Studies on the Synthesis and Electrochemistry of Crown Ether Dithiocarbamates and the Molecular Dynamics of Bis(aza-15-crown-5)thiuram Disulphide.* Crystal Structure of Cobalt Tris[(aza-15-crown-5)dithiocarbamate]†

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Reaction of aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) with sodium hydroxide and carbon disulphide yields sodium (aza-15-crown-5)dithiocarbamate (sodium 1,4,7,10-tetraoxa-13-azacyclopentadecane-13-carbodithioate), (**1**). 4′-Aminobenzo-15-crown-5 (15-aminobenzo-1,4,7,10,13-pentaoxacyclopentadecane) forms the corresponding dithiocarbamate (**2**). Oxidative dimerization of compound (**1**) yields bis(aza-15-crown-5)thiuram disulphide [13,13′-(1,4-dithioxo-2,3-dithiabutane-1,4-diyl)di(1,4,7,10-tetraoxa-13-azacyclopentadecane)], (**3**), in contrast (**2**) decomposes under the same conditions to 4′-isothiocyanatobenzo-15-crown-5. The energy barrier to rotation about the S_2C–N bond of compound (**3**), $\Delta G^{\ddagger} = 65.3 \pm 0.5$ kJ mol^{-1}, as measured by ^{13}C-{^1H} and ^1H dynamic n.m.r. spectroscopy. When 2 equivalents of $NaBPh_4$ are present $\Delta G^{\ddagger}$ falls to 54.5 ± 0.5 kJ mol^{-1}. Complexes of the crown ether dithiocarbamates with Ni, Cu, Cr, Fe, Co, and Mo have been prepared and their electrochemistry investigated. Small shifts in the values of $E_{\frac{1}{2}}$ were observed in the presence of alkali-metal cations. The molecular structure of cobalt tris[(aza-15-crown-5)dithiocarbamate] has been determined by *X*-ray crystallography.

Since the realization by Pedersen[1] of the remarkable binding properties of crown ethers with alkali-metal cations, there have been extensive studies on the chemistry of crown ethers.[2] Many crown ethers have been synthesized which incorporate a wide variety of functional groups. These compounds laid the groundwork for initial studies focusing on the analytical applications of crown ethers for the determination of alkali-metal cations in solution. Clearly if crown ethers are to serve as transducers in sensors for alkali-metal cations,[3] there must be readily measurable perturbations of one or more of the compounds' physicochemical properties upon ion binding. In recent years papers have appeared describing work in which ion binding was coupled to optical properties,[4] acidity,[5] redox potential,[6–11] and chemical shift in the n.m.r. spectrum.[12,13]

We have undertaken a programme to synthesize new crown ether complexes which will allow us to monitor ion binding electrochemically. Since transition-metal complexes of dithiocarbamate ligands are known to have extensive electrochemistry[14] these ligands were very attractive. We have focused on dithiocarbamates and related compounds, and hoped these compounds would show changes in their electrochemistry upon ion binding. Here we report results of our studies on the chemistry of crown ether dithiocarbamates and a crown ether thiuram disulphide. A preliminary account of part of this work has appeared.[15]

Results and Discussion

Reaction of an aqueous solution of aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) with 1 equivalent of sodium hydroxide and 1 equivalent of carbon disulphide gave analytically pure sodium (aza-15-crown-5)dithiocarbamate (sodium 1,4,7,10-tetraoxa-13-azacyclopentadecane-13-carbodithioate), (**1**), as a white powder, in about 60% yield. The i.r. spectrum exhibits the characteristic dithiocarbamate ν(C–N) stretch at 1 479 cm^{-1}, and the ^{13}C n.m.r. spectrum shows a singlet at δ 211.5 p.p.m. assigned to the NCS_2 carbon atom. Compound (**1**) is soluble in water and methanol, but, like other dithiocarbamates, decomposes in acidic solution. 4′-Aminobenzo-15-crown-5 (15-aminobenzo-1,4,7,10,13-pentaoxacyclopentadecane) was obtained as a viscous brown oil following the preparation described by Smid and co-workers.[16] This was similarly treated with sodium hydroxide and carbon disulphide to yield (45%) sodium (benzo-15-crown-5)dithiocarbamate (sodium benzo-1,4,7,10,13-pentaoxacyclopentadecane-15-dithiocarbamate), (**2**). Although the ^1H n.m.r. spectrum showed no peaks due to impurities this compound was not obtained analytically pure, but the unpurified material was found to be amenable for further reactions. The i.r. spectrum shows the ν(C–N) stretch at 1 511 cm^{-1}. Compound (**2**) is soluble in water and methanol, but like many dithiocarbamates of primary amines, is less stable than those of secondary amines and readily decomposes in acid and base. Characterizing data for all the new compounds are given in Table 1, and will not be discussed except where of special interest.

Oxidation of an aqueous solution of compound (**1**) with excess of potassium hexacyanoferrate(III) or ammonium peroxodisulphate produced bis(aza-15-crown-5)thiuram disulphide [13,13′-(1,4-dithioxo-2,3-dithiabutane-1,4-diyl)di(1,4,7,10-tetraoxa-13-azacyclopentadecane)], (**3**), as a white crystalline solid in 55% yield. The i.r. spectrum shows the characteristic ν(C–N) stretch at 1 494 cm^{-1}, and the ^{13}C n.m.r. spectrum shows a singlet at δ 193.0 p.p.m. assigned to the NCS_2 carbon atom. The ^1H n.m.r. spectrum exhibits a multiplet at δ 4.30 assigned to the eight hydrogen atoms α to the nitrogen atoms, and two triplets at δ 4.10 and 3.89, with coupling constants of 6.7 and 5.3 Hz respectively, assigned to two sets of four hydrogen

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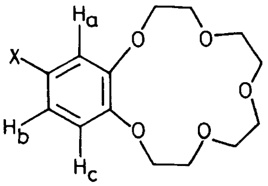
* 13,13′-(1,4-Dithioxo-2,3-dithiabutane-1,4-diyl)di(1,4,7,10-tetraoxa-13-azacyclopentadecane).

† Tris(1,4,7,10-tetraoxa-13-azacyclopentadecane-13-carbodithioato)-cobalt(III).

Supplementary data avilable: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical and spectroscopic data

