Crown-Annelated 9,10-Bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene Derivatives as Cation Sensors: Synthesis, X-ray Crystal Structures, Voltammetric and Spectroscopic Monitoring of Metal Complexation[‡]

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The synthesis of O_4S_2-crown annelated derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene using the novel Horner–Wadsworth–Emmons reagent **7** is reported. The bis- and mono-crown systems **9** and **12** function as efficient ligands in the voltammetric and UV/Vis spectroscopic recognition of Na^+ and Ag^+. Solution electrochemical studies reveal that metal complexation to the crown unit(s) leads to a significant positive shift in the potential of the first, two-electron oxidation wave of **9** and **12** [maximum shift E_1^{ox} = 115 mV for **9** in the presence of Ag^+ (ca. 10 molar equivalents)]. Considerably smaller shifts (< 30 mV) were observed for complexation of Li^+, K^+ and Ba^{2+}. UV/Vis spectrophotometric studies of metal binding (Na^+ and Ag^+) to **9** are consistent with the simultaneous formation of 1:1 and 1:2 complexes. The X-ray crystal structures of compounds **10** and **12**·CH_2Cl_2 are reported. The anthracenediylidene moiety of **12** is U-shaped due to the boat conformation of the central (quinodimethane) ring and folding of both 1,3-dithiole rings, providing an overall saddle conformation. The folding in **10** is reduced as steric crowding is relieved by removal of one of the 1,3-dithiole units.

Introduction

The chemistry of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system **1**[1] is being developed by several groups, including ourselves. Initial studies viewed this system as an extended analogue of tetrathiafulvalene (TTF). Compound **1** and its derivatives possess enhanced π-electron donor properties (relative to TTF) due to reduced intramolecular Coulombic repulsion in oxidized states,[2] and intermolecular charge-transfer complexes, e.g. with tetracyano-*p*-quinodimethane (TCNQ) have been studied.[3] The unusual features of system **1** are: (i) it displays a *two-electron* oxidation wave in solution electrochemical studies [neutral → dication, E_1^{ox} +0.30−0.35 V (in MeCN, vs. Ag/AgCl)] which is electrochemically quasi-reversible and chemically reversible;[4] (ii) the molecule adopts a saddle-shape[3a] due to steric hindance between the *peri*-hydrogens of the anthracenediylidene moiety and the sulfur atoms of the 1,3-dithiole rings.[5] X-ray crystal structures establish that upon oxidation the central anthracene ring becomes fully aromatic and planar, with the 1,3-dithiolium cations almost orthogonal to this plane.[3] These properties make system **1** fundamentally different from TTF which undergoes two, reversible, single-electron oxidation waves (sequential formation of the radical cation and dication)[6] and is essentially planar as the neutral and radical cation species,[7] although the TTF dication is twisted.[8]

Recent interest has been directed towards the study of *intra*molecular interactions in specifically functionalized derivatives of **1**.[9] We recognized the potential of this system to act as a redox-responsive centre which would be sensitive to the uptake and release of metal cations at an adjacent intramolecular ionophoric site. Crown ether derivatives of anthraquinone and ferrocene are prototype molecules in this field: cation binding induces a shift in the redox potential of the one-electron wave (E_1^{red} for anthraquinone; E_1^{ox} for ferrocene) and the complexing ability of the ligand can be switched on or off by varying the applied electrochemical potential.[10] Derivatives of TTF, e.g. **2**, have recently been studied extensively in this context.[11] Typically E_1^{ox} of TTF shifts to more positive potentials in the presence of bound metal, while E_2^{ox} is either unchanged or shifts (also positively) only very slightly. It was initially suggested that metal cation expulsion occurred at the TTF radical cation stage,[11a] although new data imply that complete expulsion does not occur until the dication stage.[11g]

Purely O-containing crown ethers are most suitable for extraction of hard ions (alkali and alkaline earth metals) and crown thioethers for soft low-valent transition metals or group Ib and IIb metals.[12] Fewer studies have addressed mixed O,S-crowns which are generally considered to be

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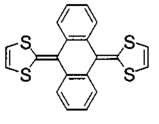
more selective towards heavy metal ions and can be used for extraction and transport of the latter,[13] although **2**[11] is responsive to Na^+, Ag^+, and Ba^{2+}. The only O_4S_2-crowns crystallographically studied to date are the saturated 1,4-dithia-crown-6,[14] a dithiomaleonitrile derivative, viz. 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile[15] and porphyrazine systems prepared from it.[15c] In the latter two systems (as in **2** and ours herein) the sulfur atoms are incorporated into a rigid moiety with a *syn* S−C−C−S configuration, which should hinder exocyclic coordination and thus favour the formation of endocyclic complexes.[16] However, the electron-donating ability of the sulfur atoms can be weakened by the electron-withdrawing effect of the CN groups.[15a] The electron-donor dithiole moiety should not produce this disadvantage.

