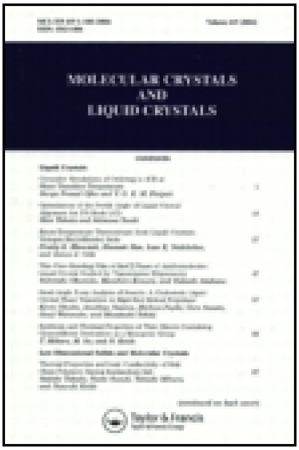

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Intramolecular Electron Transfer Across Polyenebridges

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INTRAMOLECULAR ELECTRON TRANSFER ACROSS POLYENEBRIDGES.

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Abstract: the new bipyridylpolyene bridged bimetallic complexes $[\{LMo(NO)Cl\}NC_5H_5\text{-}(C_2H_2)_n\text{-}C_5H_5N]$ (n = 2-4 all trans) have been synthesised along with their monometallic counterpart $[\{LMo(NO)Cl\}NC_5H_5\text{-}(C_2H_2)_n\text{-}C_5H_5N]$. All of the bimetallic complexes exhibit EPR spectra consistent with fast electron exchange between the metal centres and may be reduced in two 1-electron processes, the separation between which decreases by aproximately 166 mV per additional ethenyl unit.

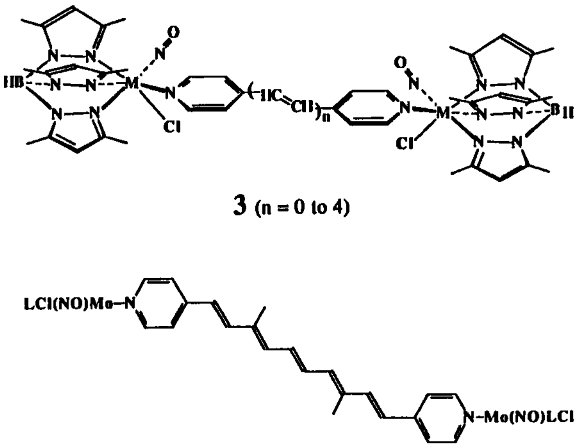
INTRODUCTION

Compounds based on polyene systems are of interest as materials for molecular electronics. They have been used as molecular wires[1], and as donor systems in molecules exhibiting charge separation.[2] It has also been postulated that they could form the basis of a molecular switch.[3-6]

Research into the latter topic has resulted in the synthesis of the isovalent complexes $[\{(NH_3)_5Ru\}_2\{4,4'\text{-}NC_5H_4\text{-}(CH{=}CH)_n\text{-}H_4C_5N\}]^{6+}$ (1;n = 2 to 4) and their mixed valence analogues $[\{(NH_3)_5Ru\}_2\{4,4'\text{-}NC_5H_4\text{-}(CH{=}CH)_n\text{-}H_4C_5N\}]^{5+}$, which are essentially extensions of a series whose first member is the well known Creutz-Taube ion[7] The extent of metal-metal electronic coupling in this series was assessed using the intervalence electron transfer band observed in their electronic spectra. The ruthenium-ruthenium electrochemical interaction in these systems is weak and no interaction is observed at all where n=2-4.[3]

SYNTHESIS

Following the synthesis of the isovalent complexes 4,-4'-[LMo(NO)Cl}NC_5H_5-$(C_2H_2)_n$-C_5H_5N] and [{LMo(NO)Cl}$_2NC_5H_5$-$(C_2H_2)_{n}C_5H_5N$] [n = 0,1; {L = HB(3,5-$Me_2C_3HN_2)_3$}][7] the new complexes [{LMo(NO)Cl}NC_5H_5-$(C_2H_2)_n$-C_5H_5N] (2; n = 2-4), [{LMo(NO)Cl}NC_5H_5-$(C_2H_2)_n$-C_5H_5N] (3; n = 2-4) and 4 (fig 1) were synthesised from [LMo(NO)Cl_2]$^-$ and the appropriate dipyridyl polyene.



3 (n = 0 to 4)

4

Figure 1 - Bimetallic molybdenum complexes

The all-trans nature of the polyene ligands has been confirmed by NMR studies[8] and, in one case, by an X-ray crystal structure[9]· An X-ray crystal structure of (3; n = 4) (fig 2) confirms the formulation of the complex and the all-trans nature of the bridge.

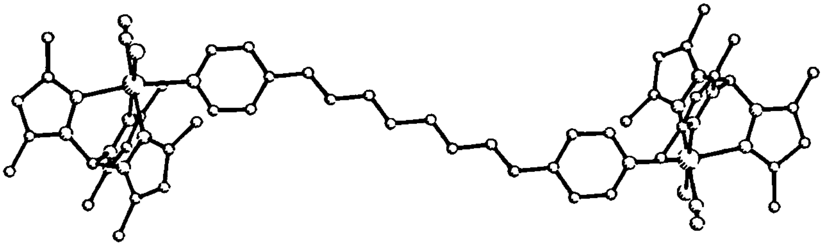


Figure 2 - X-ray crystal structure of **3** (n = 4)

ELECTROCHEMISTRY

Unlike the ruthenium systems the bimetallic complexes show an appreciable electrochemical interaction. This interaction has been investigated using cyclic voltammetry and differential pulse voltammetry. Whereas all the monometallic compounds exhibit single reduction processes between -1.09 and -1.15V (vs. SCE), the bimetallic complexes exhibit two reduction waves. The separation between these waves is dependent on the nature of the polyene bridge, decreasing with increasing chain length until, for 4, a single 2-electron wave is observed. Although the dipyridyl polyene ligands are themselves redox active, they exhibit essentially irreversible reduction processes at potentials more cathodic than those observed in the complexes. Since similar complexes which contain saturated amine ligands[10] and dipyridyl alkanes[11] also show reduction waves in the range -1.0 to -1.6 V the reduction potentials for these new compounds may be assigned to largely metal based processes.

