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The synthesis, electrochemistry and thermal properties of some molybdenum mononitrosyl complexes containing oxobiphenyl ligands which incorporate long chain alkoxy substituents

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Abstract

The new complexes $Mo(NO)LX(OC_6H_4C_6H_4OR)$ ($L = HB(3,5\text{-}Me_2C_3N_2H)_3$; $X = Cl$, I, $OC_6H_4C_6H_4OR$; $R = C_6H_{13}$, C_8H_{17}, $C_{12}H_{25}$) have been synthesised and characterised by spectroscopic methods. All undergo one-electron reduction processes at potentials ranging from −0.28 V (SCE) for the mono-substituted complexes to −0.67 V for the bis-aryloxo compounds. Differential scanning calorimetry and hot-stage polarising microscopy studies of these compounds do not reveal any liquid crystalline mesophases.

Introduction

The field of metallomesogens has attracted considerable interest in recent years, and complexes of many different metals have been found to form liquid crystal mesophases [1–5]. However, we are aware of only one report of molybdenum-containing metallomesogens [6]. These contain dimolybdenum tetracarboxylate complexes and incorporate quadruply bonded Mo–Mo cores which possess potential for exhibiting redox behaviour. The complexes $Mo_2(O_2C(CH_2)_nCH_3)_4$ form discotic mesophases for $n = 3$–9, with both the onset point and the mesophase temperature range found to vary significantly with hydrocarbyl chain length. No liquid crystal behaviour was found when $n = 1$, 2 or 16. Molybdenum mononitrosyl derivatives of formula [Mo(NO)L(X)(Y)] (L = tris(3,5-dimethylpyrazolyl)hydroborate; X and Y = halide, phenoxide) are redox-active [7–9] highly coloured species which are capable of exhibiting potentially useful molecular electronic properties including non-linear optic effects [10, 11]. These characteristics might be useful if incorporated into liquid crystalline materials. The creation of liquid crystalline complexes containing bulky trispyrazolylborate ligands would also represent a significant departure from the classes of complex currently receiving attention in the metallomesogens research field. We have previously prepared the derivatives $Mo(NO)L(X)(EC_6H_4Z)$ ($E = O$, $X = Cl$, I, $Z = CO_2C_{12}H_{25}$; $E = NH$, $X = Cl$, I, $Z = C_{10}H_{21}$) in the hope of obtaining compounds which form mesophases. However, although compounds were obtained which exhibited reduced melting points, compared to their counterparts lacking long chain alkyl substituents, no mesophases were detected [12]. In a further attempt to obtain metallomesogens containing the {Mo(NO)L} moiety we have prepared complexes from the ligands 4,4′-$HOC_6H_4C_6H_4OR$ ($R = C_6H_{13}$, C_8H_{17}, $C_{12}H_{25}$) [13, 14], which are known to form thermotropic liquid crystals, and investigated their thermal properties using polarising hot-stage microscopy and differential scanning calorimetry (DSC).

Experimental

All commercial reagents were used as supplied. $Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I_2$ [15], $Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl_2$ [16] and $HOC_6H_4C_6H_4OR$ ($R = C_6H_{13}$, C_8H_{17}, $C_{12}H_{25}$) [13, 14] were prepared according to previously described methods. Solvents used as reaction media were dried according to standard methods and freed of oxygen before use. Silica gel 60 (70–230 mesh)

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was used as the stationary phase for column chromatography with dichloromethane as eluant. All reactions were carried out under nitrogen but purification procedures were carried out in air. Elemental analyses were carried out by the Microanalytical Laboratory, University of Birmingham.

IR spectra were recorded using a PE 297 spectrometer with samples as KBr discs. 270 MHz ^{1}H NMR spectra were obtained from solutions in CDCl$_3$ using a Jeol GX 270 spectrometer. Cyclic voltammetric measurements were made using a PAR 174A polarograph. Solutions in CH$_2$Cl$_2$ were *c.* 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in [Bu^{n}N]BF$_4$ as base electrolyte. A Pt bead working electrode was used with a scan rate of 200 mV s^{-1}. An SCE reference electrode was used with ferrocene as an internal standard. Potentials are quoted relative to the SCE and under these conditions E_f for the oxidation of ferrocene was found to be 0.58 V. Differential scanning calorimetry measurements were carried out using a Perkin-Elmer DSC7 instrument with samples (typically 1.4–3 mg) being hermetically sealed in 10 μl aluminium pans. In all cases heating and cooling rates of 10 K min^{-1} were used. The microscopy studies were carried out using a CZ Scientific Labpol system equipped with a Link-Am PR600 controller and TH600 hot-stage. Heating rates were 10 K min ^{1} unless otherwise stated.

[Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}Cl(OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$)] (1)

A solution of [Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}Cl$_2$] (0.30 g, 0.61 mmol), 4-n-hexyloxy-4′-hydroxybiphenyl (0.20 g, 0.74 mmol) and hexamine (0.05 g, 0.36 mmol) in toluene (20 cm^3) was stirred under reflux for 3 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The product obtained was purified by column chromatography on silica gel using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.33 g, 75%). *Anal.* Found: C, 52.2; H, 5.9; N, 13.5%; M^+, 729. Calc. for C$_{33}$H$_{43}$BClMoN$_7$O$_3$·0.4CH$_2$Cl$_2$: C, 52.7; H, 5.8; N, 12.9%; *M*, 728. ν_{max}(NO) 1680 cm^{-1}; *δ_H(CDCl$_3$) 7.61 and 6.97 (2H, d, *J*(HH) 8.8 Hz; 2H, d, *J*(HH) 8.6 Hz, C$_6$*H*$_4$–OMo), 7.56 and 7.39 (2H, d, *J*(HH) 8.8 Hz; 2H, d, *J*(HH) 8.6 Hz, C$_6$*H*$_4$–OC$_6$H$_{13}$), 5.93, 5.89, and 5.77 (1H, s; 1H, s; 1H, s, (Me$_2$C$_3$N$_2$*H*)$_3$), 4.01 (2H, t, *J*(HH) 6.6 Hz, C$_6$H$_4$–OC*H*$_2$–C$_5$H$_{11}$), 2.60, 2.42, 2.39, 2.21 and 2.09 (3H, s; 6H, s; 3H, s; 3H, s; 3H, s, (*Me*$_2$C$_3$N$_2$H)$_3$), 1.81 (2H, qn, C$_6$H$_4$OCH$_2$–C*H*$_2$–C$_4$H$_9$), 1.48 (2H, qn, C$_6$H$_4$OC$_2$H$_4$–C*H*$_2$–C$_3$H$_7$), 1.40–1.30 (4H, c m, OC$_3$H$_6$–C$_2$*H*$_4$–CH$_3$), 0.92 (3H, t, *J*(HH) 6.7 Hz, C*H*$_3$); *m/z* 729 (M^+), 699 ($M-$NO), 693 ($M-$Cl), 460 ($M-$OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$), 430 ($M-$OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}-$NO), 424 ($M-$OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}-$Cl), 270 (HOC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$), 186 (HOC$_6$H$_4$C$_6$H$_4$OH).** $E_f = -0.33$ V, $\Delta E_p = 140$ mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}I(OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$)] (2)

This compound was prepared in identical manner to **1** using [Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}(I)$_2$]·C$_7$H$_9$ (0.40 g, 0.52 mmol) instead of [Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}(Cl)$_2$] and 4-n-hexyloxy-4′-hydroxybiphenyl (0.18 g, 0.67 mmol). A deep violet solid was obtained (0.30 g, 70%). *Anal.* Found: C, 47.1; H, 5.5; N, 11.7%; M^+, 821. Calc. for C$_{33}$H$_{43}$BIMoN$_7$O$_3$·0.4CH$_2$Cl$_2$: C, 47.0; H, 5.2; N, 11.5%; *M*, 819. ν_{max}(NO) 1670 cm^{-1}; δ_H(CDCl$_3$) 7.58 and 7.51 (2H, d, *J*(HH) 9.0 Hz; 2H, d, *J*(HH) 9.0 Hz, C$_6$*H*$_4$–OC$_6$H$_{13}$), 7.56 and 6.96 (2H, d, *J*(HH) 8.8 Hz; 2H, d, *J*(HH) 8.8 Hz, C$_6$*H*$_4$O–Mo), 5.91, 5.85 and 5.84 (1H, s; 1H, s; 1H, s, (Me$_2$C$_3$N$_2$*H*)$_3$), 4.00 (2H, t, *J*(HH) 6.6 Hz, C$_6$H$_4$–OC*H*$_2$–C$_5$H$_{11}$), 2.59, 2.45, 2.40, 2.38, 2.32 and 2.01 (3H, s; 3H, s; 3H, s; 3H, s; 3H, s; 3H, s, (*Me*$_2$C$_3$N$_2$H)$_3$), 1.81 (2H, qn, C$_6$H$_4$OCH$_2$–C*H*$_2$C$_4$H$_9$), 1.48 (2H, qn, C$_6$H$_4$OC$_2$H$_4$–C*H*$_2$–C$_3$H$_7$), 1.40–1.30 (4H, c m, OC$_3$H$_6$–C$_2$*H*$_4$–CH$_3$), 0.92 (3H, t, *J*(HH) 7.0 Hz, C*H*$_3$). *m/z* 821 (M^+), 791 ($M-$NO), 694 ($M-$I), 552 ($M-$OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$), 522 ($M-$OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}-$NO), 424 ($M-$OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}-$I), 270 (HOC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$), 186 (HOC$_6$H$_4$C$_6$H$_4$OH), 128 (I). $E_f = -0.28$ V, $\Delta E_p = 120$ mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}(OC$_6$H$_4$C$_6$H$_4$OC$_6$H$_{13}$)$_2$] (3)

