Synthesis and Electrochemistry of Crown Ether Dithiolene Complexes

Malcolm L. H. Green,* William B. Heuer, and Graham C. Saunders
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The syntheses of copper and bis(η-cyclopentadienyl)molybdenum complexes of a dithiolene ligand incorporating a trioxadithia-15-crown-5-unit [1,4,7-trioxa-10,13-dithiacyclopentadec-11-ene-11,12-dithiolate(2−)] are described. The electrochemistry of these complexes was investigated by cyclic voltammetry in acetonitrile. Upon addition of an excess of alkali-metal cations large shifts of the redox potentials of the compounds were observed.

The coupling of cation binding to shifts of the redox potential of crown ether containing redox-active compounds has been of considerable interest recently.[1–12] Such systems could find uses in the determination of cationic species in solution. Transmission of inductive and resonance effects through ligands containing amido,[7] amino,[8] arylthiolato,[9] carboxylato,[9] and porphyrin[10] groups has been reported. Recently we reported the small effect alkali-metal cations had upon the redox potential of crown ether dithiocarbamate complexes.[13] Transition metal dithiolene complexes are known to exhibit extensive electrochemistry, which has been documented.[14] Thus crown ether containing dithiolene complexes were attractive for study.

Results and Discussion

5,8,11-Trioxa-2,14,16,18-tetrathiabicyclo[13.3.0]octadec-1(15)-en-17-thione, (1), was prepared in *ca.* 12% yield by the reaction between the dithiolene dianion 4,5-dimercapto-1,3-dithiole-2-thionate(2−) [dmit^{2-}] and 3,6,9-trioxaundecane-1,11-bis(toluene-*p*-sulphonate) under high dilution conditions (Scheme). The identity of (1) was confirmed by elemental analysis and mass spectrometry (Table 1), i.r. spectroscopy, and ^{1}H and ^{13}C n.m.r. spectroscopy (Table 2). The spectral data were in close agreement with those reported.[15] The ^{23}Na n.m.r. spectrum of sodium tetraphenylborate in 1 : 1 dichloromethane–acetonitrile in the presence of one equivalent of (1) showed a peak at −6.05 p.p.m. with a width at half-height, $\Delta\nu_{\frac{1}{2}}$, of 46 Hz compared to a value of 15 Hz for sodium tetraphenylborate alone. This is consistent with a degree of equilibrium binding of sodium cations by (1), but that the binding ability of (1) was less than that of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane),[15] as expected, due to the presence of the two 'soft' sulphur atoms in the crown ether ring.[16]

