Structure and ion-complexing properties of an aza-15-crown-5 ether dye: synthesis, crystallography, NMR spectroscopy, spectrophotometry and potentiometry

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The perchlorate of 2-{2-[4-(13-aza-1,4,7,10-tetroxa-13-cyclopentadecyl)phenyl]ethenyl}-3-ethylbenzothiazolium (3) has been synthesised and its structure determined in the crystalline state by X-ray diffraction and in solution in acetonitrile by ^{1}H NMR methods. Complexation with barium and silver cations in solution has been studied in comparison with other model azacrown molecules by spectrophotometric and potentiometric methods. With the exception of the puckered azacrown moiety, the structure of 3 is remarkably planar, consistent with extensive π-conjugation throughout the remainder of the molecule in both solid and solution states. Compound 3 forms a stable 1 : 1 complex with Ba^{2+} ions in acetonitrile, with a stability constant of $K_1 = 80 \pm 10$ dm^3 mol^{-1}; the complexation results in major changes in the electronic absorption spectrum of 3, consistent with binding to the azacrown moiety. A model compound, phenylaza-15-crown-5 (2a), was found to bind Ba^{2+} to form both a 1 : 1 ligand–metal complex (LM), with a stability constant of $K_1 = (2.0 \pm 0.2) \times 10^4$ dm^3 mol^{-1}, and a 2 : 1 (L_2M) complex, with a stability constant of $K_2 = 220 \pm 20$ dm^3 mol^{-1} for binding of the second ligand. The electronic absorption and NMR spectra both indicate binding of the 'hard' Ba^{2+} cation to the azacrown oxygen atoms. However, by contrast, the evidence from NMR data shows that the 'soft' Ag^+ cation complexes with 2a mainly through a strong interaction with the azacrown nitrogen atom, giving a 1 : 1 complex with a stability constant of $K_1 = 6 \pm 1$ dm^3 mol^{-1}, determined by potentiometry. No complexation of 3 with Ag^+ is observed. Studies of the simple aza-15-crown-5 ether reveal strong complexation with both Ba^{2+} ($K_1 \times K_2 > 10^{12}$ dm^6 mol^{-2}) and Ag^+ [$K_1 = (1.15 \pm 0.10) \times 10^4$ dm^3 mol^{-1} and $K_2 = 450 \pm 20$ dm^3 mol^{-1}].

Introduction

Chromo- and fluoro-ionophores that combine an organic dye and an ionophore moiety within a single molecule provide a basis for the development of supramolecular ionic devices.[1–6] Absorption and luminescence spectroscopies are commonly used to study the affinity of such compounds for metal cations,[7–13] but these techniques provide relatively little information on the structural characteristics which are important for improved molecular design. The additional study of crystals by X-ray diffraction (XRD)[14] and of solutions by vibrational spectroscopy has been shown to provide usefully detailed information on such systems.[15–19] ^{1}H NMR spectroscopy also has been used to investigate complex formation between a styrylbenzothiazolium 15-crown-5 ether† dye and alkali and alkaline-earth metal cations.[20]

We report here the synthesis and extensive study of a styrylbenzothiazolium dye containing a phenylmonoaza-15-crown-5 ether† group, using a simple phenylaza-15-crown-5 ether for comparison. The molecular structure of the ionophores in cation-free and cation-complexed forms have been investigated in crystals by XRD and in solution by ^{1}H NMR spectroscopy, including COSY and NOESY measurements. The complexation of these ionophores with 'hard' (Ba^{2+}) and 'soft' (Ag^+) metal cations in acetonitrile has been studied also by UV–VIS absorption spectrophotometry and by potentiometry.

Results and discussion

Synthesis

The synthesis of the styrylbenzothiazolium dye **3**, containing the *N*-phenylaza-15-crown-5 group, is summarized in Scheme 1. 3-Ethyl-2-methylbenzothiazolium iodide, **1a**, was used for the preparation of the perchlorate, **1b**. The formyl derivative of phenylaza-15-crown-5, **2b**, was prepared according to the literature,[21] and the condensation of **1b** with **2b** was carried out in absolute ethanol in the presence of pyridine as a catalyst.

Crystallography

Several aspects of the structure within the crystals of dye **3**, which contain equal numbers of positively charged organic molecules and perchlorate ions, are shown in Figs. 1–3. Fig. 1(*a*) and (*b*) show the general conformational arrangement of the organic cation; its near-planarity, apart from the crown moiety, is particularly striking.

Four almost rigorously planar sub-units may be distinguished within **3**: the benzothiazolium system (plane 1), the conjugated bonds C(11)C(12)C(13)C(14) (plane 2), the phenyl ring C(14)···C(19) (plane 3), and the amino moiety C(1)C(10)C(17)N(1) (plane 4). The dihedral angles between the planes 1/2, 2/3 and 3/4 are 5.4, 6.7 and 6.5°, respectively. With

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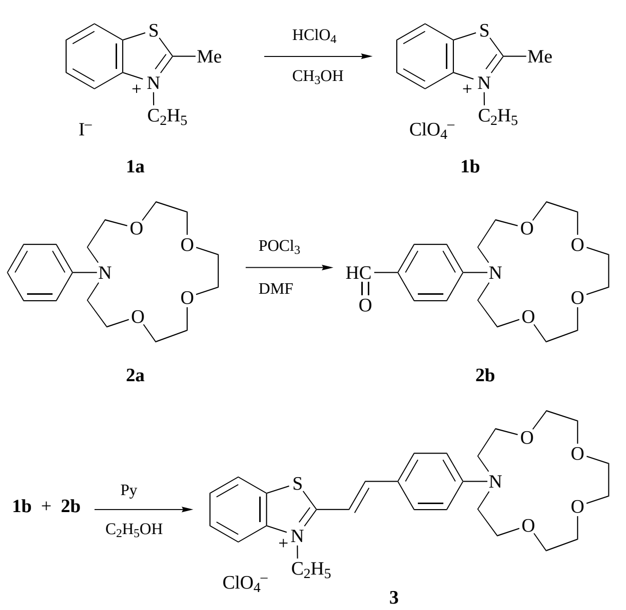
† Recommended IUPAC name for aza-15-crown-5 ether is 13-aza-1,4,7,10-tetroxacyclopentadecane.



