Transition-metal Complexes of Crown Ether Benzodithiolenes. Part 2.[1] The Effects of Alkali-metal Cation Binding

Nigel D. Lowe and C. David Garner *
Chemistry Department, University of Manchester, Oxford Road, Manchester M13 9PL, UK

The binding of Li^+, Na^+ and K^+ cations to the crown ether rings of a series of transition-metal complexes with crown ether benzodithiolene ligands has been monitored. Fast atom bombardment mass spectrometry and UV/VIS spectroscopy have been used to demonstrate the binding of the cations to the complexes, and cyclic voltammetric studies provide a quantitative measure of the perturbations which result upon cation binding. The results support the view that the electronic transitions arise primarily from sulfur-to-metal charge-transfer transitions, provide information concerning the dithiolate(2−) or dithioketonic form of the dithiolene ligand, and indicate whether a particular redox process is primarily metal- or ligand-based. Some selectivity within the series Li^+, Na^+ and K^+ is observed, with the benzo-15-crown-5 ring showing a preference for the first two and the benzo-18-crown-6 ring preferring K^+. Tris(crown ether benzodithiolene) complexes of molybdenum and tungsten show the most promise as sensors for alkali-metal cations.

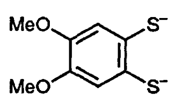
Recently we have reported the synthesis and properties of a series of transition-metal complexes of the ligands **I**–**III**.[1] Our intention in synthesising complexes of **II** and **III**, which feature benzo-15-crown-5 and benzo-18-crown-6 moieties, respectively, was to use them as 'probes' for alkali-metal cations. It was envisaged that cation binding to them would be manifest through changes in the physical properties of the complexes, particularly in the well established electrochemical behaviour of these dithiolene species.[1,2] Related studies involving transition-metal complexes of the crown ether benzothiolate,[3] dithiocarbamate[4] and dithiolene ligands[5] **IV**, **V**, **VI** have been reported recently by Green and co-workers and Beer[6] has provided a comprehensive review of developments up to 1989. It is of interest to compare the sensitivity to alkali-metal cations of each of ligands **I**–**III** with those of complexes reported previously, particularly those of ligands **IV**–**VI**. Within the series represented by structures **1**–**14**, there exist several variables which may affect the nature and extent of the response to the presence of alkali-metal cations. First, one, two or three crown ether ligands are present which should allow an assessment of the effect of the number of ion-binding sites per molecule. Secondly, an examination of the effect of the varying crown ether ring size can be made, an effect which might result in analogous complexes of ligands **I** and **III** displaying a different order of response to particular alkali-metal cations. Thirdly, the series contains various structural types which have been established to demonstrate variations within the spectrum from dithiolate-(2−) to dithioketonic in the metallodithiolene bonding;[1,7] the electronic structure of the ligand could affect the efficiency with which ion binding is transmitted to the redox-active transition-metal centre. The corresponding complexes of the veratroledithiolate (4,5-dimethoxybenzene-1,2-dithiolate) ligand **I**, have been used as 'controls', in order to prove that changes in the physical properties of the crown ether benzodithiolenes are associated with cation binding in the crown ether ring and not due to ion–molecule pairing interactions. The precedent of utilising such non-macrocyclic analogues for this purpose has been established in many previous studies in this area.[8]

Experimental

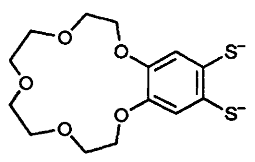
The complexes **1**–**14** were prepared according to procedures published elsewhere.[1] The electrolyte $[NBu^n{}_4][BF_4]$ was precipitated by the reaction of $Na[BF_4]$ and $[NBu^n{}_4][HSO_4]$ in water. The crude product was taken up in CH_2Cl_2 and crystalline material produced by slow addition of this solution to an excess quantity of Et_2O. The alkali-metal salts $Li[ClO_4]$, $Li[BF_4]$, $Na[ClO_4]$, $K[ClO_4]$ and $K[PF_6]$ were used as obtained from normal commercial sources. The solvents CH_2Cl_2 and MeCN were dried by prolonged reflux over CaH_2, followed by distillation under dinitrogen; dimethylformamide (dmf) was dried over anhydrous copper(I) sulfate, followed by distillation at reduced pressure.

The FAB mass spectral measurements were made in the M.S. Laboratory of Manchester University on a Kratos 'Concept' instrument using an argon source. Samples were prepared by allowing the various alkali-metal salts to equilibrate in CH_2Cl_2 solution, in the presence of each crown ether benzodithiolene complex, with the solvent being allowed to evaporate slowly overnight. Samples were applied to the probe as a matrix in *m*-nitrobenzyl alcohol with a minimum quantity of CH_2Cl_2 to aid solubility. All spectra were run in positive-ion mode. The FAB mass spectrometric experiments were performed in two different ways.[9,10] Fixed amounts of each of the alkali-metal salts were added individually to solutions of the complexes **1**–**14** and a predetermined number of scans used in accumulating the mass spectrum. The absolute intensity of each of the [complex–M^+] peaks in the spectrum was taken as being directly proportional to the concentration of that species in solution. Alternatively, a competition experiment was performed, where equal quantities of a series of alkali-metal salts were added to a solution of the macrocycle. Here the ion-binding preferences are revealed by the relative intensity of each [complex–M^+] signal in the resulting FAB mass spectrum. Both types of experiment were performed for complexes **2**, **4** and **14**, *i.e.* of the ligand **II**.

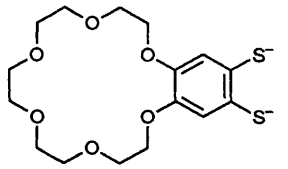
The UV/VIS spectra were recorded for solutions at room temperature on a Shimadzu 260 electronic absorption spectrometer with 0.1 cm matched silica cells. Peak positions were measured with an estimated accuracy of ±2 nm and, to facilitate comparisons of the relative energy of peaks, λ_{max} values are quoted in cm^{-1}. Two different methods were used in performing these experiments; either a solution of the crown ether complex was prepared which was 0.2 mol dm^{-3} in an