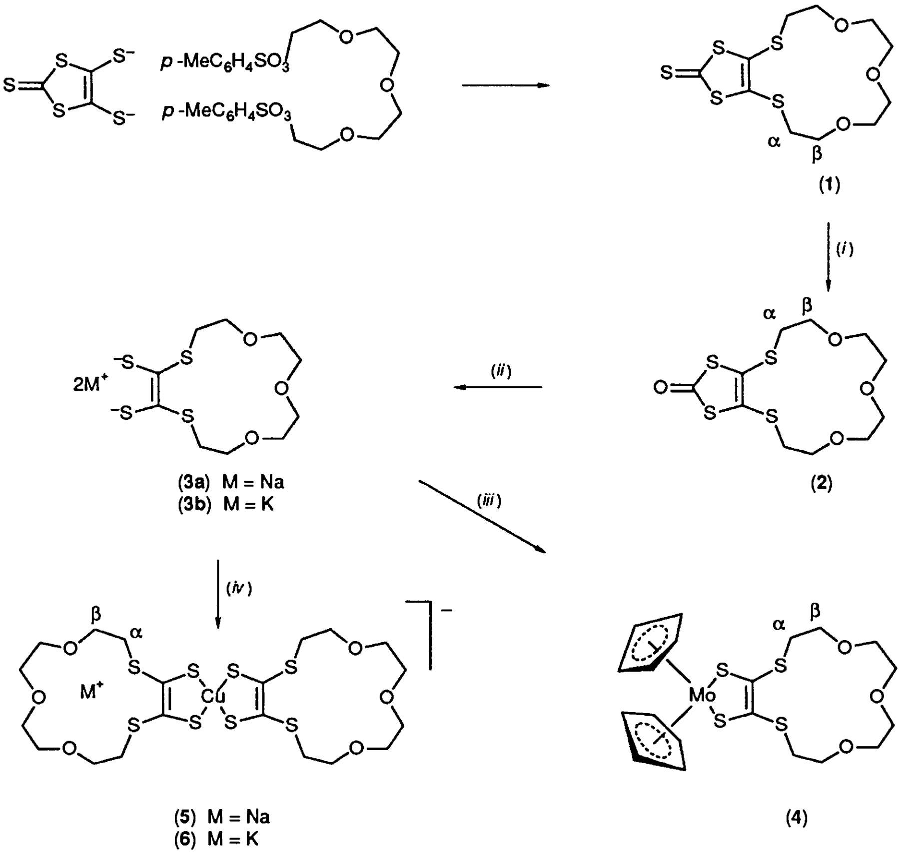
Refluxing a slurry of mercury(II) acetate and (1) in chloroform–acetic acid afforded 5,8,11-trioxa-2,4,16,18-tetrathiabicyclo[13.3.0]octadec-1(15)-en-17-one, (2), in *ca.* 80% yield (Scheme). The identity of (2) was confirmed by ^{1}H n.m.r. (Table 2) and i.r. spectroscopy. The i.r. spectrum showed a strong band at 1 674 cm^{-1} assigned to the C=O stretch. Satisfactory elemental analysis could not be obtained due to its sensitivity to light and air. Addition of two equivalents of sodium methoxide to a slurry of (2) in methanol gave a yellow solution of what was inferred to be disodium 1,4,7-trioxa-10,13-dithiacyclopentadec-11-ene-11,12-dithiolate (**3a**). The orange dipotassium analogue (**3b**) was prepared similarly from potassium methoxide and (2).

Addition of (**3a**) to dichlorobis(η-cyclopentadienyl)molybdenum produced purple crystals of the bis(η-cyclopentadienyl)molybdenum dithiolate (**4**) (Scheme). The identity of (**4**) was confirmed by elemental analysis, mass spectrometry, and i.r. and ^{1}H n.m.r. spectroscopy (Tables 1 and 2). Compound (**4**) was stable to the atmosphere in the solid state, but was oxidized rapidly in solutions exposed to air.

Addition of (**3a**) to copper(II) chloride in methanol gave a deep red solution. Aerial oxidation of the solution in the presence of an excess of tetra-n-butylammonium bromide over several hours led to the deposition of small, dark red crystals, which were soluble in dimethyl sulphoxide and slightly soluble in acetone and acetonitrile. Proton n.m.r. spectroscopy indicated the diamagnetic nature of the product and the absence of tetra-n-butylammonium cations. Further, the spectroscopic and analytical data were consistent with the sodium salt of the bis(dithiolene) monoanion (**5**). (Tables 1 and 2). The presence of sodium in (**5**) was confirmed by the ^{23}Na n.m.r. spectrum recorded in [^{2}H]$_6$dimethyl-sulphoxide, which showed a peak at −0.26 p.p.m. with a value of $\Delta\nu_{\frac{1}{2}}$ of 69 Hz. The potassium analogue, (**6**), was prepared from (**3b**) and copper(II) chloride. The identity of (**6**) was confirmed by elemental analysis, and i.r. and ^{1}H n.m.r. spectroscopy (Tables 1 and 2), and the presence of potassium was confirmed by a flame test, which showed a lilac colour. Recrystallization of (**5**) and (**6**) from acetonitrile failed to give crystals large enough for *X*-ray crystal structure determinations.

The electrochemistry of compounds (**4**)—(**6**) was investigated at a platinum disc electrode in acetonitrile with 0.1 mol dm^{3} tetra-n-butylammonium hexafluorophosphate as electrolyte. Compound (**4**) underwent two reversible oxidations at +45 and +490 mV (relative to the saturated calomel electrode). Upon changing the electrolyte to lithium or sodium tetrafluoroborate, or potassium hexafluorophosphate anodic shifts of $E_{\frac{1}{2}}$ for both couples were observed (Table 3). The magnitude of $\Delta E_{\frac{1}{2}}$ for the first oxidation was larger than that for the second, consistent with an electron being harder to remove from a cationic species.

