Synthetic and electrochemical studies on electroactive ionophores based on the di-η-cyclopentadienyl-molybendum and -tungsten fragments

Enqin Fu, Jaume Granell, Malcolm L.H. Green ★, Valerie J. Lowe, Seth R. Marder, Graham C. Saunders, and Michael Tuddenham

Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR (Great Britain)

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Abstract

The compound $[W(\eta\text{-}C_5H_5)_2Cl_2]$ reacts with $HSCH_2(CH_2OCH_2)_3CH_2SH$ in the presence of base giving the metalla-crown ether complex $[W(\eta\text{-}C_5H_5)_2SCH_2(CH_2OCH_2)_3CH_2S]$ which can undergo a reversible one-electron oxidation. Treatment of $[M(\eta\text{-}C_5H_5)_2Cl_2]$ (M = Mo or W) with 4′-carboxybenzo-15-crown-5 and base gives the complexes $[M(\eta\text{-}C_5H_5)_2\{(\text{benzo-15-crown-5})\text{-}4'\text{-carboxylato}\}_2]$, which also undergo reversible oxidation. Small changes in the $E_{1/2}(< 20\text{ mV})$ were observed upon changing the electrolyte from $(C_2H_5)_4NPF_6$ to $NaPF_6$. The new compounds, $[M(\eta\text{-}C_5H_5)_2\{(\text{benzo-15-crown-5})\text{-}4'\text{-thiolato}\}_2]$ (M = Mo or W) prepared from the sodium salt of (benzo-15-crown-5)-4′-thiol and $[M(\eta\text{-}C_5H_5)_2Cl_2]$, undergo a reversible one-electron oxidation and the $E_{1/2}$ is shifted anodically upon addition of alkali metal cations.

Introduction

Compounds which display shifts in electrochemical potentials upon ion binding or changes in ion-binding constants upon oxidation and reduction are well known [1–12]. Interest is focussed on the compounds that are highly selective towards a particular ion and show large changes in $E_{1/2}$ upon ion binding.

Here we describe studies on bent d^2 di-η-cyclopentadienyl compounds, $[M(\eta\text{-}C_5H_5)_2XY]$ (M = Mo or W), which incorporate potential ion-binding ligand systems. The systems $[M(\eta\text{-}C_5H_5)_2XY]$ were selected for two reasons. Firstly they exhibit reversible one-electron oxidations [13], and secondly, removal of an electron

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★ Dedicated to Professor Ernst Otto Fischer on the occasion of his 70th birthday on November 10th, 1988.
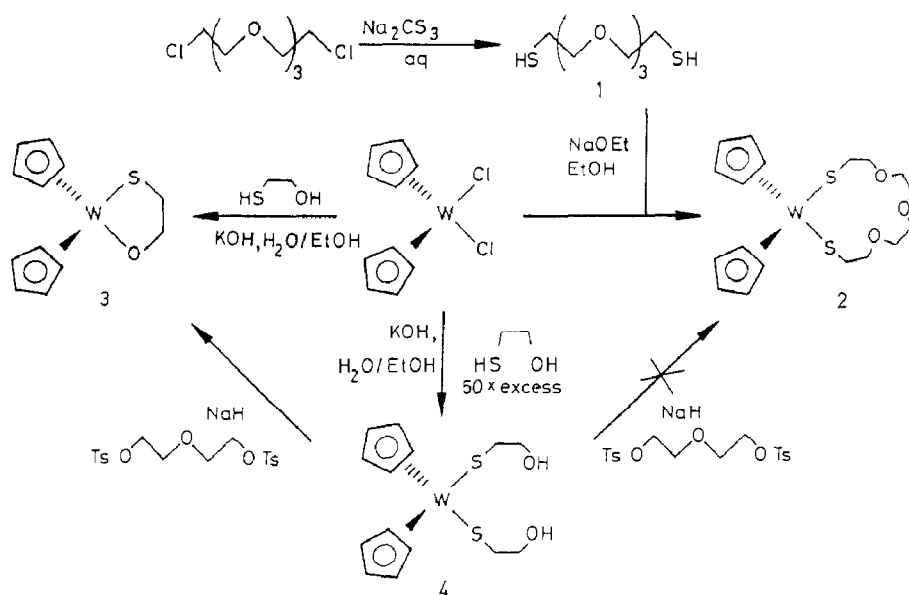
Scheme 1.

from the neutral $[M(\eta\text{-}C_5H_5)_2XY]$ systems gives mono-cations of altered geometry, in which the X–M–Y angle is increased [14]. It was thus expected that ion-binding and redox-activity would be related.

A preliminary account of this work has appeared [15].

Results

The compound $HSCH_2(CH_2OCH_2)_3CH_2SH$ (1) was prepared as described from 1,11-dichloro-3,6,9-trioxaundecane and Na_2CS_3 [16]. Compound 1 and $NaOC_2H_5$ in anhydrous ethanol were added dropwise to a stirred slurry of $[W(\eta\text{-}C_5H_5)_2Cl_2]$ in anhydrous ethanol at 65°C during 11 h. Chromatography on alumina of the involatile products followed by recrystallisation from methanol yielded orange crystals of $[W(\eta\text{-}C_5H_5)_2SCH_2(CH_2OCH_2)_3CH_2S]$ (2) in 10% yield. The structure of 2 was deduced from the ^1H and ^{13}C NMR spectra, elemental analysis, and mass spectral analysis (see Experimental section).

In an alternative approach to the preparation of compound 2, $[W(\eta\text{-}C_5H_5)_2Cl_2]$ was treated with a large excess (50 fold) of 2-hydroxyethanethiol in the presence of KOH to give the purple complex $[W(\eta\text{-}C_5H_5)_2(OCH_2CH_2S)]$ (3) in poor yield, together with the desired $[W(\eta\text{-}C_5H_5)_2(SCH_2CH_2OH)_2]$ (4) in 11% yield. However, attempts to convert 4 into 2 by treatment with NaH and 1,5-ditosyl-3-oxapentane in N,N-dimethylformamide gave 3 as the only identified product (Scheme 1).