A solution of [Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}(I)$_2$]·C$_7$H$_8$ (0.40 g, 0.52 mmol), 4-n-hexyloxy-4′-hydroxybiphenyl (0.36 g, 1.33 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in toluene (20 cm^3) was stirred under reflux for 3 h. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The product obtained was purified by column chromatography on silica gel using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a dark brown solid (0.45 g, 90%). *Anal.* Found: C, 61.4; H, 6.4; N, 9.8%; M^+, 961. Calc. for C$_{51}$H$_{64}$BMoN$_7$O$_5$·0.5CH$_2$Cl$_2$: C, 61.6; H, 6.5; N, 9.8%; *M*, 962. ν_{max}(NO) 1655 cm^{-1}; δ_H(CDCl$_3$) 7.53 and 7.23 (4H, d, *J*(HH) 8.6 Hz; 4H, d, *J*(HH) 8.6 Hz, 2×C$_6$*H*$_4$–OC$_6$H$_{13}$), 7.52 and 6.94 (4H, d, *J*(HH) 8.6 Hz; 4H, d, *J*(HH) 8.8 Hz, 2×C$_6$*H*$_4$–Mo), 5.85 and 5.76

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*NMR data, relative area and multiplicity given in parentheses; s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet with unresolved coupling, b = broad.

**Electrochemical data, E_f = formal electrode potential for reduction, ΔE_p = separation between cathodic and anodic peak potentials of cyclic voltammogram, ΔE_p(Fc) = value of ΔE_p for ferrocene present as internal standard. No compensation was made for internal resistance in the cell.

(2H, s; 1H, s $(Me_2C_3N_2H)_3$), 3.99 (4H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_5H_{11}$), 2.42, 2.41, 2.27 and 2.14 (3H, s; 6H, s; 6H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.80 (4H, qn, $2\times C_6H_4OCH_2{-}CH_2{-}C_4H_9$), 1.48 (4H, qn, $2\times C_6H_4OC_2H_4{-}CH_2{-}C_3H_7$), 1.40–1.30 (8H, c m, $2\times OC_3H_6{-}C_2H_4{-}CH_3$), 0.91 (6H, t, J(HH) 7.0 Hz, $2\times CH_3$). m/z 961 (M^+), 933 ($M-NO$), 694 ($M-OC_6H_4C_6H_4OC_6H_{13}$), 664 ($M-OC_6H_4C_6H_4OC_6H_{13}-NO$), 424 ($M-2\times OC_6H_4C_6H_4OC_6H_{13}$), 270 ($HOC_6H_4C_6H_4OC_6H_{13}$), 186 ($HOC_6H_4C_6H_4OH$). $E_f=-0.67$ V, $\Delta E_p=135$ mV, ΔE_p(Fc) = 100 mV.