Scheme 1

this geometry, the C(12)=C(13) double bond clearly is conjugated to the adjacent aromatic systems. This bond length [1.355(3) Å, see Table 1] is close to that [1.339(11) Å] generally observed for C=C–C(Ar) systems.[22] The bond lengths C(13)–C(14) [1.438(3) Å] and C(11)–C(12) [1.424(3) Å] also are close to the usual value for a conjugated C(sp^2)–C(sp^2) bond [1.455(11) Å].[22] In the benzothiazolium fragment, the N(2)–C(11) bond [1.345(2) Å] is somewhat shorter than the N(2)–C(20) bond [1.401(2) Å], which indicates some localization of the double bond. The two S–C bonds [1.734(2) and 1.737(2) Å] are almost of equal length. The benzene ring C(20)···C(25) of the benzothiazolium moiety has the expected geometry; a similar geometry for the benzothiazolium group was observed previously.[14,21,23,24] The phenyl ring C(14)··· C(19) with the C(17) amino substituent exhibits quinonoid bond lengths, with the two C–C bonds C(15)–C(16) and C(18)–C(19) being markedly shorter [1.379(3) and 1.373(3) Å] than the other four [which range from 1.411(3) to 1.423(3) Å]. The N(1)–C(17) bond length [1.368(2) Å] is typical for a C_{Ar}–$N(C_R)_2$ unit with planar NC_3 geometry [1.371(16) Å].[22]

Table 2 gives the torsional angles in the crown ether moiety of dye **3**. The conformation of the crown ether group, beginning from the N–C(1) bond, is GTG GGT TGT TGG GTG (G = *gauche*; T = *trans*). The structure of this group is qualitatively symmetrical with respect to a line from the N(1) atom to the middle of the C(5)–C(6) bond. The heteroatoms N(1)O(1)-O(2)O(3)O(4) form an irregular pentagon, with the displacements of these atoms from the mean (least-squares) plane being

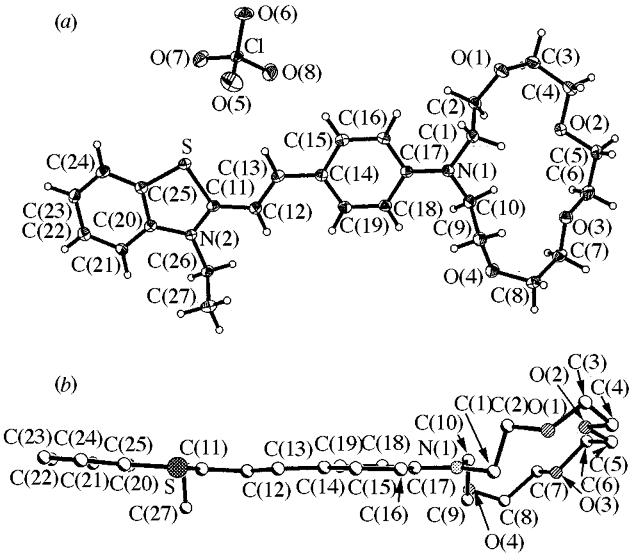


Fig. 1 Structure and numbering scheme for the dye **3** cation and anion: (*a*) top view, (*b*) side view

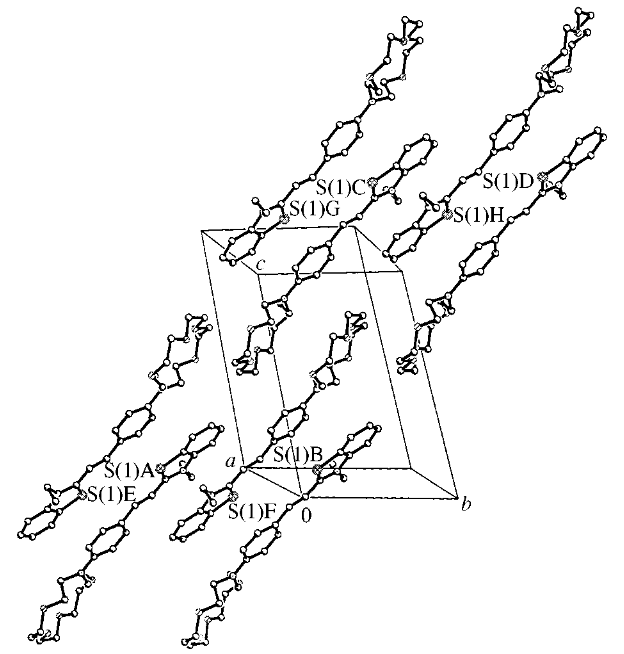


Fig. 2 Arrangement of two stacks (G-C-H-D and E-A-F-B) in the crystal. Only the S atoms of each molecule are denoted for simplicity. The E-F, A-B, G-H and C-D pairs of molecules are related by *b*-translation; any two adjacent molecules are related by a centre of symmetry.