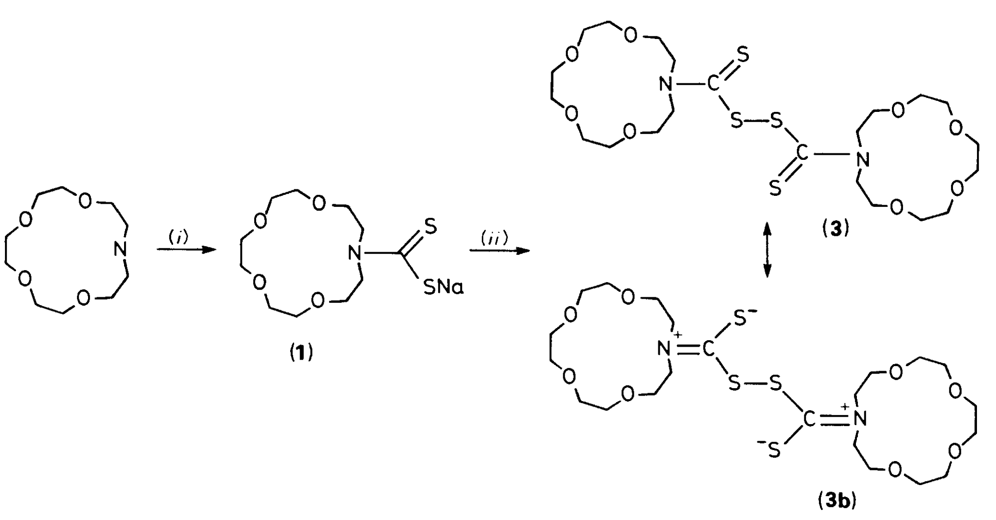


Compound	Analytical data[a] (%)			m/z (%)	$\nu_{max.}$(C–N) cm^{-1}	N.m.r. data[b]
	C	H	N			
(1)	41.4 (41.6)	6.5 (6.35)	4.35[c] (4.4)		1 479	^{1}H: 4.11 (4 H, t, *J* 6, 2-NCH$_2$), 3.76 (4 H, t, *J* 6, 2-NCH$_2$C*H*$_2$), 3.55 (12 H, m, 6-CH$_2$) ^{13}C: 211.5 (1 C, s, NCS$_2$), 69.9—68.3 (8 C, m, 8-CH$_2$), 56.1 [2 C, t, *J*(CH) 140, 2-NCH$_2$]
(2)	45.5 (47.2)	5.5 (5.3)	3.55 (3.7)		1 511	^{1}H: 6.93 [1 H, d, *J*(H$_a$H$_b$) 2.3, H$_a$], 6.86 [1 H, d, *J*(H$_b$H$_c$) 8.6, H$_c$], 6.72 (1 H, dd, H$_b$), 4.02 (4 H, m, 2-OCH$_2$), 3.75 (4 H, m, 2-OCH$_2$C*H*$_2$), 3.55 (8 H, m, 4-CH$_2$).[d]
(3)	44.8 (44.9)	6.9 (6.85)	4.7[e] (4.8)		1 494	^{1}H: 4.30 (8 H, m, 4-NCH$_2$), 4.10 (4 H, t, *J* 6.7, 2-NCH$_2$C*H*$_2$), 3.89 (4 H, t, *J* 5.3, 2-NCH$_2$C*H*$_2$), 3.66 (24 H, m, 12-CH$_2$).[f] ^{13}C-{^{1}H}: 193.0 (2 C, NCS$_2$), 70.0, 69.6, 69.4, 69.1 (12 C, OCH$_2$), 67.6, 66.5 (4 C, NCH$_2$*C*H$_2$), 58.3, 54.3 (4 C, NCH$_2$)[g]
(3)·NaBPh$_4$	59.0 (59.3)	6.4 (6.5)	2.95 (3.0)		1 477	^{1}H: 7.29 (8 H, m, BPh$_4$), 6.98 (8 H, t, *J* 7.4, BPh$_4$), 6.83 (4 H, t, *J* 7.2, BPh$_4$), 4.23 (8 H, t, *J* 5.9, 4-NCH$_2$), 3.93 (8 H, s br, 4-NCH$_2$C*H*$_2$), 3.61 (24 H, m, 12-CH$_2$)[h]
(6)	54.6 (55.4)	5.8 (5.9)	4.2 (4.3)	325 (100) 326 (20)	2 149[i]	^{1}H: 6.79 (2 H, ABq, H$_b$H$_c$), 6.73 [1 H, d, *J*(H$_a$H$_b$) 1.9, H$_a$], 4.12 (4 H, m, OCH$_2$), 3.90 (4 H, m, OCH$_2$C*H*$_2$), 3.75 (8 H, m, 4-CH$_2$)[f]
(7)	40.9 (40.8)	6.45 (6.2)	4.3 (4.3)	647 (100) 648 (30) 649 (62)	1 510	^{1}H: 3.86 (8 H, m, 4-NCH$_2$), 3.79 (8 H, m, 4-NCH$_2$C*H*$_2$), 3.64 (24 H, m, 12-CH$_2$) ^{13}C: 209.9 (2 C, s, NCS$_2$), 70.9—70.2 (12 C, m, 12-CH$_2$), 67.8 [4 C, t, *J*(CH) 145, 4-NCH$_2$C*H*$_2$], 51.6 [4 C, t, *J*(CH) 140, 4-NCH$_2$][f]
(8)	40.2 (40.5)	6.1 (6.2)	4.15 (4.3)	652 (100) 653 (30) 654 (68)	1 502, 1 490	
(9)	42.0 (42.4)	6.7 (6.5)	4.3 (4.5)	934 (100) 935 (55) 936 (43)	1 489	
(10)	42.0 (42.2)	6.3 (6.4)	4.4 (4.5)		1 490	
(11)·CH$_2$Cl$_2$	40.1 (39.8)	6.3 (6.2)	4.15 (4.1)		1 489	^{1}H: 5.30 (s, CH$_2$Cl$_2$), 3.95 (12 H, m, 6-NCH$_2$), 3.85 (12 H, m, 6-NCH$_2$C*H*$_2$), 3.66 (36 H, m, 18-CH$_2$)[f]
(12)	38.15 (37.9)	5.0 (4.5)	2.0 (2.1)	517 (55) 519 (36) 520 (67) 521 (77) 522 (53) 523 (100)	1 504	^{1}H: 7.56 (10 H, s, 2-C$_5$H$_5$), 3.95 (4 H, t, *J* 6.3, 4-NCH$_2$), 3.83 (4 H, t, *J* 6.3, 4-NCH$_2$C*H*$_2$), 3.62 (12 H, m, 6-CH$_2$)[j]
(13)	46.0 (46.5)	5.3 (5.2)	3.6 (3.6)		1 511	^{1}H: 7.06 [2H, d, *J*(H$_a$H$_b$) 2.1, 2-H$_a$], 6.92 (4 H, ABq, 2-H$_b$H$_c$), 4.01 (4 H, m, 2-OCH$_2$), 3.75 (4 H, m, 2-OCH$_2$), 3.60 (8 H, s, 4-OCH$_2$C*H*$_2$), 3.31 (16 H, m, 8-CH$_2$)[k]
(14)·CH$_2$Cl$_2$	43.05 (43.0)	4.7 (4.9)	3.45 (3.2)		1 511	

[a] Calculated values are given in parentheses. [b] Proton n.m.r. recorded at 300 MHz, ^{13}C at 62.89 MHz. Values given as chemical shift (δ) [relative intensity, multiplicity, coupling (*J* in Hz), and assignment]; s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [c] S 19.6 (20.2%). [d] In [^{2}H$_2$]water. [e] S 21.4 (21.8%). [f] In [^{2}H]chloroform. [g] In [^{2}H]chloroform–[^{2}H$_6$]acetone (1:1). [h] In [^{2}H]chloroform–[^{2}H$_3$]acetonitrile. [i] SCN band. [j] In [^{2}H$_6$]acetone. [k] In [^{2}H$_6$]dimethyl sulphoxide.

atoms β to the nitrogen atoms. The assignment of the peaks is made with the aid of integration and by comparison with the ^{1}H n.m.r. spectrum of tetraethylthiuram disulphide,[17] which exhibits a quartet assigned to the eight α-hydrogen atoms, and two triplets upfield of the quartet assigned to two sets of six β-hydrogen atoms. Both these thiuram disulphides exhibit inequivalent hydrogen atoms because there is restricted rotation about the S$_2$C–N bond due to conjugation as indicated by the canonical form **(3b)** depicted in Scheme 1. The presence of restricted rotation is confirmed by the ^{13}C-{^{1}H} n.m.r. spectrum, which shows a pair of peaks at δ 54.3 and 58.3 p.p.m. assigned to the four carbon atoms α to the nitrogen atoms, and another pair of peaks at δ 66.5 and 67.6 p.p.m. assigned to the β-carbon atoms. Variable-temperature ^{13}C-{^{1}H} n.m.r. spectra provided a value of the energy barrier to rotation about the S$_2$C–N bond, $\Delta G^\ddagger = 65.3 \pm 0.5$ kJ mol^{-1}. For uncoupled two-site exchange, the rate constant, k, at the coalescence temperature, T_c, is given by equation (1).[18] The value of $\Delta G^\ddagger$ is then

$$k = \pi\delta\nu/2 \qquad (1)$$



Scheme 1. (*i*) NaOH(aq), CS_2, 6 h; (*ii*) excess of $K_3[Fe(CN)_6]$(aq) or $[NH_4]_2[S_2O_8]$(aq)

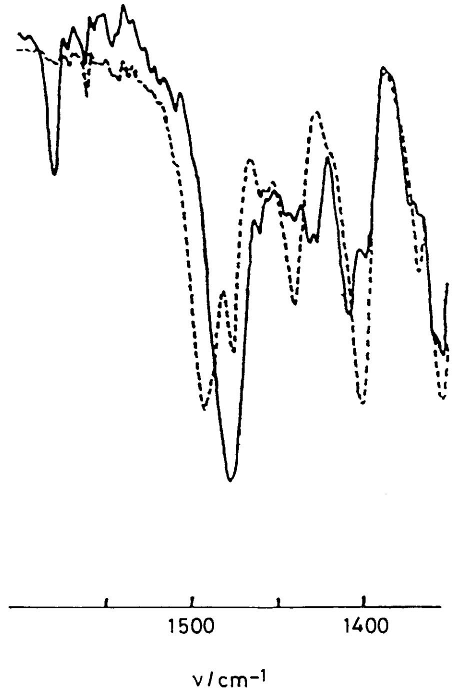


Figure 1. The S_2C–N stretching region of the i.r. transmission spectra of compound (3) (- - -) and of (3)·$NaBPh_4$ (——)

$$\Delta G^\ddagger = -RT_c \ln (hk/\kappa k_B T_c) \qquad (2)$$

obtained from the Eyring equation, (2),[19] where κ, the transmission coefficient, can be assumed to be close to or equal to unity for adiabatic reactions.[20]

Interestingly when 2 equivalents of $NaBPh_4$ were added the ^{13}C-{^1H} n.m.r. spectrum, recorded at room temperature, showed that the two peaks due to the four β-carbon atoms had collapsed into a broad singlet at δ 67.0 p.p.m., and those due to the four α-carbon atoms had collapsed into the baseline. This represents a dramatic reduction in $\Delta G^\ddagger$. When benzo-15-crown-5 was added to this solution the ^{13}C-{^1H} n.m.r. spectrum was identical to that recorded in the absence of $NaBPh_4$.