We now report the synthesis of the first ionophoric derivatives of **1** and establish that they function as efficient ligands in the voltammetric and spectrophotometric recognition of Na^+ and Ag^+ by virtue of the intramolecular electrostatic (through-space) interaction of the metallo-crown moiety with the redox-active π-system.[17]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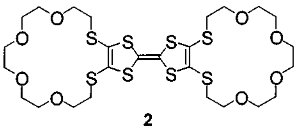
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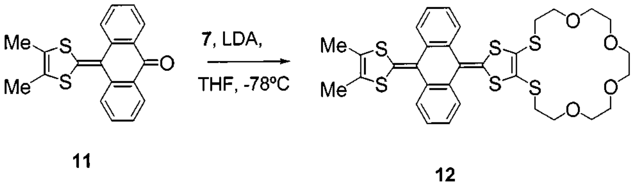
Results and Discussion

Synthesis

The synthesis of the Horner−Wadsworth−Emmons reagent **7** from thione **3**,[11a] which is based on the protocol used previously for non-crown systems,[2c,18] is shown in Scheme 1. The presence of the crown substituent meant that some steps required modification to previous reactions and/or workup and purification conditions. Methylation of **3** using methyl triflate afforded the dithiolium cation salt **4** (84% yield) which is best used immediately in the next step. Reduction of **4** with sodium cyanoborohydride yielded compound **5** (70% yield) which is stable at 20 °C for several weeks, making this compound the most suitable intermediate in Scheme 1 for shelf-storage. Compound **5** was treated with triflic acid to afford the unstable 1,3-dithiolium cation salt **6** which decomposed even upon storage in vacuo. Salt **6** was treated immediately with triethylphosphite to yield the key reagent **7**, which was isolated as a colourless oil (63% overall yield from **5**) and used within 24 h of its preparation.

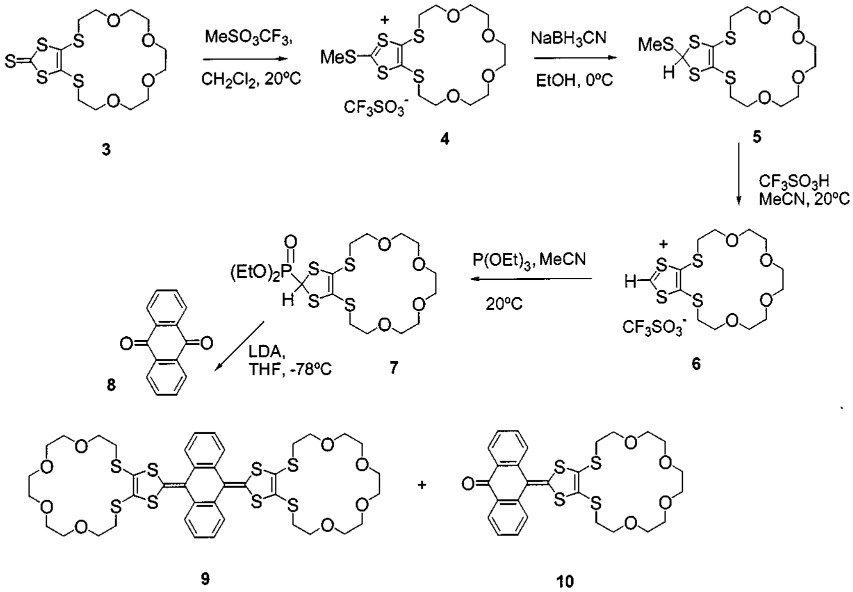
Reaction of anthraquinone **8** with the anion generated by treatment of reagent **7** (2.0 equivalents) with lithium diisopropylamide (LDA) in THF at −78 °C gave a mixture of the bis- and mono-crown annelated derivatives **9** (67% yield) and **10** (29% yield), respectively, which were readily separated by chromatography. The use of 3.0 equivalents of reagent **7** gave **9** in an optimized yield of 82%. Reaction of **11**[2c] with reagent **7**, under the same conditions gave analogue **12** in 53% yield (Scheme 2).



Scheme 2. Synthesis of compound **12**

X-Ray Crystal Structures of 10 and 12

Compounds **10** and **12** were characterised by a single-crystal X-ray diffraction study (Figure 1 and Figure 2); **12** crystallises as a 1:1 dichloromethane solvate. The chromophore moieties of both molecules adopt saddle-like con-