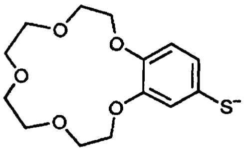
I



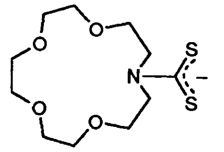
II



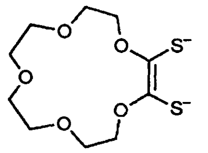
III



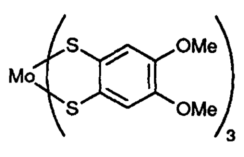
IV



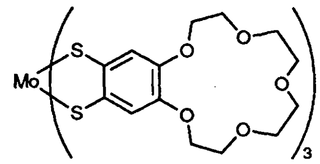
V



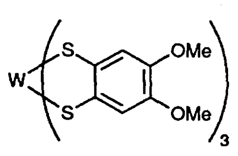
VI



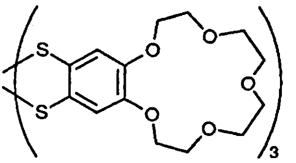
1



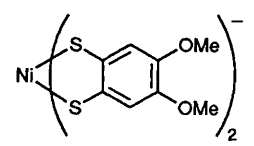
2



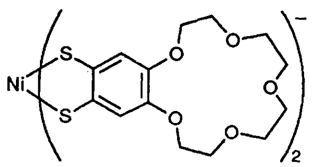
3



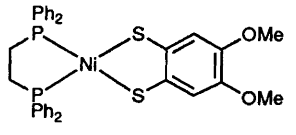
4



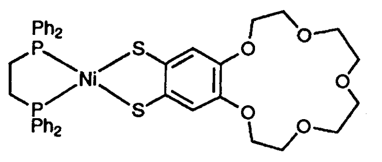
5



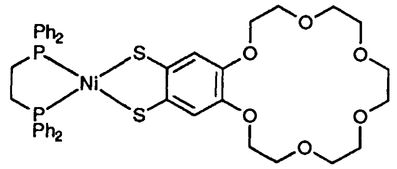
6



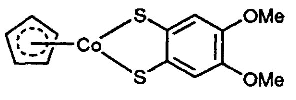
7



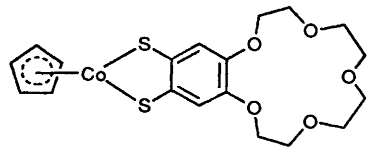
8



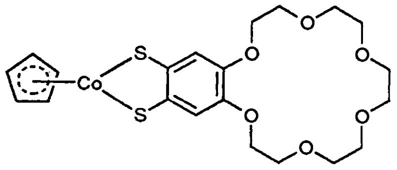
9



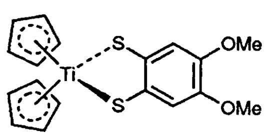
10



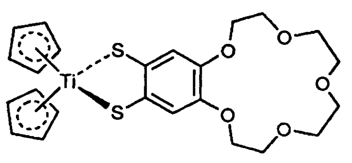
11



12



13



14

alkali-metal salt or aliquots of alkali-metal salts were added to solutions of a complex. These former solutions were used for the corresponding cyclic voltammetric studies. The UV/VIS data are reported for **2**, **4**, **11**, **12** and **14**.

The effect of alkali-metal salts on the electrochemical properties of complexes **1**–**14** was explored using cyclic voltammetry. The experiments were performed in two ways reflecting the different procedures published for similar investigations.[5] The electrochemical behaviour was monitored as successive aliquots of the solid alkali-metal salt were added to a *ca.* 1 mmol dm^{-3} solution of the complex in MeCN (though CH_2Cl_2 or dmf was used in the case of complexes **5** and **6** for reasons described previously[1]). Suitably soluble alkali-metal salts were Li[ClO$_4$], Na[ClO$_4$] and K[PF$_6$] with 0.2 mol dm^{-3} [NBu$^n_4$][BF$_4$] as the supporting electrolyte. Alternatively, cyclic voltammetry was performed with the alkali-metal salt (0.2 mol dm^{-3}) itself acting as the supporting electrolyte. Measurements were made using a Princeton Applied Research (PAR) model 173 potentiostat, model 178 electrometer and model 175 Universal Programmer, with a vitreous carbon working electrode and a platinum secondary electrode. Cyclic voltammograms were recorded on an Advance Bryans XY-plotter. Typically, scan rates of 200 mV s^{-1} were used. All potentials are quoted with an accuracy of ± 5 mV, relative to a saturated calomel electrode (SCE) connected to the cell *via* an appropriate bridge tube. The ferrocenium–ferrocene couple was measured at +0.43 and +0.56 V (ΔE_p = 80 mV, 200 mV s^{-1}) relative to the SCE in MeCN and CH_2Cl_2, respectively, under these conditions.

Results and Discussion

FAB Mass Spectrometry.—The cation-binding ability of complexes of the crown ether benzodithiolene ligands **II** and **III** can be clearly demonstrated by FAB mass spectrometry. Indeed, this technique has been widely used in the study of ion binding by macrocyclic species.[9,10] It is an extremely sensitive method and has proved capable of detecting weak complexation between species not indicated by other techniques.[10]

The FAB mass spectra of complexes **1**, **3**, **5**, **7**, **10** and **13**, which involve the ligand **I**, showed no evidence for the binding of alkali-metal cations.

Addition of equimolar quantities of each of the salts Li[BF$_4$], Na[ClO$_4$] and K[ClO$_4$] to CH_2Cl_2 solutions of complex **14** led to formation of the corresponding [ML]$^+$ complex (M = Li, Na or K), as revealed by distinct signals in the mass spectrum. In the case of Li$^+$ and Na$^+$, the signal attributable to this complex is considerably more intense than that due to free **14** (the latter comprises only *ca.* 10% of the former signal in each case) whereas, in the case of K$^+$, the signal for the [ML]$^+$ complex has *ca.* 55% of the intensity of that for free **14**. These data indicate that the K_s values for complex formation between **14** and a Li$^+$ or Na$^+$ cation are of the same order and each is significantly greater than that of the corresponding complex with K$^+$. This was confirmed by a competition experiment, the results of which are shown in Fig. 1. Here, the complex with Na$^+$ slightly predominates over that with Li$^+$, and only a very small signal is observed for the potassium analogue. The observation that Na$^+$ forms the strongest complex with **14** is consistent with hole-size arguments for benzo-15-crown-5 systems which suggest that an Na$^+$ ion is the best fit for the cavity of a crown ether of this size.[11] The almost equally strong complexation of Li$^+$ is particularly surprising in the light of previous results[9] and may reflect the influence of the solvent on measurements of this kind.[12] It is interesting that the synthesis of the benzo-15-crown-5 dithiolene ligand, **II**, involves the use of lithium metal[1] yet no bound Li$^+$ cations are evident in the FAB mass spectra of any of the transition-metal complexes of the ligand. Presumably, **II** does not bind Li$^+$ because its synthesis involves work-up in aqueous solution where the formation constant for the complex is expected to be very low. Conversely, some mass spectroscopic evidence was obtained for the sequestration of adventitious Na$^+$ and K$^+$ cations by complexes of ligands **II** and **III**. A further FAB mass spectroscopic experiment established that complex **14** forms complexes with [NH$_4$]$^+$.

Additional possibilities exist for cation binding in the case of complexes **2** and **4**, since each has not one but three crown ether sites. However, no conclusive mass spectroscopic evidence for species with more than one bound cation was obtained. The FAB mass spectra for these complexes in the presence of each of the alkali-metal salts show a signal attributable to [ML]$^+$ (M = Li, Na or K) which dominates that due to the initial complex alone but the difference in intensities is less pronounced in the case of potassium. This weaker affinity for K$^+$ is borne out by competition experiments, the results of which are shown in Figs. 2 and 3. Both reveal insignificant signals due to the potassium complex, although there are notable differences between the two spectra with respect to the other cations. Thus, **2** (Fig. 2) has a pronounced selectivity for Li$^+$ over Na$^+$ whilst the signals corresponding to the complexes of each of these cations with **4** are almost identical (Fig. 3). The reasons for this variation from **2** to **4** are not understood.