As a control experiment the dynamic ^1H and ^{13}C-{^1H} n.m.r. processes of tetraethylthiuram disulphide were examined. The spectra recorded at or near the coalescence temperatures showed no change upon addition of $NaBPh_4$. Thus the lowering of $\Delta G^\ddagger$ upon addition of $NaBPh_4$ to a solution of compound (3) is clearly due to the interaction between the sodium ions and the crown ether rings. It seems that the presence of a sodium ion in the ring reduces the electron density available for π bonding on the nitrogen atom which, in turn, reduces the bond order of the S_2C–N bond, and hence $\Delta G^\ddagger$. The i.r. spectrum of the 1:1 adduct of (3) with $NaBPh_4$, prepared by slow evaporation of a solution of (3) and 1 equivalent of $NaBPh_4$, shows a strong peak at 1 477 cm^{-1}, 17 cm^{-1} lower than for the ν(C–N) stretch for (3) alone (Figure 1), which confirms the reduction of bond order upon complexation.

Variable-temperature n.m.r. studies were undertaken to investigate the change of $\Delta G^\ddagger$ with the proportion of $NaBPh_4$. Both ^1H and ^{13}C-{^1H} n.m.r. spectra were recorded at a range of temperatures for a number of samples of compound (3) with different quantities of $NaBPh_4$ added in [^2H]chloroform–[$^2H_3$]acetonitrile (1:1) {Due to the high temperature required for coalescence of the NCH_2CH_2 carbon atoms, [$^2H_8$]toluene was used as solvent for the n.m.r. experiment for (3) without added $NaBPh_4$. However spectra recorded in [^2H]chloroform–[$^2H_3$]acetonitrile at lower temperatures were similar to those recorded in [$^2H_8$]toluene at the same temperatures, and a value of $\Delta G^\ddagger$ similar to that obtained from the spectra recorded in [$^2H_8$]toluene was calculated from coalescence temperatures of other inequivalent carbon atoms.} As expected intermolecular exchange of Na^+ was fast on the n.m.r. time-scale.[13] Thus the methylene carbon and hydrogen atoms for the crown ether moieties with Na^+ bound and those with no Na^+ bound gave rise to an averaged signal. Figures 2 and 3 show the NCH_2CH_2O part of the variable-temperature ^{13}C-{^1H} n.m.r. spectra of (3) recorded in the absence and presence of $NaBPh_4$. From the spectra values of $\Delta G^\ddagger$ were calculated, using formulae (1) and (2) for simple uncoupled two-site exchange. Figure 4 shows the change in $\Delta G^\ddagger$ upon addition of $NaBPh_4$.

Preliminary studies indicate that $LiBF_4$, when added to a solution of compound (3), causes a similar effect. We are currently investigating similar dynamic n.m.r. processes in the amides *N*-acetylaza-15-crown-5, (4) and *N*,*N*-dimethylcarbamoylbenzo-15-crown-5, (5). The barrier to rotation about the OC–N bond, $\Delta G^\ddagger$, in the latter compound is 61.0 ± 0.5 kJ mol^{-1}, but rises to 64.5 ± 0.5 kJ mol^{-1} in the presence of excess of $NaBPh_4$.

In an attempt to prepare bis(benzo-15-crown-5)thiuram disulphide, compound (2) was treated with $K_3[Fe(CN)_6]$. Following chromatography a white crystalline solid, (6), was isolated in low yield. The i.r. spectrum showed no C–N stretching band, but exhibited a very strong band at 2 149 cm^{-1},

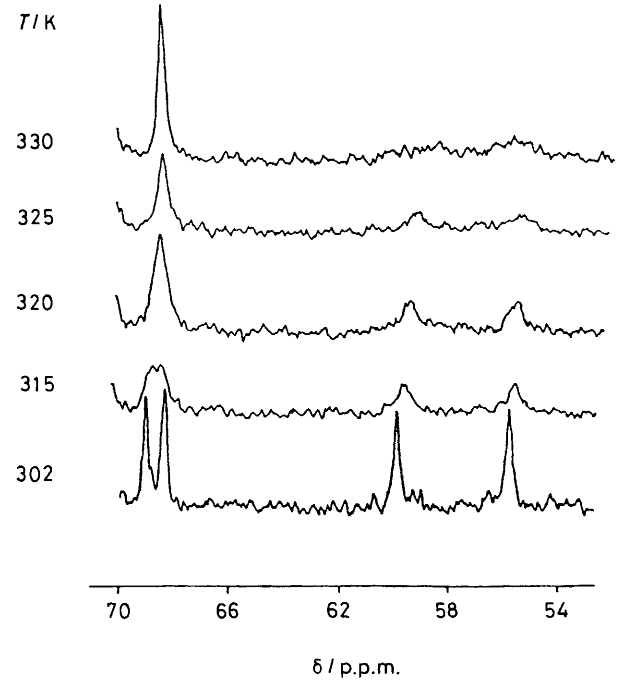


Figure 2. Variable-temperature $^{13}C-\{^1H\}$ n.m.r. spectra of compound (3) in $[^2H_8]$toluene

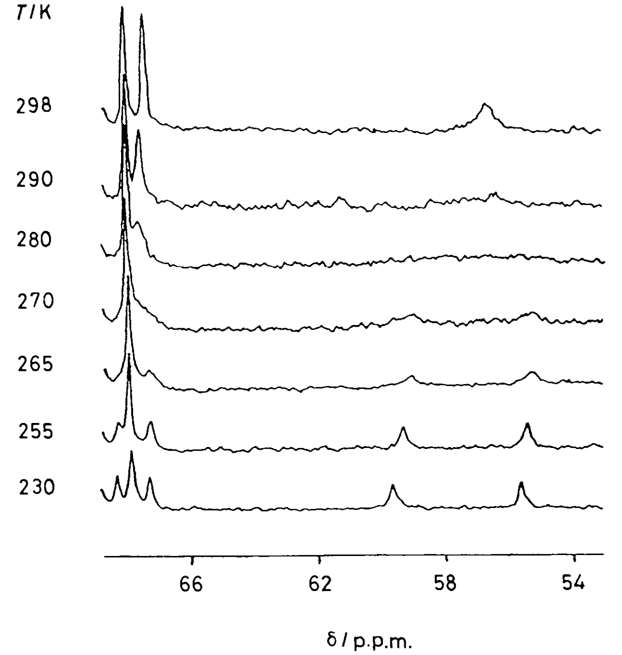


Figure 3. Variable-temperature $^{13}C-\{^1H\}$ n.m.r. spectra of compound (3) with 2 equivalents of $NaBPh_4$ in $[^2H]$chloroform–$[^2H_3]$acetonitrile (1:1)

characteristic of a thiocyanate or an isothiocyanate. Isothiocyanates are the products of decomposition of monoaryl dithiocarbamates,[21] and it is likely that the conditions of this reaction causes decomposition to 4′-isothiocyanatobenzo-15-crown-5 to occur.