The electrochemistry of compound 2 was investigated in N,N-dimethylformamide with various supporting electrolytes. In 0.1 M $(C_2H_5)_4NClO_4$ two oxidation waves were observed. The first wave had an $E_{1/2}$ of -30 mV vs. SCE. The peak separation at 20 mVs^{-1} scan rate, was 60 mV. A plot of $I_{p,a}$ against (scan rate)$^{1/2}$ was linear and $I_{p,a}/I_{p,c} = 1$, indicating the couple to be reversible [17]. The second wave, $E_{p,a} = +490$ mV vs. SCE, exhibited no cathodic peak (i.e. $I_{p,a}/I_{p,c} \gg$
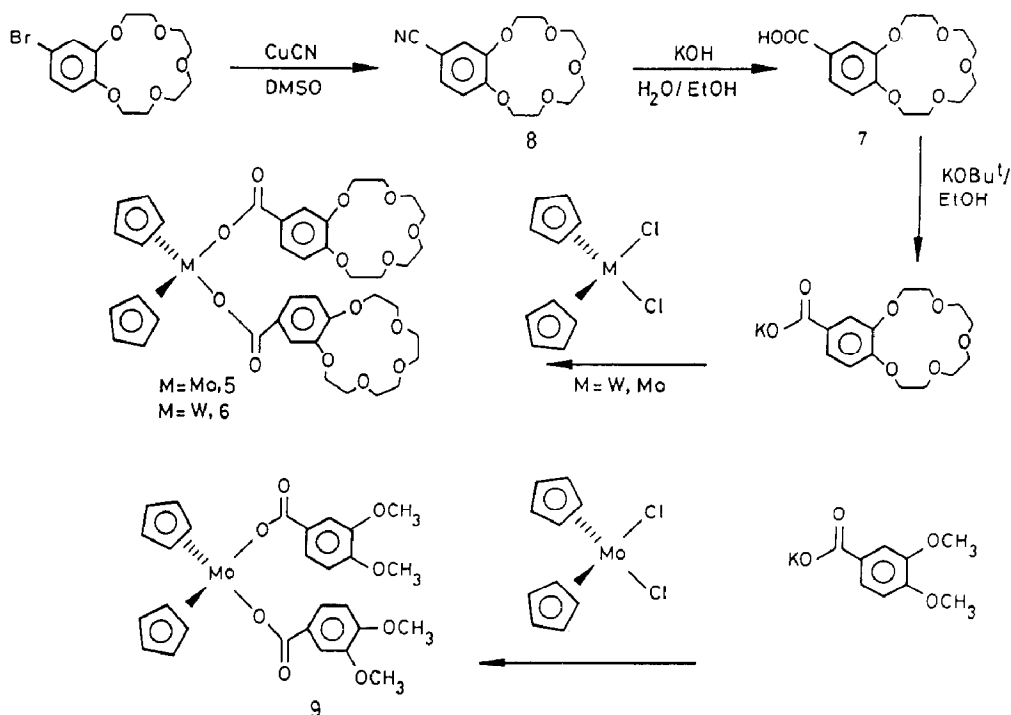
Scheme 2.

1), a feature indicative of an irreversible oxidation. This type of electrochemical behaviour has been observed previously for other di-(η-cyclopentadienyl)dithiolato-tungsten complexes [13]. Unfortunately, when the electrolyte was changed to 0.1 M p-$CH_3C_6H_4SO_3Li$, p-$CH_3C_6H_4SO_3Na$ or p-$CH_3C_6H_4SO_3K$, no significant changes ($\Delta E_{1/2} < 10$ mV) were observed in the value of $E_{1/2}$ for the reversible couple. These electrochemical results may be associated in part with the presence in the metalla-macrocycle of the "soft" sulphur atoms; these are not optimal for binding "hard" alkali metal cations [18]. We therefore directed our attention towards crown ether ligands in which all of the donor atoms were oxygen.

It is known that treatment of $[M(\eta$-$C_5H_5)_2Cl_2]$ (M = Mo or W) with benzoic acid forms the complexes $[M(\eta$-$C_5H_5)_2\{O$-$C(O)Ph\}_2]$ [19] and these can be oxidised to stable d^1 M^V cations [20]. We set out to synthesize the compounds $[M(\eta$-$C_5H_5)_2\{$(benzo-15-crown-5)-4'carboxylato$\}_2]$ (M = Mo, **5** and W, **6**). Accordingly the known compound 4'-carboxybenzo-15-crown-5 [21] (**7**) was prepared, in ca. 35% yield, by the following route. Treatment of 4'-bromobenzo-15-crown-5 with copper cyanide in refluxing dimethylsulphoxide gave 4'-cyanobenzo-15-crown (**8**), as a white solid. Hydrolysis in refluxing aqueous ethanolic potassium hydroxide followed by acidification yielded the acid **7** as a white solid.

Reaction of the potassium salt of **7** with $[Mo(\eta$-$C_5H_5)_2Cl_2]$, or $[W(\eta$-$C_5H_5)_2Cl_2]$ in hot ethanol readily yielded the desired compounds **5** and **6**, respectively (see Scheme 2). Compounds **5** and **6** exhibited a characteristic C=O stretch in the region 1620–1630 cm^{-1}, which is indicative of the carboxylato group bonding in an η^1 manner.