Scheme 1. Synthesis of compounds **9** and **10**

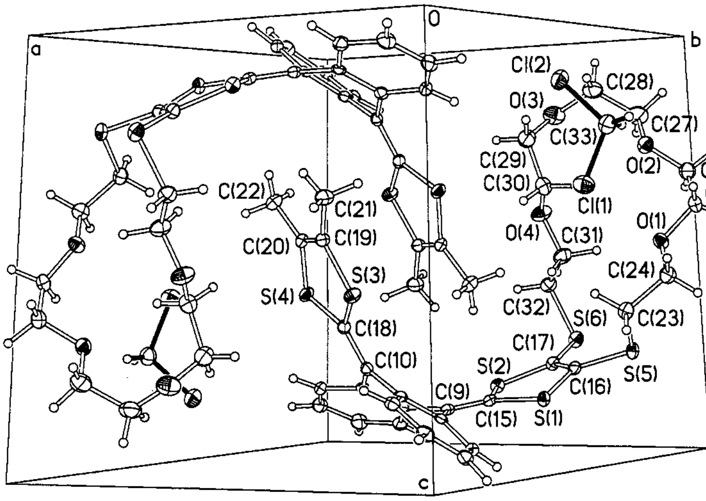


Figure 1. X-ray molecular structure of **12**·CH_2Cl_2

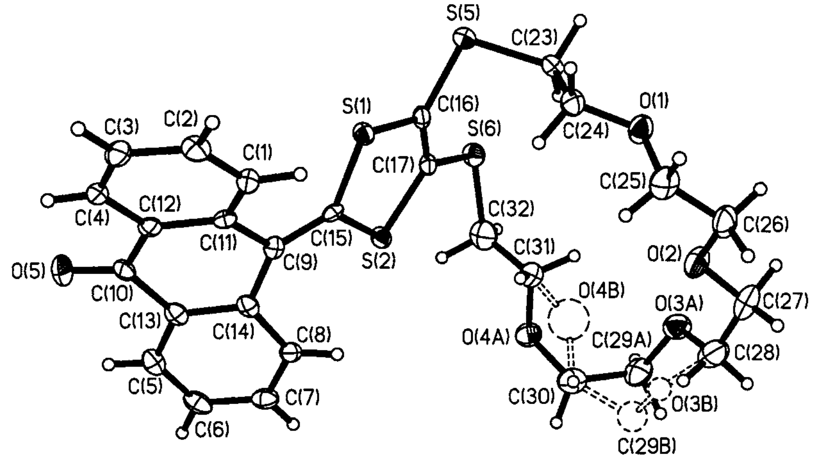


Figure 2. X-ray molecular structure of **10**

formations, characteristic for such compounds:[3c,9d,17] the anthraquinone moiety is folded (by a φ angle) along the C(9)···C(10) vector and the substituents at C(9) and C(10) are tilted in the opposite direction (in a U-shape). The distortion is caused by steric repulsion between the dithiole sulfur atoms and the peri H atoms,[5] therefore, it is stronger in the bis(dithiole) **12** (φ = 38°) than in the mono(dithiole) **10** (φ = 21°). A similar relationship was observed between the tetra (MeS) derivative of **1** (φ = 38°) and bis(MeS) analogue of **11** (φ = 27°).[19] For the same reason, the boat conformation of the central quinone ring of **10** is nonsymmetric, with the folding of 24° along the C(11)···C(14) vector, and only 9° along the C(12)···C(13) vector.

Both dithiole rings in **12** are folded inward along the vectors S(1)···S(2) by 15.5° (cf. 9.6° in **10**) and S(3)···S(4) by 8.7°. Thus the S(1)C(16)C(17)S(2) and S(3)C(21)C(22)S(4) planes form an acute dihedral angle of 81°. The crown ring folds further inward, its mean plane forming an angle of 126° with the S(1)C(16)C(17)S(2) plane. The crystal packing motif of **12** is one of pseudo-dimers: two molecules (symmetrically related by an inversion centre) mutually engulf each others' dimethyl-dithiole ends. Such a motif is adopted by almost all saddle systems[9d] and explains the tendency of bulky substituents at the dithiole ring to fold further inward, enhancing the U-bend, since the maximum packing density can be achieved by a perfectly U-shaped molecule with the terminal moieties parallel. On the contrary, in **10** the macrocycle is folded outward of the shallow U-bend [forming a dihedral angle of 85° with the S(1)C(16)C(17)S(2) plane] and the dimeric motif is not realised. Instead, the molecules are stacked in a quasi-parallel fashion.

In the crown macrocycle of **10** the O(3), O(4), and C(29) atoms are disordered between two positions with the estimated occupancies of 0.8 and 0.2. For the major conformer, the S(5), S(6), O(1), O(2), and O(3) atoms are coplanar (with the mean deviation δ of 0.14 Å) and O(4) deviates from their plane by 1.43 Å. For the minor conformer, S(5), S(6), O(1), O(2), and O(4) are coplanar (δ = 0.17 Å) and O(3) deviates by 0.98 Å. In **12** the crown-ring is ordered; S(5) and all four O atoms are coplanar (δ=0.08 Å) and S(6) deviates from their plane by 1.75 Å. The torsion angles in the macrocycles generally agree with Wolf's rules,[20] which state that a *gauche* conformation is preferable around the

C−S and C−C bonds, and an *anti* conformation around the C−O bonds, the tendency to *gauche* placement diminishing in the succession C−S>>C−C>C−O.