UV/VIS Spectroscopy.—The addition of alkali-metal salts to solutions of the complexes **1**–**14** resulted in pronounced colour changes for those involving crown ether benzodithiolene ligands (*i.e.* **2**, **4**, **6**, **8**, **9**, **11**, **12** and **14**). This was most evident for the dark red solutions of **2** which became yellow upon exposure to high concentrations of alkali-metal cations. These changes are attributed to cation binding by the crown ether benzodithiolene ligands since: (*a*) no such shifts are observed upon addition of alkali-metal salts to the complexes containing ligand **I** (**1**, **3**, **5**, **7**, **10** and **13**); (*b*) the shifts in the UV/VIS spectra are reversed upon addition of excess quantities of appropriate crown ethers (such as benzo-15-crown-5 and dibenzo-18-crown-6)* to solutions of the crown ether benzodithiolene complexes containing aliquots of alkali-metal salts.

The UV/VIS data recorded for a representative selection of the crown ether benzodithiolene complexes (**2**, **11**, **12** and **14**) alone and in the presence of 0.2 mol dm^{-3} alkali-metal salt are presented in Table 1. Thus, each of the complexes shows a significant shift in λ_{max} upon the binding of one (or more) metal cation(s). In every case, the sense of the shift is to higher energy and this is consistent with the UV/VIS transitions being primarily ligand(sulfur)-to-metal, charge transfer in character. Any interpretation of the magnitude of the shifts is complicated by the interaction of (at least) four factors: (*i*) the number of

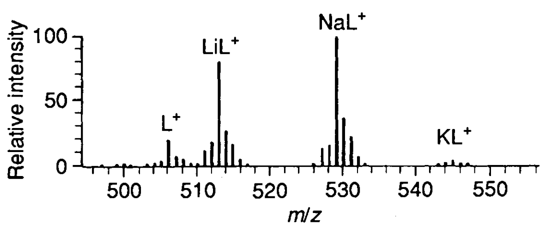


Fig. 1 The FAB mass spectrum of complex **14** (L) in the presence of equimolar quantities of Li[BF$_4$], Na[ClO$_4$] and K[ClO$_4$]

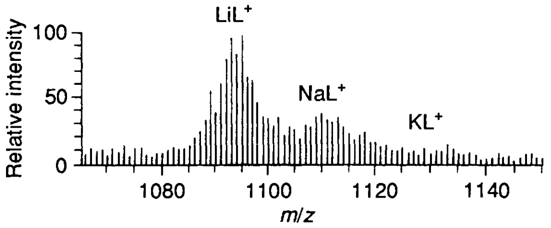


Fig. 2 The FAB mass spectrum of complex **2** (L) in the presence of equimolar quantities of Li[BF$_4$], Na[ClO$_4$] and K[ClO$_4$]

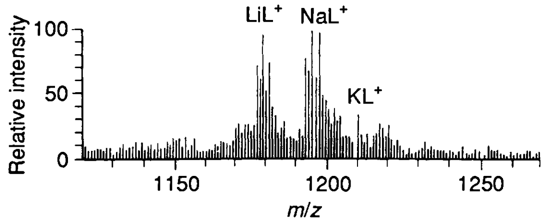


Fig. 3 The FAB mass spectrum of complex **4** (L) in the presence of equimolar quantities of Li[BF$_4$], Na[ClO$_4$] and K[ClO$_4$]

Table 1 UV/VIS absorption maxima of selected crown ether benzodithiolene complexes* and their displacement in the presence of 0.2 mol dm^{-3} alkali-metal salts

		$\Delta\lambda$/cm^{-1}		
Complex	λ_{max}/cm^{-1}	Li[ClO$_4$]	Na[ClO$_4$]	K[PF$_6$]
2	20 800, 12 900	580, 430	620, 430	620, 290
11	15 750	440	490	280
12	15 800	180	180	230
14	21 450, 15 750	230, 250	190, 200	140, 100

* 1 mmol dm^{-3} in MeCN.

---

* 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine and 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine, respectively.

Table 2 Electrochemical shifts (ΔE_1, ΔE_2/mV, see Table 3) for crown ether benzodithiolene complexes upon incremental addition of alkali-metal salts

	Complex[b]						
Added cation[a]	**2**	**4**	**6**	**8**	**11**	**12**	**14**[c]
$1Li^+$	+40, +50	+60, +60	0, +10	+20, +50	+40, +70	+10, +50	+50
$2Li^+$	+60, +70	+90, +80	+30, +30	+30, +90	+50, +100	+10, +70	*d*
xLi^+	+70, +70[e]	+90, +90[f]	+80, +70[g]	+50, +220[g]	+50, +130[e]	+40, +130[e]	+50[g]
$1Na^+$	+30, +50	+70, +60	+10, 0	+10, +110	+50, +30	+20, +70	+50
$2Na^+$	+70, +80	+90, +70	+20, +20	+10, +220	+50, +130	+20, +70	*d*
xNa^+	+100, +110[e]	+100, +80[f]	+30, +40[g]	+20, +190[g]	+50, +130[e]	+30, +70[e]	+50[g]
$1K^+$	*h*	*h*	0, 0	0, 0	+10, +40	+30, +100	+10
$2K^+$	*h*	*h*	0, 0	0, 0	+10, +40	+30, +120	*d*
xK^+	*h*	*h*	+10, 0[e]	0, 0[g]	+20, +40[e]	+30, +120[e]	+20[g]

[a] Li^+ and Na^+ added as perchlorates, K^+ as hexafluorophosphate. [b] 1 mmol dm^{-3} solutions in MeCN (except **6**, in CH_2Cl_2) containing 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$. [c] Only ΔE_1 available. [d] Data not available. [e] 6 equivalents. [f] 3 equivalents. [g] 4 equivalents. [h] See text.

cation binding sites, (*ii*) the magnitude of the stability constant(s) for $L + nM^+(solv) \rightleftharpoons [M_nL]^+(solv)$, (*iii*) the charge density of the cation, and (*iv*) the electronic structure of the dithiolene complex, especially the relative contributions of the dithiolate(2−) and dithioketonic forms of the ligand.[7]