A plot of the separation between the two reduction waves for 3 and 4 against polyene length as measured by n is shown in figure 3. Although a cubic function best fits the data for the series 3 (n = 0 to 4) there is an almost monotonic decrease in the separation of ca. 166 mV per additional -CH=CH- unit, tending to the statistical limit of 36 mV for the non-interacting metal centres of 4. These results provide the first electrochemical evaluation of the effect of increasing polyene chain length on metal-metal interactions transmitted through a polyene bridge.

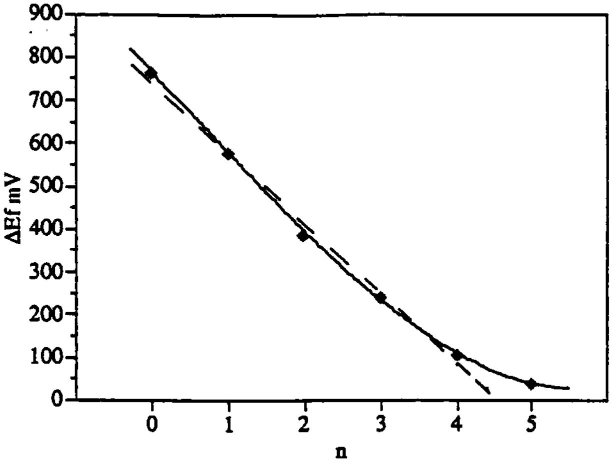


Figure 3 - A plot of the separation in the reduction potentials of 3 (n = 0-4) and 4 in mV against n. The solid line is given by the Eqn $\Delta E_f = 765 + 2.78n^3 - 6.19n^2 - 184n$ and the broken line by $\Delta E_f = 748 - 166n$

MAGNETIC AND EPR DATA

The magnetic susceptibilities of 2 (n = 4) and 3 (n = 4) have been determined over the temperature range 80 to 300K (figure 4). the magnetic moment of 2 shows a maximum at ca. 200K. This has been interpreted as the result of spin-orbit coupling.[12] A similar, less pronounced, effect is observed for the bimetallic complex. The data for 3 is consistent with an antiferromagnetic interaction.[12] Attempts to model this interaction using a simple model based on the Bleany-Bowers equation do not produce an exact fit. The best agreement with experimental data was given by a value for -2J of 100cm^{-1} (figure 4). This indicates that a moderately large interaction is present, but these results should be interpreted with caution since the effect of spin orbit coupling has not been considered. A more detailed study of this data will now be made using the completed X-ray crystal structure of 3 (n =4).

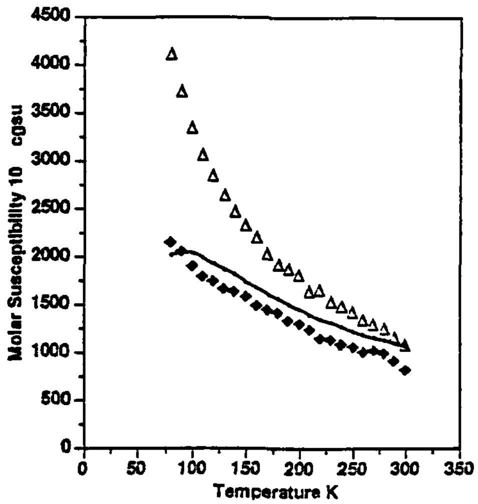


Figure 4 - Molar susceptibility data (per Mo atom) for 2 (n = 4, Δ) and 3 (n = 4, ◆) with the calculated line for the latter based on -2J = 100cm^{-1}

All of the complexes discussed are paramagnetic and exhibit EPR spectra at 300K 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. The 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 series of complexes a hyperfine pattern with A_{iso} = ca. 45 x 10^{-4} cm^{-1} is observed, typical of the $\{Mo(NO)L\}^+$ moiety . In the case of the bimetallic complexes the hyperfine pattern is that expected from two equivalent molybdenum atoms and the hyperfine splitting constant is approximately half that of the monomers (A_{iso} = ca 25 x 10^{-4} cm^{-1}). these results indicate that, in all the bimetallic compounds, the unpaired electrons are delocalised over both metal centres on the EPR timescale. This implies electron exchange rates greater than 10^{8} s^{-1} over distances in excess of 20 Å.

The spectro-elelectrochemistry of these compounds is being investigated so that the nature of the electron transfer in the analogous mixed-valence systems can also be studied.

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