UV/Vis Spectroscopic Studies

The UV/Vis absorption spectra of **9** and **12** are very similar with differences of only ±2 nm in the λ_{max} values of the main absorption peaks. This indicates that although the sulfur atoms of the crown unit are directly attached to the extended π-system, the crown substituent(s) induce only a very weak perturbation to the electronic properties of the chromophore. We sought to investigate the spectroscopic changes which accompany complexation of Na^+ and Ag^+. These cations were chosen as they induced the largest voltammetric response from a series of hard and soft cations (see below). Spectroscopic studies with compound **12** were thwarted by precipitation of the complexed salts in a range of organic solvents. This was not a problem with compound **9** and the absorption spectra in acetonitrile in the presence of sodium perchlorate and silver perchlorate are shown in Figure 3 and Figure 4, respectively. In both cases specific changes were observed in the spectra with no clear isosbestic points, indicating that, most probably, more than one species is formed, and the absorption spectra of these species are different. This is consistent with the simultaneous formation of both 1:1 and 1:2 complexes [i.e. **9**M^+ and **9**$(M^+)_2$] at similar metal cation concentrations. If one complex dominated isosbestic points would be expected for certain concentration regions. Such behaviour is documented for other bis(crown) chromoionophores.[21]

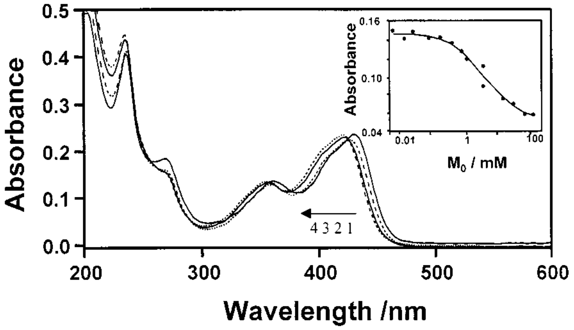


Figure 3. Absorption spectra of **9** ($2\cdot10^{-5}$ M) in MeCN (1 cm cell) containing $NaClO_4$ at concentrations of (1) 0; (2) 3.6; (3) 14; (4) 57 mM. Inset: absorption at 445 nm as a function of Na salt concentration fitted with the Equation (1)

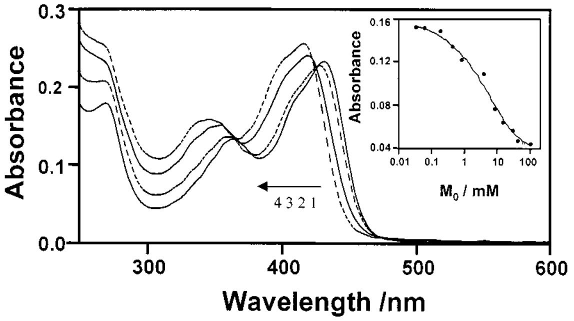


Figure 4. Absorption spectra of **9** ($2\cdot10^{-5}$ M) in MeCN (1 cm cell) containing $AgClO_4$ at concentrations of (1) 0; (2) 0.5; (3) 8.0; (4) 30 mM. Inset: absorption at 445 nm as a function of Ag salt concentration fitted with the Equation (1)

The absorbance A of a chromoionophore solution at any wavelength λ depends on the metal ion concentration M_0 as described by Equation (1), where A_0, A_1, and A_∞ are the absorbances of the free ligand L and complexes LM^+ and $L(M^+)_2$, respectively, and K_1 and K_2 are equilibrium constants for complex formation.

$$A = A_0 + \frac{K_1 * M_0 (A_1 - A_0)}{1 + K_1 * M_0 + K_2 * M_0^2} + \frac{K_2 * M_0^2 (A_\infty - A_0)}{1 + K_1 * M_0 + K_2 * M_0^2} \qquad (1)$$

Equation (1), which is derived assuming that the concentration of metal cations M_0 is much higher than the concentration of complexes, was found to fit well ($R^2 > 0.98$) the dependence of the absorbance of **9** at a fixed wavelength on the concentration of $NaClO_4$ and $AgClO_4$ in acetonitrile (Figure 3 and 4). The estimated values for K_1 and K_2 derived from these data are presented in Table 1. Although the fitting presented in Table 1 is good, the equilibrium constants K_1 and K_2 cannot be independently accurately determined because of the overlap of LM^+ and $L(M^+)_2$ formation; additional measurements clearly distinguishing formation of LM^+ and $L(M^+)_2$ complexes would be required for a more accurate estimation.