Table 1

Electrochemical data for compounds **5, 6** and **9**

Compound	Electrolyte	$E_{1/2}$ (mV)	ΔE_p (mV)
5	0.1 M $(C_2H_5)_4NPF_6$	+275	60
5	0.1 M $NaPF_6$	+280	70
6	0.1 M $(C_2H_5)_4NPF_6$	+470	70
6	0.1 M $NaPF_6$	+500	65
9	0.1 M $(C_2H_5)_4NPF_6$	+450	65
9	0.1 M $NaPF_6$	+465	75

The electrochemistry of **5** and **6** was investigated in acetonitrile with $(C_2H_5)_4NPF_6$ and $NaPF_6$ as the supporting electrolytes. The results are summarized in Table 1. With 0.1 M $(C_2H_5)_4NPF_6$ as the electrolyte, and scanning in the range -200 to $+1000$ mV, **5** and **6** each exhibited a reversible wave with $E_{1/2}$ values of $+275$ and $+470$ mV, respectively. With 0.1 M $NaPF_6$ as the electrolyte, small cathodic shifts were observed. Thus, the $E_{1/2}$ for **5** and **6** moved 5 and 30 mV to $+280$ and $+500$ mV, respectively. Under the same conditions, however, $[Mo(\eta\text{-}C_5H_5)_2\{O_2CC_6H_3(OMe)_2\}_2]$ **(9)** exhibited a reversible wave at 450 mV, and there was a 15 mV cathodic shift from the observed wave for this compound when 0.1 M $NaNPF_6$ was used as the electrolyte. Although the crown ether ligand used in **5** and **6** would be expected to bind cations, it appears that ion binding does not cause a substantial change in the redox potential of the transition metal complex.

In a procedure similar to that described by Shinkai [2b], (benzo-15-crown-5)-4'-thiol **(10)** was prepared from 4'-aminobenzo-15-crown-5 in 23% yield. Reaction of the sodium salt of **10** with $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ or $[W(\eta\text{-}C_5H_5)_2Cl_2]$ in thf at 60°C for 60 h yielded, after chromatography and crystallization, red crystals of **11** (14%) and **12** (14%), respectively, as shown in Scheme 3. The spectroscopic properties of **11** and **12** are very similar.

In the ^1H NMR spectrum of **12** the three aromatic hydrogens give rise to resonances at δ 6.95 [d, $J(H_a\text{-}H_b)$ 2.0, 2H, H_a], 6.89 [d,d, $J(H_b\text{-}H_c)$ 8.3, $J(H_b\text{-}H_a)$ 2.0, 2H, H_b] and, 6.75 [d, $J(H_c\text{-}H_b)$ 8.3, 2H, Hc]. The hydrogens of the η-cyclopentadienyl ring appear at δ 5.15 (s, 10H) and the methylene hydrogens give rise to multiplets centred at δ 4.1 (8H), 3.8(8H) and 3.7 (16H).

For the purpose of comparison the compound $[Mo(\eta\text{-}C_5H_5)_2\{SC_6H_3(OMe)_2\}_2]$ **(13)** was prepared by the reaction of $[Mo(\eta\text{-}C_5H_5)Cl_2]$ with 3,4-dimethoxy-benzenethiol, which was generated in situ from $(MeO)_2C_6H_3SO_2Cl$ (Scheme 3).

The electrochemistry of compounds **11, 12,** and **13** was investigated in acetonitrile with hexafluorophosphate salts as supporting electrolytes. Compound **12** was most thoroughly studied and most of the discussion pertains to this compound.

Scanning over the range -100 to $+1000$ mV vs. SCE compound **12** gives rise to three well-defined, major oxidation peaks (Fig. 1a). In 0.1 M $(C_2H_5)_4NPF_6$ the peaks are at $+100$, $+455$ and $+770$ mV. Additional minor waves are also observed. The reversibility of the first redox couple was found to depend on the switching potential. If the potential was switched at 320 mV or less, the $I_{p,a}/I_{p,c}$ ratio was nearly 1 and redox peak separation was equal to approximately 80 mV (v 20 mV s^{-1}), indicating at least quasi-reversible behaviour. However, if the oxidation potential was swept past $+455$ mV ($E_{p,a}$ for the second oxidation) the first couple
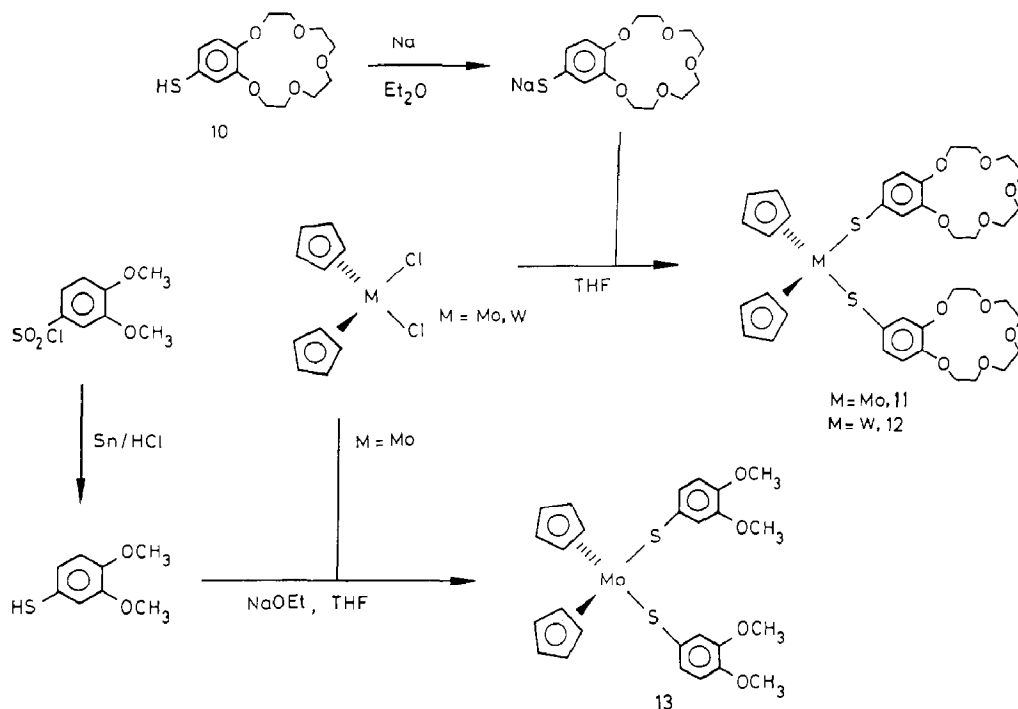
Scheme 3.

no longer had a peak current ratio of one. The anodic current of the second oxidation wave is approximately equal to the anodic current of the first oxidation wave, but the second wave appears to be irreversible at a scan rate of 20 mV s^{-1}. Kotz et al. have studied compounds of a similar form, such as $[W(\eta\text{-}C_5H_5)_2(SPh)_2]$, and have observed similar electrochemical behaviour [13].