Addressing each of these factors in turn, we observe the following in respect of the experimental data obtained. (*i*) The FAB mass spectroscopic studies provided no evidence for the binding of more than one alkali-metal cation to *e.g.* complex **2**. Furthermore, the maximum energy shift observed for **11** (Table 1) of 490 cm^{-1} is not much less than that observed for **2**, suggesting that not all of the three possible binding sites are utilised in the latter. (*ii*) The stability constant for formation of the complex must have an effect on the size of the hypsochromic shift. The absence of shifts with the analogues of **I** indicates that if the cation is not tightly bound to the ligand no changes are seen in the UV/VIS spectrum. Furthermore, the crown ether benzodithiolene complexes manifest significantly smaller hypsochromic shifts in their UV/VIS spectra than those indicated in Table 1 when presented with aliquots of the alkali-metal salts. Thus, the λ_{max} of *e.g.* **2** show progressive displacement as two (43 and 101), four (263 and 169) and six Na^+ (307 and 186 cm^{-1}) are added per mol of complex, consistent with an equilibrium (or equilibria) between the free and cation-bound forms of the complex. Since the resolution of the spectra is not sufficient to identify individual contributions to the broad bands, only the net displacement of λ_{max} can be measured. The variations identified in Table 1 between **11** (and **14**) *vs.* **12** is consistent with the benzo-15-crown-5 ring exhibiting a preference for Li^+ and Na^+ over K^+ and the benzo-18-crown-6 ring exhibiting the reverse preference, as would be expected from considerations of the cation and ring sizes. (*iii*) The smaller the alkali-metal cation the higher is its charge density and, consequently, the greater its inductive effect on the ligand. Thus, shifts in the absorption bands would be expected to be in the order $Li^+ > Na^+ > K^+$. However, this variation is not observed, possibly because any such variation in inductive effects is masked by the operation of the equilibria discussed in (*ii*). (*iv*) The ^{13}C NMR chemical shifts observed[1] for the complexes **2**, **11** and **14** (all of which contain benzo-15-crown-5 rings) imply that the amount of dithiolate(2−) character in the ligand varies in the sequence **2** < **11** < **14**. The relative shift of the λ_{max} of these complexes, for each of the cations Li^+, Na^+ and K^+ (Table 1), is the *reverse* of this trend, implying that the lowering of the sulfur-orbital energies upon cation binding increases as the dithioketonic contribution to the electronic structure of the ligand increases.

Complex **4** appeared to decompose when added to 0.2 mol dm^{-3} MeCN solutions of $K[PF_6]$, $Na[ClO_4]$ and $Li[ClO_4]$, producing a red-brown solution rather than the usual emerald-green one. The products of this decomposition have not been identified but the rate of conversion was seen to depend upon the metal salt present and was the greatest for $K[PF_6]$. This phenomenon precluded the measurement of data such as those presented in Table 1, but experiments involving the addition of aliquots of the alkali-metal salts to MeCN solutions were conducted without initiating decomposition. The maximum shift in λ_{max} observed under these circumstances required a ratio of *ca.* 8 : 1 of alkali-metal salt:**4** and was greatest for $Na[ClO_4]$ with the lower-energy transition being hypsochromically shifted some 650 cm^{-1} (from 13 400 to 14 050 cm^{-1}) and the higher-energy transition similarly displaced some 400 cm^{-1} (from 23 050 to 23 450 cm^{-1}). Similar shifts were observed upon the addition of 8 equivalents of $Li[ClO_4]$ and $K[PF_6]$ to **4** in MeCN and, again, it can be suggested that these relatively large spectroscopic shifts arise because, as indicated by ^{13}C NMR studies,[1] the electronic structure of the ligands of **4** involves a considerable contribution of the dithioketonic form.

Cyclic Voltammetry.—Table 2 summarises the *anodic* shifts resulting from addition of aliquots of alkali-metal salts to solutions of complexes of the crown ether benzodithiolene ligands **II** and **III** also containing $[NBu^n_4][BF_4]$ as an electrolyte. The magnitude of the shifts is comparable to those reported for similar systems.[3–5] The sense of the shifts is as expected and these shifts refer to the position of the couple, or irreversible wave, and not to the appearance of a new, separate feature as has been observed in some similar studies.[13] Situations where a shift in the redox wave is observed, as opposed to the appearance of an additional feature, reflect cases where the complex formed with the metal ion has a stability constant of $K_s < 10^4$ mol dm^{-3}.[14] The scan rate used in such cyclic voltammetric experiments can also have an effect on the number of waves seen.[15] The data in Tables 2–4 were all measured at scan rates of 200 mV s^{-1}. Other scan rates were investigated but generally produced no change; the few situations where a scan-rate dependence was observed are noted below. The anodic shifts produced upon addition of alkali-metal salts (Table 2) were found to be completely reversible upon addition of excess quantities of crown ethers such as benzo-15-crown-5 and dibenzo-18-crown-6. This demonstrates that the perturbations are caused by specific binding of the cations in the crown ether ligands of the complexes. Even when the alkali-metal salt was used as the supporting electrolyte (Table 3), the changes in the electrochemistry could be wholly, or essentially, reversed upon addition of excess quantities of crown ethers.

(*i*) *Complexes of ligand* **I**. No appreciable shifts were observed upon addition of alkali-metal salts to any of the complexes (**1**, **3**, **5**, **7**, **10**, **13**) of the ligand **I**. This result concurs with the FAB mass spectrometric and UV/VIS spectroscopic (see above) results, all of which suggest that the complexes of **I** do not form strong complexes with alkali-metal cations. Some anodic shifts were observed for complexes **1** and **3** when large excesses of alkali-metal salts were added but these were always < 10 mV and decreased in the order $Li^+ > Na^+ > K^+$, consistent with

Table 3 Electrochemical data (V *versus* SCE) for crown ether benzodithiolene complexes **1**–**14** using various electrolyte salts

Complex[a]	E_1[b]	E_2[b]	$E_1(\mathrm{Li}^+)$[c]	$E_2(\mathrm{Li}^+)$[c]	$E_1(\mathrm{Na}^+)$[c]	$E_2(\mathrm{Na}^+)$[c]	$E_1(\mathrm{K}^+)$[d]	$E_2(\mathrm{K}^+)$[d]
1	+0.04[e]	−0.43[f]	−0.07	−0.54	−0.09	−0.55	−0.11	−0.57
2	+0.04[e]	−0.43[f]	+0.04	−0.46	+0.05	−0.45	*g*	*g*
3	+0.05[e]	−0.56[f]	−0.06	−0.69	−0.07	−0.69	−0.10	−0.72
4	+0.05[e]	−0.56[f]	+0.01	−0.63	+0.06	−0.60	*g*	*g*
5[h]	+0.19[i]	−0.63[j]	+0.16	−0.69	+0.16	−0.69	+0.15	−0.69
6[h]	+0.19[i]	−0.61[j]	+0.17	*g*	+0.22	−0.61	+0.17	−0.65
7	−1.51[k]	+0.52[l]	−1.64	+0.38	−1.63	+0.40	−1.62	+0.42
8	−1.51[k]	+0.51[l]	−1.62	+0.48	−1.60	+0.47	−1.60	+0.50
9	−1.51[k]	+0.56[l]	−1.61	+0.46	−1.60	+0.46	−1.59	+0.52
10	−0.66[k]	+0.76[l]	−0.76	+0.65	−0.76	+0.62	−0.78	+0.64
11	−0.65[k]	+0.76[l]	−0.71	+0.78	−0.71	+0.70	−0.73	+0.76
12	−0.65[k]	+0.76[l]	−0.76	+0.66	−0.74	+0.70	−0.78	+0.74
13	−1.03[k]	+0.73[l]	−1.12	+0.62	−1.16	+0.63	−1.14	+0.62
14	−1.04[k]	+0.73[l]	−1.07	+0.73	−1.10	+0.69	−1.09	+0.72

[a] 1 mmol dm^{-3} in MeCN (except where specified). [b] Using 0.2 mol dm^{-3} $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ electrolyte. [c] Using 0.2 mol dm^{-3} $\mathrm{M[ClO_4]}$ (M = Li or Na) electrolyte. [d] Using 0.2 mol dm^{-3} $\mathrm{K[PF_6]}$. [e] [M(dithiolene)$_3$]–[M(dithiolene)$_3$]$^-$ couple. [f] [M(dithiolene)$_3$]$^-$–[M(dithiolene)$_3$]$^{2-}$ couple. [g] See text. [h] In dmf. [i] [M(dithiolene)$_2$]–[M(dithiolene)$_2$]$^-$ couple. [j] [M(dithiolene)$_2$]$^-$–[M(dithiolene)$_2$]$^{2-}$ couple. [k] [complex]–[complex]$^-$ couple. [l] Irreversible oxidation wave.

