

EPR and Electrochemical Studies of Bimetallic Seventeen-electron Molybdenum Species exhibiting Unusually Large Interactions Across Bipyridyl Bridging Ligands

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The reactions between $[\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]^-$ and L-L [$\text{HB}(\text{Me}_2\text{pz})_3 =$ hydrotris(3,5-dimethylpyrazolyl)borate and $\text{L-L} =$ 4,4'-bipyridyl, 3,3'-bipyridyl, 1,2-bis(4-pyridyl)ethane, and *trans*-1,2-bis(4-pyridyl)ethene] afford the complexes $[\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}(\text{L-L})]$ and $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}\}_2(\mu\text{-L-L})]$; the unpaired electrons in $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}\}_2(\mu\text{-L-L})]$ show large exchange interactions at 300 K.

Molecular complexes containing two redox-active metal centres provide compounds which are important in studies of intramolecular electron transfer processes,^{1,2} and allow experimental tests of theoretical models. The most extensively studied examples of mixed oxidation state bimetallic complexes are the pyrazine-bridged Creutz-Taube ion, $[(\text{NH}_3)_5\text{Ru}(\text{NC}_4\text{H}_4\text{N})\text{Ru}(\text{NH}_3)_5]^{5+}$, and related systems involving different bridging ligands and, in some cases, $[\text{Ru}(\text{bipy})_2\text{Cl}]$ (bipy = 2,2'-bipyridyl) termini.^{3,4}

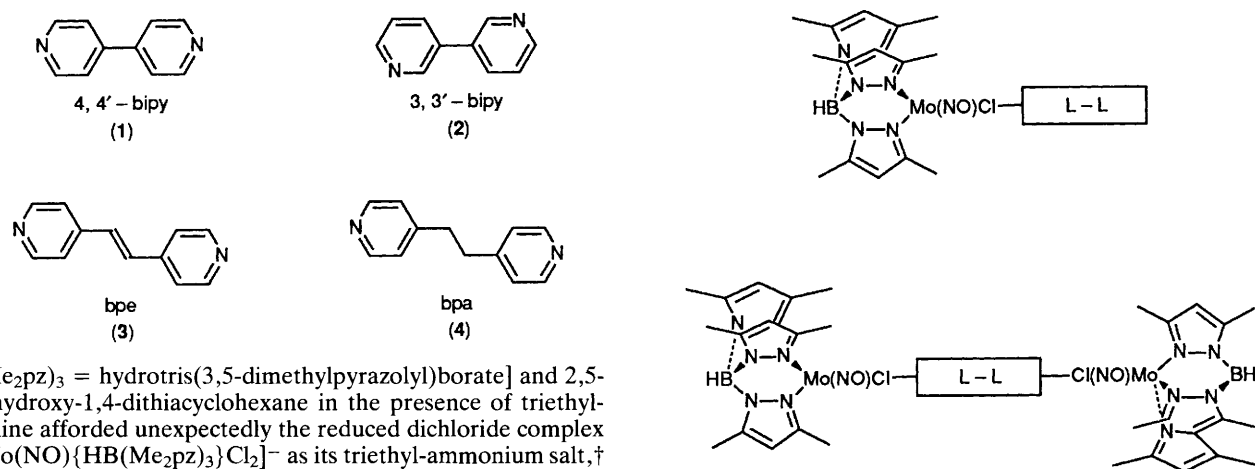
To some extent the great interest in the Creutz-Taube ion and its analogues reflects the scarcity of alternative, but equally versatile, mixed oxidation state complexes containing polyatomic bridging ligands. The $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ complexes contain d^6/d^5 metal centres and the interaction across the pyrazine bridge of the Creutz-Taube ion (as manifest in the difference between the two oxidation potentials observed for the redox system) amounts to 390 mV.⁴

The reaction between $[\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}_2]$ [H

Table 1. Electrochemical and EPR data for the complexes discussed.

$\{\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}\}_n\text{L}$		$E_{1/2}(\text{red})^a$ /mV		$\Delta E_{1/2}^b$ /mV	g_{iso}^c	Hyperfine splitting /mT	$10^4 A_{\text{iso}}^d$ /cm ⁻¹
L	n						
Pyridine	1	-1.450			1.970	4.88	45.7
4,4'-bipy	1	-1.140			1.969	4.85	45.3
4,4'-bipy	2	-0.853	-1.618	765	1.971	2.45	45.8
3,3'-bipy	1	-1.363			1.970	4.83	45.2
3,3'-bipy	2	-1.295	-1.500	205	1.971	2.49	46.6
bpe	1	-1.093			1.970	4.95	46.2
bpe	2	-0.898	-1.480	582	1.970	2.45	44.6
bpa ^e	1	-1.363			1.970	4.94	46.2
bpa ^e	2	-1.455	-1.550	105	1.970	2.51	45.4

