An EPR, Magnetic and Electrochemical Study of Electron Exchange and Intermetallic Interaction Through Polyene Bridges

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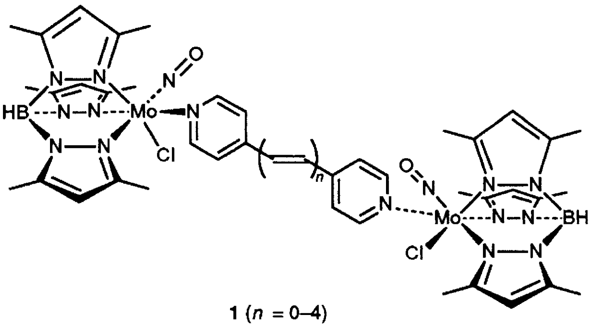
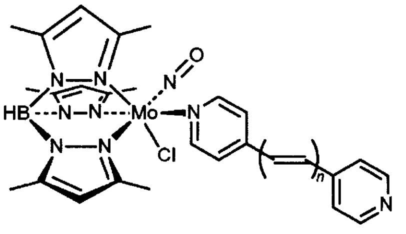
The new bipyridylpolyene bridged bimetallic complexes $[\{LCl(NO)Mo\}_2\{4,4'\text{-}NC_5H_4(CH{=}CH)_nH_4C_5N\}]$ [$L = HB(3,5\text{-}Me_2C_3HN_2)_3$; $n = 2, 3, 4$ all *trans*] may be reduced in two one-electron processes, the separation between which decreases by approximately 166 mV per additional ethenyl unit, they exhibit EPR spectra (300 K) consistent with rapid ($>10^8$ s^{-1}) electron exchange between the metal centres and magnetic measurements indicate the presence of an antiferromagnetic interaction in the compound with $n = 4$ with a coupling $-2J$ estimated to be 100 cm^{-1}.

The search for new materials with potential applications in molecular electronic or electro-optic devices has stimulated much work on compounds containing polyene moieties.[1–3] In particular *trans*-poly(acetylene) has been found to exhibit substantial third-order non-linear optic properties.[4] The mobility of the delocalised π-electrons in such systems appears to be an essential feature underlying their special properties[5] and it is possible that transition metal centres bound to polyene containing ligands might serve as sources of mobile charges within the molecule.[6–11] We have recently obtained EPR evidence for fast electron exchange between the metal centres in $[\{LCl(NO)Mo\}_2\{4,4'\text{-}NC_5H_4(CH{=}CH)_nH_4C_5N\}]$ [$L = HB(3,5\text{-}Me_2C_3HN_2)_3$; (**1**; n = 0, 1)][12] and have now linked two 17-electron [Mo(NO)LCl] moieties by a series of bridging bipyridylpolyene ligands. These compounds allow investigations to be made of the mobility of electrons through the polyene chain, the attenuation of the metal–metal interaction with increasing polyene chain length and the magnetic interaction between the metal centres separated by a large number of carbon–carbon bonds.

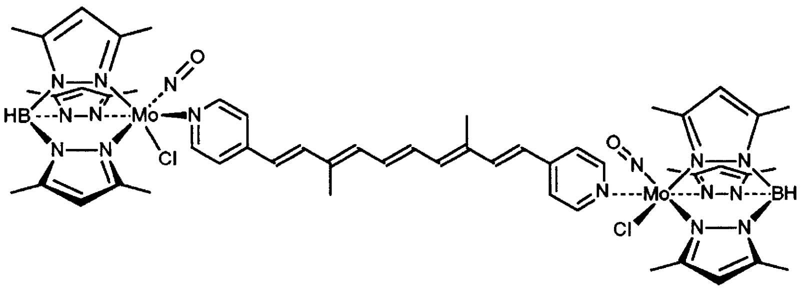
Following the syntheses of **1** and $[\{LCl(NO)Mo\}\{4,4'\text{-}NC_5H_4(CH{=}CH)_nH_4C_5N\}]$ **2** without (n = 0) and with (n = 1) a single C=C linkage,[12] we have now synthesised the analogous compounds with *trans*-polyene chains (n = 2–4). We have also synthesised compound **3** with a partially methylated chain of five double bonds.[7,13–15] In the case of **1** (n = 4) the



1 (n = 0–4)



2 (n = 0–4)



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formulation of the complex and the all-*trans* nature of the polyene bridge has been confirmed by an X-ray crystal structure.†