Table 4 Electrochemical shifts (mV) for complexes of ligands **II** and **III** compared with their **I** analogues in the presence of various electrolyte salts

Complex[a]	$\Delta E_1(\mathrm{Li}^+)$[b]	$\Delta E_2(\mathrm{Li}^+)$[b]	$\Delta E_1(\mathrm{Na}^+)$[b]	$\Delta E_2(\mathrm{Na}^+)$[b]	$\Delta E_1(\mathrm{K}^+)$[c]	$\Delta E_2(\mathrm{K}^+)$[c]
2	+110	+80	+140	+100	*d*	*d*
4	+70	+60	+130	+90	*d*	*d*
6[e]	+10	*d*	+60	+80	+20	+40
8	+20	+100	+30	+70	+20	+80
9	+30	+80	+30	+60	+30	+100
11	+50	+130	+50	+80	+50	+120
12	0	+10	+20	+80	0	+100
14	+50	+110	+60	+60	+50	+100

[a] 1 mmol dm^{-3} in MeCN (except where specified). [b] Using 0.2 mol dm^{-3} $\mathrm{M[ClO_4]}$ (M = Li or Na) electrolyte. [c] Using 0.2 mol dm^{-3} $\mathrm{K[PF_6]}$. [d] See text. [e] In dmf.

ion-pairing interactions in solution. Whilst complex **5** is insensitive to added $\mathrm{Na[ClO_4]}$ and $\mathrm{K[PF_6]}$, an anomalously large reduction current is seen for E_2 in the presence of $\mathrm{Li[ClO_4]}$.

A more complicated dependency was observed when the alkali-metal salts were employed as the electrolyte, as can be seen from the data in Table 3. For instance, substituting the $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ electrolyte by each of the salts $\mathrm{Li[ClO_4]}$, $\mathrm{Na[ClO_4]}$ and $\mathrm{K[PF_6]}$ has a significant effect on the measured redox potentials of the couples E_1 and E_2 of complex **1** (Table 3). Given that these changes in electrolyte involve changing the identity of both the anion and the cation, a complicated dependence on the nature of the electrolyte is not unexpected. In order to circumvent these problems for complexes of crown ether dithiolene ligands **II** and **III**, advantage was taken of the fact that the half-wave potentials of each of the analogous complexes of ligands **I**–**III** are virtually identical under normal conditions (*i.e.* with $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ as the electrolyte).[1] This can be seen from the first two columns in Table 3, for the groupings (**1**, **2**), (**3**, **4**), (**5**, **6**), (**7**, **8**, **9**), (**10**, **11**, **12**) and (**13**, **14**). Thus, the difference in half-wave potential between a crown ether dithiolene complex and the corresponding system involving **I** should provide a direct measure of the effect of the alkali-metal salt on the electrochemical properties of the former. These data are summarised in Table 4 for each of the crown ether dithiolene complexes.

(*ii*) *Mono(crown ether benzodithiolene) complexes.* The incremental addition of aliquots of $\mathrm{Li[ClO_4]}$, $\mathrm{Na[ClO_4]}$ and $\mathrm{K[PF_6]}$ to solutions of the monodithiolene complexes **8**, **11**, **12** and **14** in MeCN with 0.2 mol dm^{-3} $[\mathrm{NBu^n_4}][\mathrm{BF_4}]$ as electrolyte produced significant anodic shifts in the potentials. For **8**, **11** and **12** the reversible reduction feature (E_1) is relatively insensitive to the presence of alkali-metal cations, a maximum anodic shift of *ca.* 50 mV being recorded. However, the irreversible oxidation in these systems (E_2) is significantly more sensitive to the presence of alkali-metal cations and shifts of *ca.* 200 mV were observed for **8**. This behaviour suggests that, especially for **8**, the oxidation (E_2) is less metal- and more ligand-based than the reduction (E_1). Indeed, the ligand-based nature of oxidations of complexes of the type $[\mathrm{Ni(dithiolene)(Ph_2PCH_2CH_2PPh_2)}]$ has been suggested previously.[16]

The effect of the cation has some dependence upon the size of the crown-ether ring. For example, the data for complexes **11** and **12** in Table 3 are consistent with the stronger binding of Li^+ and Na^+ by the benzo-15-crown-5 ring and K^+ by the benzo-18-crown-6 ring. However, no clear, overall pattern emerges.

(*iii*) *Bis(crown ether benzodithiolene) complexes.* The magnitude of shifts in the redox potentials for the couples of complex **6**, upon addition of the alkali-metal salts (Tables 2–4), are similar to those observed for the monodithiolene complexes, perhaps indicating that only one cation becomes bound to **6**. The addition of aliquots of Li^+ and Na^+ produced significantly greater shifts than did corresponding additions of K^+ (Table 2). This was also the situation when $\mathrm{Na[ClO_4]}$ *vs.* $\mathrm{K[PF_6]}$ was used as the electrolyte (Table 4). However, anomalous effects were observed when $\mathrm{Li[ClO_4]}$ was used as the electrolyte; similar effects were also observed for the corresponding complex **5** (Fig. 4) and may arise due to strong binding of Li^+ to the anions **5** and **6**.

The electrode potentials of complexes of the ligand **VI** {such as $[\mathrm{Cu(VI)_2}]^-$}[5] are slightly more sensitive than those of **6** to the presence of significant amounts of alkali-metal cations. This might be expected since **VI** does not possess the intervening benzene ring separating the crown ether from the metallodithiolene moiety. However, it possesses 'soft' sulfur atoms in the macrocycle which may reduce the binding affinity for alkali-metal cations.[3,12] Consequently, the electrode potentials of $[\mathrm{Cu(VI)_2}]^-$ are less sensitive than those of **6** to solutions with low alkali-metal cation concentrations.

