen atoms.[23,25] The $NaIO_4$ complex of **1** isolated from MeOH also had an upper-rim bound solvent molecule, henceforth denoted as $NaIO_4$-**1**·MeOH. No encapsulated chloroform or dichloromethane complexes of **1** could be isolated and such complexes are denoted as NaX-**1** in this study. Sodium salt complexes of **1** have been widely reported in the literature[4,9–15] and NMR assignments in $CDCl_3$ were based on these reports (Table 1). All of the reported NMR spectra, including the ones reported here, and additional X-ray crystallo-

Table 1. ^1H NMR chemical shift data for NaX complexes of **1** (X = I^-, SCN^-, BPh_4^-, ClO_4^-, IO_4^-) isolated from different solvents. All spectra were recorded in $CDCl_3$.

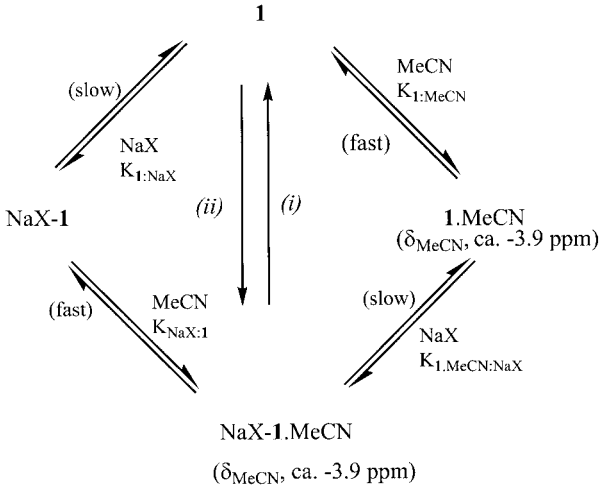
Functional group	**1**	NaI-**1**·MeCN	NaI-**1**[a]	NaSCN-**1**·MeCN	NaSCN-**1**[a]
tert-Butyl	1.07	1.17 (s)	1.14 (s)	1.15 (s)	1.14 (s)
OCH_2CH_3	1.27	1.41 (t)	1.42 (t)	1.42 (t)	1.42 (t)
Solvent signal		1.67(s)		1.50 (s)	
H_B CH_2 bridge	3.19	3.42 (d)	3.40 (d	3.40 (d)	3.40 (d)
H_A CH_2 bridge	4.85	4.25 (d)	4.24 (d)	4.25 (d)	4.25 (d)
OCH_2CH_3	4.21	4.39 (q)	4.38 (q)	4.38 (q)	4.38 (q)
$OCH_2C{=}O$	4.8	4.48 (s)	4.47 (s)	4.48 (s)	4.48 (s)
Aromatic *H*	6.77	7.16 (s)	7.12 (s)	7.13 (s)	7.12 (s)
Functional group	$NaBPh_4$-**1**·MeCN	$NaBPh_4$-**1**[a]	$NaClO_4$-**1**[a]	$NaIO_4$-**1**·MeCN	$NaIO_4$-**1**·MeOH
tert-Butyl	1.16 (s)	1.14 (s)	1.14 (s)	1.15(s)	1.14 (s)
OCH_2CH_3	1.38 (t)	1.35 (t)	1.43 (t)	1.41 (t)	1.41 (t)
Solvent signal	1.43 (s)			1.47 (s)	3.39 (s)
H_B CH_2 bridge	3.36 (d)	3.34 (d)	3.38 (d)	3.40 (d)	3.40 (d)
H_A CH_2 bridge	4.19 (d)	4.18 (d)	4.26 (d)	4.26 (d)	4.26 (d)
OCH_2CH_3	4.32 (q)	4.33 (q)	4.38 (q)	4.38 (q)	4.38 (q)
$OCH_2C{=}O$	4.42 (s)	4.42 (s)	4.48 (s)	4.48 (s)	4.48 (s)
Aromatic *H*	7.12 (s)	7.11 (s)	7.12 (s)	7.13 (s)	7.12 (s)

[a] Complexes isolated with no encapsulated solvent

graphic studies have indicated that the sodium complexes are in a fixed cone conformation in the solid and solution states. The complexation-induced shifts noted in Table 1 would indicate that the ion-pair interaction at the lower rim (as evidenced by ^{1}H NMR signals of the $OCH_2COCH_2CH_3$ and $OCH_2COCH_2CH_3$ moieties and the methylene bridges) was relatively similar for all the anions except for tetraphenylborate. This may be an indication that ion pairing with tetraphenylborate was weakest, which is consistent with the "non-coordinating" nature of this ligand, or that the phenyl groups of the anion are having an additional shielding effect at the lower rim.

^{1}H NMR signals at δ = 1.67 ppm, 1.50 ppm and 1.43 ppm in the ^{1}H NMR spectra of NaI-**1**·MeCN, NaSCN-**1**·MeCN, and $NaBPh_4$-**1**·MeCN, respectively, were assigned to MeCN in the upper rim of the complexes. In $CDCl_3$, free MeCN is known to have a chemical shift of 2.1 ppm.[26] The presence of MeCN resulted in small downfield shifts in the *tert*-butyl and aromatic signals for these complexes, relative to when MeCN was absent.

Stibor's study of the complexation of **1** with neutral molecules including MeCN in the presence and absence of sodium thiocyanate sets the context for our photolytic study of the same system in $CDCl_3$.[9] Scheme 1 shows the complexation equilibria that are set up when NaX-**1**·MeCN is dissolved in $CDCl_3$. The processes in which neutral guest MeCN complexes with **1** are fast on the NMR timescale, while Na^+ complexation processes are slow. However, the thermodynamics of these processes are reversed: Na^+ complexes very strongly with **1** with both $K_{\mathbf{1}:NaX}$ and $K_{\mathbf{1}\cdot MeCN:NaX}$ being of the order of 10^6–10^7 M^{-1}.[27] In contrast, the 1:1:1 complex formed from NaX-**1** and MeCN has a binding constant of 31 M^{-1}, while MeCN binds **1** extremely weakly with $K_{\mathbf{1}:MeCN} << 1$ M^{-1}.[9] Stibor has also determined the ^{1}H NMR properties of included MeCN in the ternary complex: from a free position of 2.1 ppm (i.e. δ_G^{MeCN}), the methyl group moves strongly upfield to a limiting value of δ_{GH}^{MeCN} = –3.9 ppm (associated with anisotropic shielding as the methyl group is inserted "head-first" into the upper rim of calixarene cavity and down into the inter-aryl space). This very large complexation-induced shift (CIS) of –6.0 ppm is probably also present in **1**·MeCN, as the geometry of NaX-**1**·MeCN and **1**·MeCN are similar, although the very weak binding precludes observation of this. If it is assumed that $K_{\mathbf{1}:MeCN}$ is < 0.3 M^{-1}, then the ratio $K_{NaX–\mathbf{1}:MeCN}/K_{\mathbf{1}:MeCN}$ is > 100; i.e. complexation of sodium at the lower rim favours complexation of MeCN at the upper rim by at least 11 kJ mol^{-1} in free energy terms.