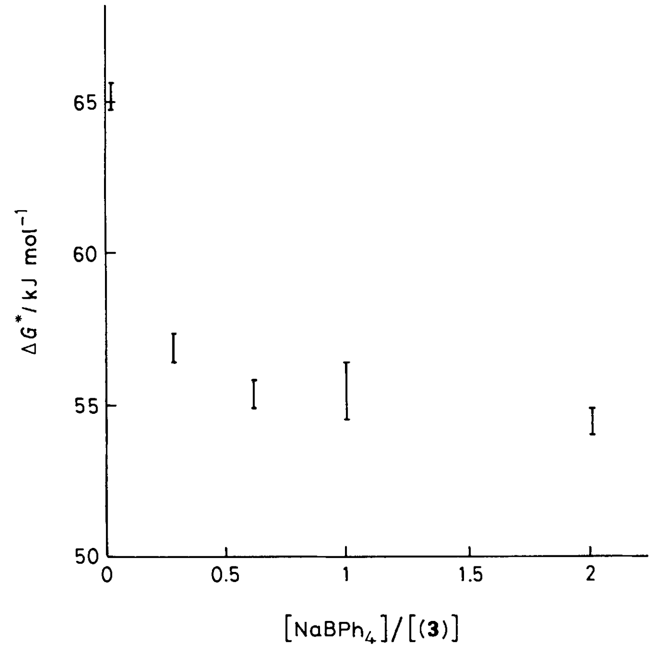
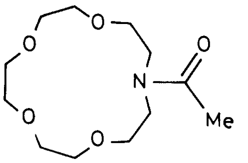
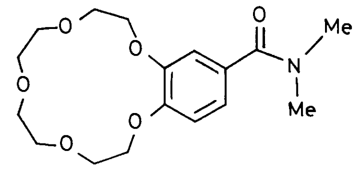


Figure 4. Plot of $\Delta G^{\ddagger}$ for S_2C–N bond rotation in compound (3) against equivalents of $NaBPh_4$ per crown ether ring

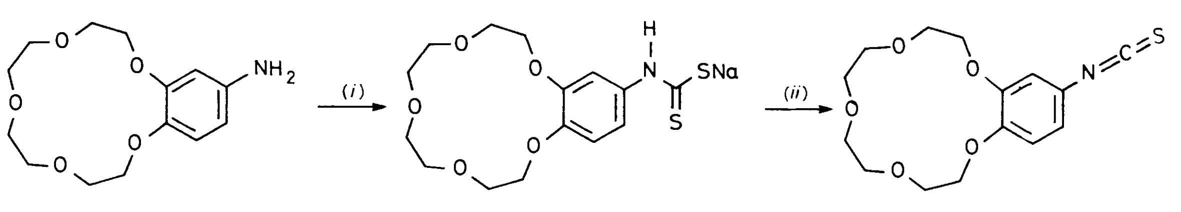


(4)



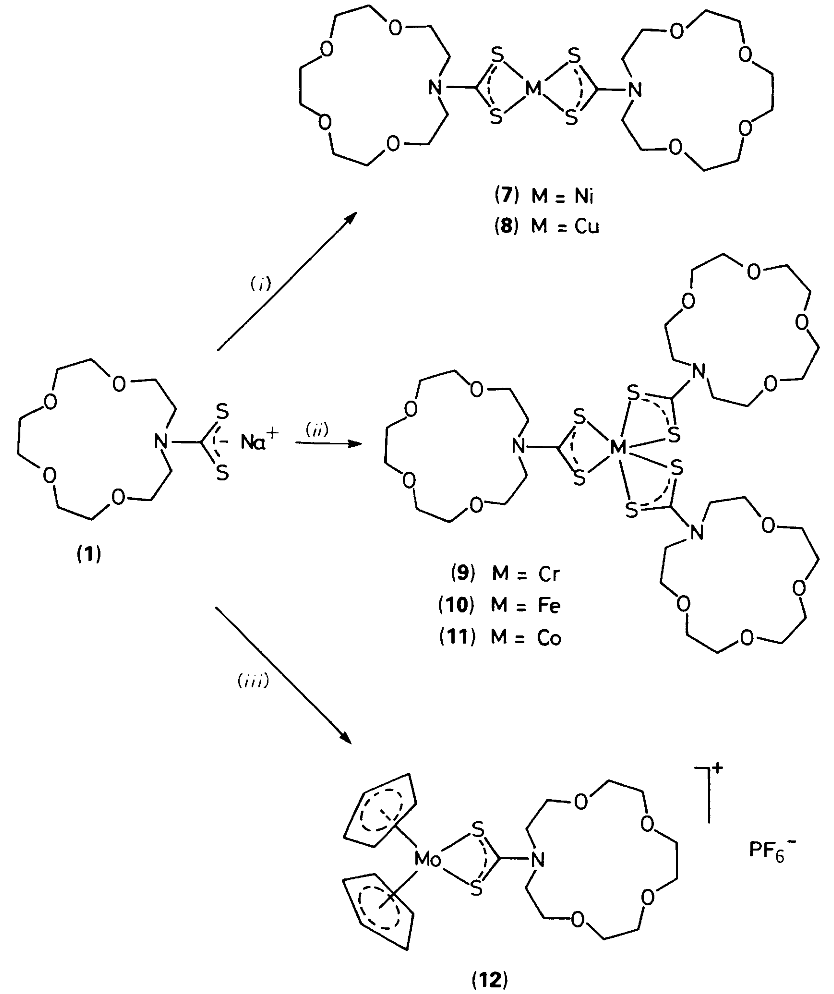
(5)

Addition of an aqueous solution of nickel chloride to an aqueous solution of 2 equivalents of compound (1) immediately produced a light green precipitate of nickel bis[(aza-15-crown-5)dithiocarbamate], (7), in 81% yield. Recrystallization from dichloromethane yielded green/red dichroic platelets. The paramagnetic copper analogue of (7), copper bis[(aza-15-crown-5)dithiocarbamate], (8), was obtained similarly as dark brown rhombohedral crystals. Compound (8) could be oxidized chemically by iodine to give highly solvated, diamagnetic, dark brown needles of what is presumed to be the tri-iodide. However, due to the high degree of solvation the salt could not be obtained pure. Chromium tris[(aza-15-crown-5)dithiocarbamate], (9), was obtained on treatment of 3 equivalents of (1) with chromium trichloride in tetrahydrofuran (thf). The product was obtained as an analytically pure, royal blue oil in 23% yield. Iron tris[(aza-15-crown-5)dithiocarbamate], (10), was obtained as a black microcrystalline powder in 60% yield upon addition of an aqueous solution of iron trichloride to an aqueous solution of 3 equivalents of (1). Attempted crystallization from dichloromethane gave only an impure dark brown oil. Addition of an aqueous solution of 2 equivalents of compound (1) to an aqueous solution of cobalt(II) sulphate, under an inert atmosphere of dinitrogen, gave a dark green precipitate. Crystallization from dichloromethane yielded dark green needles of solvated cobalt tris[(aza-15-crown-5)dithiocarbamate], (11), which looses solvent of crystallization on prolonged drying. Thus, as reported for other cobalt dithiocarbamates, the +II oxidation state is unstable with respect to oxidation to the +III state.[22] Compounds (7)—(11) are insoluble in water and acetone, slightly soluble in methanol and acetonitrile, and dissolve readily in chlorinated solvents. All are stable to the atmosphere and light, but decompose slowly in the presence of moisture. Attempts to prepare manganese tris[(aza-15-crown-5)dithiocarbamate] failed.