Qualitatively the electrochemistry of **11** was very similar to **12** under these conditions, although the potentials of the corresponding redox peaks are higher for **11**. The studies discussed above all used 0.1 M $(C_2H_5)_4NPF_6$ as supporting electrolyte. Table 2 summarizes the observed electrochemistry of the compounds **11** and **12** under various electrolyte conditions.

Table 2

Electrochemical data for compounds 11 and 12

Compound	Electrolyte	Couple I [a]		Couple III [b]	
		$E_{1/2}$(mV)	ΔE_p [c] (mV)	$E_{1/2}$(mV)	ΔE_p [c](mV)
11	0.1 M $(C_2H_5)_4NPF_6$	+150	100	+815	70
11	0.1 M NaPF$_6$	+220	180	+960	170
12	0.1 M $(C_2H_5)_4NPF_6$	+100	70	+770	70
12	0.1 M LiClO$_4$	+150	115	+815	75
12	0.1 M NaPF$_6$	+180	160	+880	150
12	0.1 M KPF$_6$	+170	150	+865	150

[a] Couple I refers to the first couple as described in the text (see also Fig. 1). [b] Couple III refers to the third couple as described in the text (see also Fig. 1). [c] The voltammograms were recorded at a scan rate of 20 mV s^{-1}.
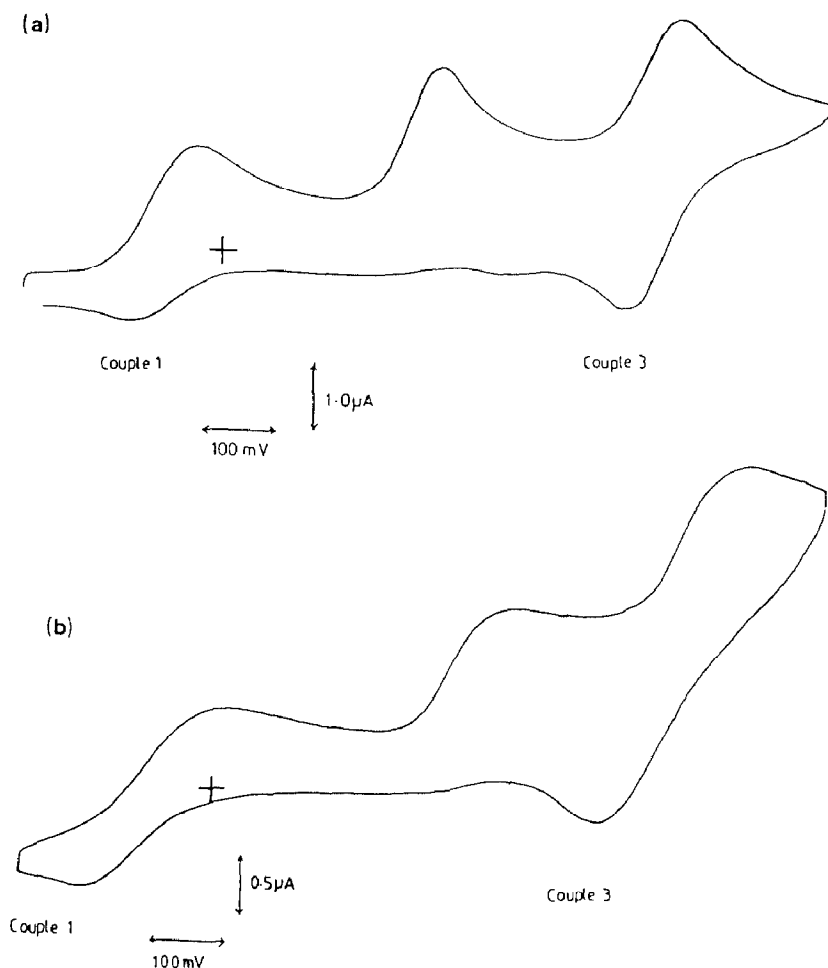
(a)

Couple 1   Couple 3

1·0μA

100 mV

(b)

0·5μA

Couple 3

Couple 1

100 mV

Fig. 1. Electrochemistry of **12** in CH_3CN with (a) 0.1 M $(C_2H_5)_4NPF_6$, and (b) 0.1 M $NaPF_6$ as electrolyte, against $Ag/AgNO_3$, ν 20 mVs^{-1}.

In 0.1 M $(C_2H_5)_4NPF_6$, the first and third redox couples of compound **12** exhibit quasi-reversible electron transfer kinetics. This contrasts sharply with the observed electrochemistry in 0.1 M $NaPF_6$ or KPF_6 supporting electrolytes, as shown in Fig. 1b. The peak potential positions have shifted to more positive potentials and redox peak separations have increased. In 0.1 M $NaPF_6$ the peak separation of the first redox couple increases by 90 mV and that of the third couple by 80 mV to 160 mV and 150 mV respectively. The $E_{1/2}$ of both couples shift to more positive potentials; the first couple $E_{1/2}$ shifts by 80 to +180 mV and the third couple shifts by 110 to +880 mV. The redox potential and peak separation shifts in 0.1 M KPF_6 were similar to those in 0.1 M $NaPF_6$.

