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SYNTHESIS, COORDINATION AND REDOX PROPERTIES OF A NOVEL TETRATHIAFULVALENE TETRA(BENZO-15-CROWN-5)ETHER LIGAND

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Abstract—A new tetrathiafulvalene tetra(benzo-15-crown-5)ether ligand (**4**) has been prepared and polymetallic alkali metal complexes of $\mathbf{4} \cdot 4Na^+$ and $\mathbf{4} \cdot 2K^+$ stoichiometries isolated. Relatively small anodic perturbations of the redox-active ligand's redox couples were observed in the presence of either alkali metal cation.

The design of new chemical sensors[1,2] and redox switchable ligands[3] has led in recent years to the syntheses of a variety of organometallic and transition metal coordinated redox-active macrocyclic receptor molecules, which have been shown to electrochemically recognize, in some cases selectively, cationic and anionic guests in polar solvents including water.[4,5] The tetrathiafulvalene (TTF) moiety is an attractive organic redox centre to incorporate or append to various macrocyclic host cavities, and indeed Otsubo and Ogura[6] and Becher *et al.*[7] have recently prepared some TTF–crown ether derivatives. We report here the synthesis, coordination and electrochemical properties of a novel TTF–tetra(benzo-15-crown-5)ether ligand including the isolation of polymetallic complexes of sodium and potassium cations.

RESULTS AND DISCUSSION

Synthesis

TTF (**1**) was treated with just over four equivalents of lithium diisopropylamide at −78°C in dry tetrahydrofuran to give the tetralithium salt (**2**).[8] Reaction of **2** with the disulphide of benzo-15-crown-5 (**3**)[9] gave the new TTF–tetra(benzo-15-crown-5)ether ligand (**4**) as a yellow solid in 41% yield (Scheme 1). ^1H and ^{13}C NMR spectroscopy, fast atom bombardment mass spectrometry (FABMS) and elemental analysis characterized the new redox-active ligand's proposed structure (see Experimental section).

Coordination studies

Refluxing **4** with acetonitrile solutions of excess amounts of sodium and potassium hexafluorophosphate salts led to the isolation of the respective alkali metal complexes as red solids in quantitative yields. The elemental analysis of the sodium complex (Table 1) indicated a $4Na^+ : \mathbf{4}$ stoichiometry in which one sodium cation is complexed within each of the benzo crown ether moieties (Fig. 1). With potassium the elemental analysis (Table 1) suggested $2K^+ : \mathbf{4}$ stoichiometry and the FABMS spectrum of the complex revealed a molecular ion at $m/z = 1620$, corresponding to

Table 1. Elemental analyses for sodium and potassium complexes of **4**

Complex	Analysis[a] (%) C	H
$[\mathbf{4} \cdot Na_4](PF_6)_4$	35.9 (36.0)	3.9 (3.7)
$[\mathbf{4} \cdot K_2](PF_6)_2$	42.7 (42.2)	4.6 (4.3)

[a] Calculated values in parentheses.