Scheme 1. Complexation equilibria established in $CDCl_3$ solution upon dissolution of NaSCN-**1**·MeCN. Processes (*i*) and (*ii*) are discussed in the text.

We can now:
(a) Estimate the position these equilibria will attain when 4.0 mmol of NaX-**1**·MeCN is dissolved per litre of $CDCl_3$;
(b) predict the expected ^{1}H NMR behaviour of the methyl signal of MeCN; and
(c) subsequently use this information to rationalize the effect of photolytic decomplexation of $Na^+(X^-)$ on (a) and (b).

Firstly consider the equilibrium:

NaX-**1** + MeCN ⇋ NaX-**1**·MeCN

with $K_{NaX–\mathbf{1}:MeCN}$ = 31 M^{-1}, dissolving compound to 4 mM will result in net dissociation of ca. 90%, leaving f_c^G (fraction of guest, MeCN, complexed) = 0.10, and $\delta_{obsd.}^G$ = 1.50 ppm, i.e. 10% of the way from 2.1 to –3.9 ppm. Neither complex should dissociate its sodium significantly; f_c^{Na} will be > 98%, assuming $K_{\mathbf{1}:NaX}$ and $K_{\mathbf{1}\cdot MeCN:NaX}$ are ca. 10^6 M^{-1}. Finally, any **1**·MeCN present will be 99.9% dissociated. Thus there will be effectively only two environments for MeCN: In the form of NaX-**1**·MeCN or free in solution.

Figure 2(a) shows the predicted ^{1}H NMR binding curve, based on Stibor's data, i.e. the movement of the MeCN methyl protons for a range of stoichiometric or initial concentrations of NaSCN-**1**·MeCN dissolved in $CDCl_3$. At low concentrations of NaSCN-**1**·MeCN, it shows linear behaviour (asymptotically). This is shown in the expansion of the range 0–5 mM in Figure 2(b) i.e $\delta_{obsd.}^G - \delta_G^{MeCN}$ (the observed CIS) is approximately proportional to $[NaSCN\text{-}\mathbf{1}\cdot MeCN]_{initial}$ in this region. When [NaSCN-**1**·MeCN] = 4.0 mM, the ternary complex is 90% dissociated and we observe δ_G^{MeCN} = 1.50 ppm, exactly as predicted by Stibor's data.

If we assume that the values of $K_{NaX\text{-}\mathbf{1}:MeCN}$ are of comparable magnitude, then all of the NaX-**1**·MeCN complexes would behave similarly once dissolved in $CDCl_3$, and $\delta_{obsd.}^{MeCN}$ for each of the complexes should also be of similar magnitude. In fact $\delta_{obsd.}^{MeCN}$ = 1.47, 1.43, 1.50 and 1.67 ppm upon dissolution of 4 mM $NaIO_4$-**1**·MeCN, $NaBPh_4$-**1**·MeCN, NaSCN-**1**·MeCN and NaI-**1**·MeCN, respectively.

The presence of encapsulated MeOH was also observed in $NaIO_4$-**1** complexes with a chemical shift of 3.39 ppm. Free MeOH in $CDCl_3$ has a chemical shift of 3.64 ppm.[25] Although crystals of suitable quality have not been isolated for solid-state structure analysis, a potassium complex of a calixarene tetraamide has been reported with a molecule of MeOH in its hydrophobic cavity.[28]

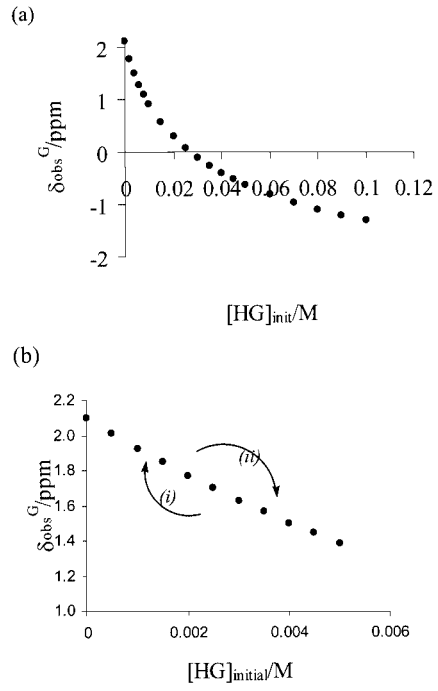


Figure 2. (a) Calculated plot of $\delta_{obsd.}{}^{MeCN}$ vs. [NaSCN-**1**·MeCN]$_{initial}$/M ($K_{NaSCN\text{-}\mathbf{1}:MeCN}$ = 31 M^{-1}, $\delta_G{}^{MeCN}$ to $\delta_{GH}{}^{MeCN}$ = 2.1 to –3.9 ppm). (b) Expansion of (a) shown in the range $\delta_{obsd.}{}^{MeCN}$ = 1.4 to 2.1 ppm, comparable to the range observed in our experiment.