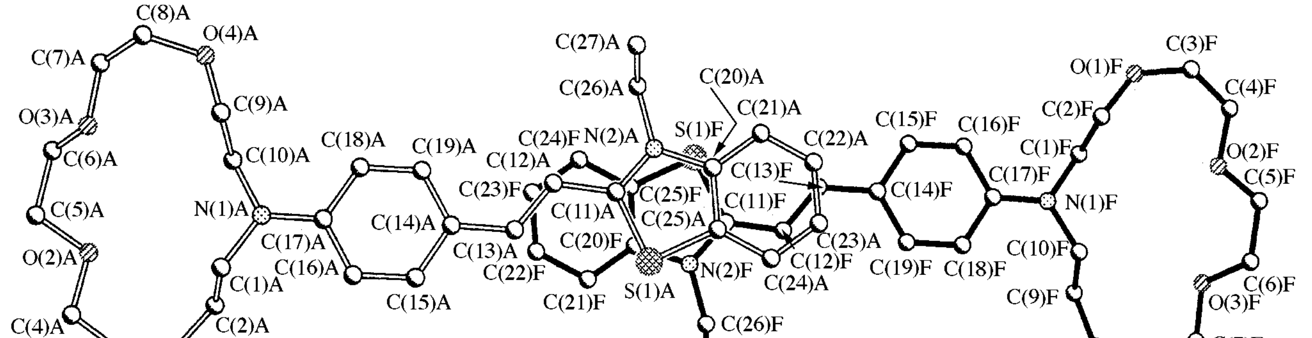


Fig. 3 Mutual arrangement of two overlapping molecules (denoted as A and F using open and solid lines) in the stack

Table 1 Selected bond lengths[a] (Å) for dye **3**, with atoms numbered as in Fig. 1

Cl–O(6)	1.438(2)	O(2)–C(5)	1.423(2)	C(14)–C(19)	1.411(3)
Cl–O(8)	1.440(2)	O(2)–C(4)	1.436(3)	C(14)–C(15)	1.414(3)
Cl–O(5)	1.440(2)	O(3)–C(6)	1.421(3)	C(15)–C(16)	1.379(3)
Cl–O(7)	1.449(2)	O(3)–C(7)	1.426(2)	C(16)–C(17)	1.421(3)
S–C(11)	1.734(2)	O(4)–C(8)	1.426(2)	C(17)–C(18)	1.423(3)
S–C(25)	1.737(2)	O(4)–C(9)	1.430(2)	C(18)–C(19)	1.373(3)
N(1)–C(17)	1.368(2)	C(1)–C(2)	1.524(3)	C(20)–C(21)	1.397(3)
N(1)–C(10)	1.463(2)	C(3)–C(4)	1.502(3)	C(20)–C(25)	1.402(3)
N(1)–C(1)	1.465(2)	C(5)–C(6)	1.503(3)	C(21)–C(22)	1.386(3)
N(2)–C(11)	1.345(2)	C(7)–C(8)	1.505(3)	C(22)–C(23)	1.399(3)
N(2)–C(20)	1.401(2)	C(9)–C(10)	1.526(3)	C(23)–C(24)	1.388(3)
N(2)–C(26)	1.485(2)	C(11)–C(12)	1.424(3)	C(24)–C(25)	1.393(3)
O(1)–C(3)	1.423(3)	C(12)–C(13)	1.355(3)	C(26)–C(27)	1.515(3)
O(1)–C(2)	1.427(2)	C(13)–C(14)	1.438(3)		

[a] Standard errors in last figures given in brackets.

Table 2 Torsional angles (°) in the crown ether group of dye **3**

C(10)N(1)C(1)C(2)	89.6	C(5)C(6)O(3)C(7)	−177.2
N(1)C(1)C(2)O(1)	−175.9	C(6)O(3)C(7)C(8)	−175.5
C(1)C(2)O(1)C(3)	124.4	O(3)C(7)C(8)O(4)	74.0
C(2)O(1)C(3)C(4)	−86.4	C(7)C(8)O(4)C(9)	−84.2
O(1)C(3)C(4)O(2)	70.1	C(8)O(4)C(9)C(10)	111.8
C(3)C(4)O(2)C(5)	172.9	O(4)C(9)C(10)N(1)	167.5
C(4)O(2)C(5)C(6)	−176.1	C(9)C(10)N(1)C(1)	98.2
O(2)C(5)C(6)O(3)	−71.5		

Table 3 Crystallographically independent short interatomic distances (Å) between adjacent molecules of dye **3** in a stack

S···N(2)	3.747	C(11)···C(20)	3.615
S···C(21)	3.587	C(12)···C(23)	3.371
S···C(20)	3.557	C(12)···C(24)	3.693
C(11)···C(24)	3.678	C(13)···C(22)	3.345
C(11)···C(25)	3.592	C(13)···C(23)	3.585

−0.036, 0.160, −0.298, 0.258 and −0.083 Å, respectively. The cavity formed by these heteroatoms is oblate in the direction perpendicular to the macrocycle symmetry line. The distance between O(1) and O(4) [6.624 Å] is the longest and the distances N(1)···O(2) [4.194 Å] and N(1)···O(3) [4.324 Å] are the shortest. The distances O(1)···O(3) and O(4)···O(2) are 5.345 and 5.261 Å, respectively.