(2) (6)

Scheme 2. (*i*) NaOH(aq), CS_2, 6 h; (*ii*) excess of $K_3[Fe(CN)_6](aq)$



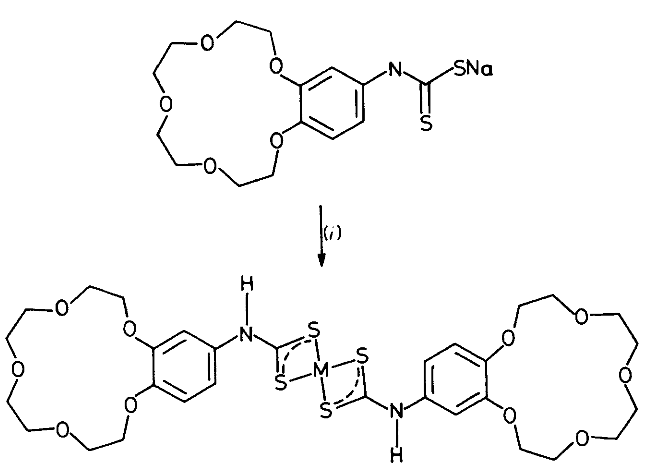
(7) M = Ni
(8) M = Cu
(1)
(9) M = Cr
(10) M = Fe
(11) M = Co
(12)

Scheme 3. (*i*) $NiCl_2(aq)$ or $CuSO_4(aq)$; (*ii*) $CrCl_3$, thf, 1.5 h, or $FeCl_3(aq)$, or $CoSO_4(aq)$; (*iii*) $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$, NH_4PF_6

Reaction of an aqueous solution of compound (**1**) with bis(η^5-cyclopentadienyl)molybdenum dichloride, under an inert atmosphere, gave a red solution. Additon of excess of ammonium hexafluorophosphate yielded a buff precipitate. Recrystallization from acetone gave small orange crystals of bis(η^5-cyclopentadienyl)molybdenum (aza-15-crown-5)dithiocarbamate hexafluorophosphate, (**12**), in 39% yield. This is stable to the atmosphere in the solid state, and soluble in acetone, acetonitrile, and chlorinated solvents.

The benzo-15-crown-5 analogues of (**7**) and (**8**) were prepared from (**2**) by a similar method to that for (**7**). Both were purified by column chromatography. Nickel bis[(benzo-15-crown-5)-dithiocarbamate], (**13**), was obtained as a green powder, and copper bis[(benzo-15-crown-5)dithiocarbamate], (**14**), as solvated red-brown needles. Both compounds are soluble in chlorinated solvents, and are air stable, but are generally less stable than the complexes of (**1**) to acid and base. Characterizing analytical and spectroscopic data for compounds (**7**)—(**14**) are given in Table 1.

The crystal structure of compound (**11**) has been determined. It crystallizes in the triclinic crystal system in space group $P\bar{1}$. The molecular structure is shown in Figure 5; fractional atomic co-ordinates are given in Table 2, and selected interatomic distances and angles in Table 3. The molecule displays trigonally distorted octahedral co-ordination about the cobalt atom, with planar S_2CN moieties, as shown in Figure 6. The bond lengths and angles of the $Co(S_2CNC_2)_3$ fragment agree closely with those of the morpholine analogue.[23] The mean $S_2C{-}N$ bond length is 1.327(8) Å, confirming the double-bond nature of this bond in the dithiocarbamate group. The carbon



(**13**) M = Ni
(**14**) M = Cu

Scheme 4. (*i*) $NiCl_2$(aq) or $CuSO_4$(aq)

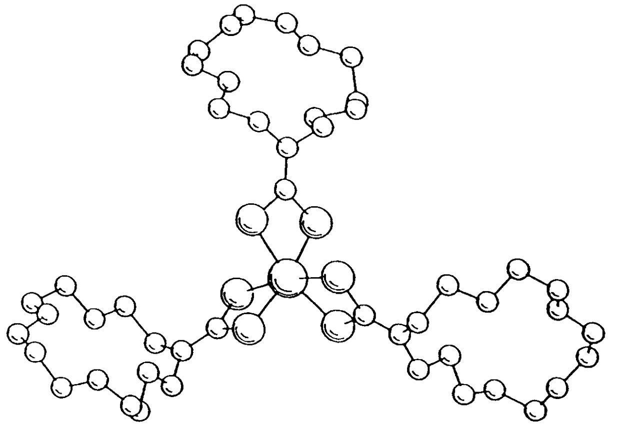


Figure 5. Molecular structure of compound (**11**)

atoms α to the nitrogen atom in each crown ether ring are essentially coplanar with the CoS_2CN moieties with a mean deviation from coplanarity of 0.15(10) Å.

The mean ring C–N–C angle is 119.5(3)°, *ca.* 5° greater than that of diaza-18-crown-6.[24] This deviation from the expected value is due to the effect of the dithiocarbamate groups and the sp^2 nature of the nitrogen atoms. The O–C bond lengths range from 1.323(7) to 1.433(9) Å with one anomalous value of 1.14(1) Å between O(12) and C(14). Discounting this anomalous distance, the mean O–C bond length is 1.40(3) Å, which is consistent with the values of 1.43(3), 1.41(1), and 1.42(1) Å for diaza-18-crown-6,[24] 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane),[25] and benzo-15-crown-5 [26] respectively. The C–C bond lengths range from 1.423(7) to 1.53(1) Å, with a mean value of 1.47(4) Å. These bond lengths are significantly shorter than the expected value of 1.54 Å for C–C bonds.[27] This is, however, consistent with values for other crown ethers.[24–6,28] Whether this shortening of C–C bonds in crown ethers is due to thermal motion, or real and due to geometric and electronic effects, is uncertain.[29–32] The C–O–C angles range from 105(8) to 133.0(8)°, with a mean value of 117(8)°. This is larger than the expected value of 112.6°,[33] and the mean values of 111.7(3), 113.5(4), and 114(1) for diaza-18-crown-6,[24] 18-crown-6,[25] and benzo-15-crown-5 [26] respectively. The O–C–C angles range from 104.5(5) to 123.2(7)°, with a mean value of 112(5)°. This is slightly larger than the mean values of 109(1), 110(3), and 110(3)° for diaza-18-crown-6,[24] 18-crown-6,[25] and benzo-15-crown-5 [26] respectively. The deviation from the values expected for crown ethers of the bond lengths and dihedral angles and the wide range of the latter is indicative of the increased strain put on the rings by the geometry imposed about the nitrogen atoms by the dithiocarbamate groups.

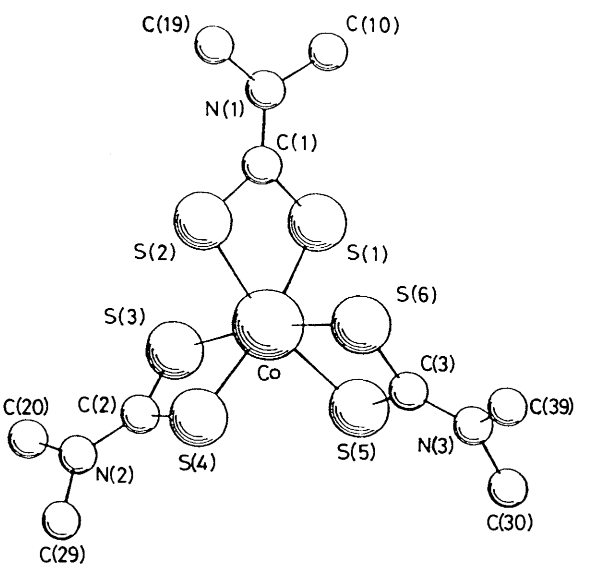


Figure 6. View of the co-ordination about the cobalt atom in compound (**11**), showing the atomic labelling

The torsional angles about one C–C bond and one C–O bond in each ring show considerable deviations from those expected for crown ethers. Crown ethers containing oxygen atoms or oxygen and nitrogen atoms generally show synclinal, or *gauche*, arrangements of the X–C–C–X fragments, with absolute values of the torsional angles of between 64 and 72°, and antiperiplanar, or *anti*, arrangements of the C–X–C–C fragments with absolute values of the torsional angles of between 165 and 180°.[24–26,28] The reasons for this conformational preference are stated by Cooper and co-workers.[34] The torsional angles of compound (**11**) are given in Table 4. Each crown ether ring has one N–C–C–O fragment adopting an *anti* conformation with a concomitant *gauche* conformation about the NCC–O bond or the NCCO–C bond. This conformation leads the oxygen atoms in these fragments to face out of the ring (*exodentate*), and the rings to be very distorted from C_{2v} symmetry, as shown in Figure 7. The rings are unrelated by symmetry and thus it is highly unlikely that the conformations adopted by the rings are due to crystal packing effects. 18-Crown-6 adopts a conformation in which there are two *anti* O–C–C–O fragments and two *gauche* C–O–C–C fragments.[26,32] Molecular mechanics show that this is the conformation of lowest energy and that crystal packing has little effect in such systems.[35,36] Upon complexation with alkali-metal cations 18-crown-6 adopts a more symmetrical conformation where all torsion angles about C–C bonds are close to 60°, and all the oxygen atoms are endodentate.[37] The crown ether rings of (**11**) cannot, however, adopt a conformation where all the heteroatoms (including nitrogen) are endodentate since the trigonal geometry around the nitrogen atom would direct the rest of the molecule towards the centre of the ring. However careful studies of molecular models indicate that conformations can be realised where an alkali-metal cation may be bound to all four endodentate oxygen atoms and held in close proximity to the nitrogen atom. The evidence presented earlier and the electrochemical data suggest that this does indeed occur.

