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THE SYNTHESES OF SOME PARAMAGNETIC STILBAZOLE COMPLEXES AND AN EVALUATION OF THEIR REDOX AND MESOGENIC PROPERTIES

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Abstract—The paramagnetic complexes [Mo(NO)(Tp*)Cl(NC$_5$H$_4$-4-{CH═CHC$_6$H$_4$-4′-OC$_n$H$_{(2n-2)}$})] {Tp* = HB(3,5-Me$_2$C$_3$HN$_2$)$_3$; n = 6, 8, 12} have been synthesized and characterized by spectroscopic methods. Polarizing hot stage microscopy studies provided no evidence of mesogenic phases.

Liquid crystal materials are important components in many electronic devices[1] and, because of their anisotropic properties, they have the potential to exhibit second-order non-linear optical properties. Many stilbene and stilbazole based compounds form liquid crystal mesophases and, recently, it has been shown that metal–organic complexes based on such ligands can also form mesophases.[2] Furthermore, such materials can form L.B. films and, in non-centric fabrications, these give rise to second-order NLO materials.[3,4] We have been investigating the possibility that redox active molybdenum mononitrosyl centres might be incorporated into molecules that form mesophases by preparing complexes containing suitably substituted ligands. However, attempts to produce diamagnetic liquid crystal materials based on alkoxystilbenol or alkoxystilbenamine derivatives containing the 16-electron {Mo(NO)Tp*Cl}$^+$ moiety have proven unsuccessful,[5] although related materials have been shown to display high efficiencies for Second Harmonic Generation (SHG).[6] If, instead of aryloxo- or arylamido-ligands, neutral ligands such as pyri-

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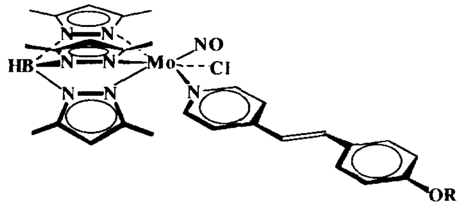
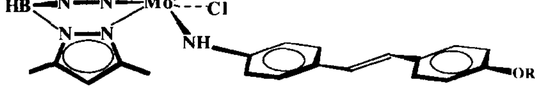
dine are attached to the {Mo(NO)Tp*Cl} group, paramagnetic 17-electron complexes are obtained.[7,8] Although, at first sight, 17-electron alkoxystilbazole complexes such as $[Mo(NO)Tp^*Cl(NC_5H_4\text{-}4\text{-}CH{=}CH\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{(2n+1)})]$ (Fig. 1) might appear structurally similar to 16-electron alkoxystilbenamide complexes such as $[Mo(NO)Tp^*Cl(NHC_6H_4\text{-}4\text{-}CH{=}CH\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{(2n+1)})]$, the removal of the amide NH and the direct attachment of the pyridyl ring to the metal will cause substantial changes in the molecular geometry. In order to assess whether or not such structural changes might be beneficial in producing metallomesogens three new complexes have been prepared and studied using polarizing hot stage microscopy.

RESULTS AND DISCUSSION

The 17-electron complex $[Et_3NH][Mo(NO)Tp^*Cl_2]$, which is known to react with pyridine and pyridyl based ligands,[7] was reacted with the stilbazoles, $NC_5H_4\text{-}4\text{-}CH{=}CHC_6H_4OC_nH_{(2n+1)}\text{-}4'$ ($n = 6$, 8, and 11), to produce a series of monometallic complexes. Optimal reaction conditions for the preparations were found to be the same in all three cases. The ligands and excess $[Et_3NH][Mo(NO)Tp^*Cl_2]$, generated *in situ*, were mixed together in refluxing toluene and heated for 3 h. The products were then separated by column chromatography, using silica gel as a stationary phase and a 99/1 v/v dichloromethane/THF mixture as an eluent. All the reactions produced $[\{Mo(NO)Tp^*Cl\}_2(\mu\text{-}O)]$ as a by-product, suggesting that water was present in the reaction mixture. Yields were improved when the stilbazole ligands used for the reaction were dried *in vacuo* before use, although some $[\{Mo(NO)Tp^*Cl\}_2(\mu\text{-}O)]$ was still found in the reaction products. Yields for all three metal organic complexes were similar and elemental analyses of the products were in agreement with the expected formulations (Table 1).



a) R = C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$



b) R = C_6H_{13}, C_8H_{17}, $C_{11}H_{23}$

Fig. 1. (a) Structural formula of $[Mo(NO)Tp^*Cl(NC_5H_4\text{-}4\text{-}CH{=}CH\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{(2n+1)})]$ ($n = 6$, 8, 11); (b) structural formula of $[Mo(NO)Tp^*Cl(NC_5H_4\text{-}4\text{-}CH{=}CH\text{-}C_6H_4\text{-}4'\text{-}OC_nH_{(2n+1)})]$ ($n = 6$, 8, 12).[5]