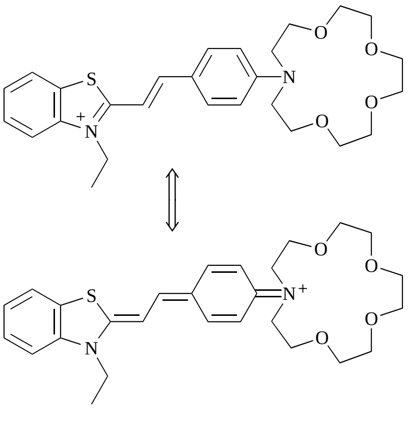
In the crystal, the conjugated molecular groups form stacks where any two adjacent molecules are related *via* symmetry centres (see Fig. 2); hence, the mean (least-squares) planes of the conjugated systems are rigorously parallel and equidistant from each other. The mean interplanar distance is 3.38 Å, which is typical of cofacially stacked aromatic systems. The stacks run along the *y*-axis. With such stacking, the benzothiazolium group and the ethylenic double bond of any one molecule overlap with the same groups of the two nearest neighbours, one above and one below (see Fig. 3). The individual, symmetrically independent, intermolecular distances for two overlapping groups are given in Table 3.

In the crystal, the crown ether moieties form channels where the crown ether groups of two neighbouring (translation related) stacks alternate, and the packing of the crown ethers within these channels is very loose. Almost all of the nearest interatomic distances between two adjacent crown ethers exceed 4 Å. Only two such distances, O(3)···C(5) [3.794 Å] and O(3)···C(4) [3.695 Å], are less than this value, but still they are greater than the sum of the van der Waals radii (*ca.* 3.1 Å).

The ClO_4^- anion has the usual tetrahedral geometry, and these anions are positioned in cavities between the stacks in the crystal. The shortest interatomic distances from the anion oxygen atoms lie within the sums of the van der Waals radii of the corresponding atoms: O···C at 3.246–3.377 Å, O···H at 2.512 Å and O···S at 3.572 Å.

NMR spectroscopy of solutions

Dye **3**, azacrown ether **2a** and their complexes with Ba^{2+} and Ag^+ have been investigated using ^1H NMR spectroscopy. An analysis of the NOESY and COSY data has enabled us to correlate the positions of the proton signals of the different molecular groups with features in the ^1H NMR spectra (see Table 4). The ^1H NMR spectrum of the crown group within **3** consists of three multiplets, assigned to the H(1,10), H(2,9) and H(3,8 and 4,7) methylene protons, and one singlet, assigned to the H(5,6) methylene protons, all occurring in the region 3.6–3.8 ppm. The crown ether group of **2a** exhibits two multiplets, assigned to H(1,10) and H(2,9), and two singlets, assigned to H(3,8 and 4.7) and H(5,6), in the same region at 3.5–3.7 ppm. The proton chemical shifts of the analogous methylene groups of **2a** and **3** differ from each other; there is a downfield shift (*i.e.* to larger δ values) of the proton signals of **3** relative to those of **2a**, this being most pronounced for the H(1,10) multiplet. The electron-donating properties of the *N*-atom within the crown ether of **2a** causes the H(1,10) signal to be shifted upfield in the ^1H NMR spectrum relative to those of the H(2,9) and H(3,8 and 4,7) protons. However, the planarity of the NC_3 moiety within the azacrown group of **3** shown by our XRD analysis, together with the quinonoid character of the benzene ring C(14)···C(19), suggests that intramolecular charge-transfer from N(1) to N(2) occurs through the involvement of resonance hybrids such as those shown in Scheme 2. Thus, the N(2) atom acts as an electron acceptor and this results in the positions of the azacrown proton signals of **3** being different from those of **2a**, for which this resonance form is not possible.



Scheme 2

The aromatic region of the ^1H NMR spectrum of **3** consists of signals arising from the benzothiazolium fragment of the molecule, of a characteristic AA′BB′ pattern arising from the phenyl ring and of two multiplets arising from the ethenylic double bond. The NOESY spectrum of **3** shows interactions between the ethenylic H(12) proton and the CH_2 and CH_3 protons in the *N*-ethyl substituent on the benzothiazolium group,

Table 4 Chemical shifts from the 500 MHz ^{1}H NMR spectra[a] of dye **3**[b] (5×10^{-3} mol dm^{-3}), crown ether **2a**[c] (1.3×10^{-1} mol dm^{-3}) and their complexes with Ba^{2+} and Ag^+ (as perchlorate salts) in CD_3CN solution (mol ratios of **3** : salt = 1 : 100, **2a** : salt = 1 : 5)

	δ														
Compound	H(1,10)	H(2.9)	H(3.8 and 4,7)	H(5.6)	H(14)	H(15,19)	H(16,18)	H(12)	H(13)	H(21)	H(22)	H(23)	H(24)	H(26)	H(27)
3	3.74 (t)	3.82 (t)	3.65 (m)	3.60 (s)		7.79 (d)	6.92 (m)	7.30 (d)	8.01 (d)	7.94 (d)	7.81 (t)	7.70 (t)	8.12 (d)	4.60 (q)	1.55 (t)
3–Ba^{2+}	3.54 (t)	3.87 (t)	3.81 (m)	3.78 (m)		7.86 (d)	7.15 (d)	7.46 (d)	8.00 (d)	7.99 (d)	7.69 (t)	7.78 (t)	8.13 (d)	4.47 (q)	1.50 (t)
2a	3.51 (t)	3.67 (t)	3.58 (s)	3.55 (s)	6.60 (t)	7.16 (t)	6.68 (d)								
2a–Ba^{2+}	3.34[d] (m)	3.81 (m)	3.81 (m)	3.81 (m)	7.10 (t)	7.40 (t)	7.19 (d)								
2a–Ag^+	3.33 (t)	3.52 (t)	3.61 (s)	3.63 (s)	7.18 (t)	7.32 (t)	7.04 (d)								

[a] s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] Numbering system as used in Fig. 1. [c] Numbering as for this group within dye **3**. [d] The most probable position (the protons have the same chemical shift as H_2O).