Table 1. Stability constants for complexes of compound **9** with Na^+ and Ag^+ cations in acetonitrile

	$\log K_{obs}$	Simultaneous 1:1 and 1:2 complexation		R^2
Na^+	2.5 ± 0.2	log K_1	≈2.6	0.982
		log K_2	≈4.3	
Ag^+	2.4 ± 0.2	log K_1	≈3.4	0.992
		log K_2	≈5.5	

For comparison, the experimental data (absorbance at a fixed wavelength vs. metal salt concentration) were fitted to Equation (2), in agreement with a simplified reaction of Equation (3).

$$A = A_\infty + (A_0 - A_\infty)/(1 + K_{obs} * M_0) \qquad (2)$$

$$\mathrm{L + M} \xleftrightarrow{K_{obs}} \text{complex} \qquad (3)$$

The observable stability constant, K_{obs}, may be wavelength dependent because of the different relative absorptivity of **9** and its complexes at different wavelengths. The fitting of the absorbance data taken at a fixed wavelength gave estimates for log K_{obs} of 2.5±0.2 and 2.4±0.2, for sodium and silver cations respectively (Table 1). The value of log K_{obs} for **9**-Na^+ complexation is very close to that reported for **2**-Na^+ complexation in acetonitrile.[11c]

Solution Electrochemical Studies

Cyclic voltammetry (CV) and square wave voltammetry (SQV) in acetonitrile showed that compounds **9** and **12** exhibit a quasi-reversible, two-electron oxidation wave at E_1^{ox}

+0.405 V and +0.345 V, respectively: the lower value for **12** reflects the stabilization of the dication due to the dimethyl substituents.[2c] As observed with previous derivatives,[4] this wave could not be separated into two separate oxidation processes even at low temperature. A second, quasi-reversible, one-electron wave, ascribed to oxidation of the anthracene system[3c,4,5] (i.e. radical trication formation) is observed at E_2^{ox} +1.620 V for both compounds **9** and **12**. The progressive addition of aliquots of metal salts (as the triflate for Li^+, Na^+, K^+, and Ag^+; perchlorate for Ba^{2+}) resulted in a positive shift of E_1^{ox} (and a similar positive shift of the coupled reductive peak on the cathodic scan) while E_2^{ox} remained essentially unchanged (± 5 mV) thereby acting as a convenient internal reference. Figure 5 shows the CVs of compound **9**, in the presence of 0 and 10 molar equivalents of $AgCF_3SO_3$. These data are consistent with expulsion of the metal cation from the ionophore prior to the second oxidation wave. The positive shifts (ΔE_1^{ox}) for **9** increase in the order: $Li^+ < K^+ < Ba^{2+} < Na^+ < Ag^+$. These data for **9** and **12** are collated in Table 2, and the shifts of E_1^{ox} for compound **9** with added K^+, Na^+ and Ag^+ in acetonitrile are shown in Figure 5.

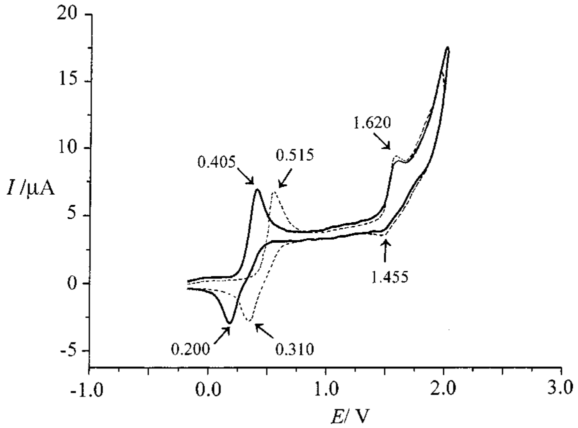


Figure 5. Cyclic voltammograms of compound **9**, in the presence of 0 and 10 molar equivalents of $AgCF_3SO_3$. Data were obtained in 0.2 M Bu_4NBF_4, MeCN, Pt disk electrode, 50 mV s^{-1}, Ag/AgCl reference electrode, referenced vs. decamethylferrocene

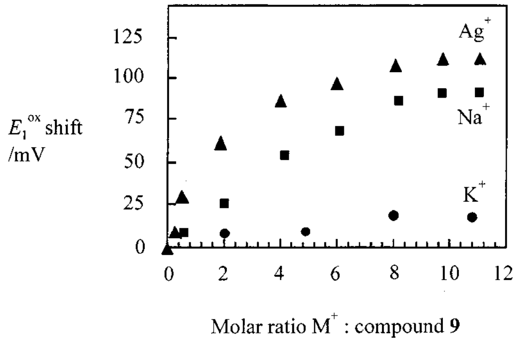


Figure 6. Plot of the shift of the potential E_1^{ox} in the cyclic voltammogram of compound **9** with added equivalents of KCF_3SO_3 (circles), $NaCF_3SO_3$ (squares), and $AgCF_3SO_3$ (triangles) under the same conditions as Figure 5

Table 2. Shift in the first oxidation potential for compounds **9** and **12** in saturated acetonitrile solutions of different metal salts

Compound	Metal cation[a]	ΔE_1^{ox}/mV[b]
9	Li^+	10−20
9	Na^+	90−100
9	K^+	15−20
9	Ba^{2+}	50−60
9	Ag^+	105−115
12	Li^+	5−15
12	Na^+	60−90
12	K^+	10−20
12	Ba^{2+}	40−55
12	Ag^+	75−85

[a] Added as the triflate salt, except for Ba^{2+}, which was added as $Ba(ClO_4)_2$. − [b] From three separate experiments with each metal salt.