The IR spectra of the complexes (Table 1) displayed the expected absorbances due to the ligand Tp* in particular $\nu_{max}(BH)$ was observed at 2550 cm^{-1}. All three complexes showed $\nu_{max}(NO)$ at *ca* 1600 cm^{-1}, in accord with their formulation as complexes containing the reduced, 17-electron {Mo(NO)Tp*Cl} group.[7–10] A band was also observed at *ca* 1540 cm^{-1} and attributed to the presence of the ethene C=C bond in the stilbazole ligand. The FAB mass spectra (Table 1) of the compounds contained molecular ions in addition to ions attributable to the loss of Cl from the molecular ion. Ion envelopes were also observed based at $m/z = 460$ due to the $\{Mo(NO)Tp^*Cl\}^+$ ion. The paramagnetic nature of the complexes resulted in their having essentially featureless ^1H NMR spectra. However, well-resolved EPR spectra were obtained from solutions at room temperature. In each case these contained a central single line signal at $g_{iso} = 1.970$ due to molecules containing molybdenum isotopes with $I = 0$, along with a sextet with $A_{iso} = 49 \times 10^{-4}\ cm^{-1}$ due to molecules containing ^{95}Mo or ^{97}Mo (total natural abundance 25.5%) with $I = 5/2$. No hyperfine coupling to any other nuclei was observed.

The UV–visible spectra of the new stilbazole complexes, obtained from dichloromethane solutions, all contain a band at 230 nm which is also present in the spectrum of Tp^{*-} and may be attributed to a π–π^* transition in this ligand. In contrast to $[Mo(NO)Tp^*(py)_2]^+$, which exhibits only weak absorptions attributed[9] to *d–d* transitions at 590 and 425 nm, each of these new complexes exhibit rather more intense absorptions at 564, 475 and 430 nm. If these bands are also *d–d* in character then the reduced molecular symmetry must lead to some relaxation of the selection rules governing the transition. Alternatively, they may involve a charge transfer process. In $[Mo(NO)Tp^*Cl(py)]$ bands are observed at 620 and 468 nm with respective molar absorbances of 150 and 1250 $dm^3\ mol^{-1}\ cm^{-1}$ but in $[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_5H_4N)\}]$ there is a band at 566 nm ($\varepsilon = 1250\ dm^3\ mol^{-1}$

Table 1. Data for the complexes $[Mo(NO)Tp^*Cl\{NC_5H_4CH{=}CHC_6H_4OC_nH_{(2n+1)}\}]$

Compound n	Elemental analysis[a] [molecular ion] (m/z)	IR data[b] ν_{max} (cm^{-1})	Electronic spectrum[c] λ_{max} (nm)	 ε ($dm^3\ mol^{-1}\ cm^{-1}$)	Electrochemical data[d] E_f (V)	 ΔE_p (mV)
6	55.1; 6.2; 14.7	1600 (NO)	564	1370	−1.280	85
(55.2)(6.1)(15.1)	1540 (C=C)	475	4111		0.603	75
	[739]		431	4453		
			363	41159		
			285	11209		
8	56.0; 6.2; 14.3	1600 (NO)	564	1329	−1.275	70
(56.3)(6.2)(14.3)	1535 (C=C)	475	3989		0.603	70
	[767]		430	4039		
			361	30600		
			287	10258		
11	57.5; 6.8; 13.4	1600 (NO)	564	1356	−1.263	75
(57.8)(6.9)(13.8)	1540 (C=C)	475	4173		0.605	75
	[809]		430	4376		
			365	34421		
			284	10874		

[a] Elemental analyses as found % and (calculated %) followed by base peak of molecular ion envelope [m/z].

[b] Recorded from KBr discs.

[c] Recorded from solutions in CH_2Cl_2 at room temperature.

[d] E_f (± 0.005 V) and ΔE_p (± 10 mV) were determined at a scan rate of 50 mV s^{-1} and E_f is quoted relative to the S.C.E.; under the conditions used the ferrocene/ferrocenium couple, used as an internal standard, had $E_f = 0.560$ V vs S.C.E. and $\Delta E_p = 70$ mV.

cm^{-1}) but no other absorbance until 298 nm. Solvatochromism studies of $[\{Mo(NO)Tp^*Cl\}_x\{NC_5H_4\text{-}4\text{-}(CH{=}CH)_4\text{-}C_5H_4N\text{-}4'\}]$ ($x = 1$, 2) have shown that, in these complexes, an absorption band in the region 540–600 nm is attributable to a MLCT process.[11] Therefore, it seems reasonable to assume that the bands between 430 and 560 nm in the spectra of the stilbazole complexes might similarly be assigned to MLCT transitions. These spectra also contain an intense band at 360–365 nm which, by comparison with the spectrum of the free stilbazole ligand, may be assigned to an intraligand π–π^* transition.