Table 5 Cation-induced shifts ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) for dye **3**[a] and crown ether **2a**[b] in CD_3CN solution (mol ratios of **3**:salt = 1:100, **2a**:salt = 1:5)

	Δδ								
Complex	H(1,10)	H(2,9)	H(3,8 and 4,7)	H(5,6)	H(14)	H(15,19)	H(16,18)	H(12)	H(13)
3–Ba^{2+}	−0.20	0.05	0.16	0.18		0.07	0.23	0.16	−0.01
2a–Ba^{2+}	−0.17[c]	0.14	0.23	0.26	0.49	0.24	0.51		
2a–Ag^+	−0.18	−0.15	0.03	0.09	0.36	0.16	0.41		

[a] Numbering system as used in Fig. 1. [b] Numbering as for this group within dye **3**. [c] The most probable position (the protons have the same chemical shift as H_2O).

and also between the ethylenic H(13) proton and H(15) on the phenyl ring, together indicating that the conformation of the dye in acetonitrile solution remains the same as that in the solid state (Fig. 1).

The complexation of **3** and **2a** with Ba^{2+} in CD_3CN was found to induce an upfield shift of the H(1,10) methylene proton signals and a downfield shift of all other proton signals of the azacrown group. Table 5 gives the chemical shift differences (Δδ) between the free and complexed forms of **2a** and **3**; all of the methylene protons of the azacrown group are influenced by the metal cation. Essentially no differences were found in the positions of the proton signals arising from the benzothiazolium group.

Complexation with a metal cation normally results in considerable conformational rearrangement within crown ether moieties.[25] In the ^1H NMR spectra, the chemical shift changes occurring on complexation result from the effects of both conformational rearrangement and the electron-withdrawing influence of the crowned cation. The Ba^{2+} cation-induced downfield shifts found for all of the azacrown ether protons except H(1,10) are of different amplitudes. Interestingly, the chemical shifts of the H(2,9), H(3,8 and 4,7) and H(5,6) protons (Table 4) are all similar for the barium complexes of **3** and **2a**, indicating that all of the crown ether protons except H(1,10) have a similar structural environment in the complexes with barium, and hence that all of the crown ether oxygens interact similarly with this cation. The upfield shift of the H(1,10) proton signals on complexation of **3** and **2a** with Ba^{2+} increases the differences between the chemical shifts for these protons and those of the other crown ether protons (Table 1). Two reasons may be suggested for the observed cation-induced upfield shift of the H(1,10) proton signal. First, the introduction of a metal cation into the crown cavity diminishes the role of the charge-transfer resonance structure (Scheme 2) in the conjugated π-bonding system. The decreased positive charge on N(1) accounts, in part, for the changes in the NMR spectrum. Secondly, the conformational changes within the crown moiety upon complex formation may modify the ring-current effects from the adjacent phenyl group on the H(1,10) methylene protons, resulting in an upfield shift. The crystal XRD data and the NOESY spectra indicate that the distances between the H(1,10) and H(2,9) methylene protons and the H(16,18) phenyl protons in non-complexed **3** are equal. In contrast, the NOESY spectra indicate that the H(1,10) methylene protons are closer to the H(16,18) protons in the complexed form, resulting in a stronger interaction than that between the H(2,9) and H(16,18) protons.

There are noticeable differences between the Ba^{2+} and Ag^+ cation-induced changes in the chemical shifts of the **2a** crown ether protons (Tables 4 and 5). Complexation with the 'soft' Ag^+ cation results in much smaller downfield shifts of the H(3,8 and 4,7) and H(5,6) proton signals than those induced by the 'hard' Ba^{2+} cation (Table 5). The influence of Ag^+ and Ba^{2+} cations on the shift of the H(2,9) proton signals is equally strong, but of opposite sign; a similarly large shift was observed for the H(1,10) and H(2,9) proton signals of the complex **2a**–Ag^+, although interference from H_2O signals causes some uncertainty in the former (Table 5). These H(1,10) and H(2,9) protons are close to the nitrogen heteroatom. All of these factors indicate that the 'soft' Ag^+ cation interacts strongly with the N(1) atom, but weakly with the oxygen atoms of the crown ether fragment of **2a**. This is consistent with earlier work in which the affinity of Ag^+ for several substituted monoazacrown ether ionophores was determined.[25] The results reported here suggest that the azacrown ether group adopts a different conformation in the **2a**–Ag^+ and **2a**–Ba^{2+} complexes. The influence of the Ag^+ and Ba^{2+} cations on the *N*-phenyl group of **2a** are qualitatively similar, *i.e.* the cation-induced chemical shifts for the H(14), H(15,19) and H(16,18) protons are similar in these two cases (Table 5).

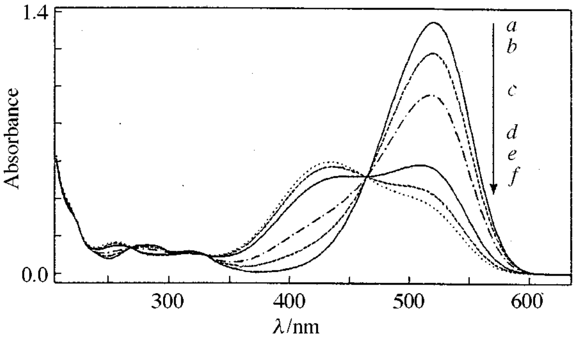


Fig. 4 UV–VIS absorption spectra of **3** (*ca.* 4×10^{-5} mol dm^{-3}) in acetonitrile containing $Ba(ClO_4)_2$ at (*a*) 0, (*b*) 2.8×10^{-3}, (*c*) 9.1×10^{-3}, (*d*) 2.1×10^{-2}, (*e*) 4.9×10^{-2} and (*f*) 9.6×10^{-2} mol dm^{-3}