Compounds (**5**) and (**6**) showed essentially the same behaviour to each other, undergoing irreversible oxidations at *ca.* +240 mV and reversible reductions at −700 mV (Figure 1). A small reduction peak was also present at *ca.* −150 mV. This wave disappeared on scanning from −1 to 0 V, indicating that it was associated with decomposition of the compounds following oxidation. The results of changing the electrolyte to lithium or sodium tetrafluoroborate, or adding an excess of potassium hexafluorophosphate are shown in Table 4. An anodic shift of $E_{\frac{1}{2}}$ of 175 mV was obtained with sodium tetrafluoroborate as electrolyte, and smaller shifts were caused by lithium or potassium cations. The magnitude of the shifts of $E_{\frac{1}{2}}$ and the order of $Na^+ > Li^+ > K^+$ indicate that simple ion-pairing alone cannot be invoked to explain the shifts of $E_{\frac{1}{2}}$, and thus cation binding must have a significant effect upon the value of $E_{\frac{1}{2}}$. Anodic shifts of $E_p{}^A$ for the irreversible oxidation also



Scheme 1. (*i*) $Hg(O_2CMe)_2$, $CHCl_3$-$MeCO_2H$ at 80 °C, yield 80%; (*ii*) 2 M(OMe) (M = Na or K), MeOH; (*iii*) $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$, MeOH at 60 °C for 20 min, yield 71%; (*iv*) $CuCl_2{\cdot}2H_2O$, MeOH; air, M = Na^+ (yield 40%) or K^+ (yield 38%)

Table 1. Analytical and mass spectral data

	Analysis[a] (%)			
Compound	C	H	S	m/z[b] (%)
(1)	36.7 (37.05)	4.3 (4.5)	43.4 (45.0)	356 (93), 357 (100), 358 (37)
(2)	37.9 (38.8)	4.5 (4.7)	35.8 (37.7)	
(4)	44.4 (44.6)	4.9 (4.9)	22.8 (23.8)	537 (64), 538 (78), 539 (69), 540 (100)
(5)	33.8 (33.8)	4.8 (4.5)		
(6)	33.0 (33.0)	4.45 (4.4)		

[a] Calculated values given in parentheses. [b] Fast-atom bombardment.

Table 2. N.m.r. data

Compound	N.m.r. data[a]
(1)	^{13}C: 211.2 (s, $S_2C{=}S$), 136.5 [t, $^4J(CH)$ 6, $S_2C{=}CS_2$], 71.2 [t, $^1J(CH)$ 141, OCH_2], 70.7 [t, $^1J(CH)$ 141, OCH_2], 69.7 [t, $^1J(CH)$ 143, OCH_2], 36.4 [t, $^1J(CH)$ 141, SCH_2][b]
(2)	^1H: 3.80 [t, $^3J(H^{\alpha}H^{\beta})$ 6.3, 4 H, H^{α} or H^{β}], 3.68 (m, 8 H, OCH_2), 3.04 (t, 4 H, H^{α} or H^{β})[b]
(4)	^1H: 5.29 (s, 10 H, η-C_5H_5), 3.70 (m and t, 8 H, OCH_2 and H^{α} or H^{β}), 3.63 (m, 4 H, OCH_2), 3.10 [t, $^3J(H^{\alpha}H^{\beta})$ 7.3, 4 H, H^{α} or H^{β}][b]
(5)	^1H: 3.65 [t, $^3J(H^{\alpha}H^{\beta})$ 7.0, 8 H, H^{α} or H^{β}], 3.55 (m, 16 H, OCH_2), 2.96 (t, 8 H, H^{α} or H^{β})[c]
(6)	^1H: 3.65 [t, $^3J(H^{\alpha}H^{\beta})$ 7.05, 8 H, H^{α} or H^{β}], 3.51 (m, 16 H, OCH_2), 2.97 (t, 8 H, H^{α} or H^{β})[c]