The electrochemistry of compound **13** was investigated in 0.1 M $(C_2H_5)_4NPF_6$, and 0.1 M $NaPF_6$; no shifts in redox potentials were observed with change of supporting electrolyte. Thus it is proposed that these changes in electrochemistry of compound **12** are mainly, due to specific ion binding rather than ion pairing influences, although the data do not permit distinction of the relative contributions

of ion pairing and of ion binding to the observed change in redox potential. This proposal is supported by the fact that the electrochemistry is less perturbed in 0.1 M $LiPF_6$ (with respect to 0.1 M $(C_2H_5)_4NPF_6$) than in 0.1 M $NaPF_6$; the $E_{1/2}$ of the first couple increases by 50 mV, and that of the third couple by 45 mV; the peak separations are 115 and 75 mV, respectively. If ion pairing in non-aqueous solvents was responsible for this change in electron transfer characteristics, then Li^+ would be expected to exert a greater effect than Na^+. The smaller changes in redox potential of compound **13** with supporting electrolyte variation indicates that the perturbation must be due to specific ion binding by the crown ether functionalities.

The effect of titrating Na^+ into 0.1 M $(C_2H_5)_4NPF_6$ (**12**) is illustrated in Fig. 2.
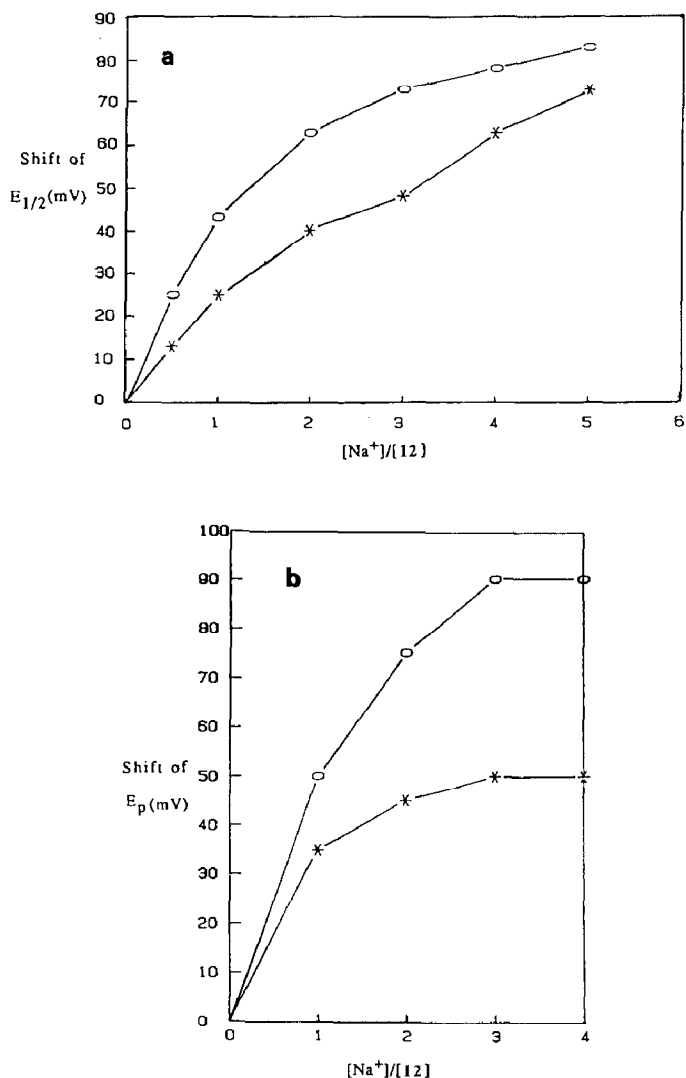

Fig. 2. (a) Plot of redox peak shifts of **12** in CH_3CN, with 0.1 M $(C_2H_5)_4NPF_6$ as electrolyte, against concentration of Na^+. $\circ$ = 1st couple, * = 3rd couple. (b) Plot of differential redox peak shifts for the 1st couple of **12** in CH_3CN, with 0.1 M $(C_2H_5)_4NPF_6$ as electrolyte, against concentration of Na^+. $\circ$ = anodic peak, * = cathodic peak.

Addition of Na$^+$ results in a shift of the redox potential of the first couple that is greater than that of the third couple (Fig. 2a). The peak separations also start to increase. Addition of further Na$^+$ accentuates this peak separation shift, although the redox potential shifts are not great in the range of 2 to 4 equivalents. There is also a differential rate of peak shift; the reduction peak of the first couple shifts little in comparison to the oxidation peak (Fig. 2b). This may be due to differential binding of the reduced and oxidized form of the compound. Presumably, the positively charged product arising from one electron oxidation will not bind ions as well as the neutral form. The differential peak shift could also be due to slower electron-transfer kinetics superimposed on an increase in redox potential; this should give rise to similar peak shapes. The increase in oxidation potential on ion binding is probably due to increased electronegative inductive effects on the metal centre by the ion binding ligand.

After careful titration, analysis of the results revealed no sign of two or more differing species undergoing electron transfer. In some ionophore redox systems studied, two independent species have been observed at a ligand/metal ratio of 2/1 [3]. In this case, the observed shift in redox potential is a gradual process with no individual species of compound/ion complexes observed. This is probably due to the rapid equilibrium between binding and unbinding compounds, resulting in the observation of an averaged redox potential. Qualitatively the effect on the third redox peak is the same as that of the first, although the magnitude of the effect at low Na$^+$ concentrations is smaller, presumably due to the reduced ion binding ability of this multiply charged species.

The effects observed with both Na$^+$ and K$^+$ ions are very similar in magnitude. The benzo-15-crown-5 ligand has been shown to display selectivity for Na$^+$ rather than K$^+$, but K$^+$ can also form sandwich-type complexes with benzo-15-crown-5. The geometry of the di-η-cyclopentadienyl compounds may allow binding of a metal ion in this manner. It appears that these compounds do not distinguish between K$^+$ and Na$^+$. Benzo-15-crown-5 does not bind Li$^+$ well, and this is reflected in the smaller changes in the observed electrochemistry with 0.1 M LiClO$_4$ supporting electrolyte.