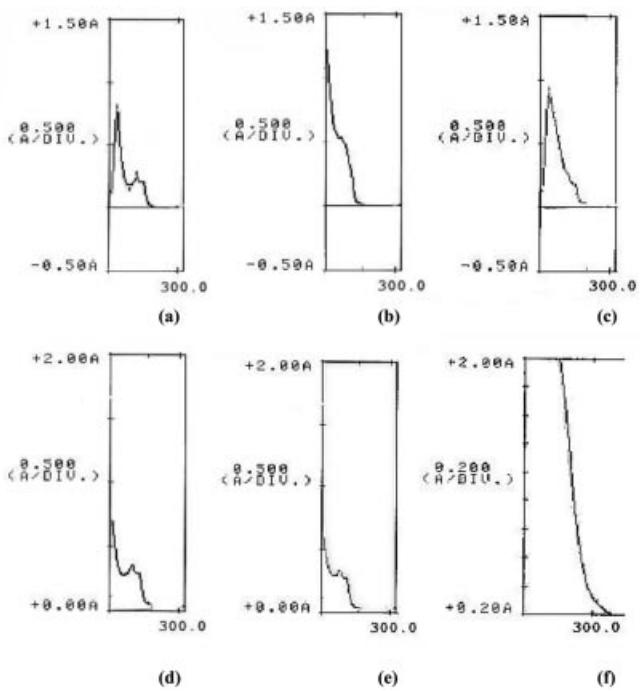


Figure 3. UV/Vis absorbance spectra recorded in $CDCl_3$ of (a) uncomplexed calixarene (**1**), (b) $NaBPh_4$-**1**·MeCN, (c) NaI-**1**·MeCN, (d) NaSCN-**1**·MeCN, (e) $NaIO_4$-**1**·MeCN, and (f) a pyrex NMR tube. Concentrations of complexes and calixarene approximately 1×10^{-5} M.

Photodecomplexation Studies of NaX-1, NaX-1·MeCN and $NaIO_4$-1·MeOH

Our previous work had shown that irradiation of $NaBPh_4$-**1** in $CDCl_3$ generated products consistent with the photooxidation of the tetraphenylborate anion.[17] In this study, we monitored the fate of the other anions upon photoexcitation of the macrocyclic complexes. The choice of excitation source was a low-pressure mercury lamp operating at room temperature, which emits primarily one band of radiation at 253.6 nm. Exposure of calixarene complexes to this wavelength leads to extensive photochemical reaction and breakdown of the host compound. However, the output of low-pressure mercury lamps includes a number of weak lines above 280 nm, including 289.4, 296.7, 302.2 and 312.6 nm. Use of this lamp with an appropriate UV filter, in this case a pyrex NMR tube, ensured that all photochemical decomplexations were clean and could be monitored over reasonable time-scales. Figure 3 shows the absorption spectra of the calixarene host compound **1** and some of its complexes, together with the transmission characteristic of a typical pyrex NMR tube.

The pyrex NMR tube effectively cuts out all radiation at the main excitation wavelength of the lamp and is only 10% transmitting at 280 nm, but increases thereafter. With this experimental set-up, decomplexation of the complexes of **1** could be monitored with good reproducibility over reasonable time scales.[29] The presence of the tetraphenylborate and iodide anions do alter the UV/Vis spectrum of its complexes, but for the remaining complexes the two main absorption bands of the calixarene varied little in position upon coordination; however, they varied somewhat in intensity. Table 2 gives the absorption data of free calixarene and its complexes at a number of wavelengths.

Table 2. UV/Vis absorbance data for host compound, **1**, and its NaI, NaSCN, and $NaIO_4$ complexes in $CDCl_3$.

Compound	λ (nm)	ε (cm^{-1} mol^{-1}) × 10^3
1	275	3.49
	281	3.54
	308	0.06
NaI-**1**·MeCN	272	4.73
	282	2.90
	308	0.25
NaI-**1**	272	4.71
	282	3.15
	308	0.28
NaSCN-**1**·MeCN	273	3.51
	282	3.41
	308	0.49
NaSCN-**1**	273	3.55
	282	3.44
	308	0.50
$NaIO_4$-**1**·MeCN	274	3.00
	283	2.58
	308	0.12
$NaIO_4$-**1**·MeOH	273	2.94
	282	2.59
	308	0.11

The unphotolysed samples of NaX-**1** had two main absorption bands at ca. 272 nm and 283 nm, characteristic of the complexed calixarene. The latter was assigned to the S_0

$\rightarrow S_1$ transition of the aryl ether moiety.[30,31] The primary wavelengths of excitation, centred around 308nm, correspond to the shoulder of the $S_0 \rightarrow S_1$ transition and the anion-centred absorptions. Photoexcitation of aryl ethers usually leads to the ejection of an electron from the arene excited (π,π^*) state and the formation of a radical cation. The subsequent activation of the aromatic ring is primarily at the *para* position but also at the *ortho* position.[32] In our case, a *tert*-butyl and a methylene group occupy these two positions, and so the expected further reactions would be inhibited. The other chromophoric species in solution are the counter-anionic species i.e. the iodide, thiocyanate, tetraphenylborate or periodate ions that have weak absorptions at these wavelengths (perchlorate ions have no absorption bands in this region).[33]

The % decomplexations of NaX-**1** complexes upon irradiation in $CDCl_3$ at timed intervals are shown in Table 3. The values for % decomplexation are calculated from the ^{1}H NMR spectra of the photolysed solutions by the integration of the aryl protons of the free and complexed species, as distinct signals can be seen for both species in the spectrum. These results indicated a significant anion dependence on the extent of decomplexation with up to 85% decomplexation being achieved with BPh_4^- and SCN^- as anions, but no decomplexation occurring for the sodium perchlorate complex and little for the periodate complex (14%). There was no apparent relationship between the extent of ion pairing at the lower rim and the extent of photodecomplexation, a factor we had previously thought to be important.[17] If this were the case, a $NaBPh_4$-**1** complex, which from the NMR results looks to be the least ion-paired of the complexes, would show the least % decomplexation. However, this was not the case. If fresh solutions of salt were added to the NMR tubes, full recomplexation of **1** occurred, indicating the integrity of the calixarene host was maintained during decomplexation. The presence of encapsulated MeCN within the upper cavity reduced the initial % photodecomplexation of the tetraphenylborate and periodate complexes. In all cases at extended irradiation times, where MeCN was present in the sample, recomplexation was seen to occur to some extent. Irradiation over a two-hour period of the free host, **1**, showed that the calixarene remained intact throughout.