The electrochemistry of compounds (**7**)—(**14**) was investigated by cyclic voltammetry in acetonitrile with NEt_4PF_6 as supporting electrolyte, and was consistent with that observed

Table 2. Fractional atomic co-ordinates (× 10^4) for compound (**11**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Co	930.9(5)	8 085.8(4)	1 229.4(9)	C(13)	−5 350(5)	6 218(5)	−5 100(16)
S(1)	−655(1)	7 461.5(7)	−673(2)	C(14)	−6 013(7)	7 059(5)	−4 328(15)
S(2)	262(1)	8 947.0(7)	102(2)	C(15)	−5 897(6)	7 784(5)	−3 648(14)
S(3)	685(1)	8 274.6(8)	3 576(2)	C(16)	−4 476(6)	8 797(5)	−1 992(11)
S(4)	2 415(1)	8 846.4(8)	3 293(2)	C(17)	−3 618(4)	9 272(4)	−1 930(9)
S(5)	1 402(1)	7 082.2(8)	1 644(2)	C(18)	−2 110(4)	9 362(3)	−2 010(8)
S(6)	1 490(1)	7 906.8(8)	−712(2)	C(19)	−1 661(4)	8 996(4)	−2 903(8)
O(11)	−3 615(4)	6 600(2)	−4 355(7)	C(20)	1 739(6)	9 267(4)	7 166(8)
O(12)	−5 397(7)	6 882(4)	−4 451(25)	C(21)	1 202(4)	9 826(3)	6 796(8)
O(13)	−5 116(5)	8 350(5)	−3 505(10)	C(22)	1 473(4)	11 075(3)	7 315(8)
O(14)	−3 114(3)	8 943(2)	−2 624(6)	C(23)	2 230(4)	11 768(3)	8 365(8)
O(21)	1 904(3)	10 518(2)	7 613(5)	C(24)	3 749(6)	12 554(4)	8 800(12)
O(22)	2 949(3)	11 925(3)	7 792(5)	C(25)	4 556(6)	12 641(6)	8 410(14)
O(23)	5 023(4)	12 097(4)	8 879(7)	C(26)	5 051(12)	11 800(6)	7 464(14)
O(24)	4 757(4)	10 586(4)	7 999(11)	C(27)	5 279(8)	11 141(6)	7 505(19)
O(31)	2 201(5)	5 065(4)	645(9)	C(28)	3 732(5)	10 334(4)	6 892(9)
O(32)	2 009(10)	3 874(7)	−2 039(17)	C(29)	3 403(5)	9 593(4)	7 166(10)
O(33)	1 100(5)	4 427(3)	−4 903(8)	C(30)	2 523(5)	6 233(4)	441(10)
O(34)	1 817(4)	5 939(3)	−3 984(6)	C(31)	1 757(6)	5 511(4)	−393(9)
N(1)	−1 591(3)	8 296(3)	−2 535(6)	C(32)	1 610(8)	4 327(5)	115(15)
N(2)	2 310(4)	9 232(3)	6 246(6)	C(33)	2 068(17)	3 837(9)	−428(21)
N(3)	2 227(4)	6 802(3)	−410(7)	C(34)	1 311(10)	3 473(6)	−3 690(16)
C(1)	−800(4)	8 242(3)	−1 231(7)	C(35)	1 342(11)	3 802(6)	−5 013(12)
C(2)	1 875(4)	8 848(3)	4 628(7)	C(36)	1 256(8)	4 843(5)	−5 962(11)
C(3)	1 764(4)	7 197(3)	95(7)	C(37)	1 090(7)	5 533(4)	−5 693(10)
C(10)	−2 360(4)	7 630(4)	−3 754(8)	C(38)	1 721(6)	6 604(4)	−3 587(10)
C(11)	−3 138(4)	7 299(3)	−3 264(8)	C(39)	2 522(5)	6 978(4)	−1 730(10)
C(12)	−4 350(5)	6 159(4)	−4 041(13)				

Table 3. Selected bond lengths (Å) and angles (°) for compound (**11**) with e.s.d.s in parentheses

Co–S(1)	2.252(2)	Co–S(2)	2.295(1)
Co–S(3)	2.265(2)	Co–S(4)	2.266(2)
Co–S(5)	2.278(1)	Co–S(6)	2.256(2)
S(1)–C(1)	1.700(5)	S(2)–C(1)	1.727(5)
S(3)–C(2)	1.711(6)	S(4)–C(2)	1.714(6)
S(5)–C(3)	1.703(6)	S(6)–C(3)	1.699(6)
N(1)–C(1)	1.319(7)	N(1)–C(10)	1.476(8)
N(1)–C(19)	1.470(8)	N(2)–C(2)	1.328(7)
N(2)–C(20)	1.447(9)	N(2)–C(29)	1.488(9)
N(3)–C(3)	1.335(7)	N(3)–C(30)	1.471(8)
N(3)–C(39)	1.469(9)		
S(2)–Co–S(1)	76.16(5)	S(3)–Co–S(1)	96.83(6)
S(3)–Co–S(2)	94.10(6)	S(4)–Co–S(1)	170.23(6)
S(4)–Co–S(2)	96.94(5)	S(4)–Co–S(3)	76.54(6)
S(5)–Co–S(1)	93.82(6)	S(5)–Co–S(2)	165.71(6)
S(5)–Co–S(3)	97.24(6)	S(5)–Co–S(4)	94.15(6)
S(6)–Co–S(1)	93.40(6)	S(6)–Co–S(2)	93.85(6)
S(6)–Co–S(3)	168.30(6)	S(6)–Co–S(4)	93.98(6)
S(6)–Co–S(5)	76.36(6)	C(1)–S(1)–Co	87.8(2)
C(1)–S(2)–Co	85.8(2)	C(2)–S(3)–Co	86.7(2)
C(2)–S(4)–Co	86.6(2)	C(3)–S(5)–Co	85.9(2)
C(3)–S(6)–Co	86.7(2)	C(10)–N(1)–C(1)	118.5(5)
C(19)–N(1)–C(1)	121.3(5)	C(19)–N(1)–C(10)	119.8(5)
C(20)–N(2)–C(2)	120.4(5)	C(29)–N(2)–C(2)	120.2(6)
C(29)–N(2)–C(20)	119.3(5)	C(30)–N(3)–C(3)	120.9(5)
C(39)–N(3)–C(3)	119.6(5)	C(39)–N(3)–C(30)	119.3(5)
S(2)–C(1)–S(1)	109.9(3)	N(1)–C(1)–S(1)	125.0(4)
N(1)–C(1)–S(2)	125.1(4)	S(4)–C(2)–S(3)	110.0(3)
N(2)–C(2)–S(3)	124.5(5)	N(2)–C(2)–S(4)	125.5(4)
S(6)–C(3)–S(5)	110.9(3)	N(3)–C(3)–S(5)	125.7(4)
N(3)–C(3)–S(6)	123.4(5)		

for other dithiocarbamate complexes.[38] The complexes of (**1**), except (**7**) and (**9**), exhibited at least one reversible redox couple. Compounds (**13**) and (**14**) showed no reversible electrochemisty. It is likely that this is due to the decreased stability of dithiocarbamates of primary amines,[21] and no reversible electrochemistry for this class of compounds has been reported. For (**8**), (**10**), (**11**), and (**12**) cyclic voltammograms were also recorded with $NaPF_6$ as the supporting electrolyte. Shifts of up to 35 mV in the redox potentials were observed, as recorded in Table 5. The larger shifts were observed for the tris(dithiocarbamate) complexes, and these were further investigated with KPF_6 as the supporting electrolyte. Smaller shifts of the redox potentials were observed with KPF_6 than with $NaPF_6$. Recently Andrews *et al.*[10] reported that larger shifts of the redox potentials of aza-15-crown-5 ferrocene compounds occurred with lithium cations than with sodium cations. To investigate whether the same was true for dithiocarbamate complexes, the cyclic voltammogram of compound (**8**) was recorded with $LiBF_4$ as electrolyte. As is shown in Table 5, a similar effect was not observed.

