The Synthesis and Electrochemistry of Novel Redox Responsive Molybdenum Complexes Containing Cyclic Polyether Cation Binding Sites

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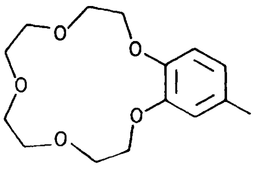
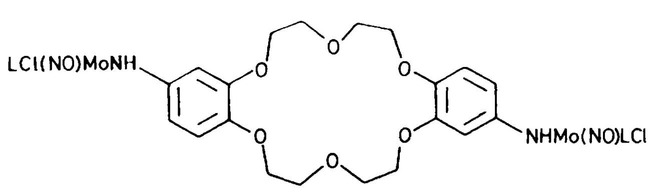
The binding of Na^+ to cyclic polyether sites incorporated in molybdenum complexes has been shown to shift the reduction potentials of the $\{Mo(NO)\}^{3+}$ centres present to more anodic potentials by up to 320 mV.

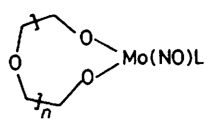
There is considerable current interest in the synthesis and properties of molecules which contain both a redox-active transition metal centre and a host site at which a guest ion or molecule might bind.[1—6] The species reported to date usually contain ferrocenyl groups which might undergo an electrochemical oxidation, but the effect of guest binding on the oxidation potential of the complex has not been reported. We have now prepared a series of novel complexes (**1**)—(**5**), which contain a redox-active 16-electron $\{Mo(NO)\}^{3+}$ core as well as a cyclic polyether moiety. The compounds (**1**) and (**2**) were prepared from the reactions between $[Mo(NO)LCl_2]$; L^- = tris(3,5-dimethylpyrazolyl)hydroborate, and the appropriate amine-substituted crown ether.[7—9] The compounds (**3**), (**4**), and (**5**) were prepared from the reactions between $[Mo(NO)LI_2]$ and tetra-, penta-, or hexa-ethylene glycol respectively in the presence of triethylamine.[10] These latter complexes provide transition metal analogues of the previously reported cyclic polyether (**6**) which contains a quinone as the redox site.[11] The new complexes were characterised by i.r., mass, and ^{13}C and ^{1}H n.m.r. spectroscopy and gave satisfactory elemental analyses. The mass spectra of (**3**) and (**4**) exhibited parent ion (P^+) envelopes at *m/z* 617 and 661 (^{11}B, ^{98}Mo) respectively as well as envelopes at $(P-30)^+$ attributed to the loss of NO. In the case of (**5**) only the $(P-30)^+$ envelope was observed at *m/z* 675. The 400 MHz ^{1}H and 100 MHz ^{13}C n.m.r. spectra of (**1**) and (**2**) were measured in $CDCl_3$ solution, and upon the addition of a 2:1 molar excess of $NaBPh_4$ they exhibited changes consistent with the



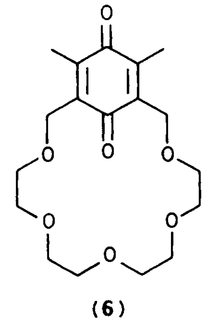
(1)



(2)



(3) $n = 3$
(4) $n = 4$
(5) $n = 5$



(6)

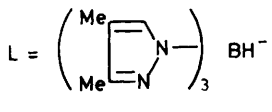


Table 1. Electrochemical and i.r. data.

Complex	ν_{NO}[a] /cm^{-1}	$E_{\frac{1}{2}}$[b] /V	ΔE_p[c] /mV	$\Delta E_{\frac{1}{2}}$[d] /mV
(1)	1645	−0.95	110	60
(1) + Na$^+$		−0.89	80	
(2)	1650	−0.96[e]	80	70
(2) + Na$^+$		−0.89[e]	60	
(3)	1635	−1.32	80	320
(3) + Na$^+$		−1.00	80	
(4)	1640	−1.28	80	280
(4) + Na$^+$		−1.00	80	
(5)	1640	−1.24	100	180
(5) + Na$^+$		−1.06	100	