The analogous data for **12** showed more variation between different experiments, especially at higher concentrations of the metal salt, possibly as a result of precipitation of the complex, as noted above. The trend is that the values of ΔE_1^{ox} are only slightly lower for the mono-crown system **12** compared to the bis-crown **9**, whereas in the TTF series, e.g. compound **1** and analogues, a significantly larger shift is observed for bis-crowns.[11a,11c] This could be a consequence of intramolecular steric interactions between the crown rings of **9**, and/or sandwich complexation between the two crowns, favoured by the rigid saddle conformation.

A comparison with related crowned TTF systems[11] reveals two important features of system **9**. (1) The positive shifts of E_1^{ox} which accompany Na^+ and Ag^+ complexation are larger, and (2) system **9** is significantly more sensitive than some TTF crowns, with saturation being achieved with < 10 equivalents of cation (Figure 6) (cf. compound **2** for which ΔE_1^{ox} = 80 mV saturating with 200 equivalents of Na^+ [11a]). We note that Gorgues et al. have recently reported that a structurally different TTF-cage molecule is very selective and responsive to Ba^{2+} ions: ΔE_1^{ox} 100 mV for a stoichiometric amount of added metal.[11g] The voltammetric response of **9** is a consequence of the unusual electronic and structural features of this system. The two-electron wave of compound **9** (rather than the one-electron wave of TTF) should serve to enhance the Coulombic repulsion with the bound metal cation(s). Upon electrochemical oxidation each dithiole ring of **9** acquires a full positive charge which is not delocalized into the anthracene system to any significant extent, due to the orthogonality of the anthracene and dithiolium systems.[3a][3c] This situation is different from the TTF radical cation, which is formed by the first oxidation process, where the +1 charge is partly delocalized over the two rings, with the maximum charge density located on the central $S_2C{=}CS_2$ fragment.[22] Studies on a TTF derivative with pendant (rather than fused) crown substituents,[23] and a vinylogous system where the HOMO is localized on the central $S_2C{=}C{-}C{=}CS_2$ fragment,[24] both of which show no voltammetric response to metal cations, confirm that the binding site should be situated close to the region of maximum charge density in the oxidized state for an efficient voltammetric response.

As with TTF-crowns, monitoring the E_2^{ox} wave of **9** provides confirmation that cation expulsion has occurred: this is a clear advantage of these transducer units over comparable ferrocene based ligands, although larger potential shifts (> 150 mV) accompany metal binding in some ferrocene ionophores.[10]

Conclusions

We have synthesized the first crown annelated derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene and exploited their chromophoric and strong π-electron donor properties in the spectrophotometric and voltammetric sensing of metal cations. The electroregulated cation binding data herein further establish this extended π-system as a versatile building block in supramolecular chemistry. Reactions of the new reagent **7** should be applicable to the synthesis of other crown-annelated 1,3-dithiole derivatives suitable for development as chemosensor devices.[25]

Experimental Section

^{1}H and ^{13}C NMR Spectra were obtained on Oxford 200, Varian Unity 300, and Varian VXR 400S spectrometers operating at 199.992 (^{1}H) and 50.293 (^{13}C), 299.908 (^{1}H) and 75.420 (^{13}C), and 400.0 (^{1}H) and 100.6 (^{13}C) MHz, respectively. − Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV. − Infra-red spectra were recorded using a golden gate on a Paragon 1000 FTIR spectrometer operated from a Grams Analyst 1600. − Electronic absorption spectra were measured using a Perkin−Elmer Lambda 9 UV/Visible absorption spectrophotometer. − Melting points were obtained on a Philip Harris melting point apparatus and are uncorrected. − All reagents were of commercial quality; all reaction solvents were dried using standard procedures. − All reactions were performed under an inert atmosphere of argon in pre-dried glassware. − Cyclic voltammetric data were measured with iR compensation using a BAS CV50 electrochemical analyser. The experiments were carried out at 20 °C with 5 mL of a ca. 10^{-4} M solution of the compound in acetonitrile containing 0.2 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte, at scan rate 100 mV s^{-1}. The oxidation potentials were measured versus a platinum wire quasi-reference electrode and corrected versus decamethylferrocene/decamethylferrocenium^{+} by adding decamethylferrocene to the studied solution after the experiment, and referenced versus Ag/AgCl.[26] Metal salts for electrochemical cation recognition experiments were purchased from Fluka and were dried in vacuo before use.