[a] Proton n.m.r. data recorded at 300 MHz, ^{13}C at 75.47 MHz. Values given as chemical shift (δ) [multiplicity, coupling constant (*J* in Hz), relative intensity, and assignment]; s = singlet, t = triplet and m = multiplet. [b] Recorded in $[^2H]$chloroform. [c] Recorded in $[^2H]_6$dimethyl sulphoxide.

resulted from the presence of alkali-metal cations. The result of titrating sodium tetrafluoroborate against compound (**5**) is shown in Figure 2. The value of $E_{\frac{1}{2}}$ increased by *ca* 3 mV per equivalent of sodium cations added up to 35 equivalents, and from 40 equivalents upward the value of $E_{\frac{1}{2}}$ increased by *ca.* 0.25 mV per equivalent of sodium cations added. The large amount of sodium cations necessary to achieve the maximum shift of $E_{\frac{1}{2}}$ for compound (**5**) may be ascribed to the low value of the binding constant *K*, as expected due to the presence of two sulphur atoms in each crown ether ring.[17] The relatively large shifts of $E_{\frac{1}{2}}$ compared to those for amido,[7] amino,[8] carboxylato,[9] and dithiocarbamato[13] complexes may be explained by the extensive π delocalization in dithiolene complexes, which causes bound cations to have a stronger interaction with the redox-active centre than if the electron density was localised on the central metal atom.

However, we conclude that these ionophores are not sufficiently selective towards cation binding to have useful applications.

Experimental

Proton n.m.r. spectra were recorded at 300 MHz, ^{13}C n.m.r. spectra at 75.47 MHz, and ^{23}Na n.m.r. spectra at 79.35 MHz on a Brüker AM300 spectrometer. Proton n.m.r. spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane (δ = 0), ^{13}C n.m.r. spectra were referenced internally using the solvent ^{13}C resonance relative to tetramethylsilane (δ = 0 p.p.m.), and ^{23}Na n.m.r. spectra were referenced externally to 3 mol dm^{-3} sodium chloride in D_2O (δ = 0 p.p.m.). 4,5-Bis(thiobenzoyl)1,3-dithiole-2-thione,[18] dichlorobis(η-cyclopentadienyl)molybdenum,[19] and 3,6,9-trioxaundecane-1,11-bis(toluene-*p*-sulphonate)[20] were prepared by the literature methods. Acetonitrile suitable for electrochemical studies was distilled under nitrogen from over calcium hydride and then from over phosphorus pentoxide.

Preparation of (**1**).—In a typical preparation a solution (26 cm^3) of 1.8 mol dm^{-3} sodium methoxide (0.048 mol) in methanol was added to 4,5-bis(thiobenzoyl)-1,3-dithiole-2-thione (9.90 g, 0.024 mol) slurried in methanol (450 cm^3) under nitrogen and stirred for *ca.* 1 h until no crystals of 4,5-bis(thiobenzoyl)-1,3-dithiole-2-thione remained. The resulting deep red solution was added to methanol (800 cm^3) simultaneously, and at the same rate, as 3,6,9-trioxaundecane-1,11-bis(toluene-*p*-sulphonate) (11.94 g, 0.024 mol) in methanol (450 cm^3) with stirring over 12 h. The resulting red solution was stirred for a further 12 h. The solvent was removed by rotary evaporation and the product was extracted into dichloromethane (3 × 500 cm^3). The dichloromethane was removed by rotary evaporation and the resulting red oil was chromatographed on alumina. Using light petroleum (b.p. 40—60 °C)–dichloromethane (10:1) as eluant methyl benzoate and unreacted ditosylate were eluted. The yellow product was then eluted with light petroleum (b.p. 40—60 °C)–dichloromethane (1:1). Removal of the solvent by rotary evaporation gave a yellow solid and a red oil. Recrystallization of the yellow solid from light petroleum (b.p. 40—60 °C) gave yellow crystals of the title compound. Typical yield *ca.* 1.0 g (12%). I.r.: ν(C=S) at 1 069 cm^{-1}.