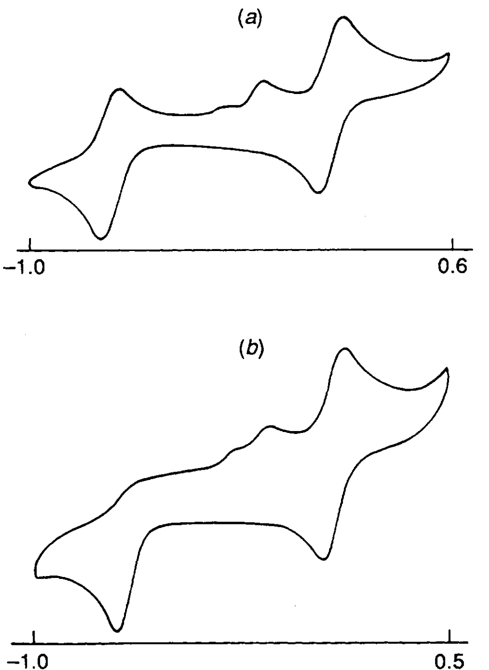


Fig. 4 Cyclic voltammograms recorded at 200 mV s^{-1}, in dmf solution, with 0.2 mol dm^{-3} $Li[ClO_4]$ supporting electrolyte for complexes (*a*) **5** and (*b*) **6**

(*iv*) *Tris*(*crown ether benzodithiolene*) *complexes*. The tris(dithiolene) complexes **2** and **4** showed the greatest anodic shifts of *reversible* couples upon addition of the alkali-metal salts. Addition of aliquots of $Li[ClO_4]$ and $Na[ClO_4]$ salts to MeCN solutions of **2** leads to anodic shifts of up to 110 mV (Table 2) which are fully reversible upon addition of excess quantities of benzo-15-crown-5. The effects of $Li[ClO_4]$ and $Na[ClO_4]$ are similar but when 1 equivalent of $K[PF_6]$ is added to **2** the behaviour shown in Fig. 5(*b*) results. The distorted shape of this cyclic voltammogram is possibly the result of the overlap of an adsorption feature with the normal reverse wave and, thus, may be indicative of the weak adsorption of a species formed during the scan onto the electrode surface.[17]

A 'normal' cyclic voltammogram was obtained with $Li[ClO_4]$ as electrolyte with anodic shifts of 110 and 80 mV occurring in the couples E_1 and E_2, respectively. However, complicated behaviour for complexes **2** and **4** was observed when $Na[ClO_4]$ and $K[PF_6]$ were used as electrolytes. With 0.2 mol dm^{-3} $Na[ClO_4]$ as the electrolyte, additional features were seen in the cyclic voltammogram with the profile being dependent upon the scan rate used (Fig. 6). At a scan rate of 500 mV s^{-1} [Fig. 6(*c*)] the cyclic voltammogram appears 'normal' and, as compared with the analogue **1** under the same conditions, yields anodic shifts of 140 and 100 mV for E_1 and E_2, respectively. These are the largest anodic shifts measured for reversible redox couples in this study. At lower scan rates the features A–F [Fig. 6(*a*)] were identified. The reduction waves, A and B, appear normal and occur at the same potential as those in Fig. 6(*c*); the oxidation wave C appears to be the Nernstian return wave associated with the reduction at B, and F appears to bear the same relationship to reduction A. Thus, the extra features which require special consideration are the oxidation waves D and E.

A possible explanation of these observations is as follows. The reduction potential of E_1 is shifted to positive potential (A) as a result of a weak interaction of the neutral complex **2** with Na^+ cations. Since there is only a weak interaction (*i.e.* $K_s < 10^4$), only an average positively shifted peak is seen, rather than separate peaks corresponding to the reduction of the bound and unbound complexes.[14] The same arguments apply to the reduction E_2 (B), demonstrating that the K_s is also small for the complex formed between Na^+ cations and the monoanionic 'molybdenum(v)' species. The dianionic 'molybdenum(IV)' species forms a stronger complex with Na^+ than either the neutral or monoanionic forms of **2**. Consequently, two oxidation waves are seen for E_2; C is attributed to the oxidation of the unbound dianionic species $\mathbf{2}^{2-}$ and D to the oxidation of the cation-bound dianionic species $[NaL]^-$ ($L = \mathbf{2}^{2-}$), the latter appearing at a potential some 70 mV more positive than the former. The shape of the oxidation wave E is indicative of an adsorption process[17] and, since it is not seen in the cyclic voltammogram of **2** in the absence of metal ions, is considered to

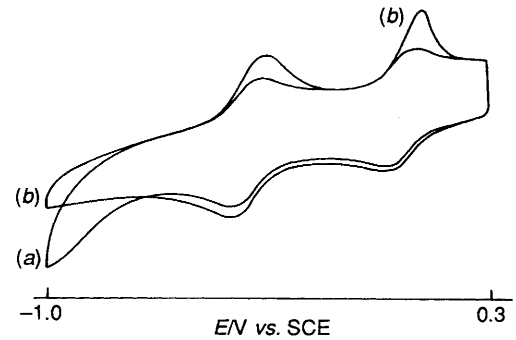


Fig. 5 Cyclic voltammograms of complex **2** recorded at 200 mV s^{-1}, in MeCN solution, with 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ supporting electrolyte, (*a*) alone and (*b*) + 1.0 equivalent $K[PF_6]$

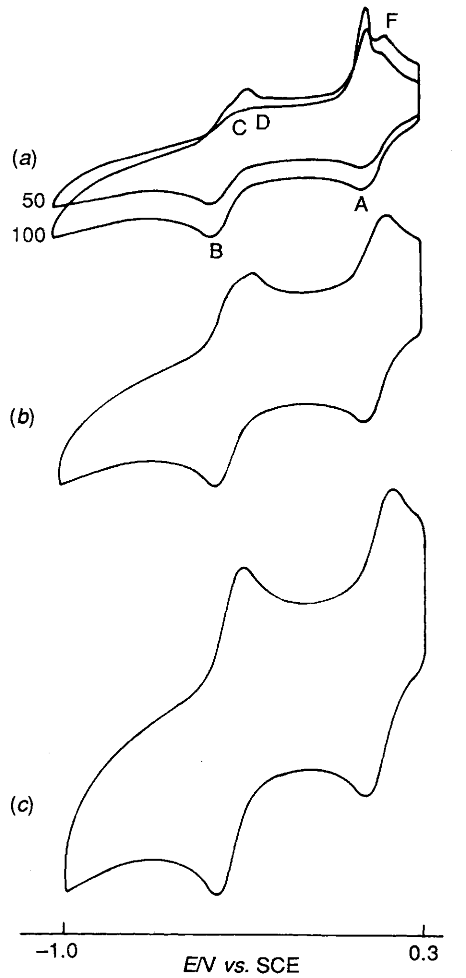


Fig. 6 Cyclic voltammograms of complex **2** recorded in MeCN solution, 0.2 mol dm^{-3} in $Na[ClO_4]$, recorded at scan rates of (*a*) 50 and 100, (*b*) 200 and (*c*) 500 mV s^{-1}

be associated with the product of the oxidation D. The complex [NaL] produced at D could be adsorbed onto the electrode surface, giving rise to the feature at E when oxidation to the neutral form of **2** occurs. The oxidation wave F is attributed to the oxidation of the $\mathbf{2}^-$ species which undergoes a weak interaction with Na^+ cations, causing a slight positive shift of the Nernstian return wave relative to that recorded for **2** in the absence of cations.

