

## Redox Responsive Metal Complexes Containing Cation Binding Sites

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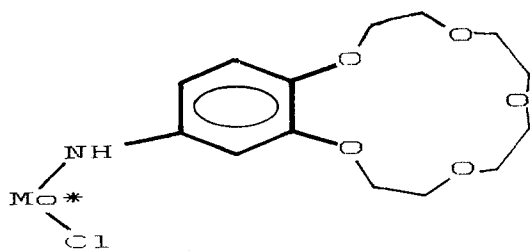
**Abstract.** A series of cyclic polyethers, which incorporate the redox active  $\{\text{Mo}(\text{NO})\}^{3+}$  moiety, have been prepared and characterised. The electrochemistry of these complexes has been investigated and their reduction potentials found to undergo anodic shifts upon the binding of alkali metal cations to the cyclic polyether moiety. The magnitude of the shift appears relatively insensitive to the size of the cyclic polyether ring, but is substantially reduced when  $\text{K}^+$  is used in place of  $\text{Na}^+$ .

**Key words:** Molybdenum, nitrosyl, pyrazolylborate, electrochemistry, cyclic polyether, complexation, sodium, potassium.

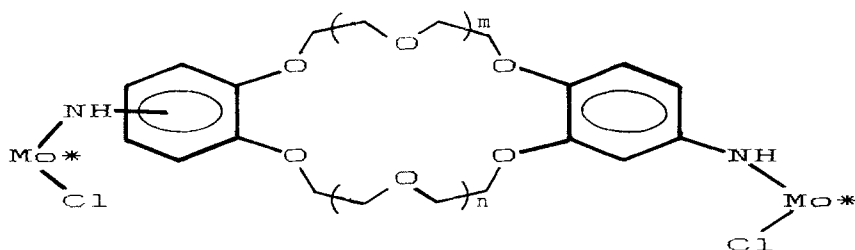
The sterically demanding tripodal ligand  $\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{N}_2\text{H}_3)\}^-$ ,  $\text{L}^*$ , restricts the coordination spheres of metals to which it is bound so that only complexes having essentially octahedral or tetrahedral geometries may form. In the case of the  $\{\text{Mo}(\text{NO})\}^{4+}$  core this results in the formation of formally 16-electron complexes of formula  $[\text{Mo}(\text{NO})\text{L}^*\text{XY}]$  in which X and/or Y is halide, amide, alkoxide or thiolate. These electron deficient compounds undergo one-electron reduction reactions at potentials which vary substantially depending on the nature of X and Y [1]. Thus in the complexes  $[\text{Mo}(\text{NO})\text{L}^*\text{Cl}\{\text{NHC}_6\text{H}_4\text{Z}\}]$ , in which Z is one of a variety of *para* substituents, the reduction potential of the  $\{\text{Mo}(\text{NO})\}^{3+}$  core is linearly related to the substituent constant,  $\sigma_p$ , with a reaction constant of 6.7 [2, 3].

We have extended these studies by investigating the effects of non-covalently bonded charged moieties located in close proximity to the redox centre. Our initial experiments have involved a study of the effects of cation binding on the electrochemical properties of complexes which contain cyclic polyether cation binding sites. The synthesis and electrochemistry of the redox active compounds **I**, **II** ( $n = m = 1$ ) and **III** ( $a = 0, 1, 2, 3$ ) has been reported previously [4]. It was found that the binding of  $\text{Na}^+$  to the cyclic polyether moiety in these complexes could produce anodic shifts in their reduction potentials. In the case of complexes of type **III**, the magnitude of these shifts varied from 180 to 320 mV depending upon the size of the polyether ring. We have now synthesised further complexes of type **II** so that the effect of polyether ring size on anodic shift could also be assessed in these complexes. In addition we have investigated the effect of changing the nature of the bound cation on the anodic shifts produced. Finally, to provide an example of a

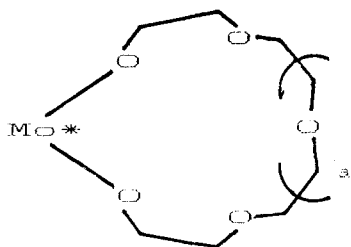
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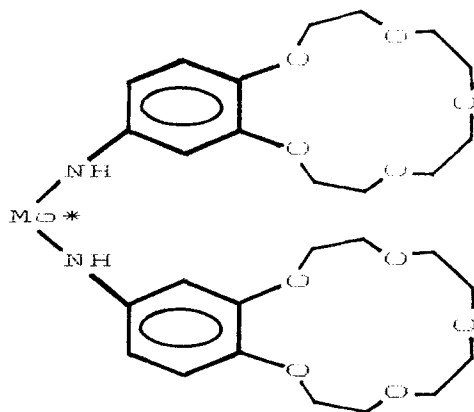
I



II



III



IV

bis-crown ether system, we have also prepared a complex containing two cyclic polyether rings and one redox centre.