The relatively small shifts in redox potentials upon addition of alkali-metal cations is likely to be due to two reasons. Firstly, the alkali-metal cation is not strongly bound to the crown ether. The value of log *K*, where *K* is the equilibrium constant for binding sodium cations, for aza-15-crown-5 in methanol is only 2.06,[39] compared to *ca.* 3.25[40] for 15-crown-5, and is likely to be further reduced by the MS_2C centre withdrawing electron density from the nitrogen atom. The low degree of binding is confirmed by ion-selective electrode and extractability studies on compounds (**8**) and (**10**). The more positive nature of the nitrogen atom is also suggested by the lack of any increase in the shift of redox potential on changing the alkali-metal cation to lithium which, as Andrews *et al.*[10] have shown, is primarily bound to the nitrogen atom in aza-crowns. Secondly, the shifts may be small because of poor communication between the transition metal and the cation. It has become apparent from recent literature and our own studies that electronic effects are not transmitted as well by groups where there is localization of charge as by groups which have more delocalization. Thus carboxylato,[9] amino,[8] dithiocarbamate, and porphyrin[7] groups

Table 4. Torsional angles (°) X–C–C–X and C–O–C–C for the crown ether rings of compound (**11**)

N(1)–C(10)–C(11)–O(11)	−165.63	C(14)–C(15)–O(13)–C(16)	−122.57
C(10)–C(11)–O(11)–C(12)	175.86	C(15)–O(16)–C(16)–C(17)	169.40
C(11)–O(11)–C(12)–C(13)	90.94	O(13)–C(16)–C(17)–O(14)	−49.59
O(11)–C(12)–C(13)–O(12)	−73.07	C(16)–C(17)–O(14)–C(18)	−158.95
C(12)–C(13)–O(12)–C(14)	−143.89	C(17)–O(14)–C(18)–C(19)	−176.07
C(13)–O(12)–C(14)–C(15)	−178.34	O(14)–C(18)–C(19)–N(1)	−64.15
O(12)–C(14)–C(15)–O(13)	16.81		
N(2)–C(20)–C(21)–O(21)	−72.35	C(24)–C(25)–O(23)–C(26)	127.64
C(20)–C(21)–O(21)–C(22)	178.98	C(25)–O(23)–C(26)–C(27)	−166.49
C(21)–O(21)–C(22)–C(23)	173.45	O(23)–C(26)–C(27)–O(24)	48.73
O(21)–C(22)–C(23)–O(22)	66.57	C(26)–C(27)–O(24)–C(28)	61.66
C(22)–C(23)–O(22)–C(24)	−175.41	C(27)–O(24)–C(28)–C(29)	157.77
C(23)–O(22)–C(24)–C(25)	169.26	O(24)–C(28)–C(29)–N(2)	174.42
O(22)–C(24)–C(25)–O(23)	−66.84		
N(3)–C(30)–C(31)–O(31)	−179.58	C(34)–C(35)–O(33)–C(36)	170.42
C(30)–C(31)–O(31)–C(32)	−179.93	C(35)–O(33)–C(36)–C(37)	−174.07
C(31)–O(31)–C(32)–C(33)	116.51	O(33)–C(36)–C(37)–O(34)	64.60
O(31)–C(32)–C(33)–O(32)	−74.02	C(36)–C(37)–O(34)–C(38)	−179.53
C(32)–C(33)–O(32)–C(34)	−93.17	C(37)–O(34)–C(38)–C(39)	179.06
C(33)–O(32)–C(34)–C(35)	161.91	O(34)–C(38)–C(39)–N(3)	−86.19
O(32)–C(34)–C(35)–O(33)	−64.24		

Table 5. Electrochemical data for compounds (**8**), (**10**)—(**12**)[a]

Compound	Electrolyte (0.1 mol dm^{-3})	$E_{\frac{1}{2}}$[b]/mV	ΔE_p[c]/mV	$\Delta E_{\frac{1}{2}}$/mV
(**8**)	NEt_4PF_6	+420	75	
	$NaPF_6$	+430	75	10
(**10**)	NEt_4PF_6	−450	60	
	$LiBF_4$	−415	90	35
	$NaPF_6$	−415	80	35
	KPF_6	−410	80	30
	NEt_4PF_6	+345	70	
	$LiBF_4$	+360	115	15
	$NaPF_6$	+350	70	5
	KPF_6	+355	70	10
(**11**)	NEt_4PF_6	+810	80	
	$NaPF_6$	+825	95	15
	KPF_6	+820	90	10
(**12**)	NEt_4PF_6	+1 095	75	
	$NaPF_6$	+1 100	80	5
	KPF_6	+1 100	85	5

[a] The voltammograms were recorded in acetonitrile at a scan rate of 20 mV s^{-1}. [b] *vs.* s.c.e. [c] $E_p^A - E_p^C$.

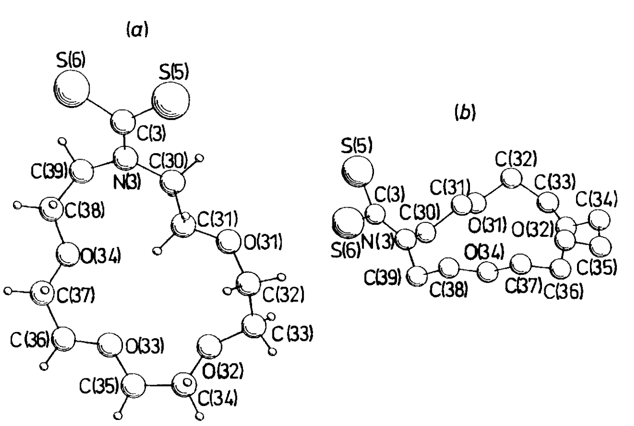


Figure 7. Two views of one of the crown ether rings of compound (**11**). Molecular projections (*a*) almost parallel to C(3)–N(3) (hydrogen atoms included), and (*b*) almost parallel to C(34)–C(35), showing the atomic labelling scheme

are not as good at transmitting any effect as arenethiolato,[9] and conjugated straight-chain and ring systems.[10,11]

Experimental

Proton n.m.r. spectra were recorded using a Bruker WH300 spectrometer (300 MHz), ^{13}C n.m.r. spectra on a Bruker AM250 spectrometer (62.89 MHz). Spectra were internally referenced using the solvent resonance relative to $SiMe_4$ ($\delta = 0$ p.p.m.). Infrared spectra were recorded on CsI discs on a Perkin-Elmer 1710 Fourier-transform spectrometer or on a Mattson Polaris Fourier-transform spectrometer. Mass spectra were recorded on an AEI M.S. 902 spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services Ltd., or on a VG Micromass 2AB 1F or VG 20-250 spectrometer fast atom bombardment (f.a.b.). Chromatography was carried out on columns of deactivated neutral alumina (6% water) made up in light petroleum (b.p. 40—60 °C).

Cyclic voltammetry experiments were performed using an Oxford Instruments potentiostat and recorded on a Gould 3000 X-Y chart recorder. A platinum disc (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 silver wire dipped in 0.01 mol dm^{-3} silver nitrate and isolated by a Vycor frit.[41] Ferrocene was added at the end of each experiment as an internal reference;[42] its potential against the standard calomel electrode (s.c.e.) was measured as +355 mV.[43] A two-compartment cell was used.[44] The working compartment had a working volume of *ca.* 25 cm^3 and contained the working and counter electrodes. The reference electrode was isolated from the test solution by a medium-grade porous frit. The gas-tight cell was suitable for use under anaerobic conditions. Sample loading was carried out using Schlenk-line techniques or by use of syringes. Experiments were carried out under dinitrogen at room temperature in *ca.* 0.1 mol dm^{-3} electrolyte solution. Acetonitrile was dried by distillation from over calcium hydride and then from over phosphorus pentoxide, under dinitrogen, and stored over activated molecular sieves. The salt NEt_4PF_6 was recrystallized from ethanol four times and dried *in vacuo*; $NaPF_6$, KPF_6, and $LiBF_4$ were dried by heating *in vacuo* prior to dissolution.