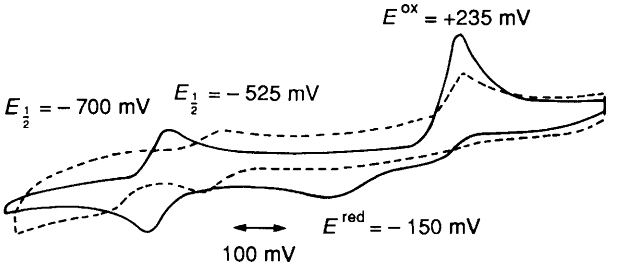


Figure 1. Cyclic voltammogram of compound (**5**) recorded in acetonitrile at a scan rate of 50 mV s^{-1} with $NBu^n{}_4PF_6$ (——) and $NaBF_4$ (– – – –) as electrolyte

Table 3. Electrochemical data for compound (**4**)

Electrolyte	$E_{\frac{1}{2}}^{ox1\,a}$/mV	$\Delta E_p^{1\,b}$/mV	$E_{\frac{1}{2}}^{ox2\,a}$/mV	$\Delta E_p^{2\,b}$/mV
$NBu^n{}_4BF_4$	+45	60	+490	60
$LiBF_4$	+80	60	+500	65
$NaBF_4$	+75	60	+510	65
KPF_6	+105	55	+510	60

[a] Relative to the saturated calomel electrode. [b] Separation between the anodic and cathodic peak potentials, $\Delta E_p = E_p{}^A - E_p{}^C$.

Preparation of (**2**).—In a typical preparation (**1**) (1.10 g, 3.08 mmol) in chloroform (7 cm^3) was added to a slurry of mercury(II) acetate (*ca.* 2.2 g, 7 mmol) in glacial acetic acid (20 cm^3). The resulting white slurry was refluxed for 1 h. The volatiles were removed by rotary evaporation and the product extracted into refluxing chloroform (2 × 25 cm^3). The chloroform extracts were washed with water (2 × 50 cm^3), aqueous sodium carbonate (50 cm^3) and water (50 cm^3) again, and dried over anhydrous magnesium sulphate. Following filtration the solvent was removed by rotary evaporation to give a white solid. This was found to be suitable for further reaction, but could be recrystallized from ethanol–water. Yield: 0.84 g (80%). The product decomposed slowly and was used immediately or stored under nitrogen in the dark. Repeated recrystallizations failed to give satisfactory elemental analyses. I.r.: ν(C=O) at 1 674 cm^{-1}.

Preparation of (**4**).—Sodium methoxide (0.15 g, 2.8 mmol) was added to (**2**) (0.33 g, 0.97 mmol) slurried in methanol (50 cm^3) under nitrogen. The mixture was stirred until all the (**2**) had reacted and a pale yellow solution of (**3a**) had developed (*ca* 10 min). Dichlorobis(η-cyclopentadienyl)molybdenum (0.29 g, 0.97 mmol) was added under nitrogen and the mixture heated to

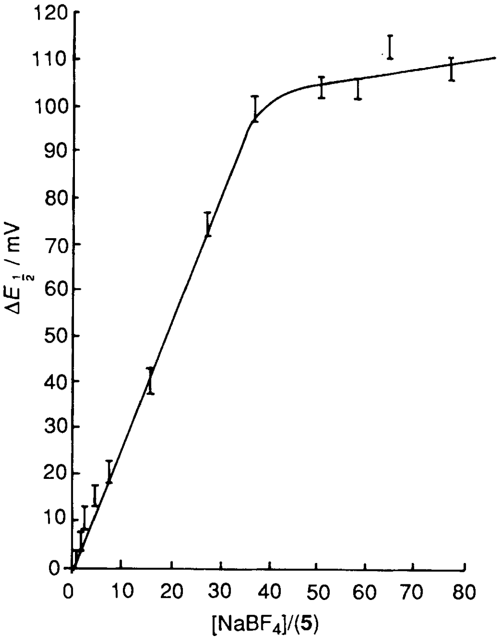


Figure 2. Plot of $\Delta E_{\frac{1}{2}}$ for the reversible reduction of (**5**) against equivalents of $NaBF_4$ added