Interesting decomplexation behaviour was noticed upon irradiation of NaX-**1**·MeCN complexes. Figure 4 illustrates the relationship between the amount of calixarene remaining complexed to a sodium cation and the chemical shift of the ^{1}H NMR peak for MeCN measured for three sodium complexes. At the concentrations of NaX-**1**·MeCN used in these experiments, ca. 4.0 mM, the ternary complex is 90% dissociated. As stated earlier, for the NaSCN-**1**·MeCN complex we observe $\delta_G^{MeCN} = 1.50$ ppm. Photolysis now causes net decomplexation of Na^+, and the rapid nature of the reaction

1 + MeCN ⇋ **1**·MeCN

means MeCN dissociates too. Thus the degree to which the sodium is decomplexed can be represented as a movement up the binding curve shown in Figure 2(b): 50% decomplexation will cause $\delta_{obsd.}^{MeCN}$ to move to 1.80 ppm (halfway back to 2.1 ppm) while 100% decomplexation will completely free all the MeCN ($\delta_{obsd.}^{MeCN} = \delta_G^{MeCN} =$ 2.1 ppm). This is represented by process (i) of Figure 2(b) and in Scheme 1. The ordinate-intercept value of the graphs is consistent within experimental error with the value 2.1 ppm for free MeCN in $CDCl_3$,[26] although experimentally 100% decomplexation was not observed in any of the complexes studied. This is because on the slower timescale of many minutes post-photolysis, the sodium will recomplex, moving the acetonitrile position back down the binding curve, represented by process (ii) of Figure 2(b) and in

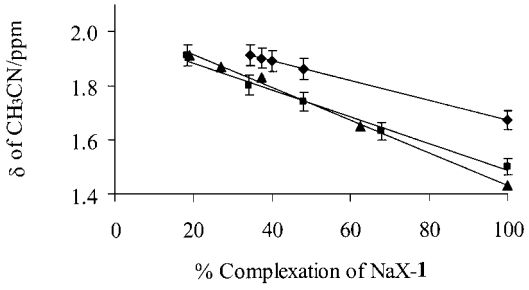


Figure 4. The relationship between the % complexation of NaX-**1** and the chemical shift, δ, of upper-rim bound acetonitrile; NaSCN-**1** (■), NaI-**1** (♦), $NaBPh_4$-**1** (▲). Concentration of each solution is 4 mM and each value is an average of 3 replicate experiments.

Table 3. Decomplexation (%) of NaX-**1** complexes (typical concentration 4.5 mM), before and after irradiation in $CDCl_3$ as determined by ^{1}H NMR spectroscopy. Each value is the average of 6 replicate experiments. Complexes with encapsulated MeCN and MeOH are indicated by NaX-**1**·MeCN or NaX-1·MeOH, respectively.

	% Decomplexation of NaX-**1** complexes								
Irradiation time [minutes]	NaI-**1**·MeCN	NaI-**1**	NaSCN-**1**·MeCN	NaSCN-**1**	$NaBPh_4$-**1**·MeCN	$NaBPh_4$-**1**	$NaClO_4$-**1**	$NaIO_4$-**1**·MeCN	$NaIO_4$-**1**·MeOH
0	0%	0%	0%	0%	0%	0%	0%	0%	0%
15	56±5%	55±6%	31±2%	25±1%	30±3%	44±9%	0%	7%	9%
30	64±2%	67±2%	62±4%	67±5%	65±5%	82±5%	0%	6%	16%
45	62±3%	65±2%	81±2%	81.5±3%	81±2%	87±1%	0%	10%	14%
60	53%	65%	68±3%	83.5±1%	72±3%	86±1%	0%	16%	14%

Scheme 1. This recomplexation can be accelerated by adding fresh excess NaX.

The behaviour of the other anions should be similar with any variability being due to variation in $K_{NaX-1:MeCN}$ values due to the anion. This variability is reflected in the differing slopes of the plots in Figure 4 and Figure 5(b). Such variations would be expected to be small based on the observed values for $\delta_{obsd.}^{MeCN}$ for the four complexes isolated in this study. Determination of the value of K for NaX-**1** with MeCN in the presence of different anions at the lower rim is now a feature of a further study by our group.

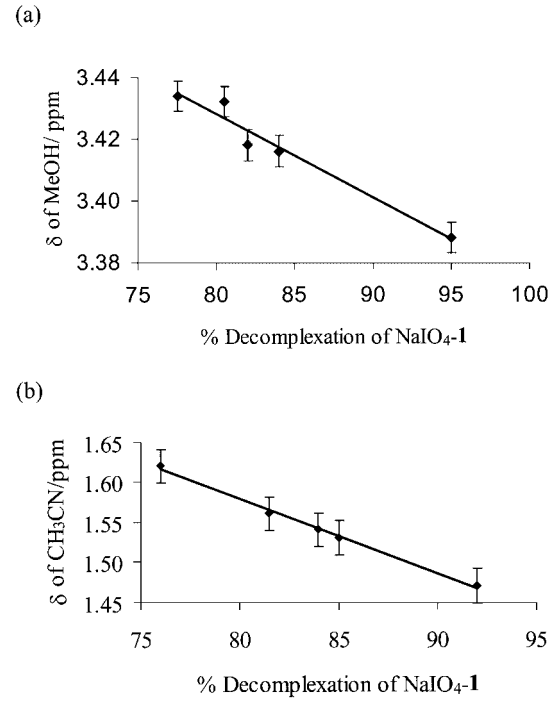


Figure 5. The relationship between (a) the % complexation of $NaIO_4$-**1**·MeOH and the chemical shift, δ, of upper-rim bound methanol and (b) the % complexation of $NaIO_4$-**1**·MeCN and the chemical shift, δ, of upper-rim bound acetonitrile. Concentration of each solution is 4 mM and each value is an average of 3 replicate experiments.