The new complexes **1**, **2** (n = 2–4) and **3** exhibit EPR spectra at 300 K in CH_2Cl_2–toluene (5 : 1 v/v) and all contain signals with the same value of g_{iso} = 1.97 to within experimental error. These spectra show the characteristic patterns expected for the molybdenum isotopes in natural abundance (I = 0, 74.5%; I = 5/2, 25.5%) and in the monometallic complexes a hyperfine pattern with $A_{iso} \approx 45 \times 10^{-4}$ cm^{-1} is observed, typical of the monomeric [Mo(NO)L]$^+$ moiety.[12,17–19] In the case of the bimetallic complexes the hyperfine pattern is that expected from two equivalent molybdenum atoms and, furthermore, the hyperfine splitting constant, $A_{iso} \approx 25 \times 10^{-4}$ cm^{-1} is, as expected, approximately half that in the monomers. The overall pattern of these results indicates that, in each of the bimetallic compounds, the unpaired electrons are delocalised over both metal centres on the EPR timescale. This implies rates of electron exchange greater than 10^8 s^{-1} over distances in excess of 20 Å in the case of **1** (n = 4) and **3**.

The magnetic susceptibilities of **1** (n = 4) and **2** (n = 4) have been determined over the temperature range 80 to 300 K as shown in Fig. 1. The monometallic complex exhibits simple Curie law behaviour with a plot of $1/\chi_m$ against temperature having a zero intercept. The χ_m per metal atom of the bimetallic compound is smaller and also shows a smaller rate of increase with decreasing temperature compared to that of the monometallic compound. This behaviour is consistent with an antiferromagnetic interaction in **1** (n = 4) as confirmed by a plot of $1/\chi_m$ against temperature which is linear with a negative intercept on the temperature axis and a Weiss constant of 67 K.[20] Attempts were made to model the interaction between the molybdenum centres in **1** (n = 4) using a simple spin exchange model based on the Bleaney–Bowers equation[21] and the observed solution g value of 1.97. An exact fit was not obtained but the trend in the magnetic susceptibility of **1** (n = 4) with temperature was followed best using a value for $-2J$ of 100 cm^{-1} (Fig. 1). This result suggests that a moderately large interaction is present, although the value of $-2J$ must be interpreted with caution since the effects of spin-orbit coupling have not been considered. We were unable to find other examples involving paramagnetic low-oxidation state molybdenum complexes for comparison.

The electrochemical properties of the new complexes have been investigated using cyclic voltammetry and, where necessary, differential pulse voltammetry. In the potential range 0 to −1.8 V (standard calomel electrode) the monometallic compounds **2** (n = 2–4) exhibit a single reduction process at potentials which fall within the narrow range of −1.09 to −1.15 V. This represents an anodic shift of some 300 mV compared to the reduction of the related pyridine complex

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† The structure of **1** (n = 4) has been refined[16] to a current R value of 0.073 and is as expected revealing bond alternation in the polyene chain with C–C 1.433(12)–1.459(18) Å and C=C 1.326(13) and 1.342(14) Å. There is a centre of symmetry in the molecule. In accord with their formulation as 17-electron systems the new complexes exhibit ν_{NO} bands in the region 1595 to 1625 cm^{-1}.[17,18] The bimetallic complexes **2** (n = 3 and 4) exhibited two bands in this region but only one band was observed for **2** (n = 2). In addition to bands attributable to the ligand L and the π–π* absorption of the bipyridylpolyene moiety, the electronic spectra of the bimetallic complexes contained an absorption at *ca.* 550 nm. Solvatochomism studies of **1** (n = 4), **2** (n = 4) and **3** indicate that this band is due to metal to ligand charge transfer process. All of the new compounds give satisfactory elemental analyses.