The reversibility of effects of Na$^+$ addition to a solution of compound **11** in 0.1 M (C$_2$H$_5$)$_4$NPF$_6$ can be demonstrated by addition of an excess of benzo-15-crown-5 which causes the position of the redox peaks to return to those observed in pure 0.1 M (C$_2$H$_5$)$_4$NPF$_6$.

Experimental

All preparations and reactions were carried out under nitrogen, by standard Schlenk-tube and vacuum line techniques when required.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of nitrogen. Solvents were pre-dried over molecular sieves and then distilled under nitrogen from potassium (tetrahydrofuran (thf)), sodium-potassium alloy (light petroleum (b.p. 40–60°C), diethyl ether), phosphorous pentoxide (dichloromethane), calcium hydride followed by phosphorous pentoxide (acetonitrile) or magnesium ethoxide (ethanol) under nitrogen. HPLC grade N,N-dimethylformamide (Aldrich) was dried over molecular sieves. Deuterated solvents were stored over activated molecular sieves and transferred by vacuum distillation.
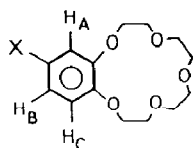
Fig. 3. Labelling Scheme for benzo-15-crown-5 compounds.

Elemental analyses were performed by the Analysis Department in this laboratory. Chromatography was carried out on columns of deactivated neutral alumina (6% H_2O) made up in light petroleum (b.p. 40–60°C).

Infrared spectra were recorded on a Perkin–Elmer 1510 Infrared Fourier Transform spectrometer. Mass spectra were recorded on a VG Micromass 2AB 1F or a VG 20-250 mass spectrometer. ^1H NMR spectra were measured using a Bruker WH300 spectrometer (300 MHz). ^{13}C NMR spectra were measured on a Bruker AM250 spectrometer (62.89 MHz). Chemical shifts (δ) are reported in ppm and coupling constants in Hz. Abbreviations used in multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Spectra were referenced internally using the solvent resonance relative to $SiMe_4$ (δ 0 ppm). Assignments of aromatic protons in 4'-substituted benzo-15-crown-5 derivatives are according to the labelling scheme (Fig. 3).

Cyclic voltammetry experiments were performed using an Oxford Instruments Potentiostat and recorded on a Gould 3000 X-Y chart recorder. The reference electrode in acetonitrile was a silver wire dipped in 0.01 M silver nitrate and isolated by a Vycor frit [22]. Ferrocene was added at the end of an experiment as an internal reference point; its potential against the Standard Calomel Electrode (SCE) was measured as +355 mV [23]. All potentials are referred to the SCE. This reference electrode (Radiometer 1401) was used for studies in N,N-dimethylformamide. A platinum disc (diameter 3 mm) sealed in glass was used as the working electrode. A platinum gauze served as the counter electrode. A three compartment cell was used; the working compartment has a working volume of 2.5 cm³, the counter electrode was isolated by a medium grade porous frit and the reference electrode by a Luggin capillary. The cell was suitable for use under anaerobic conditions. Sample loading was carried out using Schlenk line techniques or by use of gas-tight syringes. A micro-magnetic follower was used for ease of sample mixing and for renewal of the diffusion layer adjacent to the electrode. $(C_2H_5)_4NPF_6$ (Fluka) was recrystallized from ethanol four times and dried in vacuo. $(C_2H_5)_4NClO_4$ was recrystallized from ethanol and dried in vacuo. The salts $LiClO_4$, $NaPF_6$, KPF_6, and p-$CH_3C_6H_4SO_3M$ (M = Li, Na, K) were dried by heating in vacuo prior to dissolution in solvent.

1,11-dithio-3,6,9-trioxaundecane (1) was prepared as described [16].

[W(η-C_5H_5)$_2$SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S] (2)

The compound $HSCH_2(CH_2OCH_2)_3CH_2SH$ (1) (0.66 g, 4.8 mmol), and $NaOC_2H_5$ (0.07 g, 10 mmol) in ethanol (50 cm³) were added dropwise during 11 h to a slurry of [W(η-C_5H_5)$_2$Cl$_2$] (1.0 g, 2.6 mmol) in ethanol (150 cm³). After the addition was complete, the solution was stirred for 1 h, and the mixture was then filtered and the residue extracted into ethanol (10 cm³). The extract was filtered and combined with the filtrate. The solvent was removed under reduced pressure to leave an oily orange solid, which was washed with diethyl ether (50 cm³) to yield an

orange powder that was dissolved in dichloromethane and chromatographed. Elution with 5% ethanol in dichloromethane gave an orange band, which was collected and concentrated to yield an oil. Prolonged washing with ethanol (15 cm^3) yielded, after filtration, an orange powder. Recrystallization from methanol yielded orange crystals. Yield 0.13 g, 11%.

Analysis . Found C, 40.2; H, 4.85. $C_{18}H_{26}O_3S_2W$ calcd.: C, 40.2; H, 4.8%. Mass spectrum (FAB): M/e 539 ($M + H^+$). ^{1}H NMR in [^{2}H] chloroform: δ 5.18 (s, 10H, η-C_5H_5), 3.58 (m, 8H, OCH_2), 3.48 [t, J(H–H) 6.8, 4H, OCH_2CH_2S], 2.58 [t, J(H–H) 6.8, 4H, CH_2S]. $^{13}C\{^1H\}$ NMR in [^{2}H] chloroform: δ 92.03 (η-C_5H_5), 71.01, 70.60, 70.24 (OCH_2), 39.45 (SCH_2).

Preparation of [W(η-C_5H_5)$_2$(SCH_2CH_2OH)$_2$] (4)

2-Hydroxyethanethiol (4.0 g, 5.2 mmol) and potassium hydroxide (2.9 g, 5.2 mmol) in water (3 cm^3) were added to a slurry of [W(η-C_5H_5)$_2$Cl$_2$] (0.05 g, 1.3 mmol) in ethanol (10 cm^3). The mixture was refluxed for 1 min to give an orange solution, and this was cooled and the solvent was removed under reduced pressure.