Table 4. Electrochemical data for compounds (**5**) and (**6**)

Compound	Electrolyte	$E_{\frac{1}{2}}{}^{a}$/mV	$\Delta E_p{}^{b}$/mV	$\Delta E_{\frac{1}{2}}$/mV	E^{ox}/mV
(**5**)	$NBu^n{}_4PF_6$	−700	60	—	+235
(**6**)	$NBu^n{}_4PF_6$	−700	75	—	+245
(**5**)	$LiBF_4$	−560	115	140	+330
(**5**)	$NaBF_4$	−525	60	175	+245
(**6**) + KPF_6	$NBu^n{}_4PF_6$	−565	75	135	+265[c]

[a] Relative to the saturated calomel electrode. [b] Separation between the anodic and cathodic peak potentials, $\Delta E_p = E_p{}^A - E_p{}^C$. [c] Recorded with $NBu^n{}_4PF_6$ as electrolyte and an excess of KPF_6 added.

reflux for 20 min. The resulting red solution was filtered, the solvent removed under reduced pressure, and the product chromatographed. The purple product eluted with dichloromethane–methanol (5%). Recrystallization from dichloromethane–light petroleum (b.p. 40—60 °C) gave small purple crystals of (**4**), which were washed with light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 0.37 g (71%).

Preparation of (**5**).—Sodium methoxide (0.10 g, 1.85 mmol) was added to (**2**) (0.25 g, 0.73 mmol) slurried in methanol (60 cm^3) under nitrogen. The mixture was stirred until all the (**2**) had reacted and a pale yellow solution of (**3a**) had developed (*ca.* 15 min). Copper(II) chloride dihydrate (0.06 g, 0.35 mmol) in methanol (20 cm^3) was added under nitrogen. A red-brown solution and a dirty green precipitate formed. The solution was filtered and the residue extracted with acetone (*ca.* 100 cm^3). The combined extract and filtrate were exposed to the atmosphere. Small dark red crystals were deposited over 24 h. These were recrystallized from acetonitrile, washed with light petroleum (b.p. 40—60 °C), and dried *in vacuo*. Yield: *ca* 0.1 g (40%).

Preparation of (**6**).—Potassium hydride (0.16 g of a 35% w/w dispersion in oil, 1.4 mmol) was washed with light petroleum (b.p. 40—60 °C) (20 cm^3). Methanol (20 cm^3) was added slowly, followed by (**2**) (0.15 g, 0.44 mmol). The mixture was stirred until almost all the (**2**) had reacted and a pale orange solution of (**3b**) had developed (*ca* 30 min). Copper(II) chloride dihydrate (0.03 g, 0.18 mmol) in methanol (20 cm^3) was added. An orange solution and a dirty green precipitate were formed. The solution was filtered and the residue extracted with hot methanol (20 cm^3, several portions). The combined filtrate and extracts were concentrated to *ca.* 80 cm^3 and exposed to the atmosphere. Dark red microcrystals were deposited over 24 h. The crystals were washed with methanol (50 cm^3) and light petroleum (b.p. 40—60 °C; 2 × 20 cm^3), and dried *in vacuo*. Yield: *ca.* 50 mg (38%).

Electrochemistry.—Cyclic voltammetry studies were carried out using an Oxford Instruments potentiostat and recorded on a Rikadenki *X*–*Y* chart recorder. A platinum disc of diameter 3 mm sealed in glass was used as the working electrode. A platinum gauze served as the counter electrode. The reference electrode was a platinum 'pigtail' electrode. Ferrocene was added during or at the end of each experiment as an internal reference; its potential was taken as +355 mV against the saturated calomel electrode.[21] Experiments were carried out using *ca.* 20 cm^3 of *ca.* 0.1 mol dm^{-3} electrolyte solution containing *ca.* 5 mg of sample under nitrogen at ambient temperature (20 ± 5 °C). Potentials measured in this way were accurate to the nearest 5 mV.

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