$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl(OC_6H_4C_6H_4OC_8H_{17})]$ *(4)*

This compound was prepared in similar manner to **1** using 4-n-octyloxy-4′-hydroxybiphenyl (0.22 g, 0.74 mmol) in place of 4-hexyloxy-4′-hydroxybiphenyl. The product was purified by column chromatography on silica gel using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.37 g, 80%). *Anal.* Found: C, 55.9; H, 6.3; N, 12.6%; M^+, 757. Calc. for $C_{35}H_{47}BClMoN_7O_3$: C, 55.6; H, 6.3; N, 13.0%; M, 756. ν_{max}(NO) 1675 cm^{-1}; $\delta_H(CDCl_3)$ 7.61 and 6.97 (2H, d, J(HH) 8.8 Hz; 2H, d, J(HH) 8.8 Hz, $C_6H_4{-}OMo$), 7.56 and 7.39 (2H, d, J(HH) 8.8 Hz; 2H, d, J(HH) 8.6 Hz, $C_6H_4{-}OC_8H_{17}$), 5.93, 5.89 and 5.77 (1H, s; 1H, s; 1H, s, $(Me_2C_3N_2H)_3$), 4.00 (2H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_7H_{15}$), 2.60, 2.42, 2.41, 2.39, 2.21 and 2.09 (3H, s; 3H, s; 3H, s; 3H, s; 3H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.80 (2H, qn, $C_6H_4OCH_2{-}CH_2{-}C_6H_{13}$), 1.48 (2H, qn, $C_6H_4OC_2H_4{-}CH_2{-}C_5H_{11}$), 1.40–1.30 (8H, c m, $OC_3H_6{-}C_4H_8{-}CH_3$), 0.88 (3H, t, J(HH) 6.7 Hz, CH_3). m/z 757 (M^+), 727 ($M-NO$), 460 ($M-OC_6H_4C_6H_4OC_8H_{17}$), 430 ($M-OC_6H_4C_6H_4OC_8H_{17}-NO$), 298 ($HOC_6H_4C_6H_4OC_8H_{17}$), 186 ($HOC_6H_4C_6H_4OH$). $E_f=-0.33$ V, $\Delta E_p=120$ mV, ΔE_p(Fc) = 100 mV.

$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}I(OC_6H_4C_6H_4OC_8H_{17})]$ *(5)*

This compound was prepared in identical manner to **4** using $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(I)_2]\cdot C_7H_8$ (0.40 g, 0.52 mmol) instead of $[MO(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(Cl)_2]$ and 4-n-octyloxy-4′-hydroxybiphenyl (0.20 g, 0.67 mmol). A deep violet solid was obtained (0.32 g, 73%). *Anal.* Found: C, 49.3; H, 5.5; N, 11.8%; M^+, 849. Calc. for $C_{35}H_{47}BIMoN_7O_3$: C, 49.6; H, 5.6; N, 11.6%; M, 847. ν_{max}(NO) 1665 cm^{-1}; $\delta_H(CDCl_3)$ 7.58 and 7.51 (2H, d, J(HH) 9.0 Hz; 2H, d, J(HH) 9.0 Hz, $C_6H_4{-}OC_8H_{17}$), 7.56 and 6.96 (2H, d, J(HH) 8.8 Hz; 2H, d, J(HH) 8.8 Hz, $C_6H_4{-}Mo$), 5.91, 5.85 and 5.84 (1H, s; 1H, s; 1H, s, $(Me_2C_3N_2H)_3$), 4.00 (2H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_7H_{15}$), 2.59, 2.45, 2.40, 2.38, 2.32 and 2.01 (3H, s; 3H, s; 3H, s; 3H, s; 3H, s; 3H, s $(Me_2C_3N_2H)_3$), 1.81 (2H, qn, $C_6H_4OCH_2{-}CH_2{-}C_6H_{13}$), 1.48 (2H, qn, $C_6H_4OC_2H_4{-}CH_2{-}C_5H_{11}$), 1.40–1.30 (8H, c m, $OC_3H_6{-}C_4H_8{-}CH_3$), 0.89 (3H, t, J(HH) 7.0 Hz, CH_3). m/z 849 (M^+), 819 ($M-NO$), 722 ($M-I$), 552 ($M-OC_6H_4C_6H_4OC_8H_{17}$), 522 ($M-OC_6H_4C_6H_4OC_8H_{17}-NO$), 424 ($M-OC_6H_4C_6H_4OC_8H_{17}-I$), 298 ($HOC_6H_4C_6H_4OC_8H_{17}$), 186 ($HOC_6H_4C_6H_4OH$), 128 (I). $E_f=-0.28$ V, $\Delta E_p=110$ mV, ΔE_p(Fc) = 95 mV.