The residue was extracted into a mixture of dichloromethane and ethanol (2/1) and chromatographed. Elution with dichloromethane separated 3. Further elution with ethanol (20%) in dichloromethane eluted an orange band which was collected and concentrated. Cooling yielded orange crystals which were filtered and washed with light petroleum (b.p. 40–60°C) and dried in vacuo. Yield 0.07 g, 11%.

Analysis. Found C, 36.1; H, 4.3; S, 13.1. $C_{14}H_{20}O_2S_2W$ calcd.: C, 35.9; H, 4.5; S, 13.7%. IR data (Nujol): 3500–3100 br, ν(OH). ^{1}H NMR in [^{2}H]$_2$-dichloromethane: δ 5.16 (s, 10H, η-C_5H_5), 3.40 [q, J(H–H) 7.0, 4H, CH_2OH], 2.55 [t, J(H–H) 7.0, 4H, CH_2S], 2.25 [t, J(H–H) 7.0, 2H, OH].

4'-Cyanobenzo 15-crown-5 (8)

4'-Bromobenzo-15-crown-5 [24] (13.0 g, 37 mmol) and copper cyanide (4.5 g, 50 mmol) in dimethylsulphoxide (100 cm^3) were refluxed for 8 h. The solution was allowed to cool and added to a solution of ferric chloride (40 g) in 2 M hydrochloric acid (400 cm^3) in a fume-cupboard. The resulting mixture was extracted with chloroform (5 × 100 cm^3). The combined extracts were washed with 2 M sodium hydroxide, and water, and then dried over sodium sulphate. Following filtration, the solvent was removed under reduced pressure to give solid, which was recrystallised from heptane to yield white crystals of 8. Yield, 5.94 g, 54%.

Analysis, Found: C, 61.0; H, 6.85; N, 4.8. $C_{15}H_{19}O_5N$ calcd.: C, 61.4, H, 6.5, N, 4.8%. IR data (CsI pellet): 2225 cm^{-1}, ν(C≡N). ^{1}H NMR in [^{2}H]-chloroform: δ 6.81 [d, J(H_c–H_b) 8.3, 1H, H_c], 7.02 [d, J(H_a–H_b) 1.8, 1H, H_a], 7.24 [dd, J(H_b–H_c), 8.4, J(H_b–H_a) 1.8, 1H, H_b], 4.09 (m, 4H, $ArOCH_2$), 3.87 (m, 4H, $ArOCH_2CH_2$), 3.71 (m, 8H, OCH_2).

4'-Carboxybenzo-15-crown-5 (7)

The compound 8 (4.0 g, 14 mmol) in ethanol (170 cm^3) was refluxed for 24 h with a solution of potassium hydroxide (100 g) in water (100 cm^3). The mixture was allowed to cool, water (150 cm^3) was added and then the solution extracted with chloroform to remove unreacted 8. The aqueous layer was acidified (pH 1–2) with 2 M hydrochloric acid and extracted with chloroform (3 × 200 cm^3). The chloroform layer was washed with water and dried over sodium sulphate. The solvent was

removed under reduced pressure, and the white residue recrystallised from ethanol to give 4'-carboxybenzo-15-crown-5. Yield, 2.9 g, 66%. The spectroscopic and analytical properties were in good agreement with those reported previously [21].

Di-η-cyclopentadienylbis[(benzo-15-crown-5)-4'-carboxylato]molybdenum (5)

4'-Carboxybenzo-15-crown-5 (0.15 g, 0.48 mmol) and potassium t-butoxide (0.053 g, 0.46 mmol) in ethanol (10 cm^3) were refluxed for 5 min and stirred for a further 2 h. [Mo(η-C$_5$H$_5$)$_2$Cl$_2$] (0.08 g 0.26 mmol) was added and the mixture refluxed to give a blue-grey solution. The solvent was removed under reduced pressure and the residue extracted with thf. Concentration of the extract gave a grey powder which was recrystallized from thf and light petroleum (b.p. 40–60 °C) to give a blue-grey microcrystalline product. Yield, 0.035 g, 16%. Repeated recrystallizations failed to give satisfactory analyses, and characterization was based on the spectroscopic data and by comparison to analogous compounds [19].

Analysis: Found: C, 56.6; H, 5.7. C$_{40}$H$_{48}$O$_{14}$Mo calcd.: C, 55.8; H, 6.2%. IR data (CsI Pellet): 1622 cm^{-1}, ν(C=O). ^{1}H NMR in [^{2}H]$_2$-dichloromethane: δ 7.58 [dd, J(H$_b$–H$_c$) 8.2, J(H$_b$–H$_a$) 1.9, 2H, H$_b$], 7.51 [d, J(H$_a$–H$_b$) 1.9, 2H, H$_a$], 6.79 [d, J(H$_c$–H$_b$) 8.2, 2H, H$_c$], 5.73 (s, 10H, η-C$_5$H$_5$), 4.11 (m, 8H, ArOCH$_2$), 3.84 (m, 8H, ArOCH$_2$CH$_2$), 3.68 (m, 16H, OCH$_2$).

Bis(η-cyclopentadienyl)bis[(benzo-15-crown-5)-4'-carboxylato]tungsten (6)

This was prepared in the way described for 5 but from [W(η-C$_5$H$_5$)$_2$Cl$_2$] (0.010 g, 0.26 mmol). Recrystallization of the product from thf and light petroleum (b.p. 40–60 °C) yielded dark red crystals. Yield 0.02 g, 8%. Repeated recrystallizations failed to give satisfactory analyses. Characterization was based on spectroscopic data and comparison with analogous compounds [19].

