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COMMUNICATION

The syntheses, electrochemistry and magnetism of some paramagnetic metallomacrocycles containing molybdenum(V) centres

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Abstract—The reactions between $[Mo(=O)\{HB(3,5\text{-}Me_2pz)_3\}Cl_2]$ and the bifunctional ligands $1,3\text{-}(HO)_2C_6H_4$ ($\mathbf{1H_2}$), $1,3\text{-}(HS)_2C_6H_4$ ($\mathbf{2H_2}$), $2,7\text{-}(HO)_2C_{10}H_6$ ($\mathbf{3H_2}$) and $4,4'\text{-}\{(HO)C_6H_4\}_2CH_2$ ($\mathbf{4H_2}$) afford the metallomacrocycles. $[Mo(=O)\{HB(3,5\text{-}Me_2pz)_3\}X]_2$. (X = **1, 2, 3** and **4**) and $[Mo(=O)\{HB(3,5\text{-}Me_2pz)_3\}X]_3$ (X = **1, 3** and **4**). Electrochemical studies provide evidence for the presence of strongly interacting metal centres in the resorcinol bridged species. © 1997 Elsevier Science Ltd

Keywords: macrocycle; cyclophane; molybdenum(V); electrochemistry; magnetism.

The potential uses of transition metal centres in the construction of cyclophanes [1] have only recently been recognised and the number of metal centres which have been shown to form metallocyclophanes is still limited, though increasing. The metallocyclophanes known to date are, for the most part, diamagnetic. Many have been prepared using metals in the lower oxidation states (I) or (II) and with coordination number four. In particular square planar Cu^{II}, Pd^{II} or Pt^{II} centres, or tetrahedral Cu^{I} centres, have been used [2–5]. Examples of metallocyclophanes containing octahedral W^0 and Re^I centres have also been reported [6,7] and some of the earlier work on metallomacrocycles provides examples containing eight coordinate Zn^{IV} centres [8]. In our laboratory we have demonstrated the formation of metallocyclophanes using $\{M(NO)\}^{3+}$ (M = Mo, W) moieties, which formally contain Mo^{II} in octahedral sites [9]. In seeking to extend the range of metal oxidation states present in metallocyclophanes and introduce paramagnetic centres we have attempted to synthesise new examples incorporating octahedral Mo(V) centres.

Unlike $[Mo(tp^*)(NO)I_2]$, which reacts readily with $1,3\text{-}HECH_2C_6H_4CH_2EH$ (E = O, S) and $1,4\text{-}HECH_2C_6H_4CH_2EH$ to form the bimetallomacrocycles $[Mo(tp^*)(NO)(ECH_2C_6H_4CH_2E)]_2$ [9,10], the reactions of $[Mo(tp^*)(=O)(Cl)_2$ [11] with these proligands failed to afford macrocyclic products. More promising results were obtained with the bifunctional proligands $1,3\text{-}(HO)_2C_6H_4$ ($\mathbf{1H_2}$), $1,3\text{-}(HS)_2C_6H_4$ ($\mathbf{2H_2}$), $2,7\text{-}(HO)_2C_{10}H_6$ ($\mathbf{3H_2}$), and $4,4'\text{-}\{(HO)C_6H_4\}_2CH_2$ ($\mathbf{4H_2}$) (Fig. 1). Initially one step reactions between $[Mo(tp^*)(=O)(Cl)_2]$ and the bifunctional proligand were conducted in the presence of NEt_3 and/or $Ag(O_2CMe)$, which were added to stimulate the substitution of chloride. Mass spectrometric studies of the products of these reactions showed that bimetallomacrocycles were being formed but these could only be separated from the other reaction products in very low yields. The prior synthesis of the bimetallic complexes $[\{Mo(tp^*)(=O)(Cl)\}_2(\mathbf{BL})]$ (**BL** = **1** and **4**) followed by reaction with further BLH_2 gave improved yields of $[\{Mo(tp^*)(=O)\}(\mathbf{BL})]_2$ (**BL** = **1** and **4**) although these were still low being *ca* 5% overall from $[Mo(tp^*)(=O)(Cl)_2]$. In the case of $3H_2$ prior synthesis of the monometallic precursor $[\{Mo(tp^*)(=O)(Cl)\}(\mathbf{3H})]$ followed by reaction with further $3H_2$ afforded $[\{Mo(tp^*)(=O)\}_2(\mathbf{3})]_2$ in 2% overall yield. These yields are much lower than those obtained using [Mo(tp*)