The new complexes **II** ( $n = 1, m = 2$ ;  $n = m = 2$ ) have been prepared from the reaction between two moles of  $[\text{Mo}(\text{NO})\text{L}^*\text{Cl}_2]$  and the appropriate diaminodibenzo-crown ether. The bis complex **IV** was also prepared from the reaction between the monoiodide derivative,  $[\text{Mo}(\text{NO})\text{L}^*\text{I}\{\text{NHC}_6\text{H}_3\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{O}\}]$ , and  $\{\text{NH}_2\text{C}_6\text{H}_3\text{OCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{O}\}$  in the presence of sodium naphthalenide. These new complexes were characterised by elemental analysis and by infrared,  $^1\text{H-NMR}$  and mass spectroscopy. In the cases where  $n = m = 1$  and  $n = 1, m = 2$  it proved possible to separate the *cis* and *trans* isomers of the diaminodibenzo-crown ether precursors and in these cases only one isomer of the bimetallic complex was synthesised and used in the subsequent studies. However, in the case where  $n = m = 2$  separation of the *cis* and *trans* isomers was not possible and the complex characterised was a mixture of the two isomeric forms. Since the single isomers and the mixture exhibited similar spectral properties and behaved in a similar manner in the electrochemical experiments it would appear that there are no electrochemically detectable differences between the *cis* and *trans* isomers.

The electrochemical properties of the new compounds have been investigated using cyclic voltammetry and differential pulse techniques. The results obtained, along with previously reported results for **I** and **II** ( $n = m = 1$ ), are summarised in the Table. The observed reduction potentials are in accord with the formulations of **I** and **II** as monoarylamide derivatives,  $[\text{L}^*\text{Mo}(\text{NO})\text{Cl}\{\text{NHAr}^1\}]$ , and of **IV** as a bis-arylamide derivative,  $[\text{L}^*\text{Mo}(\text{NO})\{\text{NHAr}^1\}_2]$  [6]. In the case of the complexes **II**, coulometric studies have confirmed that a two electron reduction reaction occurs. This is in accord with their formulation as bimetallic complexes containing non-interacting redox centres [5]. Cyclic voltammogram and differential pulse polarogram traces showing the effect of adding up to 2 molar equivalents of  $\text{NaBPh}_4$  or

Table I.

Complex	<b>I</b>	<b>II</b>			<b>IV</b>
		$n = m = 1$	$n = 1, m = 2$	$n = m = 2$	
$E_f$ (V) <sup>a</sup>	-0.95	-0.96	-0.94	-0.92	-1.36
$\Delta E_p$ (mV) <sup>b</sup>	110	80	80	80	120
$\Delta E(\text{Na})$ (mV) <sup>c</sup>	60	70	85	85	90
$\Delta E(\text{K})$ (mV) <sup>c</sup>	—	40	40	40	40

<sup>a</sup> Obtained in MeCN solution containing 0.2M  $[\text{Bu}_4\text{N}]\text{BF}_4$  as supporting electrolyte. Solutions were ca.  $2 \times 10^{-3}$  M in complex and potentials were determined with reference to ferrocene as internal standard but are quoted relative to the S.C.E..

<sup>b</sup> Separation between anodic and cathodic peak potentials of cyclic voltammograms.

<sup>c</sup> Shift in reduction potential produced by the presence of  $\text{Na}^+$  or  $\text{K}^+$  added as their  $\text{BPh}_4^-$  salts, in solution, and in aliquots to provide up to 2 molar equivalents with less than 5% volume change in the solution. Broadening of the cyclic voltammogram trace was observed when between 0.2 and 1.0 equivalents of  $\text{Na}^+$  or  $\text{K}^+$  had been added. After ca. 1.2 equivalents had been added the trace returned to its original shape and no further changes were observed on adding an additional 0.8 equivalents to give a cation/complex molar ratio of 2. These shifts may be compared with the effects of adding aliquots of  $\text{NaBPh}_4$  to solutions containing  $[\text{Mo}(\text{NO})\text{L}^*\text{Cl}\{\text{NHC}_6\text{H}_4\text{-3, 4-(OMe)}_2\}]$  or  $[\text{Mo}(\text{NO})\text{L}^*\{\text{NHC}_6\text{H}_4\text{-3, 4-(OMe)}_2\}_2]$  for which shifts in reduction potential of less than 10 mV were found under similar conditions.

KBPh<sub>4</sub> to the electrochemical cell were also obtained. The results of these experiments are also summarised in the Table.

In the case of the complexes **II**, the anodic shifts produced by cation addition appear relatively insensitive to the size of the cyclic polyether ring. A more notable effect is the consistent difference in the  $\Delta E$  value on going from Na<sup>+</sup> to K<sup>+</sup>. The larger potassium ion, having the smaller charge:radius ratio produces about half the shift of the Na<sup>+</sup> ion. A similar effect is apparent with the complex **IV** but, although the electrochemical titrations suggest a 1:1 stoichiometry for cation:complex binding with both Na<sup>+</sup> and K<sup>+</sup>, further studies are needed before an unequivocal interpretation of the electrochemical data can be given for **IV**. The results obtained with the type **II** complexes suggest that the polarising power of the cation is of great importance in determining the magnitude of the anodic shift in  $E_f$  produced by cation binding.

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