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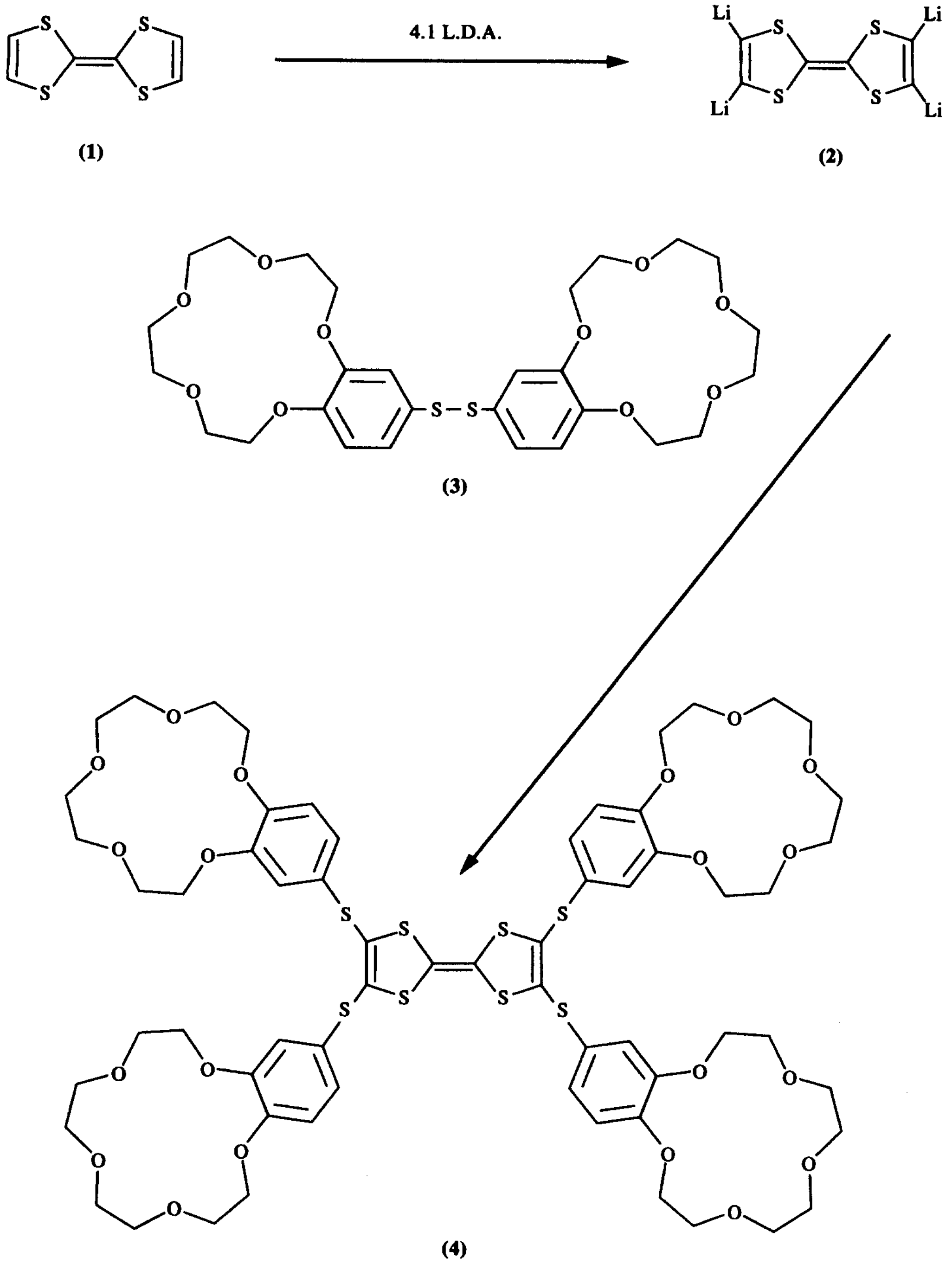


Scheme 1.

$[4 \cdot K_2PF_6]^+$. As a consequence of the potassium cation being larger in size than the cavity of the benzo-15-crown-5 ether ligand, it is well documented that this alkali metal cation forms inter- and intramolecular sandwich complexes with mono- and bis-benzo-15-crown-5 ethers respectively.[10,11] Taking this known coordination chemistry into account, two possible structures for the potassium complex of **4** can be proposed. Figure 2a shows two K^+ ions bound by one molecule of **4** and Fig. 2b the dimeric $4K^+ : 2(\mathbf{4})$ analogue. Repeated attempts at obtaining crystals suitable for single crystal X-ray analysis have failed; however, molecular modelling and CPK models suggest the structure shown in Fig. 2a is highly strained. In addition, there are solid state examples of charge-transfer complexes of TTF with acceptors such as TCNQ (tetracyanoquinodimethane), where the TTF radical cations stack vertically[12] suggesting that the structure in Fig. 2b may be favoured for the pot-