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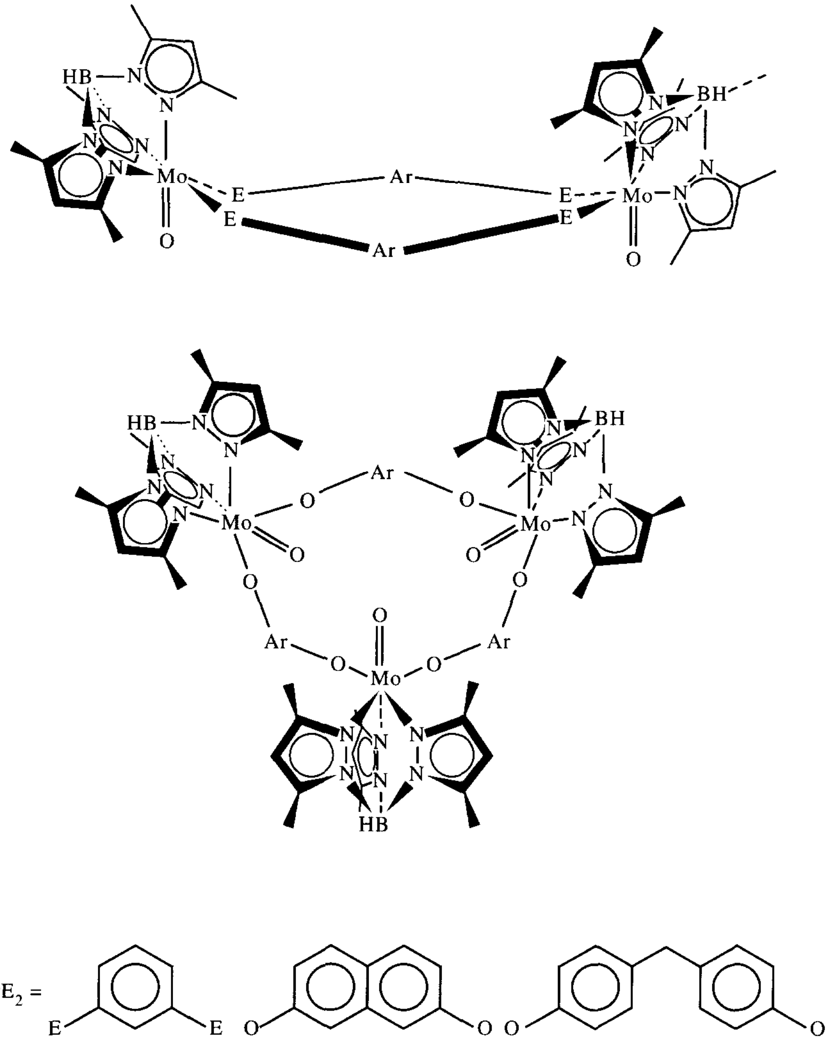
(NO)I$_2$] or [Mo(tp*) (NO)Cl$_2$] in similar reactions. Subsequently improved yields of metallomacrocycles were obtained by treating a solution of **BL**H$_2$ in toluene with sodium before adding [Mo(tp*)(NO)(Cl)$_2$]. Using this approach it was possible to isolate [{Mo(tp*) (=O)}$_2$(**BL**)]$_2$ (**BL** = **1**, 15%; **2**, 41%; **3**, 18%; **4**, 12%) as well as the cyclic trimers [{Mo(tp*)(=O)}$_2$(**BL**)]$_3$ (BL = **1**, 9%; **3**, 11%; **4**, 7%) [12,13].