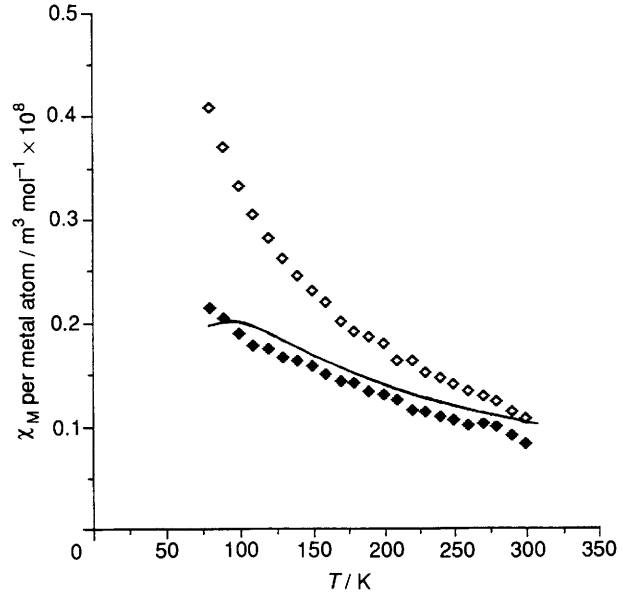

Fig. 1 χ_m data (per molybdenum atom) for $[Mo(NO)LCl\{NC_5H_4(CH{=}CH)_4C_5H_4N\text{-}4,4'\}]$ ◇ and $[\{Mo(NO)LCl\}_2\{NC_5H_4(CH{=}CH)_4C_5H_4N\text{-}4,4'\}]$ ◆ with the calculated line (—) for the latter based on the Bleaney–Bowers eqn. with $g = 1.97$ and $-2J = 100\ cm^{-1}$

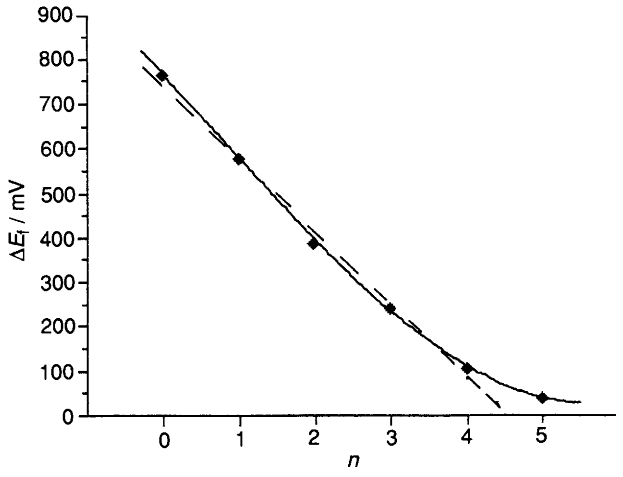

Fig. 2 A plot of the separation between the two reduction potentials of $[\{Mo(NO)LCl\}_2\{NC_5H_4(CH{=}CH)_nC_5H_4N\text{-}4,4'\}]$ (**1**, n = 0–4) and **3**, ΔE_f in mV, against n where n = 5 in **3**. The solid line is given by the eqn. $\Delta E_f = 765 + 2.78n^3 - 6.19n^2 - 184n$ and the broken line by $\Delta E_f = 748 - 166n$.

$[Mo(NO)LCl(NC_5H_5)]$. The bimetallic complexes **1** (n = 2–4) exhibit two reduction waves. The first of these appears at −1.0 V compared to respective values of −0.86 and −0.90 V for **1** (n = 0, 1).[12] The second reduction process appears at a potential more cathodic than the first by an amount which decreases with increasing polyene chain length. In the case of **3** a single two-electron wave is seen and any metal–metal interaction is too small to resolve. The bipyridylpolyene ligands themselves are also redox active but exhibit reduction processes at potentials more cathodic than −1.5 V and beyond the range of potentials at which **1** and **2** reduce. Since the 17-electron complexes $[Mo(NO)LCl(NHC_mH_{2m})]$ (m = 4, 5), which contain saturated cyclic amine ligands, also exhibit reduction processes in the range −1.0 to −1.6 V,[18] the two reduction potentials for **1** may be assigned to processes largely associated with the [Mo(NO)LCl] moiety. No further cathodic processes were observed which might correspond with the original ligand reductions. A plot of the separation between the two reduction waves (ΔE_f in mV) for **1** (n = 0–4) and **3** against polyene chain length, measured by n (n is taken as 5 for **3**) is shown in Fig. 2. Over the series **1** (n = 0–4) there is an almost monotonic decrease in ΔE_f of *ca.* 166 mV per added -CH=CH- unit. In the case of **3** the interaction is not experimentally distinguishable from the statistical limit of ΔE_f = 36 mV for non-interacting metal centres.

These results provide the first electrochemical evaluation of the effect of increasing polyene chain length on metal–metal interactions transmitted through polyene bridges. The attenuation with distance of the intermetallic interaction in **1** corresponds with a factor of 7.3 decrease with an increase in metal–metal distance (n = 0 to n = 4) of *ca.* 9 Å. The EPR data confirm that the paramagnetic metal centres can act as sources of mobile charges in polyene containing complexes and the magnetic measurements indicate that substantial antiferromagnetic interactions can be transmitted through unsaturated hydrocarbon bridges over distances of *ca.* 20 Å.

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