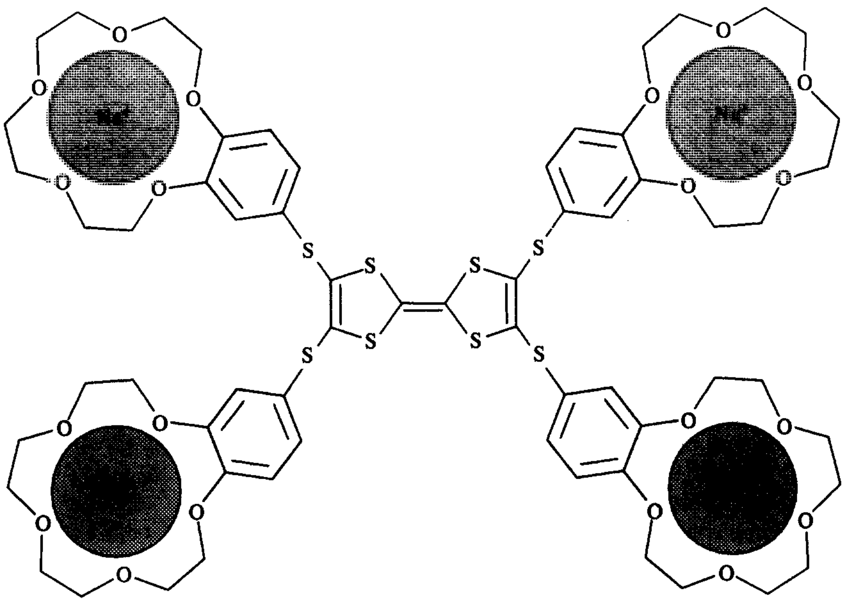
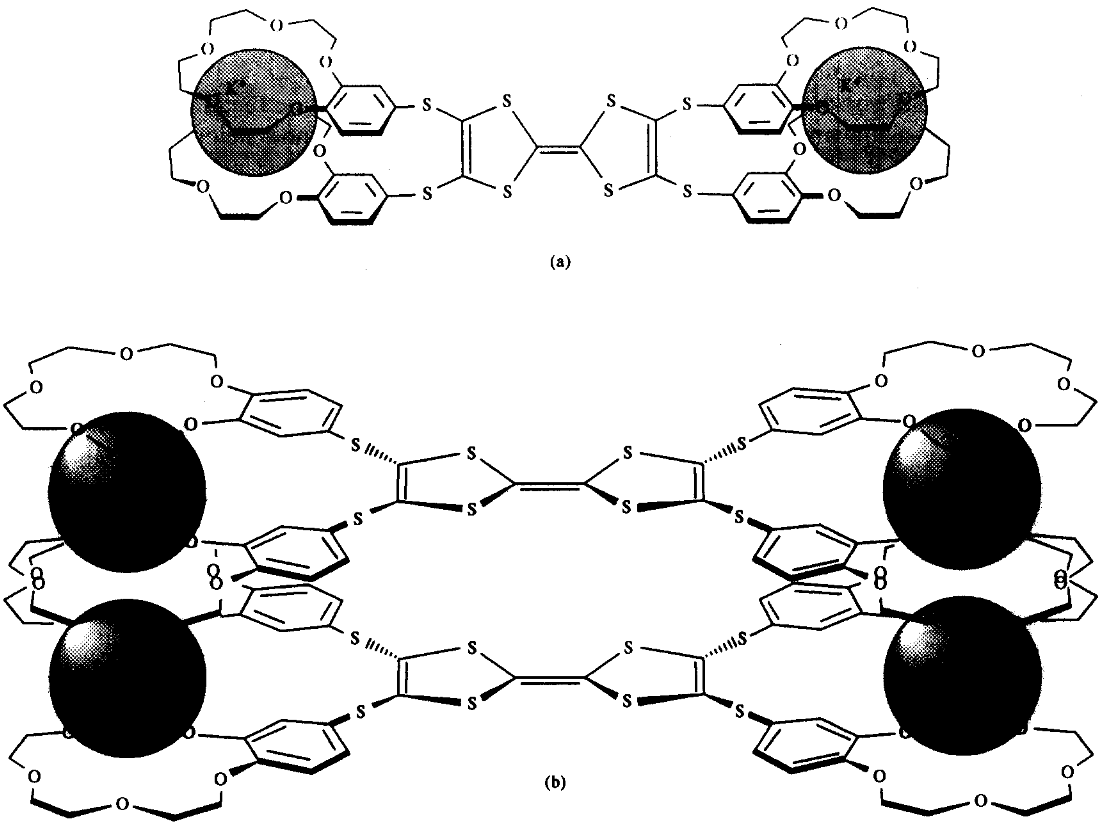


Fig. 1. Proposed structure of polymetallic **4**·sodium cation complex.



(a)

(b)

Fig. 2. Proposed structures of polymetallic **4**·potassium cation complexes.

assium complex of **4**. Unfortunately, solubility problems prevented solution ^1H and ^{13}C NMR coordination studies to be undertaken with either Na^+ or K^+ cations.