$NaIO_4$-**1** complexes with encapsulated solvent were also examined. The extent of decomplexation noted here was considerably less than in the thiocyanate, tetraphenylborate and iodide complexes. After irradiation of $NaIO_4$-**1**·MeOH, the MeOH peak shifted marginally downfield, consistent with the small extent of decomplexation noted for this anion, but again was found to be linearly dependent (presumably asymptotically) upon the extent of photodecomplexation [(a) in Figure 5]. A similar result was found for the corresponding $NaIO_4$-**1**·MeCN complex [(b) in Figure 5]. Stability constants for ternary complexes with methanol have not been determined yet but the behaviour of theses complexes upon irradiation would appear to be similar to the acetonitrile complexes of NaI-**1**, NaSCN-**1** and $NaBPh_4$-**1**.

From Table 3 it can be seen that the *extent* of neutral guest decomplexation depended on the identity of the counter anion at the lower rim, and the role of this anion in the decomplexation process was important to determine.

Photoreactivity of the Counter Anions of NaX-1

Potentiometric titration of aqueous extracts of the irradiated $CDCl_3$ solutions of NaI-**1** and NaI-**1**·MeCN (Table 4) indicated that the concentration of iodide was reduced upon irradiation, but that reduction did not correlate exactly with the decomplexation of the calixarene. In fact, while most of the iodide had reacted after 10 minutes, partial complexation of the calixarene at this and later times indicated the presence of another anion in solution. UV/Vis analysis indicated that triiodide was produced, presumably from the initial reaction of iodine radicals to form iodine followed by further reaction with iodide to form triiodide.[34] Chloride was also detected in reasonable concentrations (Table 4). A white precipitate isolated from the photolysed solutions was identified as NaCl. If a fresh source of counter anion, in the form of *tert*-butylammonium iodide was added to the NMR tubes, full recomplexation of **1** occurred. *tert*-Butylammonium is a cation that is too large to fit into the lower-rim hydrophilic cavity of **1**, and thus recomplexation of **1** must be with any sodium cation present (Table 4).

Replicate 1-mL samples of chloroform were irradiated for up to 90 minutes, under the same conditions described above, and in each case, no chloride was detected. Solutions of **1** in $CDCl_3$, irradiated for 60 minutes, showed no degradation of the calixarene. However, a potentiometric titration showed that chloride was present in these solutions, but at a significantly reduced level (1.69 ± 0.04 mM) than that recorded following irradiation of the sodium complexes of **1**. In a separate series of experiments *tert*-butylammonium iodide (TBAI) was irradiated for timed intervals and

Table 4. Autotitration results for NaI-**1** complexes before irradiation, and after irradiation for 10 (*) and 45 (#) minutes. Results are average of six replicate experiments (n.d. = not detectable).

	Complexed calixarene [%]	Complexed calixarene [mM]	Uncomplexed calixarene [mM]	Iodide concentration [mM]	Chloride concentration [mM]
NaI-**1**	100	8.76	0	8.56	n.d.
	74*	6.47 ± 0.65	2.29 ± 0.8	5.5 ± 1.5	0.92 ± 1
	36#	3.05 ± 0.14	5.70 ± 0.14	n.d.	6.63 ± 0.5
NaI-**1**·MeCN	100	8.76	0	8.64	n.d.
	66*	5.74 ± 0.2	3.02 ± 0.2	3.16 ± 0.6	n.d.
	38#	3.38 ± 0.2	5.38 ± 0.21	n.d.	6.53 ± 0.3

analysed by both ^{1}H NMR and potentiometry; TBA cation has no absorption bands above 280 nm. After just 15 minutes no iodide could be detected in solution and chloride, in an equivalent amount to that of iodide initially present, was detected [(a) in Figure 6]. The presence of triiodide in these solutions was confirmed by UV/Vis spectroscopy. The results confirmed that direct photooxidation of the anion could result in the production of triiodide from iodide and lead to the generation of chloride from the solvent.

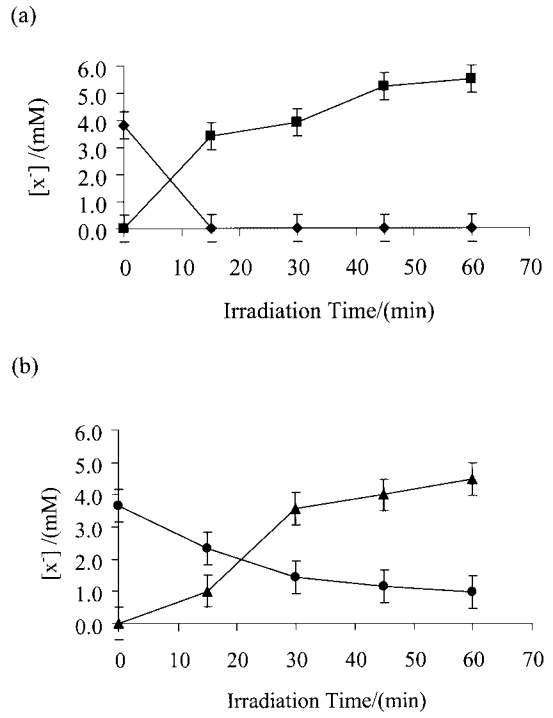


Figure 6. Plots showing (a) the relationship between concentration in mmol of iodide (♦) and chloride (■) ions in $CDCl_3$ solution on irradiation of 3.8 mmol TBAI at 15 minute intervals and (b) the relationship between concentration in mmol of thiocyanate (●) and chloride (▲) ions in solution on irradiation at 15 minute intervals of ca. 3.7 mmol TBASCN. Each value is an average of 3 replicate experiments.