Spectrophotometry and potentiometry of solutions

The UV–VIS absorption spectrum of **3** (*ca.* 4×10^{-5} mol dm^{-3}) in acetonitrile solution was found to change on addition of $Ba(ClO_4)_2$ at $>10^{-3}$ mol dm^{-3} (Fig. 4), and a colour change from dark pink to ochre was observed. Such changes are typical of metal ion complexation to the azacrown. The concentration dependence of the absorbance, *A*, at a fixed wavelength fits well to eqn. (1), where A_o and A_i are the absorbance at zero

$$A = (A_o + A_i K_1[M])/(1 + K_1[M]) \qquad (1)$$

and infinite metal ion concentrations, [M], respectively. This indicates that 1:1 ligand–cation complexes are formed in accordance with reaction (2), where L is the ligand;[9] eqn. (1) is

$$M + L \overset{K_1}{\rightleftharpoons} ML \qquad (2)$$

valid for [M] ⩾ [L], which was the case for these experiments. The stability constant for complex formation, K_1, was estimated to be 80 ± 10 dm^3 mol^{-1} for **3**–Ba^{2+}. The large changes in the spectrum on cation complexation indicate that the electronic structure of **3** is altered significantly, and may be attributed to coordination of Ba^{2+} to the azacrown ether. This results in charge redistribution within the extended chromophore, as studied previously by Raman spectroscopy for several styrylbenzothiazolium dyes containing different benzocrown ether groups.[15,16,18]

The complexation of **2a** with Ba^{2+} was studied similarly by spectrophotometric titration: a solution of $Ba(ClO_4)_2$ (10^{-2} mol

Table 6 Stability constants for complex formation (K_1, K_2 and $K' = K_1 \times K_2$) between **3**, **2a** and N-15-C-5, and Ba^{2+} (as perchlorate) and Ag^+ (as perchlorate or nitrate) in acetonitrile

	$Ba^{2+\,a}$			$Ag^{+\,b}$	
Compound	K_1/dm^3 mol^{-1}	K_2/dm^3 mol^{-1}	K'/dm^6 mol^{-2}	K_1/dm^3 mol^{-1}	K_2/dm^3 mol^{-1}
3	80	—	—	—	—
2a	2.0×10^4	220	—	6	—
N-15-C-5	—	—	$>1 \times 10^{12}$	1.15×10^4	450

[a] Spectrophotometry. [b] Potentiometry.

dm^{-3}) and **2a** (8×10^{-4} mol dm^{-3}) was added to a solution of **2a** (8×10^{-4} mol dm^{-3}) in acetonitrile and changes in the absorbance were determined at 315 nm. In this case, the dependence of $a = (A_o - A)/(A_o - A_i)$ on the total concentration of metal cation (*i.e.* free and complexed), $[M]_{tot}$, was found to fit to eqn. (3),

$$\frac{[M]_{tot}}{a} = \frac{1 + K_1(1-a)[L]_{tot} + K_1K_2(1-a)^2[L]_{tot}^2}{K_1(1-a)[1 + 2K_2(1-a)[L]_{tot}]} \qquad (3)$$

where $[L]_{tot}$ is the total concentration of the ligand, in accordance with both reactions (2) and (4).[12] Thus, the two stability

$$ML + L \underset{}{\overset{K_2}{\rightleftharpoons}} ML_2 \qquad (4)$$

constants for complex formation, K_1 and K_2, were calculated to be $(2.0 \pm 0.2) \times 10^4$ and 220 ± 20 dm^3 mol^{-1}, respectively.

By contrast with **2a**, for which complexation to form ML_2 proceeds in two distinguishable steps, a 2:1 complex was observed to form immediately on spectrophotometric titration of a 0.99×10^{-4} mol dm^{-3} solution of the simple aza-15-crown-5 ether (N-15-C-5) with $Ba(ClO_4)_2$. In this case, the experimental dependence of $a = (A_o - A)/(A_o - A_i)$, measured at 200 nm, on $[M]_{tot}$ fits well to eqn. (5), where $K' = K_1 \times K_2$ is

$$[M]_{tot} = \frac{a}{2K'(1-a)^2[L]_{tot}} + \frac{a[L]_{tot}}{2} \qquad (5)$$

the observed stability constant for ML_2 complex formation in accordance with reaction (6).

$$M + 2L \overset{K'}{\rightleftharpoons} ML_2 \qquad (6)$$

The stability constant for the formation of N-15-C-5–Ba^{2+} was estimated to be $K' > 1 \times 10^{12}$ dm^6 mol^{-2}. The very high value of K' precludes a more precise determination by spectrophotometry; the K_1 and K_2 values for the individual reactions (2) and (4) could not be determined.

A solution of **3** in acetonitrile was studied by spectrophotometry on addition of $AgClO_4$. No complex formation was observed by this method, with $AgClO_4$ concentrations up to 0.1 mol dm^{-3}.

Potentiometry was used to study the complexation of **2a** with Ag^+ (as both $AgClO_4$ and $AgNO_3$) in acetonitrile, using a large excess of the ligand ($[Ag^+] = 10^{-3}$ and $[\mathbf{2a}] = 10^{-1}$ mol dm^{-3}). These measurements gave a stability constant for formation of **2a**–Ag^+ of $K_1 = 6 \pm 1$ dm^3 mol^{-1}. This value contrasts dramatically with that of $K_1 = (1.15 \pm 0.10) \times 10^4$ dm^3 mol^{-1} and $K_2 = 450 \pm 20$ dm^3 mol^{-1} obtained by a similar potentiometric titration of N-15-C-5 with Ag^+ in acetonitrile. The stability constant values obtained here are summarized in Table 6.