Electrochemical investigations

The electrochemical properties of **4** were investigated by cyclic voltammetry in an anhydrous ace-

Table 2. Electrochemical data

	TTF (1)		4	
	1st redox wave	2nd redox wave	1st redox wave	2nd redox wave
$E_{1/2}$ (V)[a]	0.42	0.82	0.60	0.87
ΔE_p (mV)[b]	70	80	80	95
ΔE_{Na^+} (mV)[c]	—	—	$\leqslant 10$	$\leqslant 10$
ΔE_{K^+} (mV)[c]	—	—	$\leqslant 10$	$\leqslant 10$

[a] Obtained in acetonitrile–dichloromethane (1 : 1) solution containing 0.2 mol dm^{-3} Bu_4N BF_4 as supporting electrolyte. Solutions were *ca* 2×10^{-3} in compound and potentials were determined with reference to a standard calomel electrode (SCE).

[b] Separation between anodic and cathodic peak potentials.

[c] Anodic shifts produced by presence of excess amounts of alkali metal cations (10 equivalents) added as their hexafluorophosphate salts.

tonitrile–dichloromethane (1 : 1) solvent system using tetrabutylammonium tetrafluoroborate as base electrolyte, and the results are summarized in Table 2. The cyclic voltammogram of **4** exhibited two reversible one-electron oxidation redox couples (Fig. 3), which are significantly anodically shifted compared to TTF (**1**) itself under analogous electrochemical solution conditions, $\Delta E = 180$ and 50 mV for the first and second oxidation potentials, respectively (Table 2). Related simple alkyl thio substituted TTF derivatives also display more anodic oxidation redox couples than TTF itself.[13]

Disappointingly, alkali metal cation electrochemical recognition studies revealed that the addition of excess amounts of sodium or potassium cations to an electrochemical solution of **4** did not perturb the position of either redox couple by a significant amount ($\Delta E \leqslant 10$ mV). This suggests that the binding of the metal cations at the crown ether moieties is not being efficiently electrostatically communicated either through bonds or through space to the TTF redox centre. However, it is noteworthy that in the case of the sodium cation addition, the current increased steadily with increasing equivalents of metal cation. A graphical representation of change in current ΔI_{pa} versus molar equivalents of sodium cations is shown in Fig. 4. The resulting titration curve plateaus at approximately four equivalents of Na^+, suggesting that **4** in solution forms the tetra-sodium complex shown in Fig. 1. A similar plot could not be drawn

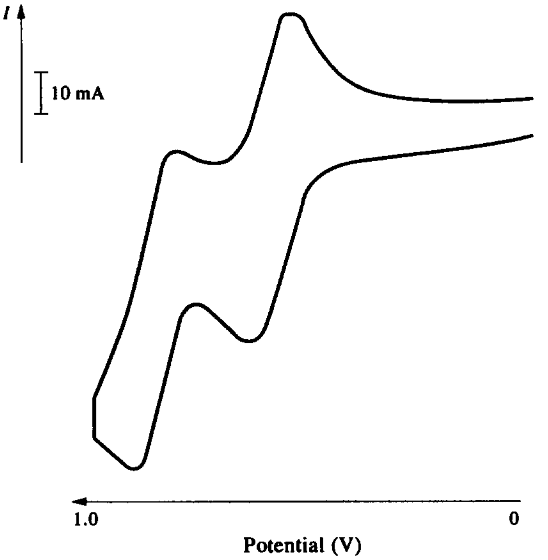


Fig. 3. Cyclic voltammogram of **4** in acetonitrile–dichloromethane (1 : 1) solution.

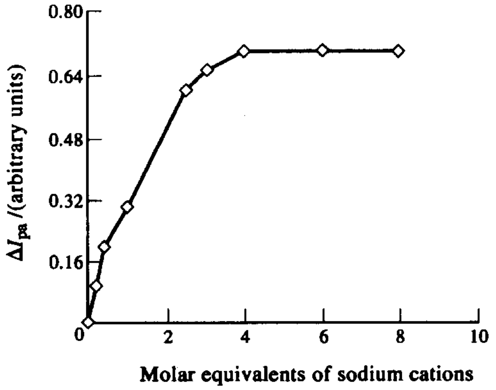
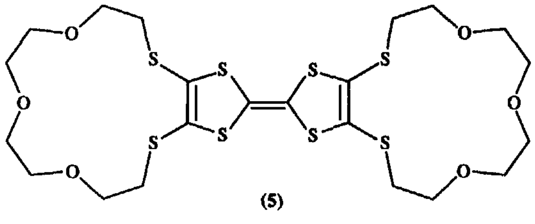


Fig. 4. Titration curve of change in I_{pa} current of **4** versus equivalents of Na^+ in acetonitrile–dichloromethane (1 : 1) solution.

for potassium because the increase in I_{pa} current was much less marked.