As expected, the complexes are paramagnetic and their magnetic susceptibilities have been measured over the range of 6–300K using a SQUID magnetometer. In all cases Curie–Weiss law behaviour is seen below 100K. The χT *vs* T plots indicate a temperature dependence for the magnetic moment in all cases except for the cyclic trimer [{Mo(tp*)(=O)}(**4**)]$_3$, which exhibits no temperature dependence. The curvature observed in the other χT *vs* T plots is in keeping with antiferrimagnetic exchange between the formally d^1 Mo^V centres and the nature and extent of this coupling is being further investigated. The room temperature solution EPR spectra of [{Mo(tp*)(=O)}$_2$(**BL**)]$_2$ (**BL** = **1**, **3**, **4**) and [{Mo(tp*)(=O)}$_2$(**BL**)]$_3$ (**BL** = **1**, **4**) exhibit signals at g = 1.93 which show some hyperfine interactions but have widely differing linewidths. Further studies are in progress to produce a detailed analysis of the EPR data and of the solid state magnetic properties of these materials.

Previously Enemark and co-workers have reported that [Mo(tp*)(=O)(OPh)$_2$] undergoes a chemically reversible one-electron reduction in MeCN at −0.88 V (vs Ag/AgCl) [11]. This reduction is metal centred and assigned to the Mo^V/Mo^{IV} couple. Furthermore, the acyclic dinuclear complex [{Mo(tp*)(=O)(Cl)}$_2$ (**1**)] has been shown to undergo two stepwise one electron reductions at −1.2 and −1.4 V (CH$_2$Cl$_2$ *vs*



E =0: 1
S: 2

3

4

Fig. 1. Structural formulae of the new compounds

SCE), both reductions being metal centred and therefore involving the Mo^{V}/Mo^{IV} couple [14]. The cyclic dimer [Mo(tp*)(=O)(**1**)]$_2$ should therefore exhibit two stepwise one-electron reductions and the cyclic trimer [Mo(tp*)(=O)(**1**)]$_3$ three stepwise one-electron reductions. This would be in keeping with results obtained for metallomacrocycles containing the {Mo(NO)Tp*}$^{2+}$ centre [9d]. This is in fact observed and the cyclic voltammogram of [Mo(tp*)(=O)(**1**)]$_2$ contains two reversible reduction processes at $E_f = -0.92$ and -1.24 V (CH$_2$Cl$_2$ *vs* SCE; *Fc*/*Fc*$^+$ $E_f = +0.55$ V). The negative shift of the potential for the second reduction process is 120 mV more than for the acyclic dimer [{Mo(tp*)(=O)(Cl)}$_2$(**1**)]. Thus the presence of a second bridging ligand significantly increases the degree of coupling between the two metal centres. In the case of [Mo(tp*)(=O)(**1**)]$_3$ three reduction processes are observed at $E_f = -1.03$, -1.23 and -1.46 V. These results are similar to those obtained with the diamagnetic Mo(II) complexes [Mo(tp*)(NO)(**1**)]$_n$ (n = 2, 3) [9,15]. In the complexes containing a saturated bridge in the form of —OC$_6$H$_4$CH$_2$C$_6$H$_4$O— (**4**) the metal–metal interactions will be attenuated compared to the resorcinol bridged complexes. In accord with this expectation only a single broadened reduction wave is observed at $E_f = -1.08$ V for the cyclic dimer [Mo(tp*)(=O)(**4**)]$_2$ and $E_f = -0.98$ V for the cyclic trimer [Mo(tp*)(=O)(**4**)]$_3$. Earlier work on complexes containing the {Mo(tp*)(NO)}$^{2+}$ redox centre has indicated that the electrochemical behaviour of thiolate complexes such as [Mo(tp*)(NO)(SPh)$_2$] [16] and [{Mo(tp*)(NO)(Cl)}$_2$(**2**)] [17] is very similar to that of their oxygen containing counterparts [Mo(tp*)(NO)(OPh)$_2$] [16] and [{Mo(tp*)(NO)(Cl)}$_2$(**1**)] [17]. However, this similarity does not extend to the Mo(V) complexes [Mo(tp*)(=O)(**1**)]$_2$ and [Mo(tp*)(=O)(**2**)]$_2$. The cyclic voltammogram of the latter complex contains two reduction waves at -0.48 and -0.60 V (CH$_2$Cl$_2$ *vs* SCE; *Fc*/*Fc*$^+$ $E_f = +0.55$ V), respectively some 430 and 640 mV more positive than for their oxygen containing counterparts. This shift is in accord with the potentials reported earlier [11] for [Mo(tp*)(=O)(OPh)$_2$] (-0.877 V, *vs* Ag/AgCl) and [Mo(tp*)(=O)(SPh)$_2$] (-0.282 V *vs* Ag/AgCl). Consistent with the stronger π-donating properties of oxygen in the Mo^{V} systems producing more negative reduction potentials, the oxygen ligand **1** supports a larger separation between the reduction processes ($\Delta E_f = 320$ mV) than the sulphur ligand **2** ($\Delta E_f = 115$ mV), although these figures must be treated with some caution as the reduction processes for [Mo(tp*)(=O)(**2**)]$_2$ do not appear to be fully reversible. The presence of a 2,7-naphthalenediyl bridge in place of 1,3-benzenediyl leads to an expected reduction in the metal-metal interaction as judged from the difference between successive reduction potentials. Thus reduction potentials are observed at $E_f = -0.86$ and -1.07 V for the cyclic dimer [Mo(tp*)(=O)(**3**)]$_2$ and at $E_f = -0.90$, -1.01 and -1.14 V for the cyclic trimer [Mo(tp*)(=O)(**3**)]$_3$.