GC and GC-MS analysis of the irradiated $CDCl_3$ solutions of both the calixarene and TBA iodide complexes showed that the primary organic products formed were deuterio-dichloromethane and -dichloroiodomethane ($CDCl_2I$) and traces of deuterio-1,1,2,2-tetrachloroethane. It is known that reduction of chloroform generates short-lived radical anions which eject chloride immediately upon formation.[35] The generated radicals can undergo disproportionation and recombination processes as well as further attack on solvent and this is evidenced by the photoproducts identified above. In all cases the photolysis by-products were present in much larger quantities for experiments carried out on the complexes rather than on the free ligand. In addition no organic photoproducts were identified upon extended irradiation of $CDCl_3$ solutions (or CD_2Cl_2 solutions, vide infra). In other studies, UV/Vis irradiation of metal coordination complexes where iodide is present either as an axial ligand or as a counter anion leads to the generation of an I$^{\cdot}$ radical, with concomitant reduction of the solvent by charge transfer to solvent (CTTS).[36–44] For those studies carried out in chlorinated solvents generation of iodide radicals has resulted in the production of chloride from chlorinated solvents.[40,41]

The pattern of destruction of counter anion and production of chloride can be seen again in the irradiation of NaSCN-**1** and NaSCN-**1**·MeCN This was shown firstly by quantitative FT-IR spectroscopy which indicated that irradiation of the NaSCN-**1** solutions resulted in the concentration of thiocyanate anions falling to undetectable levels after 30 minutes. A similar pattern was noted by potentiometric studies as shown in Figure 7. However, the complexes were once again noted by ^{1}H NMR spectroscopy to be only partially decomplexed over the same time period. The main anion present from photolysis of thiocyanate solutions, as detected by potentiometry, was again chloride and NaCl could be recovered as a precipitate from solution. Elemental sulfur also precipitated out of solution and was identified by microanalysis.

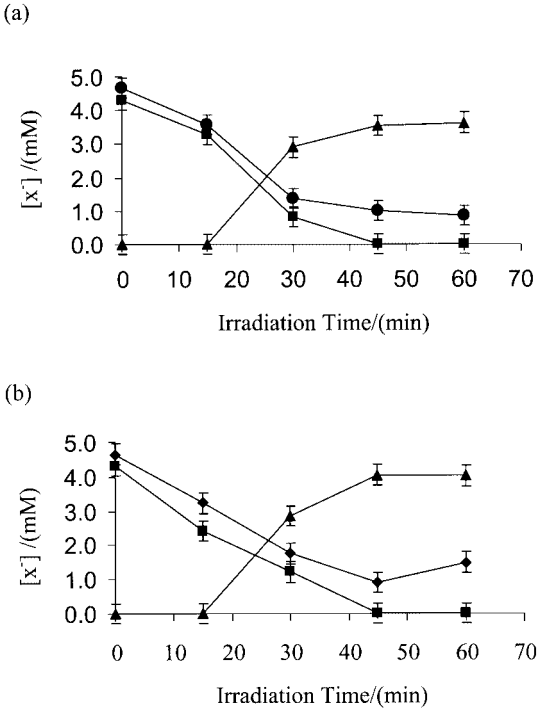


Figure 7. The relationship between (a) the concentration of NaSCN-**1** (●) and (b) the concentration of NaSCN-**1**·MeCN (♦) and those of chloride (▲) and thiocyanate (■) upon irradiation of the respective complexes in $CDCl_3$ at timed intervals. Each value is the average of six replicate measurements.

Irradiation of *tert*-butylammonium thiocyanate (TBASCN) over 60 minutes in $CDCl_3$ also showed the destruction of the SCN anion, though at lower levels than recorded for NaSCN-**1** [(b) in Figure 6]. Thus again the production of chloride in solution could be linked to the photoreaction of the counter-anionic species. GC-MS analysis of irradiated solutions of both TBASCN and NaSCN-**1** showed the formation of mainly deuterated dichloromethane as a photoproduct of the solvent.

These results confirm what other workers have noted on irradiation of thiocyanate complexes in nonaqueous solvents.[39,40,42] Initially irradiation leads to production of thiocyanate radicals which can then form sulfur and cyanide anion. The proposed reaction is:

$$SCN^- + h\nu \rightarrow SCN^{\cdot} + e^-_{solvated} \quad (1)$$

$$SCN^- + h\nu \rightarrow S + CN^- \quad (2)$$

followed by complex reactions in which cage recombination and further reactions with SCN^- are central:

$$SCN^- + SCN^{\cdot} \leftrightharpoons (SCN)_2^{\cdot -} \quad (3)$$

$$2\ (SCN)_2^{\cdot -} \rightarrow (SCN)_2 + 2\ SCN^- \quad (4)$$

$$S + SCN^- \rightarrow S_2 + CN^- \quad (5)$$

$$2\ SCN^{\cdot} \rightarrow (SCN)_2 \quad (6)$$

Elemental sulfur was recovered following photolysis of both NaSCN-**1** and TBASCN, but there was no evidence for the presence of cyanide from auto-titration or FT-IR studies. The cyanide anion itself can be further photolysed to the cyano radical, which can oxidise the solvent or form cyanogen gas, and this may be what has happened here.[42]

Electrochemical Studies

The experiments on the thiocyanate and iodide complexes, taken together with our previous work on tetraphenylborate, has confirmed that the oxidation of the counter-anionic species is critical to the decomplexation process. The non-reaction of perchlorate and minimal reaction of periodate complexes would support this. The electrochemical oxidation of the anions in $CDCl_3$, as TBAX salts and as the complexes NaX-**1**, was examined by cyclic voltammetry. The results indicated that the iodide, thiocyanate and tetraphenylborate anions in the form of the TBAX salts had oxidation potentials at 0.86, 1.20 and 0.85 V, respectively. In the corresponding calixarene NaX-**1** complexes, these oxidation potentials were recorded at 0.55, 0.95, and 0.80 V, respectively. Thus complexation with the calixarene lowers the oxidation potential of the anion which is consistent with the anion being effectively shielded from the bound cation. The relative ease of electrochemical oxidation of the anions was approximately in the same order as their photochemical oxidation (taking irradiation results after 15 minutes in Table 3, which is before equilibrium is reached).

Irradiation of NaX-1 in Other Deuterated Solvents

The % decomplexation of NaI-**1** and NaSCN-**1** were recorded after irradiation in CD_3OD, CD_3CN, and CD_2Cl_2 (Figure 8). No decomplexation of the complexes occurred in CD_3OD or CD_3CN. While ion pairing is minimised in these solvents it should also be noted that these solvents are not easily reduced by CTTS. The extent of decomplexation of both complexes was significantly less in CD_2Cl_2 than in $CDCl_3$ and both autotitration and IR measurements indicated that, while destruction of the anions had occurred, it was to a far lesser extent than in $CDCl_3$. Although the extent of ion pairing would be similar for these solvents, this difference in reactivity is thought to reflect the relative ease of reduction of these solvents [chloroform, –1.67 V ($E_{1/2}$) vs. dichloromethane –2.33 V ($E_{1/2}$)][45] resulting in the formation of chloride as well as other photoproducts.