It is even more surprising that the redox couples of **4** are electrochemically insensitive to either Na^+ or K^+ cations when considering a recent publication by Becher and co-workers,[14] who report that the TTF–crown ether derivative (**5**) undergoes anodic perturbations of up to 80 mV with 100 equivalents of Na^+, although only a 10 mV shift was noted with K^+.


(**5**)

CONCLUSIONS

A novel tetrathiafulvalene tetra(benzo-15-crown-5)ether ligand (**4**) was synthesized and shown to form polymetallic alkali metal complexes of $\mathbf{4}\cdot 4Na^+$ and $\mathbf{4}\cdot 2K^+$ stoichiometries. Disappointingly, addition of sodium or potassium cations to an electrochemical solution of **4** did not significantly perturb the redox couples of the ligand, indicating that alkali metal cation complexation is not being communicated to the TTF redox centre.

EXPERIMENTAL

Solvent and reagent pre-treatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was predried over 4 Å molecular sieves (4–8 mesh) and then distilled from CaH_2. Tetrahydrofuran was distilled from sodium using benzophenone as indicator.

Unless otherwise stated, commercial grade chemicals were used without further purification. Bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclodecin-16-yl)disulphide (**3**) was prepared according to a literature procedure.[9]

All elemental analyses were carried out by the Inorganic Chemistry Laboratory Microanalysis Service. The NMR spectra were recorded on a Brüker AM300 instrument, operating at 300 MHz for ^1H NMR and 75.42 MHz for ^{13}C NMR spectra. IR spectra were recorded on a Mattson 10410E "polaris" Fourier Transform Spectrometer. Electrochemical measurements were conducted on a Princeton Applied Research Potentiostat/Galvanostat Model 273. FABMS were carried out by the SERC mass spectrometry service at University College, Swansea. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

Synthesis

Tetra(2,3,5,6,8,9,11,12 - *octahydro*-1,4,7,10,13 - *benzopentaoxacyclodecin* - 16 - *yl*) - 1,2,3,4 - *tetrathiafulvalenylsulphide* (**34**). To a solution of LDA, generated at 0°C with diisopropylamine (1.4 cm^3, 10 mmol) and n-butyllithium (1.6 M in hexane, 6.3 cm^3 10 mmol) in anhydrous THF (150 cm^3), was added tetrathiafulvalene (0.5 g, 2.45 mmol) dropwise in dry THF (60 cm^3) at −78°C under nitrogen. A yellow suspension resulted and the mixture was stirred at −78°C for 1 h. To the mixture was slowly added a solution of **3** (6.18 g, 10.3 mmol) in THF (60 cm^3) at −78°C. The resulting mixture was stirred for 1 h and then slowly allowed to warm to room temperature with stirring (15 h). The precipitate was collected, washed with THF (60 cm^3) and recrystallized from $CHCl_3$–MeOH to give a yellow solid, 1.4 g, 41%. Melting point: 170–172°C. Mass spectrum (FAB): *m/z* at 1397 = M+1. Calc. for $C_{62}H_{76}S_8O_{20}$: C, 53.3; H, 5.4%. Found: C, 53.3; H, 5.2. ^1H NMR ($CDCl_3$): δ 3.78 (32H, s, OCH_2CH_2O), 3.90 (16H, m, $ArOCH_2\underline{CH_2}$), 4.10 (16H, m, $ArOC\underline{H_2}CH_2$), 6.75–7.10 (12H, m, ArH). ^{13}C NMR ($CDCl_3$): δ 69.13, 69.45, 70.53, 71.18 (OCH_2), 114.16, 117.74, 124.05, 125.64, 149.31, 149.90 (ArC and TTF—C).

Sodium and potassium complexes of **4**

To an acetonitrile solution of **4** was added an excess amount of sodium or potassium hexafluorophosphate. The mixture was refluxed for 30 min and on cooling a red precipitate was collected by filtration in quantitative yields. Elemental analyses of the respective complexes are shown in Table 1.

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