Analysis, Found: C, 50.8; H, 5.2. C$_{40}$M$_{48}$O$_{14}$W calcd.: C, 51.3; H, 5.9%. IR data (CsI pellet): 1630 cm^{-1}, ν(C=O). ^{1}H NMR in [^{2}H]$_2$-dichloromethane: δ 7.57 [dd, J(H$_b$–H$_c$) 8.3, J(H$_b$–H$_a$) 1.9, 2H, H$_b$], 7.52 [d, J(H$_a$–H$_b$) 1.9, 2H, H$_a$], 6.79 [d, J(H$_c$–H$_b$) 8.3, 2H, H$_c$], 5.67 (s, 10H, η-C$_5$H$_5$), 4.10 (m, 8H, ArOCHCH$_2$), 3.84 (m, 8H, ArOCH$_2$CH$_2$), 3.68 (m, 16H, OCH$_2$). ^{13}C NMR in [^{2}H]$_2$-dichloromethane: δ 174.4 (CO$_2$), 152.0, 148.6, 127.8, 123.7, 115.0 (Ar), 97.0 (η-C$_5$H$_5$), 71.3-60.0 (OCH$_2$).

(Benzo-15-crown-5)-4'-thiol (10)

4'-Aminobenzo-15-crown-5 [24] (2.23 g, 7.9 mmol) in 3 M hydrochloric acid (12 cm^3) was cooled to 0 °C and a cold solution of sodium nitrite (0.55 g, 8.0 mmol) in water (5 cm^3) was added dropwise with stirring at such a rate that the temperature did not rise above 5 °C. The resulting diazonium salt was treated with KSC(S)OC$_2$H$_5$ (1.27 g, 7.9 mmol) in water (10 cm^3) at 40–45°C in a dropwise manner with vigorous stirring. After the addition was complete, the solution was stirred for an additional 30 min to ensure complete decomposition of the diazonium salt. The red-brown oily material was extracted into chloroform (3 × 15 cm^3) to give a solution which was washed with aqueous sodium carbonate and water, and then dried over sodium sulphate. The chloroform extract was added dropwise to a suspension of lithium aluminium hydride (0.30 g) in anhydrous ether (30 cm^3) at such a rate that the diethyl ether refluxed gently without external cooling. Stirring was continued at room temperature for 1.5 h. After the addition was complete, water (2.5 cm^3) was added dropwise (very carefully), followed by 15% hydrochloric

acid (13 cm^3) to dissolve the precipitated alumina. The organic layer was separated and the aqueous phase extracted with chloroform. The combined extracts were washed thoroughly with water and dried over anhydrous calcium chloride. The chloroform was removed, affording a brown oily product. Extraction into diethyl ether gave a yellow solution and a brown residue (20 mg), which was separated by filtration. Removal of the diethyl ether gave a yellow oil which was used without further purification. Yield 0.54 g, 23%.

Di-η-cyclopentadienylbis[benzo-15-crown-5]-4'-thiolato]molybdenum (11)

The sodium salt of **10** was generated by addition of an excess of sodium metal the yellow oil (0.54 g, 1.8 mmol) in diethyl ether (10 cm^3). The mixture was refluxed for 24 h. to give a fine white precipitate, which was readily separated from the lumps of remaining sodium. The solvent was removed to give a white powder (0.49 g).

A suspension of [Mo(η-C$_5$H$_5$)$_2$Cl$_2$] (0.125 g, 0.42 mmol) and the sodium salt of 4'-thiobenzo-15-crown-5 (0.28 g, 0.87 mmol) was stirred in thf (50 cm^3) at 80 °C for 100 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane to give a red-brown extract, which was chromatographed. Elution with 2% ethanol in dichloromethane yielded first a green band, which was discarded, and then an orange band, which was collected. The solvent was removed from the eluate and the residue was recrystallized from thf to give red crystals. Yield 0.05 g, 14%.

Analysis, Found: C, 55.05; H, 5.8. C$_{38}$H$_{48}$S$_2$O$_{10}$Mo calcd.:C, 55.3; H, 6.0%. Mass Spectrum (FAB). M/e 825 (M + H)$^+$. ^{1}H NMR in [^{2}H]$_2$-dichloromethane: δ 6.96 [d, J(H$_a$–H$_b$) 2.0, 2H, H$_a$], 6.76 [dd, J(H$_b$–H$_c$) 8.3, J(H$_b$–H$_a$) 2.0 2H, H$_b$], 6.69 [d, J(H$_c$–H$_b$) 8.3, 2H, H$_c$], 5.16 (s, 10H, η-C$_5$H$_5$), 4.05 (m, 8H, ArOCH$_2$), 3.82 (m, 8H, ArOCH$_2$CH$_2$), 3.68 (m, 16H, OCH$_2$).

Di-η-cyclopentadienylbis[(benzo-15-crown-5)-4'-thiolato]tungsten (12)

The procedure was identical to that described for **11**. Treatment of [W(η-C$_5$H$_5$)$_2$Cl$_2$] (0.29 g, 0.75 mmol) with the sodium salt of 4'-thiobenzo-15-crown-5 (0.49 g, 1.50 mmol) gave **12** as red-brown crystals. Yield, 0.095 g (14%).

Analysis, Found: C, 55.05; H, 6.0. C$_{38}$H$_{48}$MoS$_2$O$_{10}$ calcd.: C, 55.3; H, 5.8%. Mass spectrum, (FAB). M/e 825 (M + H$^+$). ^{1}H NMR in [^{2}H]$_2$-dichloromethane: δ 6.95 [d, J(H$_a$–H$_b$) 2.0, 2H, H$_a$], 6.89 [dd, J(H$_b$–H$_c$) 8.3, J(H$_b$–H$_a$) 2.0, 2H, H$_b$], 6.75 [d, J(H$_c$–H$_b$) 8.3, 2H, H$_c$], 5.15 (s, 10H, η-C$_5$H$_5$), 4.10 (m, 8H, ArOCH$_2$), 3.82 (m, 8H, ArOCH$_2$CH$_2$), 3.68 (m, 16H, OCH$_2$).

Acknowledgements

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