Electrochemical studies

The electrochemistry of the new complexes was investigated using cyclic voltammetry. All three complexes displayed both a reduction and an oxidation process, each involving one electron. The oxidation waves were observed at $E_f = 0.60$ V (Table 1) and the shape parameter ΔE_p was found to vary with sweep rate suggesting that the oxidations were not fully reversible. The value of i_p^a/i_p^c was close to unity for this couple so the process appears to be chemically reversible. This oxidation potential is similar to those of 0.598, 0.590 and 0.600 V found[12] respectively for $[Mo(NO)Tp^*Cl(NC_5H_5)]$, $[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_5H_4N\text{-}4')\}]$ and $[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH_2CH_2C_5H_4N\text{-}4')\}]$, indicating that changes in the nature of the pyridyl ligand do not have a significant affect on the oxidation potential in these examples. The reduction couples of the new complexes were found to be quasi-reversible (Table 1), all appearing at about the same potential (1.275 ± 8 mV), which is intermediate between the values reported for the corresponding monometallic complexes containing the bipyridyl ethene (−1.093 V) and bipyridyl ethane (−1.455 V) ligands.[7b] Molecular orbital calculations on the free ligands using the AM1 MO method of the MOPAC package[13] show that the LUMO (π^*-orbital) of the stilbazole, which is the acceptor orbital in the MLCT, is intermediate in energy between those of bipyridyl ethane and bipyridyl ethene (Fig. 2); whereas the HOMO (filled π-orbital) is higher in energy than in pyridine or these two bipyridyl derivatives. This may be the result of π-donation from the alkoxy group increasing the LUMO energy and reducing the π-acceptor capacity of the substituted stilbazoles. Similar π-donation effects have been proposed to account for the small aryl–aryl torsion angle in $[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(C_6H_4\text{-}4'\text{-}OMe)\}]$.[14] The trend in

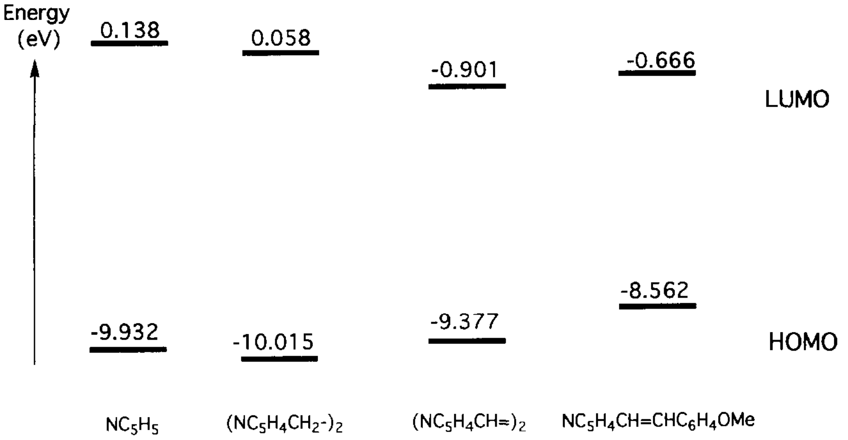


Fig. 2. Schematic representation of the calculated HOMO and LUMO energies in the free ligands NC_5H_5, NC_5H_4-4-($CH_2CH_2C_5H_4N$-4′), NC_5H_4-4-(CH=CH-C_5H_4N-4′), and NC_5H_4-4-(CH=CH-C_6H_4-4′-OCH_3).

reduction potentials for the stilbazole complexes qualitatively follows that of the LUMO energy in the free ligands, rather than that of the HOMO. This suggests that the LUMO of the complex contains some ligand LUMO character and that the stilbazole functions as a π-acceptor ligand towards the 17-electron molybdenum centre rather than as a π-donor.

Testing for mesogenic properties

The three complexes were examined in the Sheffield Centre for Molecular Materials, Department of Chemistry, University of Sheffield, using the technique of polarizing hot stage microscopy. However, on heating, no mesophases were observed before the complexes melted with decomposition.