As for F, the oxidation C is shifted to a slightly more positive potential by the presence of alkali-metal salts. This implies that a weak complexation effect with, *e.g.* Na^+, cations is operating. Therefore, it appears that the dianionic form of complex **2** can form two different types of complex with Na^+, one with a higher binding constant than that of the other. The weaker complex responsible for C results, presumably, from the weak binding of one (or more) Na^+ cation(s) to one (or more) individual crown ether ligand(s), producing a positive shift in potential. The stronger complex formed (and considered to be responsible for the features D and thence E) appears to involve a time-dependent conformational change which cannot occur when scan rates of 500 mV s^{-1} are used [Fig. 6(*c*)]. This change may involve the binding of one Na^+ cation by two crown ether ligands of the same molecule, as has been seen in related systems.[18] Such binding may be facilitated by distortions in the shape of the complex which occur upon its progression from the neutral to the dianionic form.[19] Also, the larger cation Na^+ (and K^+, see below), in contrast to Li^+, may 'lock' the dianion in this conformation, making reoxidation more difficult. The phenomenon of 'cation lock' has been reported previously.[20]

These changes in the cyclic voltammogram were reversed when an excess of dibenzo-18-crown-6 was added to the MeCN solution of complex **2** containing 0.2 mol dm^{-3} $Na[ClO_4]$. This shows that the effects arise due to binding of Na^+.

The consequences of using 0.2 mol dm^{-3} $K[PF_6]$ in MeCN as the electrolyte for complex **2** (Fig. 7) are similar to those seen for 0.2 mol dm^{-3} $Na[ClO_4]$ (Fig. 6). However, several differences are noted. (1) At low scan rates [100 mV s^{-1}, Fig. 7(*a*)] there is evidence that the reduction wave corresponding to B [in Fig. 6(*a*)] is actually due to two overlapping waves. This implies that a strong potassium complex of the monoanionic form of **2** is slowly being formed. (2) At low scan rates there is no oxidation wave corresponding to C [in Fig. 6(*a*)] implying that, in the presence of K^+ ions, there is almost complete conversion into the 'strong' complex. (3) The oxidation wave corresponding to D is shifted to much more positive potentials, as compared with D in Fig. 4(*a*), implying that the larger K^+ cation provides a stronger 'cation lock'. (4) Even at 1000 mV s^{-1} [Fig. 7(*d*)], the equivalent behaviour to that shown in Fig. 6(*c*) is not observed, although the features corresponding to the oxidations C and F of Fig. 4(*c*) do grow relative to D and E. This implies that the 'strong' potassium complex with the dianionic form of **2** is formed more quickly than is the corresponding sodium complex, as well as having a greater formation constant. (5) The positions of the 'normal' reversible couples E_1 and E_2 observed in Fig. 7(*d*) for **2** have been shifted to values 110 and 70 mV more positive than the equivalent values for **1**. The magnitudes of these shifts are less than those seen for Na^+ [Fig. 6(*c*)] and are of the same order as those seen with Li^+.

The effects of adding aliquots of $Li[ClO_4]$ and $Na[ClO_4]$ to solutions of complex **4** (Table 2) were similar to those seen for **2**. The addition of aliquots of $K[PF_6]$ produced different behaviour which was very similar to that seen for $K[PF_6]$ with **2** (Fig. 5).

Further similarities between complexes **2** and **4** emerge when the alkali-metal salts are used as electrolytes with **4**. Thus, 'normal' behaviour results with $Li[ClO_4]$, with anodic shifts for E_1 and E_2 of 70 and 60 mV, respectively, whilst extra features are seen with $Na[ClO_4]$ (Fig. 8) and $K[PF_6]$ (Fig. 9). In Fig. 8 anodic shifts of 130 mV for E_1 and 90 mV for E_2 (Table 4) were observed at the high-scan-rate limit [Fig. 8(*c*)]. At lower scan rates [Fig. 8(*a*)] the presence of two oxidation waves for the 'W^V–W^{IV}' couple (E_2) can clearly be seen. In contrast to the cyclic voltammograms obtained for **2** with the $Na[ClO_4]$ electrolyte (Fig. 6), there is no effect on the 'W^{VI}–W^V' (E_1) couple in the case of **4**. Fig. 9 shows the cyclic voltammogram of **4** recorded at 500 mV s^{-1} in MeCN with $K[PF_6]$ as electrolyte. The form of this is similar to that measured for **2** under the same conditions (Fig. 7) except that, in this case, the oxidation waves corresponding to C and D are barely visible and waves E and F are not resolved. The reasons for the detailed differences in behaviour between **2** and **4** with $K[PF_6]$ as the electrolyte are not apparent. If dibenzo-18-crown-6 is added to the $K[PF_6]$ electrolyte solution of **4** the cyclic voltammogram approaches, but does not attain, 'normal' behaviour as a two-couple cyclic voltammogram.

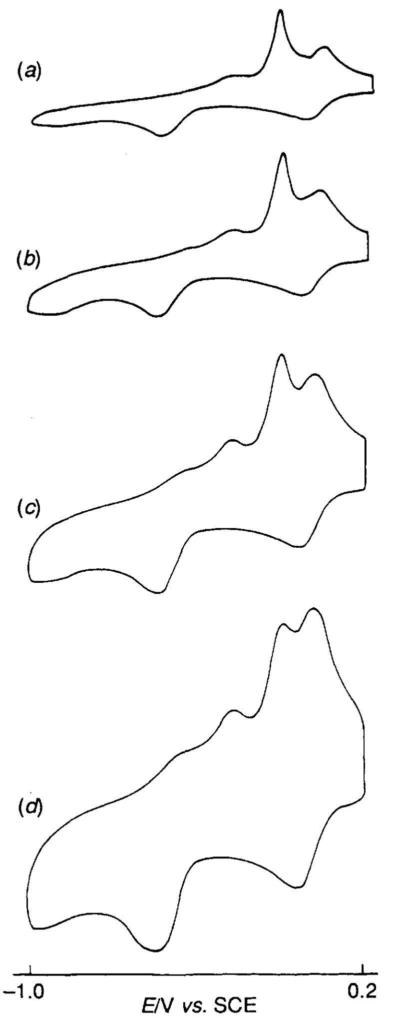


Fig. 7 Cyclic voltammograms of complex **2** recorded in MeCN solution, 0.2 mol dm^{-3} in $K[PF_6]$, recorded at scan rates of (*a*) 100, (*b*) 200, (*c*) 500 and (*d*) 1000 mV s^{-1}

The complicated electrochemical behaviour observed for the tris(crown ether benzodithiolene) complexes in the presence of alkali-metal cations requires further investigation, not least to establish which effects are due to solution equilibria and which to surface phenomena such as adsorption.

Conclusion

The FAB mass spectral results demonstrated that the crown ether benzodithiolene complexes do bind one alkali-metal ion (Li^+, Na^+ or K^+) but, even when two or three potential binding sites are available, no evidence was obtained for the binding of more than one cation.