Triflate Salt 4: Into a solution of **3**[11a] (2.7 g, 6.8 mmol) in dichloromethane (50 mL) was added methyl triflate (1.2 g, 7.3 mmol). The solution was stirred at 20 °C for 5 h to give a dark brown solution. The solvent was partially evaporated in vacuo (to leave ca. 5 mL) and diethyl ether was added (100 mL) and the mixture was stirred for 30 min. The solvent was decanted off and the residual oil dried in vacuo to afford **4**, as a brown oil (3.2 g, 84%) of high purity suitable for use in the next step without further purification. − ^{1}H NMR (CD_3CN): δ = 3.23 (s, 3 H), 3.33 (s, 12 H), 3.57 (t, *J* = 4.5 Hz, 4 H), 3.95 (t, *J* = 4.5 Hz, 4 H). − $C_{15}H_{23}F_3O_7S_6$ (564.0): calcd. C 31.91, H 4.08; found C 31.64, H 4.27.

Compound 5: Into an ice cooled solution of **4** (2.36 g, 4.2 mmol) in ethanol (75 mL) was added sodium cyanoborohydride portionwise (284 mg, 4.5 mmol) at 0 °C and the mixture was stirred at 0 °C for 1 h. The solvent was then evaporated in vacuo and the residue was purified by column chromatography on silica gel with ethyl acetate as the eluent to afford 5, as a red oil (0.72 g) which was crystallized from hot ethyl acetate with cooling in acetone/dry ice to yield an off-white waxy solid (1.20 g, 70%). − ^{1}H NMR ($CDCl_3$): δ = 5.77 (s, 1 H), 3.71 (t, *J* = 2.6 Hz, 4 H), 3.70 (s, 12 H), 2.98−3.16 (m, 4 H), 2.24 (s, 3 H). − *m/z* (EI): 416 [M^{+}]. − $C_{14}H_{24}O_4S_5$ (416.0): calcd. C 40.38, H 5.76; found C 40.25, H 5.84.

Triflate Salt 6: Into a solution of **5** (0.5 g, 1.2 mmol) in acetonitrile (5 mL) was added triflic acid (1 mL, 10 mmol) and the mixture was stirred at 20 °C for 10 min to give a deep red-orange solution. Workup as described for **4**, gave **6** as an unstable brown oil (0.52 g, 84%) of high purity (^{1}H NMR analysis) suitable for use in the next step without further purification. − ^{1}H NMR (CD_3CN): δ = 3.38 (s, 12 H), 3.55 (t, *J* = 4.5 Hz, 4 H), 3.85 (t, *J* = 4.5 Hz, 4 H), 9.22 (s, 1 H).

Compound 7: To a stirred suspension of freshly-prepared salt **6** (540 mg, 1.0 mmol) in dry acetonitrile (5 mL) at 20 °C, was added triethylphosphite (0.17 mL, 1.0 mmol) and the mixture was stirred for 1 h. Then the solvent was evaporated in vacuo and the residue extracted into ethyl acetate (2× 50 mL), filtered, dried ($MgSO_4$), and evaporated in vacuo. Column chromatography on silica gel with ethyl acetate as the eluent afforded **7** as a colourless oil (0.40 g, 75%) of high purity (^{1}H NMR analysis) suitable for use in the next step without further purification. − ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, *J* = 7.0 Hz, 6 H), 2.86−2.96 (m, 2 H), 2.99−3.12 (m, 2 H), 3.62 (s, 4 H), 3.64 (s, 8 H), 3.74 (t, *J* = 6.2 Hz, 2 H), 3.75 (t, *J* = 6.8 Hz, 2 H), 4.18 (dt, $J_{H\text{-}H} = J_{H\text{-}P}$ = 7.0 Hz, 4 H), 4.63 (s, 1 H). − HRMS: $C_{17}H_{31}O_7PS_4$ (506.7): calcd. 506.0759; found 506.0759.