The results described here establish that paramagnetic redox active metallocyclophanes containing the Mo(V) {Mo(tp*)(=O)}$^{2+}$ centre can be prepared from [Mo(tp*)(=O)(Cl)$_2$], although the syntheses are more problematic than for their counterparts containing the Mo(II) {Mo(tp*)(NO)}$^{2+}$ centre. Significant metal–metal interactions can be detected electrochemically in the Mo^{V} compounds as for the Mo^{II} compounds but the former show a dependence on donor atom type, on going from oxygen to sulphur, not seen in the Mo(II) systems. Preliminary magnetic measurements suggest that magnetic interactions are occurring and these are the subject of further study.

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12. As the compounds are paramagnetic they have been characterised by IR spectroscopy, mass spectrometry and elemental analyses for C, H and N. The IR spectra of the new complexes all contain bands attributable to the presence of the tp* ligand including ν_{max}(B–H) at 2550 cm^{-1} and to the bridging aryl group. In each case a band attributable to ν_{max}(Mo=O) is also present in the range 935–950 cm^{-1}. Satisfactory elemental analyses have also been obtained and mass spectra contain molecular ions at *m*/*z* values in accord with their formulations. The absence of ions attributable to higher cyclic oligomers confirm that single cyclic oligomers have been isolated in the cases of the bimetallomacrocycles. Thin layer chromatographic measurements confirm that the cyclic trimers are free of the cyclic dimers which have different R_f values. The complexes also exhibit EPR spectra in accord with the presence of paramagnetic Mo(V) centres. One isomer of [{Mo(tp*)(=O)}(**1**)]$_2$ have been isolated. Preliminary single crystal X-ray diffraction studies [13] show it to be the *syn*-isomer. Only one isomer of [{Mo(tp*)(=O)}(**3**)]$_2$ has been isolated but two isomers of [{Mo(tp*) (=O)}(**4**)]$_2$ have been separated, each in 6% yield. The isomeric distribution in the cyclic trimers has not yet been determined.
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