This dramatic difference in the affinity of different azacrown ethers for silver cations may be attributed to the important role which the nitrogen heteroatom plays in complexation with soft metal cations. The substitution of nitrogen for oxygen heteroatoms within the crown is known to strengthen the affinity of 18-crown-6 ethers for the 'soft' Ag^+ cation.[26] In general, the affinity of crown ethers for silver cations is high when the ratio of N:O heteroatoms within the ring is high, while their affinity for alkali-metal cations is higher than for Ag^+ when the N:O ratio is low.[27] Several factors may contribute to the change in the magnitude of the stability constant for complexes of monoazacrown ethers with substituted alkyl side-chains attached to the nitrogen atom.[25,27] A decrease in the basicity of the nitrogen atom, arising from partial charge transfer to electron-accepting substituents, has been reported to reduce the stability constant for complex formation with Ag^+ by up to two orders of magnitude,[27] although in this case the inductive effect was restricted because of the presence of an ethyl spacer between the nitrogen heteroatom and the *para*-substituted phenyl ring. For the molecule studied here, the absorption spectra indicate that the nitrogen heteroatoms in **2a**, and especially in **3**, are strongly involved in the π-conjugation system of the chromophores. Thus they may be expected to exhibit the effect of lowered Ag^+ affinity more strongly than molecules without an extended π-system. Furthermore, the nitrogen heteroatom carries a partial positive charge due to the charge-transfer resonance form of dye **3**, as already discussed and illustrated in Scheme 2. Together, these effects result in the low and very low (*ca.* zero) affinity of the **2a** and **3** ionophores for Ag^+ in acetonitrile.

The studies described above establish that the nitrogen heteroatom plays a crucial role in determining the different complexing properties of **3** and **2a** with Ba^{2+} and Ag^+ in acetonitrile. We have characterised the nature of the nitrogen heteroatom further by studying the protonation of **3** and **2a** in aqueous solution. A spectrophotometric titration of **3** (2×10^{-5} mol dm^{-3}) with $HClO_4$ in aqueous solution was carried out at 506 nm, where the protonated form does not absorb, and gave $K_1 = 19.5 \pm 0.9$ dm^3 mol^{-1}, where K_1 is the stability constant for protonation [as given by reaction (2) when H^+ is substituted for M]. A similar titration of **2a** (6×10^{-5} mol dm^{-3}) with $HClO_4$ was made at 253.5 nm, where the protonated form does not absorb, and gave $K_1 = (4.8 \pm 0.2) \times 10^4$ dm^3 mol^{-1}. The proton may be expected to locate at the nitrogen atom, with the oxygen atoms within the remainder of the azacrown exerting only a minor influence.[28] Therefore, the stability constants for protonation report directly on the nitrogen heteroatom and their values show that its basicity is much weaker in **3** than in **2a**. The finding is entirely consistent with our interpretation of the role of this heteroatom in determining the different complexing properties of **3** and **2a** with Ba^{2+} and Ag^+ in acetonitrile.

Conclusions

The remarkable planarity of the non-crown part of **3** revealed by our XRD data evidently is conserved in solution, as shown by our NMR results. Complexation of **3** and **2a** with the 'hard' metal ion Ba^{2+} results in conformational changes at the azacrown ether binding site, with the four oxygen atoms binding to the metal cation. Complexation of **2a** with the 'soft' metal ion Ag^+, however, involves mainly interaction with the nitrogen atom of the azacrown group. Our spectrophotometric and potentiometric data are consistent with this interpretation, in that they show dramatically different stability constants for Ba^{2+} and Ag^+ complexes, with Ba^{2+} complexation being far more stable for both **3** and **2a** azacrowns. Delocalization of positive charge from the benzothiazolium moiety in **3** by π-conjugation through to the azacrown group is identified as the cause of the much higher stability of the Ba^{2+} complex with **2a** than with **3**.

Experimental

Synthesis

The iodide of 3-ethyl-2-methylbenzothiazolium (**1a**), *N*-phenylaza-15-crown-5 (**2a**), and $AgNO_3$ were purchased from the Aldrich Chemical Company and used as received. $Ba(ClO_4)_2$ (Aldrich) and $AgClO_4{\cdot}H_2O$ (Fluka) were dried in vacuum before use.

***N*-(4-Formylphenyl)aza-15-crown-5 ether (2b).** **2b** was prepared according to the literature,[21] yield 75%, mp 86–88 °C (lit. 87–88 °C).

Perchlorate of 3-ethyl-2-methylbenzothiazolium (1b). Compound **1a** (0.314 g) was dissolved in hot methanol and 56% $HClO_4$ (0.55 cm^3) was added. After 3 h the precipitate formed was filtered and dried. The yield of **1b** was 0.25 g (86%), mp 177–179 °C (Found: C, 43.02; H, 4.47; N, 4.95. Calc. for $C_{10}H_{12}ClNO_4S$: C, 43.32; H, 4.37; N, 5.05%).