Compounds 9 and 10: Into a solution of **7** (558 mg, 1.10 mmol) in dry tetrahydrofuran (70 mL) at −78 °C, was added lithium diisopropylamide (0.74 mL of 1.5 M solution in cyclohexane, 1.11 mmol). The reaction was stirred for 3 h at −78 °C until a cloudy solution formed. Anthraquinone **8** (115 mg, 0.552 mmol) was added and the reaction was allowed to warm overnight to 20 °C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel with ethyl acetate as eluent. The first product to elute was **10** as a red oil which solidified on standing (90 mg, 29%). M.p. 123−124 °C (from dichloromethane/hexane). − $C_{27}H_{28}O_5S_4$ (560.8) calcd. C 57.8, H 5.0; found C 57.7, H 5.0. − *m/z* (EI) 560 [M^{+}]. − ^{1}H NMR ($CDCl_3$): δ = 3.04 (t, *J* = 6.0 Hz, 4 H), 3.58 (m, 16 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.66 (m, 2 H) 7.76 (d, *J* = 7.6 Hz, 2 H), 8.27 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 35.8, 69.6, 70.4, 70.6, 119.5, 126.3, 126.9, 127.2, 127.3, 130.6, 131.9, 138.6, 140.1, 197.9. − ν_{max} (Golden Gate): 1646 (C=O) cm^{-1}. − Continued elution with ethyl acetate/acetone (3:1 v/v) afforded **9** as a yellow solid (335 mg, 67%) (from dichloromethane/hexane). M.p. 216−218 °C. − $C_{40}H_{48}O_8S_8$ (913.3) calcd. C 52.6, H, 5.3; found C 52.3, H 5.4. − *m/z* (EI): 912 [M^{+}]. − ^{1}H NMR ($CDCl_3$): δ = 3.05 (m, 8 H), 3.66 (m, 32 H), 7.33 (m, 4 H), 7.56 (m, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 19.4, 26.5, 116.1, 116.4, 120.4, 120.9, 126.2, 127.8, 128.7, 129.8, 131.3, 132.9, 135.5, 135.7, 136.6, 153.2.

Reaction as above using **7** and LDA (both 3.0 equiv.) gave **9** as the sole product in 82% yield, after separation from traces (< 5%) of **10**.

Compound 12: Into a solution of **7** (250 mg, 0.494 mmol) in tetrahydrofuran (50 mL) at −78 °C, was added lithium diisopropylamide (0.33 mL of 1.5 M solution in cyclohexane, 0.495 mmol). The reaction was stirred for 3 h at −78 °C until a cloudy solution formed.

Compound **11**[2c] (159 mg, 0.494 mmol) was added, then the reaction was allowed to warm overnight to 20 °C. The reaction mixture was evaporated in vacuo and the residue was purified by column chromatography on silica gel, initially with ethyl acetate (to remove unchanged starting material) then with ethyl acetate/acetone (3:1 v/v) as the eluent to afford **12** as a yellow/orange solid (178 mg, 53%). M.p. 223−225 °C (from dichloromethane/hexane). − ^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 6 H), 3.00 (m, 4 H), 3.58 (m, 16 H), 7.29 (m, 4 H), 7.52 (m, 2 H), 7.68 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 13.1, 35.4, 53.4, 69.8, 70.4, 70.5, 70.6, 76.7, 77.0, 77.3, 120.8, 123.8, 125.3, 125.8, 126.1, 129.9, 133.4, 134.4, 135.1. − *m/z* (EI): 674 [M^+]. − HRMS $C_{32}H_{34}O_4S_6$ (675.0) requires 674.0883; found 674.0883.

X-ray Crystallography: X-ray diffraction experiments were carried out on a SMART 3-circle diffractometer with a 1 K CCD area detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 gas crysostat. A combination of 3 sets of ω scans, each set a different φ and/or 2θ angles, covered over a quadrant (**10**) or a hemisphere (**12**) of reciprocal space. Absorption corrections by numerical integration[27] were negligible. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[28] The absolute structure of crystal **10** was determined from anomalous scattering by Flack's method;[29] absolute structure parameter 0.07(8). Crystal data and experimental details are summarised in Table 3. The structures have been briefly reported earlier[17] and deposited with the Cambridge Crystallographic Data Centre, no. CCDC 182/1511.

Table 3. Crystal data and experimental details

Compound	**10**	**12**
Empirical formula	$C_{27}H_{28}O_5S_4$	$C_{32}H_{34}O_4S_6 \bullet CH_2Cl_2$
Formula mass	560.73	759.88
T [K]	150	120
Symmetry	Orthorhombic	Triclinic
Space group	$P2_12_12_1$ (# 19)	$P\bar{1}$ (# 2)
a [Å]	7.600(1)	11.891(2)
b [Å]	18.395(1)	12. 546(1)
c [Å]	18.566(4)	12.691(2)
α [°]	90	104.93(1)
β [°]	90	97.02(1)
γ [°]	90	106.60(1)
V [Å^3]	2595.6(4)	1713.4(4)
Z	4	2
No. of refl. total	10781	9437
Refl. unique	4235	7137
$R_{int.}$	0.037	0.025
$2\theta_{max}$ [°]	53	55
Refl. with $I > 2\sigma(I)$	3920	6205
No. of variables	418	551
$R[I > 2\sigma(I)]$	0.038	0.037
$wR(F^2)$, all data	0.083	0.089

Supporting Information Available: Torsion angles in the macrocycle of **10** and **12**, as determined by X-ray crystallography (see also footnote on the first page of this article).

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