That liquid crystal mesophases were not observed for these complexes is not entirely surprising. Despite the ability of stilbazoles to coordinate to metals producing mesomorphic complexes, the head group, {Mo(NO)Tp*}, is very large and will destroy the anisotropy required for mesophase formation. That this is so is demonstrated by complexes obtained using related stilbazoles coordinated to {$W(CO)_5$} where some evidence for mesophase formation was obtained.[15] However, the stilbazole used was much longer and the head group, {$W(CO)_5$}, much smaller than those described here. Indeed, long, strongly mesomorphic rod-like ligands would appear to be important in forming liquid-crystals based on high coordination number metal centres.[16]

CONCLUSIONS

The electrochemical properties of the new complexes demonstrate how the reduction couple of the {Mo(NO)Tp*Cl} centre in these 17-electron systems is dependent on the nature of the co-ligands bound to the metal, pyridyl ligands with greater π-acceptor capacity giving rise to more anodic reduction potentials. The EPR spectra indicate that the unpaired electron in these paramagnetic complexes is located in a metal-based orbital and no evidence is seen to suggest that it is delocalized on to the stilbazole ligand in the ground state. Unfortunately no mesogenic properties have been observed. This probably results from the bulky nature of the {Mo(NO)Tp*Cl} terminus which destroys the inherent liquid crystal forming capacity of the alkoxy stilbazole ligand to which it is bound. Thus, whilst the steric bulk of the {Mo (NO)Tp*Cl} terminus can have favourable effects in forming second-order NLO materials,[6,17] it apparently does not have a favourable influence on the formation of mesogenic materials.

EXPERIMENTAL

The stilbazole ligands used were synthesized and fully characterized in Sheffield and were used without further purification.[18] [Mo(NO)Tp*Cl_2] was prepared according to a previously reported method.[19] Toluene used as reaction medium was dried and freed of oxygen before use by distillation from sodium/benzophenone under dinitrogen. Reactions were carried out under nitrogen but purification procedures were carried out in air. Silica Gel 60 (70–230 mesh) was used as the stationary phase for column chromatography. Elemental analyses were carried out by the Microanalytical Laboratories in the School of Chemistry at the University of Birmingham.

IR spectra were recorded using KBr pellets and a Perkin–Elmer PE297 spectrometer, 270MHz ^1H NMR spectra were obtained from solutions in $CDCl_3$ using a JEOL GX 270 spectrometer and FAB mass spectra were recorded from a NOBA matrix using a Kratos MS80 spectrometer. UV–visible spectra were obtained using a Shimadzu UV-240 or Perkin–Elmer 13 spectrometer. Solvent background corrections were made in all cases. Cyclic voltammetric measurements were made using a Pt bead electrode with a PAR 174A polarograph and 10^{-3} mol dm^{-3} solutions of complex in CH_2Cl_2 containing 0.2 mol dm^{-3} $[Bu_4N][BF_4]$ as base electrolyte. Values are quoted relative to the S.C.E. but ferrocene was also added and used as an internal standard. Electron paramagnetic resonance spectra were obtained using a Bruker ESP 300 spectrometer. Samples were dissolved in a dichloromethane/toluene mixture as solvent.

$[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_6H_{13})\}]$

$[Mo(NO)Tp^*Cl_2]$ (300 mg, 0.61 mmol) and $NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_6H_{13})$ (140.7 mg, 0.5 mmol) were added to toluene (60 cm^3) containing triethylamine (0.5 cm^3). The mixture was stirred and heated under reflux for 2 h and the toluene removed by evaporation *in vacuo*. The resulting solid was redissolved in dichloromethane and the solution passed down a silica gel chromatography column using 99:1 v/v dichloromethane/THF as the eluent. The main red-brown fraction was collected and the solvent was removed *in vacuo* to give a black solid (174 mg, 47% with respect to the ligand).

$[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_8H_{17})\}]$

This was prepared in a similar manner to the previous compound using $NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_8H_{17})$ (154.75 mg, 0.5 mmol) and $[Mo(NO)Tp^*Cl_2]$ (300 mg, 0.61 mmol) to give $[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_8H_{17})\}]$ (155 mg, 44% with respect to the ligand).

$[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_{11}H_{23})\}]$

This was prepared in a similar manner to the previous compound using $NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_{11}H_{23})$ (176 mg, 0.5 mmol) and $[Mo(NO)Tp^*Cl_2]$ (300 mg, 0.61 mmol) to give $[Mo(NO)Tp^*Cl\{NC_5H_4\text{-}4\text{-}(CH{=}CHC_6H_4\text{-}4'\text{-}OC_{11}H_{23})\}]$ (132 mg, 33% with respect to the ligand).