$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(OC_6H_4C_6H_4OC_8H_{17})_2]$ *(6)*

This compound was prepared from $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(I)_2]\cdot C_7H_8$ (0.40 g, 0.52 mmol) and 4-n-octyloxy-4′-hydroxybiphenyl (0.40 g, 1.34 mmol) using the procedure described for **1** except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A dark brown solid was obtained (0.50 g, 95%). *Anal.* Found: C, 61.7; H, 6.7; N, 9.8%; M^+, 1019. Calc. for $C_{55}H_{72}BMoN_7O_5\cdot 0.75\,CH_2Cl_2$: C, 61.9; H, 6.8; N, 9.1%; M, 1018. ν_{max}(NO) 1650 cm^{-1}; $\delta_H(CDCl_3)$ 7.53 and 7.23 (4H, d, J(HH) 8.6 Hz; 4H, d, J(HH) 8.6 Hz, $2\times C_6H_4{-}OC_8H_{17}$), 7.52 and 6.94 (4H, d, J(HH) 8.6 Hz; 4H, d, J(HH) 8.8 Hz, $2\times C_6H_4O{-}Mo$), 5.85 and 5.76 (2H, s; 1H, s $(Me_2C_3N_2H)_3$), 3.99 (4H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_7H_{15}$), 2.42, 2.41, 2.27 and 2.14 (3H, s; 6H, s; 6H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.80 (4H, qn, $2\times C_6H_4OCH_2{-}CH_2{-}C_6H_{13}$), 1.47 (4H, qn, $2\times C_6H_4OC_2H_4{-}CH_2{-}C_5H_{11}$), 1.40–1.30 (16H, c m, $2\times OC_3H_6{-}C_4H_8{-}CH_3$), 0.91 (6H, t, J(HH) 7.0 Hz, $2\times CH_3$). m/z 1019 (M^+), 722 ($M-OC_6H_4C_6H_4OC_8H_{17}$), 648 ($M-OC_6H_4C_6H_4OC_8H_{17}-C_5H_{11}$), 424 ($M-2\times OC_6H_4C_6H_4OC_8H_{17}$), 298 ($HOC_6H_4C_6H_4OC_8H_{17}$), 186 ($HOC_6H_4C_6H_4OH$). $E_f=-0.67$ V, $\Delta E_p=150$ mV, ΔE_p(Fc) = 100 mV.

$[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Cl(OC_6H_4C_6H_4OC_{12}H_{25})]$ *(7)*

This compound was prepared in similar manner to **1** using 4-n-dodecyloxy-4′-hydroxybiphenyl (0.26 g, 0.73 mmol) in place of 4-hexyloxy-4′-hydroxybiphenyl. The product was purified by column chromatography on silica using 50% dichloromethane/n-hexane as eluent. Recrystallisation from dichloromethane/n-hexane yielded a deep violet solid (0.45 g, 91%). *Anal.* Found: C, 56.2; H, 7.1; N, 12.0%; M^+, 813. Calc. for $C_{39}H_{55}BClMoN_7O_3\cdot 0.33CH_2Cl_2$: C, 56.2; H, 6.7; N, 11.7%; M, 812. ν_{max}(NO) 1680 cm^{-1}; $\delta_H(CDCl_3)$ 7.61 and 6.97 (2H, d, J(HH) 8.8 Hz; 2H, d, J(HH) 8.8 Hz, $C_6H_4{-}OMo$), 7.56 and 7.39 (2H, d, J(HH) 8.8 Hz; 2H, d, J(HH) 8.6 Hz, $C_6H_4{-}C_{12}H_{25}$), 5.93, 5.89 and 5.77 (1H, s; 1H, s; 1H, s, $(Me_2C_3N_2H)_3$), 4.00 (2H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_{11}H_{23}$), 2.60, 2.42, 2.39, 2.21 and 2.09 (3H, s; 6H, s; 3H, s; 3H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.81 (2H, qn, $C_6H_4OCH_2{-}CH_2{-}C_{10}H_{21}$), 1.48 (2H, qn, $C_6H_4OC_2H_4{-}CH_2{-}C_9H_{19}$), 1.27 (16H, br s, $OC_3H_6{-}C_8H_{16}{-}CH_3$), 0.88 (3H, t, J(HH) 6.7 Hz, CH_3). m/z 813 (M^+), 783 (M − NO), 777 (M − Cl), 460 ($M - OC_6H_4C_6H_4OC_{12}H_{25}$), 430 ($M - OC_6H_4C_6H_4OC_{12}H_{25} - NO$), 354 ($HOC_6H_4C_6H_4OC_{12}H_{25}$), 186 ($HOC_6H_4C_6H_4OH$). $E_f = -0.33$ V, $\Delta E_p = 110$ mV, ΔE_p(Fc) = 100 mV.

[Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}I(OC$_6$H$_4$C$_6$H$_4$OC$_{12}$H$_{25}$)] (8)

This compound was prepared in identical manner to 7 using $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(I)_2]\cdot C_7H_8$ (0.40 g, 0.52 mmol) instead of $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(Cl)_2]$ and 4-n-dodecyloxy-4′-hydroxybiphenyl (0.24 g, 0.68 mmol). A deep violet solid was obtained (0.36 g, 77%). *Anal.* Found: C, 49.9; H, 6.0; N, 10.9%; M^+, 905. Calc. for $C_{39}H_{55}BIMoN_7O_3\cdot 0.5CH_2Cl_2$: C, 50.2; H, 6.0; N, 10.4%; M, 904. ν_{max}(NO) 1665 cm^{-1}, δ_H($CDCl_3$) 7.58 and 7.51 (2H, d, J(HH) 9.0 Hz; 2H, d, J(HH) 9.0 Hz, $C_6H_4{-}OC_{12}H_{25}$), 7.56 and 6.96 (2H, d, J(HH) 8.8 Hz; 2H, d, J(HH) 8.8 Hz, C_6H_4-Mo), 5.91, 5.85 and 5.84 (1H, s; 1H, s; 1H, s, $(Me_2C_3N_2H)_3$), 4.00 (2H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_{11}H_{23}$), 2.59, 2.45, 2.40, 2.38, 2.32 and 2.01 (3H, s; 3H, s; 3H, s; 3H, s; 3H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.81 (2H, qn, $C_6H_4{-}OCH_2{-}C_{11}H_{23}$), 2.59, 2.45, 2.40, 2.38, 2.32 and 2.01 (3H, s; 3H, s; 3H, s; 3H, s; 3H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.81 (2H, qn, $C_6H_4OCH_2{-}CH_2{-}C_{10}H_{21}$), 1.48 (2H, qn, $C_6H_4OC_2H_4{-}CH_2{-}C_9H_{19}$), 1.27 (16H, br s, $OC_3H_6{-}C_8H_{16}{-}CH_3$), 0.88 (3H, t, J(HH) 6.6 Hz, CH_3). m/z 905 (M^+), 875 (M − NO), 778 (M − I), 552 ($M - OC_6H_4C_6H_4OC_{12}H_{25}$), 522 ($M - OC_6H_4C_6H_4OC_{12}H_{25} - NO$), 424 ($M - OC_6H_4C_6H_4OC_{12}H_{25} - I$), 354 ($HOC_6H_4C_6H_4OC_{12}H_{25}$), 186 ($HOC_6H_4C_6H_4OH$), 128 (I). $E_f = -0.28$ V, $\Delta E_p = 105$ mV, ΔE_p(Fc) = 95 mV.

[Mo(NO){HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}(OC$_6$H$_4$C$_6$H$_4$OC$_{12}$H$_{25}$)$_2$] (9)