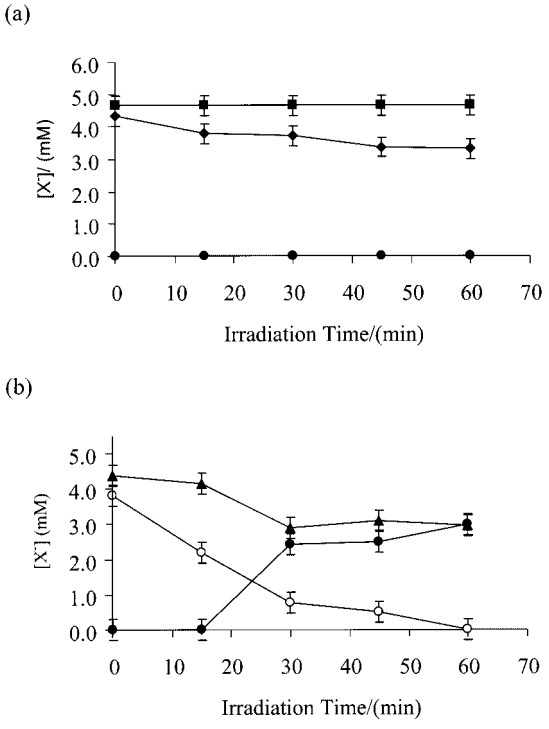
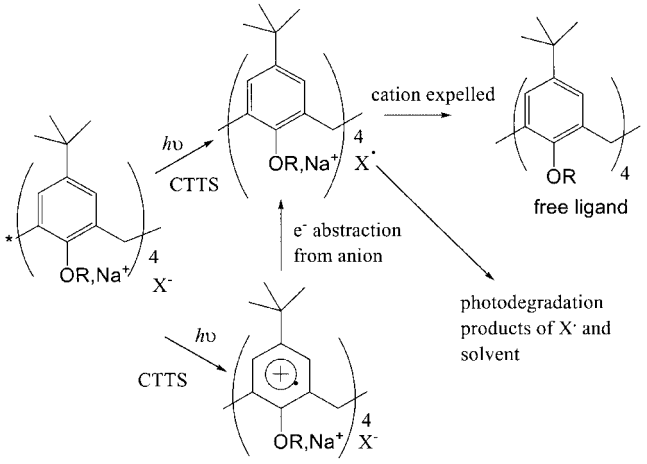


Figure 8. Variation in the concentrations of (a) NaSCN-**1** (■), thiocyanate (♦) and chloride (●) and (b) NaI-**1** (▲), iodide (○) and chloride (●) upon photolysis of the sodium complexes in CD_2Cl_2. Each value is an average of six replicate measurements.

Proposed Mechanism

In Scheme 2 the proposed mechanism for the decomplexation process is shown. Irradiation of NaX-**1** in $CDCl_3$ results in the possible generation of two excited species, a radical aryl cation and the direct oxidation of the counter-anionic species. While the experiments with TBA salts

would indicate that excitation of the counter anion predominates, some excitation of the aryl cation does occur as evidenced by the production of chloride ions, albeit at low levels, from the solvent upon irradiation of **1** on its own. However, although a radical aryl cation may be generated initially, abstraction of an electron from the counter anion or solvent is likely to have occurred quickly, as no photoproducts of the host compound were detected in any of the experiments.



R = $CH_2OCOCH_2CH_3$

X = I^-, SCN^-, BPh_4^-

Scheme 2. Proposed decomplexation mechanism for the sodium salt complexes of **1**. Encapsulated solvent is omitted for clarity.

Excitation of the counter-anionic species resulted in a charge transfer to solvent with the subsequent generation of a number of photoproducts of both the solvent and anion. The generation of a radical from the anion leads to the break-up of the ion pair and the subsequent expulsion of the sodium cation. This cation remains available for recomplexation if a suitable counter anion is added to solution post-photolysis or indeed is generated during the photolysis process, i.e. triiodide, chloride.

The products of iodide oxidation were ultimately triiodide and iodine, sulfur was isolated from irradiated thiocyanate solutions, and chloride ion was generated from CTTS to the solvent in both cases. The poor solubility of sodium chloride in chloroform, even in the presence of the macrocycle, precluded full recomplexation. The NMR spectrum recorded after irradiation showed the complex peaks to be at slightly shifted positions relative to the initial complex and these positions are consistent with the complex being present as NaY-**1** (Y = product anion i.e. I_3^-, Cl^-).[17] While photoproducts of the solvent, including the deuterated forms of 1,1,2,2-tetrachloroethane, dichloromethane and dichloroiodomethane, could be detected by GC-MS, there were no photoproducts of the macrocycle itself indicated by NMR or GC-MS.

Conclusions

This study involved the irradiation of a series of sodium salt complexes of **1**. Some of the complexes were isolated in the solid sate with a moleclue of solvent bound at the upper rim. Upon dissolution, however, the upper-rim guest largely dissociated, with about 10% of the solvent molecule remaining associated with the upper rim at any given time. Decomplexation of the sodium cation and immediate subsequent expulsion of upper-rim bound guest could be triggered by the oxidation of the counter anion at the lower rim and the extent of decomplexation varied as a function of the anion. The lower the oxidation potential of the anion the greater the extent of initial decomplexation, with iodide, thiocyanate and tetraphenylborate complexes being easily decomplexed whereas the perchlorate complex was unreactive, as expected. Addition of fresh solutions of anion (in the form of *tert*-butylammonium iodide/thiocyanate etc.) allowed full recomplexation to occur, indicating that the integrity of both the cation and macrocycle were maintained during irradiation.

Potentiometric studies of the inorganic species in solution indicated that there was not a linear correlation between photooxidation of the anion and decomplexation of the calixarene. Photolysis of the anions resulted in the production of other anionic species which could allow recomplexation to occur to some extent. The overall % decomplexation measured was found to be determined by the amount of NaY-**1** present *in solution* at the end of the experiment.