Crystal Structure Determination of Compound (**11**).—*Crystal data.* $C_{33}H_{60}CoN_3O_{12}S_6$, $M = 942.12$, triclinic, space group $P\bar{1}$, $a = 15.636(5)$, $b = 19.695(6)$, $c = 8.808(5)$ Å, $\alpha = 96.39(4)$, $\beta = 115.14(4)$, $\gamma = 103.35(2)°$, $U = 2\,321$ Å^3, $Z = 2$, $D_c = 1.35$ Mg m^{-3}, $\mu(\text{Mo-}K_\alpha) = 6.808$ cm^{-1}, $T = 293$ K, $F(000) = 996$, crystal size *ca.* 0.2 × 0.15 × 0.25 mm.

A dark green crystal of (**11**) was mounted on the end of a glass fibre and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Data were collected ($2\theta_{max.} = 47°$) using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å) and ω—2θ scan mode. Unit-cell parameters were calculated from the setting angles of 25 accurately centred reflections. Negligible fluctuation was observed for three intensity standards measured repeatedly at 2-h intervals. An absorption correction based on an azimuthal scan was applied (maximum correction = 1.13) and the data were corrected for Lorentz and polarization effects. Equivalent reflections were merged ($R_{merge} = 0.016$) and 4 953 reflections were considered unique $[I > 3\sigma(I)]$ out of the 6 848 reflections measured. The locations of the cobalt, nitrogen, and sulphur atoms were determined using SHELXS,[45] and the carbon and oxygen atoms located from subsequent difference maps. Hydrogen atoms were placed in calculated positions and refined riding on their supporting atoms with a thermal parameter 1.3 times that of the carbon atom. The non-hydrogen atoms were refined anisotropically with the exception of those in the O(31)–C(32)–C(33)–O(32) fragment of one of the crown ether rings. No simple model for disorder in this fragment could be constructed. Blocked-matrix least-squares refinement of 478 least-squares parameters and application of a three-term Chebychev weighting scheme (parameters 11.64, 4.276, and 9.416) led to final agreement factors of $R = 0.077$ and $R' = 0.092$. All calculations were performed using CRYSTALS suite[45] on the VAX11/750 computer in the Chemical Crystallography Laboratory, Oxford.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Sodium 1,4,7,10-*Tetraoxa*-13-*azacyclopentadecane*-13-*carbodithioate* (**1**).—Carbon disulphide (1.11 g, 0.015 mol) was added to aza-15-crown-5[46] (3.20 g, 0.015 mol) and sodium hydroxide (0.58 g, 0.015 mol) in water (50 cm^3) at 0 °C, and stirred for 6 h. The water was removed under reduced pressure and the product recrystallized from methanol and diethyl ether. Yield 3.17 g (68%).

Sodium Benzo-1,4,7,10,13-*pentaoxacyclopentadecane*-15-*dithiocarbamate*, (**2**).—Carbon disulphide (0.91 g, 0.012 mol) was added to 4-aminobenzo-15-crown-5[10] (3.40 g, 0.012 mol) and sodium hydroxide (0.48 g, 0.012 mmol) in water (150 cm^3) at 0 °C and stirred for 6 h. The water was removed under reduced pressure and the dark brown residue washed with dichloromethane, cold methanol, and diethyl ether. The impure, off-white product was dried *in vacuo*. Yield 2.06 g (45%). Repeated recrystallizations of the product from water or methanol and diethyl ether failed to give satisfactory analyses. Characterization was based on the spectroscopic data and on the reaction products.

13,13′-(1,4-*Dithioxo*-2,3-*dithiabutane*-1,4-*diyl*)*di*(1,4,7,10-*tetraoxa*-13-*azacyclopentadecane*), (**3**).—Compound (**1**) (0.60 g, 1.9 mmol) and $K_3[Fe(CN)_6]$ (1.40 g, 4.2 mmol) in water (10 cm^3) were stirred for 5 min. The aqueous solution was decanted off and the resultant oil extracted into acetone. The solvent was removed under reduced pressure and the oil washed with water and light petroleum (b.p. <40 °C) and dried *in vacuo* giving a white crystalline solid. Yield 0.31 g (55%).

15-*Isothiocyanatobenzo*-1,4,7,10,13-*pentaoxacyclopentadecane*, (**6**).—Potassium hexacyanoferrate(III) (1.05 g, 3.3 mmol) in water (40 cm^3) was added with stirring to compound (**2**) (0.60 g, 1.6 mmol) in water (100 cm^3). The resulting precipitate was filtered off and chromatographed using dichloromethane containing 1% methanol as eluant. The solvent was removed under reduced pressure and the product recrystallized from dichloromethane and light petroleum (b.p. 100—120 °C) giving small white crystals. Yield *ca.* 50 mg (5%).

Nickel Bis(1,4,7,10-*tetraoxa*-13-*azacyclopentadecane*-13-*carbodithioate*), (**7**).—Compound (**1**) (0.50 g, 1.6 mmol) in water (20 cm^3) was added to nickel chloride (0.19 g, 0.8 mmol) in water (10 cm^3). The green precipitate was filtered off and washed with water. Recrystallization from dichloromethane and light petroleum (b.p. 100—120 °C) gave red/green platelets. Yield 0.42 g (81%).

Copper Bis(1,4,7,10-*tetraoxa*-13-*azacyclopentadecene*-13-*carbodithioate*), (**8**).—This was prepared analogously to (**7**) using compound (**1**) (0.56 g, 1.7 mmol) and copper sulphate (0.22 g, 0.9 mmol) giving red-brown rhombohedral crystals. Yield 0.52 g (91%).

Chromium Tris(1,4,7,10-*tetraoxa*-13-*azacyclopentadecane*-13-*carbodithioate*), (**9**).—Compound (**1**) (0.44 g, 1.4 mmol) and chromium trichloride (0.12 g, 0.45 mmol) in thf (50 cm^3) were stirred for 1.5 h. The blue solution was filtered and the solvent removed under reduced pressure yielding a blue oil. Attempts to crystallize the product failed and the oil was dried *in vacuo*. Yield 0.10 g (23%).

Iron Tris(1,4,7,10-*tetraoxa*-13-*azacyclopentadecane*-13-*carbodithioate*), (**10**).—This was prepared analogously to (**7**) using compound (**1**) (0.50 g, 1.6 mmol) and iron trichloride (0.14 g, 0.5 mmol). The black solid was washed with water and light petroleum (b.p. 40—60 °C) and dried *in vacuo*. Yield 0.30 g (64%).

Cobalt Tris(1,4,7,10-*tetraoxa*-13-*azacyclopentadecane*-13-*carbodithiate*), (**11**).—This was prepared similarly to (**7**) using compound (**1**) (0.50 g, 1.6 mmol) and cobalt(II) sulphate (0.22 g, 0.8 mmol), giving dark green needles. Yield 0.34 g (68%).

Bis(η^5-*cyclopentadienyl*)(1,4,7,10-*tetraoxa*-13-*azacyclopentadecane*-13-*carbodithiato*)*molybdenum Hexafluorophosphate*, (**12**).—Under an inert atmosphere of nitrogen, compound (**1**) (0.53 g, 1.7 mmol) and bis(η^5-cyclopentadienyl)molybdenum dichloride (0.50 g, 1.7 mmol) in water (30 cm^3) were stirred for 1 h. The resulting red solution was filtered and excess of ammonium hexafluorophosphate (0.50 g) added. The buff precipitate was washed with water and recrystallized from acetone and ethanol yielding orange crystals. Yield 0.44 g (39%).

Nickel Bis(*benzo*-1,4,7,10,13-*pentaoxacyclopentadecane*-15-*dithiocarbamate*), (**13**). Compound (**2**) (0.16 g, 0.4 mmol) in water (100 cm^3) was added with stirring to nickel chloride (0.05 g, 0.2 mmol) in water (10 cm^3). The resulting green precipitate was filtered off, washed with water and chromatographed. With dichloromethane containing 4% methanol as eluant a green band was eluted and collected. The product was precipitated with light petroleum (b.p. 100—120 °C), filtered off, and dried *in vacuo*. Yield *ca.* 50 mg (16%).

Copper Bis(*benzo*-1,4,7,10,13-*pentaoxacyclopentadecane*-15-

dithiocarbamate), (**14**).—This was prepared analogously to (**13**) using compound (**2**) (0.20 g, 0.55 mmol) and copper sulphate (0.065 g, 0.28 mmol). The product was recrystallized from dichloromethane and light petroleum (b.p. 100—120 °C) affording solvated red-brown crystals. Yield 0.12 g (56%).

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