This compound was prepared from $[Mo(NO)\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(I)_2]\cdot C_7H_8$ (0.40 g, 0.52 mmol) and 4-n-dodecyloxy-4′-hydroxybiphenyl (0.48 g, 1.35 mmol) using the procedure described for **1** except that triethylamine (0.5 cm^3, 3.7 mmol) was used in place of hexamine. A dark brown solid was obtained (0.55 g, 94%). *Anal.* Found: C, 63.4; H, 7.4; N, 8.6%; M^+, 1129. Calc. for $C_{63}H_{88}BMoN_7O_5\cdot CH_2Cl_2$: C, 63.3; H, 7.5; N, 8.1%; M, 1130. ν_{max}(NO) 1650 cm^{-1}; δ_H($CDCl_3$) 7.53 and 7.23 (4H, d, J(HH) 8.6 Hz; 4H, d, J(HH) 8.6 Hz, $2\times C_6H_4{-}OC_{12}H_{25}$), 7.52 and 6.94 (4H, d, J(HH) 8.6 Hz; 4H, d, J(HH) 8.8 Hz, $2\times C_6H_4O$-Mo), 5.85 and 5.76 (2H, s; 1H, s $(Me_2C_3N_2H)_3$), 3.99 (4H, t, J(HH) 6.6 Hz, $C_6H_4{-}OCH_2{-}C_{11}H_{23}$), 2.42, 2.41, 2.27 and 2.14 (3H, s; 6H, s; 6H, s; 3H, s, $(Me_2C_3N_2H)_3$), 1.80 (4H, qn, $2\times C_6H_4OCH_2{-}CH_2{-}C_{10}H_{21}$), 1.47 (4H, qn, $2\times C_6H_4OC_2H_4{-}CH_2{-}C_9H_{19}$), 1.27 (32H, br s, $2\times OC_3H_6{-}C_8H_{16}{-}CH_3$), 0.88 (6H, t, J(HH) 6.6 Hz, $2\times CH_3$). m/z 1129 (M^+), 776 ($M - OC_6H_4C_6H_4OC_{12}H_{25}$), 648 ($M - OC_6H_4C_6H_4OC_{12}H_{25} - C_5H_{11}$), 424 ($M - 2\times OC_6H_4C_6H_4OC_{12}H_{25}$), 354 ($HOC_6H_4C_6H_4OC_{12}H_{25}$), 186 ($HOC_6H_4C_6H_4OH$). $E_f = -0.67$ V, $\Delta E_p = 180$ mV, ΔE_p(Fc) = 100 mV.

Results and discussion

Synthetic studies

The new complexes (Fig. 1) were synthesised according to established procedures [7]. In the case of the phenoxide derivatives hexamine was used to selectively induce monosubstitution of iodide in $[Mo(NO)LI_2]$ and triethylamine to induce bis-substitution. All of the new complexes exhibit ν_{BH} at *c.* 2550 cm^{-1} in their IR spectra. In addition ν_{NO} appears at 1675–1680 cm^{-1} in the mono-aryloxo chloro complexes, 1665–1670 cm^{-1} in the mono-aryloxo iodo complexes and 1650–1655 cm^{-1} in the bis-aryloxo complexes. These values are consistent with those found previously for related aryloxo derivatives containing linear NO ligands [7].

The ^{1}H NMR spectra of the mono-substituted complexes contain three signals due to the pyrazolyl 4-H protons in accord with the absence of a plane of symmetry in the molecule. Six discrete signals due to the pyrazolyl-3- and 5-methyl groups might also be expected but in two cases signal overlap results in five signals one of which has relative area 6 rather than 3. The spectra of the bis-substituted complexes contain two signals of relative areas 2:1 attributable to the pyrazolyl 4-H protons and four signals of relative areas 6:6:3:3 attributable to the pyrazolyl methyl protons and in accord with the presence of a plane of symmetry in these molecules. In addition signals of the appropriate relative area are present in the region 6.9–7.6 ppm arising from the aryl protons of the biphenyl moiety and in the region 2.0–0.8 ppm due to the aliphatic protons. The protons on the α-carbon of the alkoxy substituent appear as a triplet at 4.0 ppm.

All of the mono- and bis-substituted oxobiphenyl complexes show molecular ion envelopes. Owing to the

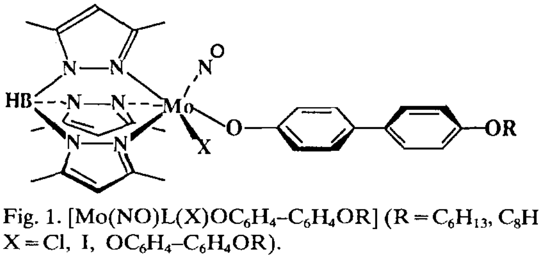

Fig. 1. $[Mo(NO)L(X)OC_6H_4{-}C_6H_4OR]$ ($R = C_6H_{13}, C_8H_{17}, C_{12}H_{25}$; $X = Cl$, I, $OC_6H_4{-}C_6H_4OR$).

presence of a large number of possible isotope combinations of the elements Mo, B, Cl, and I these envelopes have complex forms with the highest peak often not corresponding to exactly the fragmental mass calculated from relative atomic mass values. In most cases the highest peak and not the averaged fragment mass is quoted.