These studies have also helped to understand the relationship between a guest binding at the lower rim of a calixarene and the "allosteric effect" that this confers on upper-rim binding of neutral species.[8,9,25,46] In the example studied here the difference in binding constant for the two guests confers essentially a "one-way allosterism" and removal of the lower-rim bound guest, in this case by photodecomplexation, results in the immediate expulsion of the upper-rim guest. Thus the possibility for a novel control mechanism for the complexation of neutral guest at the upper rim of calixarenes, by choice of lower rim counter anion or level of irradiation, has been identified. Importantly, the photoreaction of the nonchromophoric TBA salts followed similar patterns to the calixarene complexes suggesting that controlled photodecomplexation of bound guests by other macrocyclic systems such as cryptands or resorcinarenes should be possible. The development of high level control of switching systems is obviously desirable and such a system offers potential as an analogue switching device for the control of complexation of neutral species. The dependence of the binding constants at the upper and lower rim as a function of the nature of the counter anion, cation and upper-rim guest is currently being investigated.

Experimental Section

Complexes of *p-tert*-Butylcalix[4]arene Tetraethyl Ester: This calixarene was synthesised and supplied as pure from Prof. M. A. McKervey, Queen's University Belfast and from Loctite (Irl) Ltd. All salts used in this study were supplied by Sigma–Aldrich and were dried overnight at 110 °C prior to use. The following solvents were used in this study: HPLC MeCN, HPLC MeOH (Riedel de

Haan); and HPLC chloroform, HPLC dichloromethane, [D_3]-MeCN, [D]chloroform, [D_2]dichloromethane and [D_4]MeOH (Aldrich). Anhydrous chloroform was supplied by Sigma–Aldrich. Hydrogen, air, nitrogen and helium were supplied by Air Products.

The complexes were prepared by mixing equimolar amounts of ligand and salt (typically 0.5 mmol) in ca.50 mL of MeCN, chloroform, dichloromethane or MeOH overnight in the dark. The solvent was allowed to evaporate naturally and passing a stream of N_2 over the complex dried the isolated salt. Full complexation was verified from ^{1}H NMR and FTIR data. Micro-analytical data, recorded at the micro-analytical laboratory at the National University of Ireland, Dublin, showed that the solid-state complexes, that contained solvent within the upper cavity, contained 1:1 mol ratios of solvent to complex in all cases.

Spectroscopic Techniques: Solutions of the analytes were typically 10^{-4} mol·L^{-1}. UV/Vis spectra were recorded with a double beam Shimadzu 160A Spectrophotometer. Their spectra were measured using a 10-mm path-length quartz cell. Infrared spectra were recorded with a Nicolet Impact 410 FTIR Spectrometer and the spectra processed on an attached PC using Omnic v.3.1a software. NMR spectra were recorded with a JEOL 300 MHz FT NMR spectrometer. Typically 20 mg of analyte was dissolved in 0.5 mL of a deuterated solvent and placed in a precision pyrex NMR tube.

Irradiation Procedure: The photolysis lamp used in this study was a Pen-Ray 5.5-Watt low-pressure cold cathode mercury vapour lamp with a 150 V (60 Hz) power supply. An external transformer was added to enable direct use of the mains power supply (220 V, 50 Hz). Previous irradiation studies with this lamp showed that a UV filter needed to be used in order to avoid ligand decomposition.[17] This filter was simply a glass NMR tube into which the irradiation sample was placed. Typically, 1 mL of a 4.5 mM solution of a complex in an appropriate solvent was placed into a Pyrex NMR tube. Another 1 mL aliquot of the irradiation sample was placed in the dark during the irradiation time as a reference sample. Before irradiation the solution was degassed for ca. 10 minutes to remove any dissolved oxygen from the sample.

Potentiometric Titration: A 1 mL aliquot of a 4 mM irradiated solution, in chloroform or dichloromethane, was washed with 5 mL ultra-pure water in order to extract all water-soluble inorganic species from the organic solvent. The aqueous layers were collected and transferred to a 50 mL plastic beaker where 2 mL of 2 M HNO_3 was added. The volume in the beaker was made up to ca. 25 mL with doubly distilled water. The solution was then titrated with 0.01 M $AgNO_3$ using a Metrohm 702 SM Titrino autotitrator with a Metrohm 703 Ti stand. The end point was determined potentiometrically using a combined silver ring electrode.

GC-MS Analysis: A GC method was developed using a Shimadzu GC system incorporating a GC-14A gas chromatograph fitted with an FID detector and a Supelco SBP-5 fused silica capillary column (15 m × 0.20 mm, 0.20 μm film thickness). Spectra were obtained from a Shimadzu C-R5A integrator. Samples were introduced to the GC with a Hamilton 10 μL syringe. A GC-MS method was developed using a Shimadzu GC system incorporating a GC-17A gas chromatograph, fitted with an FID detector and a Supelco SBP-5 fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness), and a QP-5000 mass spectrometer. Spectra were obtained using the "Class-5000" software package, and samples were introduced to the system with a Shimadzu AOC-20i auto injector.

Electrochemical Analysis: A CHI630A Electrochemical Analyser was used with a Pt wire as the auxillary electrode, a Ag/Ag^+ non-aqueous reference electrode, and a glassy carbon working electrode. A 0.1 M solution of *tert*-butylammonium hexafluorophosphate in chloroform was used as the electrolyte. 0.1 M solutions of *tert*-butylammonium thiocyanate and iodide were prepared in chloroform, and the solution to be analysed contained 6 mL of the electrolyte + 1 mL of the individual anion solutions. A 1 mM solution of *tert*-butylammonium tetraphenylborate was prepared in the electrolyte and was analysed undiluted. All solutions were degassed using nitrogen for 10 minutes prior to analysis. The technique used was CV, sweeping in a positive direction, looking at oxidation between 0 and 1.8 V, and the reverse as far as –0.6 V. The scan rate was 0.1 V/s, four segments were carried out (two full sweeps forward and reverse from –0.6 to 1.8 V), and the sensitivity was 2×10^{-5} A/V.

Acknowledgments

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