Perchlorate of 2-{2-[4-(13-aza-1,4,7,10-tetroxa-13-cyclopentadecyl)phenyl]ethenyl}-3-ethylbenzothiazolium (3). A mixture of the benzothiazole derivative **1b** (0.25 g, 0.9 mmol), arylaldehyde **2b** (0.32 g, 1 mmol) and pyridine (0.15 cm^3) was suspended in 10 cm^3 of absolute ethanol and heated for 8 h at 90 °C in an oil bath. After cooling, the crude product was filtered and dried. The dye obtained was purified by recrystallization from acetonitrile; the yield was 0.35 g (67%), mp 237–239 °C (Found: C, 54.93; H, 6.00; N, 4.64. Calc. for $C_{27}H_{35}ClN_2O_8S{\cdot}0.5H_2O$: C, 54.81; H, 6.12; N, 4.74%); δ_H([$^2H_6$]DMSO) 1.4 (3H, t, CH_3), 3.3 (4H, s, $2CH_2O$), 3.6 (12H, m, $6CH_2O$), 3.7 (4H, m, $2CH_2O$), 4.8 (2H, q, CH_2N), 6.8 (2H, d, *J* 8.9, ArH), 7.6 (1H, d, *J* 15.5, α-H), 7.7 (1H, t, ArH), 7.8 (1H, t, ArH), 7.88 (1H, d, *J* 8.9, ArH), 8.0 (1H, d, *J* 15.5, β-H), 8.1 (1H, d, ArH), 8.29 (1H, d, ArH).

Crystallography

Crystal data. $C_{27}H_{35}ClN_2O_8S$, $M = 583.08$, triclinic, $a = 9.2021(1)$, $b = 9.8491(2)$, $c = 16.3792(1)$ Å, $\alpha = 106.503(1)$, $\beta = 98.009(1)$, $\gamma = 98.217(1)°$ (refined from all collected reflections during data reduction[29]), $V = 1383.17(3)$ Å^3, space group *P*-1, $Z = 2$, $D_c = 1.400$ g cm^{-3}, $F(000) = 616$, μ(Mo-Kα) = 0.266 mm^{-1}.‡

Data collection, structure solution and refinement. The single crystal of **3**, of approximate dimensions 0.6 × 0.18 × 0.05 mm, was mounted in inert oil on the top of a glass fibre and transferred to a cold nitrogen stream on a Siemens SMART CCD diffractometer.

A total of 10 187 reflections (6278 unique, $R_{int} = 0.0334$) were measured using graphite monochromatized Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at 100.0(2) K. Data were collected in the range $1.32 < \theta < 27.53$ ($-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-21 \leqslant l \leqslant 16$). The omega scan mode with a scan step of 0.3° (35 s per step) was used. Siemens SAINT software was applied for data reduction.[29] Absorption correction was not performed because it did not result in any improvement of the data.[30] 6104 reflections with $I > -3\sigma(I)$ were used in further calculations. The structure was solved by direct methods[31] and refined by full matrix least-squares[32] on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were found from difference Fourier syntheses and refined in an isotropic approximation. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (0.0096P)^2 + 1.5446P$, where $P = (2F_c^{\,2} + F_o^{\,2})/3$. The final residuals were: $R1 = 0.0426$, $wR2 = 0.0855$ for 5156 reflections with $I > 2\sigma(I)$ and 0.0620, 0.1099 for all data and 493 parameters. Goof = 1.111, maximum shift/e.s.d. = 0.000, maximum $\Delta\rho = 0.34$ e Å^{-4}.

NMR spectroscopy

^1H NMR spectra were recorded at 300 K on a Bruker AMX500 spectrometer, with tetramethylsilane as the standard; *J* values are given in Hz. ^1H–^1H COSY and NOESY spectra were acquired in the phase-sensitive mode using the time-proportional phase incrementation method. NOESY spectra were obtained with a mixing time of 800 ms.

Spectrophotometry

UV–VIS absorption spectra were measured using either a Hitachi U-3000 or a Shimadzu UV-3100 spectrophotometer using 1 or 2 cm pathlength cells. All measurements were made at room temperature (*ca.* 18 °C). The data were fitted using the SPSS statistical package, which allowed non-linear regression analysis to be performed.

The protonation of **3** and **2a** in aqueous solution was studied at 20 °C using a Specord M40 spectrophotometer; pH values were measured with a I-500 ionometer (accuracy ± 0.01 pH).

Potentiometry

Potentiometric experiments were carried out with an I-1201 ion meter with 1 mV resolution in an experimental cell consisting of two glass vessels joined by a salt bridge. The reference compartment of the cell contained a Ag/(0.01 mol dm^{-3} $AgNO_3$ in CH_3CN) electrode. The working compartment of the cell contained a silver electrode and was fitted with a magnetic stirrer. The salt bridge solution was 0.01 mol dm^{-3} tetramethylammonium perchlorate (TMAP) in acetonitrile.

The stability constants K_1 and K_2 for complexes of $AgClO_4$ with aza-15-crown-5 were determined by potentiometric titration of a $AgClO_4$ solution (0.01 mol dm^{-3} $AgClO_4$–0.01 mol dm^{-3} TMAP–CH_3CN). The emf values obtained with different ligand concentrations (28 values) gave the free Ag^+ ion concentration. K_1 and K_2 were calculated as $K_1 = [LAg^+]/[Ag^+]_{free}[L]_{free}$ and $K_2 = [L_2Ag^+]/[LAg^+][L]_{free}$, using the mass balance equations: $[Ag^+]_{tot} = [Ag^+]_{free} + [LAg^+] + [L_2Ag^+]$ and $[L]_{tot} = [L]_{free} + [LAg^+] + 2[L_2Ag^+]$.

The stability constant for formation of **2a**–Ag^+ was calculated similarly using the emf value obtained for a 10^{-3} mol dm^{-3} solution of $AgNO_3$ (or $AgClO_4$) and a 10^{-1} mol dm^{-3} solution of **2a** in acetonitrile.

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‡ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/102.

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