REFERENCES

1. L. M. Blinov, *Electro-optical and Magneto-optical Properties of Liquid Crystals*. Wiley Interscience, Chichester (1983); G. W. Gray (Ed.), *Thermotropic Liquid Crystals*. Wiley, Chichester (1987).
2. D. W. Bruce, *J. Chem. Soc., Dalton Trans.* 1993, 2983; D. W. Bruce, in *Inorganic Materials* (Edited by D. W. Bruce and D. O'Hare), Chapter 8, p. 407. Wiley, Chichester (1992).
3. D. W. Bruce and A. Thornton, *Mol. Cryst. Liq. Cryst.* 1993, **231**, 253.
4. (a) T. Richardson, A. Topaçli, W. H. Abd Majid, M. B. Greenwood, D. W. Bruce, A. Thornton and J. R. Marsden, *Adv. Mater. Opt. Electron.* 1994, **4**, 243; (b) T. Richardson, A. Topaçli, W. H. Abd Majid, M. B. Greenwood, D. W. Bruce, A. Thornton and J. R. Marsden, *Int. J. Elec.*, in press.
5. (a) B. J. Coe, C. J. Jones, J. A. McCleverty and D. W. Bruce, *Inorg. Chem. Acta*, 1993, **206**, 41; (b) B. J. Coe, C. J. Jones, J. A. McCleverty and D. W. Bruce, *Polyhedron* 1993, **12**, 45.
6. (a) B. J. Coe, C. J. Jones, J. A. McCleverty, D. Bloor, P. V. Kolinsky and R. J. Jones, *J. Chem. Soc., Chem. Commun.* 1989, 1485; (b) B. J. Coe, Ph.D Thesis, University of Birmingham (1991).
7. (a) N. Al-Obaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty, K. Paxton, A. J. Howes and M. B. Hursthouse, *Polyhedron* 1988, **7**, 1931; (b) S. L. W. McWhinnie, C. J. Jones, J. A. McCleverty, D. Collison and F. E. Mabbs, *J. Chem. Soc., Chem Commun.* 1990, 940.
8. S. L. W. McWhinnie, C. J. Jones, J. A. McCleverty, D. Collison and F. E. Mabbs, *Polyhedron* 1993, **11**, 2639.
9. N. Al. Obaidi, A. J. Edwards, C. J. Jones, J. A. McCleverty, B. D. Neaves, F. E. Mabbs and D. Collison, *J. Chem. Soc., Dalton Trans.* 1989, 127.
10. J. A. McCleverty, *Chem. Soc. Rev.* 1983, **12**, 331.
11. J. A. Thomas, C. J. Jones, J. A. McCleverty, D. Collison, F. E. Mabbs, C. J. Harding and M. G. Hutchings, *J. Chem. Soc., Chem Commun.* 1990, 940; J. A. Thomas, C. J. Jones, J. A. McCleverty and M. G. Hutchings, unpublished results; J. A. Thomas, Ph.D Thesis, University of Birmingham (1993).
12. S. L. W. McWhinnie, Ph.D Thesis, University of Birmingham (1989).
13. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. Stewart, *J. Am. Chem. Soc.* 1985, **107**, 3902; QCPE Program 455 Version 6.0, Department of Chemistry, Indiana University, Bloomington, IN 47405, U.S.A.
14. A. Das, J. C. Jeffrey, J. P. Maher, J. A. McCleverty, E. Schatz, M. D. Ward and G. Wollermann, *Inorg. Chem.* 1993, **32**, 2145.

15. D. W. Bruce and J. P. Rourke, *J. Organomet. Chem.*, submitted.
16. (a) D. W. Bruce and X.-H. Liu, *J. Chem. Soc.*, *Chem. Commun.* 1994, 729; (b) D. W. Bruce, *Adv. Mater.* 1994, **6**, 1017.
17. (a) B. J. Coe, C. J. Jones, J. A. McCleverty, D. Bloor, P. V. Kolinsky and R. J. Jones, *Polyhedron* 1994, **13**, 2107; (b) B. J. Coe, C. J. Jones, J. A. McCleverty, D. Bloor and G. H. Cross, *J. Organomet. Chem.* 1994, **464**, 225; (c) B. J. Coe, J.-D. Foulon, T. A. Hamor, C. J. Jones, J. A. McCleverty, D. Bloor, G. H. Cross and A. L. Axon, *J. Chem. Soc.*, *Dalton Trans.* 1994, 3427.
18. D. W. Bruce, D. A. Dunmur, E. Lalinde, P. M. Maitlis and P. Styring, *Liq. Cryst.* 1988, **3**, 385.
19. S. Trofimenko, *Inorg. Chem.* 1969, **8**, 2675.