Electrochemical studies

The electrochemical properties of the complexes have been determined by cyclic voltammetry. All show chemically reversible reduction waves (i_p^c/i_p^a in the range 1.00 to 1.02) but the electron transfer is subject to some kinetic control (ΔE_p(complex) > ΔE_p(ferrocene)). Previous work has shown that the reduction potentials of the complexes [Mo(NO)L(X)(Y)] are highly sensitive to the nature of X and Y. Thus for X = halide and Y = phenoxide a reduction potential of *c.* -0.4 V might be expected compared to *c.* -0.8 V for X = Y = phenoxide [8]. However, the presence of substituents on the aryl ring also has a significant effect on the reduction potentials [9, 17]. Thus the reduction potentials of the mono-oxobiphenyl complexes [Mo(NO)L(Cl)($OC_6H_4C_6H_4OR$)] reveal a cathodic shift of 130 mV as compared to [Mo(NO)L(Cl)($OC_6H_4CO_2C_{12}H_{25}$)] [12]. The corresponding bis-aryloxide derivatives show an even larger cathodic shift of 230 mV. This large difference arises from the fact that the ester function is a relatively strong electron withdrawing group and effective communication via the phenyl ring enables it to significantly deplete the electron density at the metal. Not surprisingly, the length of the alkyl chain has no detectable influence on the reduction potentials.

Thermal studies

The mono-substituted oxobiphenyl complexes [Mo(NO)L(X)($OC_6H_4C_6H_4OR$)] (X = Cl, I; R = C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$) proved to be extremely high melting. For both chloride and iodide complexes it was found that the hexyloxy and octyloxy derivatives melt at around the same temperature, whilst the dodecyloxy derivatives have somewhat lower melting points. All three iodide complexes were observed to melt at higher temperatures than their chloride analogues. These complexes represent materials which have higher melting points than [Mo(NO)L(Cl)(OC_6H_4-4-Me)] and, since no birefringence was detected under the polarising microscope, the compounds were not studied further using DSC. Approximate melting points for these complexes are summarised in Table 1.

The bis-substituted biphenyloxy complexes [Mo(NO)L($OC_6H_4C_6H_4OR$)$_2$] proved to have greatly reduced melting points when compared to their mono-substituted counterparts. However, these values are still somewhat higher than those of the mono-aryl ligand complexes prepared previously [12]. When viewed under the microscope at a heating rate of 10 K min^{-1} all three showed fairly wide range melting behaviour with no birefringence at all, and a single broad endothermic melting event was observed in their DSC traces. The results of these DSC studies are summarised in Table 2. The hexyloxy derivative **3** showed an extremely broad second event with $T_{peak} = 137$ °C, the origin of which is unclear. It is perhaps of some interest to note that the hexyloxy, **3**, and dodecyloxy, **9**, complexes have very similar melting points but that the octyloxy derivative **6** melts at about 40 °C higher than these two. None of these samples showed any thermal evidence of solidification in the cooling trace which implies that the compounds cool to form amorphous glassy solids. In keeping with this observation, repeating the heating process failed to show the endothermic events found in the initial traces. There was no evidence for any liquid crystalline behaviour.

TABLE 1. Approximate melting points for mono-substituted biphenyloxy complexes [Mo(NO)L(X)($OC_6H_4C_6H_4OC_nH_{2n+1}$)]

X	*n*	m.p. (°C)	Complex no.
Cl	6	230	**1**
	8	230	**4**
	12	195	**7**
I	6	245	**2**
	8	245	**5**
	12	225	**8**

TABLE 2. DSC data for bis-substituted biphenyloxy complexes [Mo(NO)L($OC_6H_4C_6H_4OC_nH_{2n+1}$)$_2$]

n	T_{ON} (°C)	ΔH (J g^{-1})	T_{peak} (°C)	Complex no.
6	106.3	9.2	115	**3**
8	142.4	37.5	149	**6**
12	102.4	28.5	110	**9**

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