[a] KBr disc. [b] Obtained at a Pt bead electrode in acetonitrile solutions containing 0.2 M $[Bu^n_4N]BF_4$ supporting electrolyte with a standard calomel electrode as reference at 0.3 V s^{-1} scan rate with and without $NaBPh_4$ added in 1 : 1 molar ratio to the complex present at concentrations in the range (2—3) × 10^{-3} M. [c] Difference between cathodic and anodic peak potentials. Typical values for ferrocene were found to be 80—100 mV. $E_{\frac{1}{2}}$, ΔE_p, and $\Delta E_{\frac{1}{2}}$ values were obtained without compensation for cell resistance. [d] Change in $E_{\frac{1}{2}}$ value produced by $NaBPh_4$ addition. [e] Values are for a two-electron process associated with two negligibly interacting redox sites in the molecule. They represent the centre of the wave and not the true $E_{\frac{1}{2}}$ values of the two one-electron transfers which were not resolved.

binding of Na$^+$ to the cyclic polyether moiety as have been described by other workers.[2—4] The 400 MHz ^{1}H n.m.r. spectra of **(3)**, **(4)**, and **(5)** were also measured in $CDCl_3$ solution. As has been noted previously,[10] the methylene protons adjacent to the molybdenum-bound oxygen atoms appeared as AB pairs shifted to low field. In the case of **(5)** for example these protons appeared as quintets at δ 5.42 and 5.72. After the addition of an excess of $NaBPh_4$ these signals were shifted upfield to δ 4.67 and 4.94 respectively. Similar effects were found on adding $NaBPh_4$ to $CDCl_3$ solutions of **(3)** and **(4)**. Changes were also apparent in the signals attributable to the pyrazoyl methyl groups in L. In the case of **(5)** these appeared as two resonances in the area ratio 12 : 6 at δ 2.30 and 2.53. After the addition of $NaBPh_4$ they appeared as four resonances of area ratio 3 : 6 : 3 : 6 at δ 2.26, 2.37, 2.39, and 2.51. Again similar changes were observed in the ^{1}H n.m.r. spectra of **(3)** and **(4)**.

We were particularly interested in the effect of Na$^+$ binding to these molecules on the redox properties of the $\{Mo(NO)\}^{3+}$ centre. The electrochemistry of the new complexes was investigated in acetonitrile solution by cyclic voltammetry with $[Bu^n_4N]BF_4$ as the supporting electrolyte. Cyclic voltammograms were also recorded after adding $NaBPh_4$ to the solutions and the results obtained are presented in Table 1, along with the nitrosyl stretching frequencies of **(1)**—**(5)**. The ν_{NO} values and reduction potentials of the new compounds were consistent with their formulations as chloro-mono-arylamide [**(1)** and **(2)**] or bis-alkoxide [**(3)**—**(5)**] derivatives containing the $\{Mo(NO)L\}^{2+}$ moiety.[12—15] The addition of $NaBPh_4$ in 1 : 1 molar ratio produced respective anodic shifts of 60 and 70 mV in the reduction potentials of **(1)** and **(2)**. More substantial effects were found with **(3)**—**(5)** with the smallest polyether ring giving rise to the largest anodic shift of 320 mV in $E_{\frac{1}{2}}$. The addition of $NaBh_4$ in 1 : 1 molar ratio to solutions containing $[Mo(NO)L(OEt)_2]$ produced a shift of only 40 mV while no detectable shift was found under similar conditions using $[Mo(NO)LCl\{NHC_6H_3(OMe)_2\text{-}3,4\}]$.

Studies of the effect of aryl substituents, Z, on the reduction potentials of $[Mo(NO)L(NHC_6H_4Z)]$ have demonstrated a linear relationship between $E_{\frac{1}{2}}$ and the Hammett σ parameter for Z.[15,16] On the basis of these findings, the binding of Na$^+$ to **(1)** produced an anodic shift in $E_{\frac{1}{2}}$ equivalent to a change in σ of 0.16. It is interesting to compare the results obtained using **(3)**—**(5)** with those reported[11] for **(6)**. The molybdenum redox centre is rather more sensitive to cation binding than the quinone moiety for which the largest reported shift was 130 mV. Furthermore these effects described here were observed at 1 : 1 mole ratios of Na$^+$ to complex whereas, in the case of **(6)**, Na$^+$ was present in large excess as a component of the supporting electrolyte.

Although we have yet to establish the selectivity of these new complexes for alkali metal or organic cation substrates, the results obtained so far do demonstrate that substrate binding can significantly affect the redox potentials of the $\{Mo(NO)\}^{3+}$ centres present to an extent which depends on the structure of the host molecule. These prototype compounds suggest the promise of future reagents which may effect stereospecific electron transfer reactions on bound organic substrates.

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