The sense of the shifts observed in the UV/VIS absorption bands of the crown ether benzodithiolene complexes is

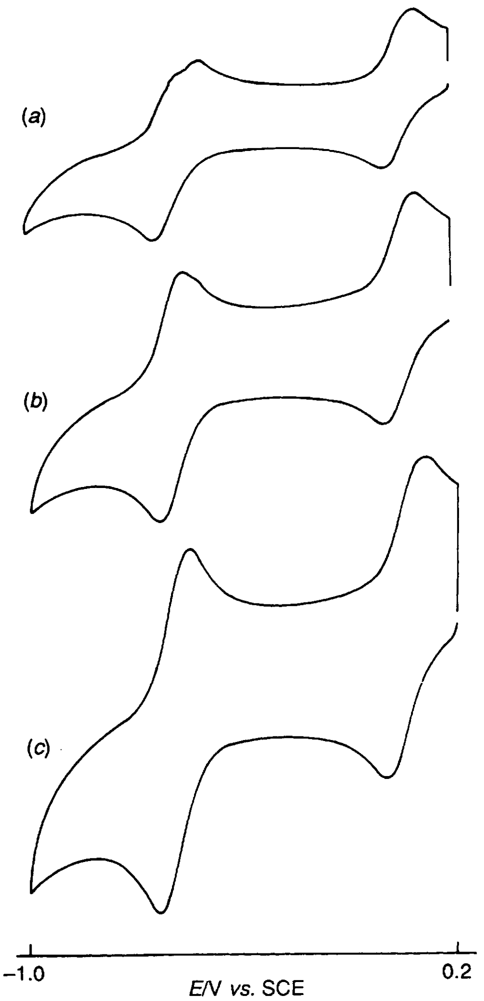


Fig. 8 Cyclic voltammograms of complex **4** recorded in MeCN solution, 0.2 mol dm^{-3} in Na[ClO$_4$], recorded at scan rates of (*a*) 50, (*b*) 100 and (*c*) 200 mV s^{-1}

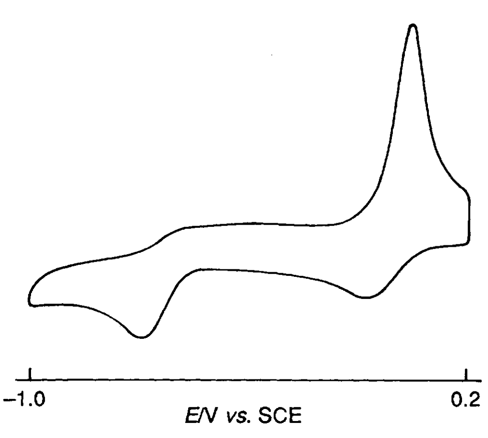


Fig. 9 Cyclic voltammogram of complex **4** recorded at 500 mV s^{-1}, in MeCN solution, with 0.2 mol dm^{-3} K[PF$_6$] supporting electrolyte

consistent with these absorptions arising from sulfur-to-metal charge-transfer transitions.[7] The magnitude of the shifts was greatest for the molybdenum and tungsten tris(dithiolene) complexes (**2** and **4**) and the trends observed, when considered with reference to ^{13}C NMR data,[1] imply that the relative shifts in λ_{max} are proportional to the involvement of the dithioketonic form in the electronic structure of the dithiolene ligands.

Positive shifts in the half-wave potentials of the redox processes of all the transition-metal complexes of the crown ether benzodithiolene ligands were observed in the presence of Li^+, Na^+ and K^+. These shifts were generally small and < 150 mV. However, they are comparable with many that have been reported for similar systems.[3–6] Features other than anodic shifts were apparent in the cyclic voltammograms only in the case of the tris(crown ether benzodithiolene) complexes **2** and **4**. These effects were essentially reversible upon addition of an excess of a crown ether.

In the FAB mass spectroscopic measurements a clear cation preference was seen, with the benzo-15-crown-5 ring binding more strongly to Li^+ and Na^+ than to K^+. The UV/VIS and electrochemical data were consistent with this pattern and preference of the benzo-18-crown-6 ring for K^+ over Li^+ and Na^+ was also observed.

In view of the greater magnitudes of the perturbation of the λ_{max} and redox potential values, the tris(crown ether benzodithiolene) complexes **2** and **4** show the most promise as sensors for alkali-metal cations.

Acknowledgements

We thank the SERC for provision of a Studentship (to N. D. L.).

References

1 Part 1, N. D. Lowe and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1993, 2197.

2 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.

3 E. Fu, M. L. H. Green, V. J. Lowe and S. R. Marder, *J. Organomet. Chem.*, 1988, **341**, C39; E. Fu, J. Granell, M. L. H. Green, V. J. Lowe, S. R. Marder, G. C. Saunders and M. Tuddenham, *J. Organomet. Chem.*, 1988, **355**, 205.

4 M. L. H. Green, S. R. Marder, G. C. Saunders and N. M. Walker, *J. Chem. Soc., Dalton Trans.*, 1988, 1697; J. Granell, M. L. H. Green, V. J. Lowe, S. R. Marder, P. Mountford, G. C. Saunders and N. M. Walker, *J. Chem. Soc., Dalton Trans.*, 1990, 605.

5 M. L. H. Green, W. B. Heuer and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1990, 3789.

6 P. D. Beer, *Chem. Soc. Rev.*, 1989, **18**, 409.

7 E. I. Stiefel, R. Eisenberg, R. C. Rosenberg and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 2956; M. J. Baker-Hawkes, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 4870; R. B. King and C. A. Eggers, *Inorg. Chem.*, 1968, **7**, 340.

8 A. Kaifer, L. Echegoyen, D. A. Gustowski, D. M. Goli and G. W. Gokel, *J. Am. Chem. Soc.*, 1983, **105**, 7168; R. E. Wolf, jun., and S. R. Cooper, *J. Am. Chem. Soc.*, 1984, **106**, 4646.

9 R. A. W. Johnstone and M. E. Rose, *J. Chem. Soc., Chem. Commun.*, 1983, 1268.

10 J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer and G. W. Gokel, *J. Am. Chem. Soc.*, 1992, **114**, 10583.

11 R. M. Izatt, D. J. Eatough and J. J. Christensen, *Struct. Bonding (Berlin)*, 1973, **16**, 161.

12 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271.

13 F. R. Fronczek, V. J. Gatto, R. A. Schultz, S. J. Jungk, W. J. Colucci, R. D. Gandour and G. W. Gokel, *J. Am. Chem. Soc.*, 1983, **105**, 6717; S. Akabori, Y. Habata, Y. Sakamoto, M. Sato and S. Ebine, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 537; C. D. Hall, N. W. Sharpe, I. P. Danks and Y. P. Sang, *J. Chem. Soc., Chem. Commun.*, 1989, 419.

14 S. R. Miller, D. A. Gustowski, Z. C. Chen, G. W. Gokel, L. Echegoyen and A. E. Kaifer, *Anal. Chem.*, 1988, **60**, 2021.

15 D. A. Gustowski, M. Delgado, V. J. Gatto, L. Echegoyen and G. W. Gokel, *J. Am. Chem. Soc.*, 1986, **108**, 7553.

16 G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1982, **21**, 2403 and refs. therein.

17 R. Greef, R. Peat, L. M. Peter, D. Pletcher and J. Robinson, Southampton Electrochemistry Group, *Instrumental Methods in Electrochemistry*, Ellis Horwood, Chichester, 1985, pp. 206–212.

18 P. D. Beer and A. S. Rothin, *J. Chem. Soc., Chem. Commun.*, 1988, 52; *Polyhedron*, 1988, **7**, 137.

19 S. Boyde, C. D. Garner, J. H. Enemark and R. B. Ortega, *Polyhedron*, 1986, **5**, 377; *J. Chem. Soc., Dalton Trans.*, 1987, 297 and refs. therein.

20 J. P. Desvergne, N. Bitit and H. Bouas-Laurent, *J. Chem. Res.*, 1984, (*S*) 214, (*M*) 1901.

Received 24*th May* 1993; *Paper* 3/02948D