^a Electrochemical measurements were made at a Pt bead electrode in dichloromethane containing 0.2 mol dm⁻³ Bu₄NBF₄ and were referenced to a standard calomel electrode. In all cases ferrocene was used as an internal reference and was observed to oxidise at +0.555 V. Measurements were made by CV unless otherwise stated. Errors: $E_{1/2} \pm 0.005$ V. ^b Separation between first and second one-electron reduction processes. Errors: $\Delta E_{1/2} \pm 10$ mV. ^c Spectra obtained at room temperature in dichloromethane/toluene solution. Errors: $g_{\text{iso}} \pm 0.001$. ^d Errors: when $n = 1$, $A_{\text{iso}} \pm 0.5 \times 10^{-4}$ cm⁻¹; when $n = 2$, $A_{\text{iso}} \pm 1.0 \times 10^{-4}$ cm⁻¹. ^e Data obtained by differential pulse voltammetry.

**Figure 1.** Structural formulae of products.

(Me₂pz)₃ = hydrotris(3,5-dimethylpyrazolyl)borate] and 2,5-dihydroxy-1,4-dithiacyclohexane in the presence of triethylamine afforded unexpectedly the reduced dichloride complex [Mo(NO){HB(Me₂pz)₃}Cl₂]⁻ as its triethyl-ammonium salt,† rather than the bimetallic alkoxide derivative. In contrast to [Mo(NO){HB(Me₂pz)₃}I₂], which reacts with excess pyridine⁵ to produce the seventeen-electron cation [Mo(NO){HB(Me₂pz)₃}(NC₅H₅)₂]⁺, [Mo(NO){HB(Me₂pz)₃}Cl₂]⁻ reacts to form the green neutral complex [Mo(NO){HB(Me₂pz)₃}Cl(NC₅H₅)] which exhibits $\nu(\text{NO})$ at 1623 cm⁻¹.† Earlier attempts to prepare the iodo-analogue of this chloro-complex were unsuccessful. Cyclic voltammetry (CV) of [Mo(NO){HB(Me₂pz)₃}Cl(NC₅H₅)] in dichloromethane revealed an irreversible one-electron oxidation at +0.60 (*vs.* standard calomel electrode, SCE), and a one-electron reduction at -1.45 which was chemically reversible on the CV time-scale, but showed electron transfer kinetics slightly slower than diffusion controlled. The EPR spectrum contained a signal at g_{iso} 1.970 with additional hyperfine coupling to the $I = 5/2$ isotopes [⁹⁵Mo (15.9%) and ⁹⁷Mo (9.6%)] of 48.6×10^{-4} cm⁻¹.

The reactions between [Mo(NO){HB(Me₂pz)₃}Cl₂]⁻ and L-L [L-L = 4,4'-bipy (1), 3,3'-bipy (2), bpe (3), and bpa (4)] afford mixtures of the mono- and bi-metallic complexes, [Mo(NO){HB(Me₂pz)₃}Cl(L-L)] and [(Mo(NO){HB(Me₂pz)₃}Cl)₂(L-L)] respectively, which are air-stable and may be separated by column chromatography on silica gel using CH₂Cl₂ as eluant. Thus far, all attempts to prepare an

analogue of the Creutz-Taube ion, with a pyrazine ligand bridging two {Mo(NO)} centres have failed.

The electrochemical and EPR spectral data for the new complexes are summarised in Table 1, and EPR spectra are shown in Figure 2(a-d). In addition to an irreversible one-electron oxidation process these complexes also exhibited reduction processes. The reduction potentials of the mono-metallic complexes are sensitive to the nature of L-L, varying by 270 mV from L-L = bpe to L-L = bpa. For the bimetallic complexes two separate one-electron reduction processes are observed which straddle the potential for the corresponding monometallic complex. The separation between these two waves varies from 105 mV for L-L = bpa to 765 mV for L-L = 4,4'-bipy. This latter figure may be compared with a value of only 76 mV for the related complex containing two {Ru(NH₃)₅} centres separated by 4,4'-bipy. In the case of [(Ru(NH₃)₅)₂(*u*-bpe)]⁴⁺ a separation of 68 mV is observed⁴ compared with 582 mV in the related dimolybdenum complex. These figures reveal an electronic coupling between the {Mo(NO)} centres which is an order of magnitude larger than that of their {Ru(NH₃)₅} counterparts. In the case of the related complexes containing {Ru(bipy)₂Cl} termini linked by L-L, no electronic coupling is observed between the metal centres by electrochemistry, comproportionation constants of *ca.* 4 being quoted.⁴

† The new complexes have been characterised by elemental analyses for C, H, and N, IR and electronic spectral measurements, and by EPR spectroscopy.

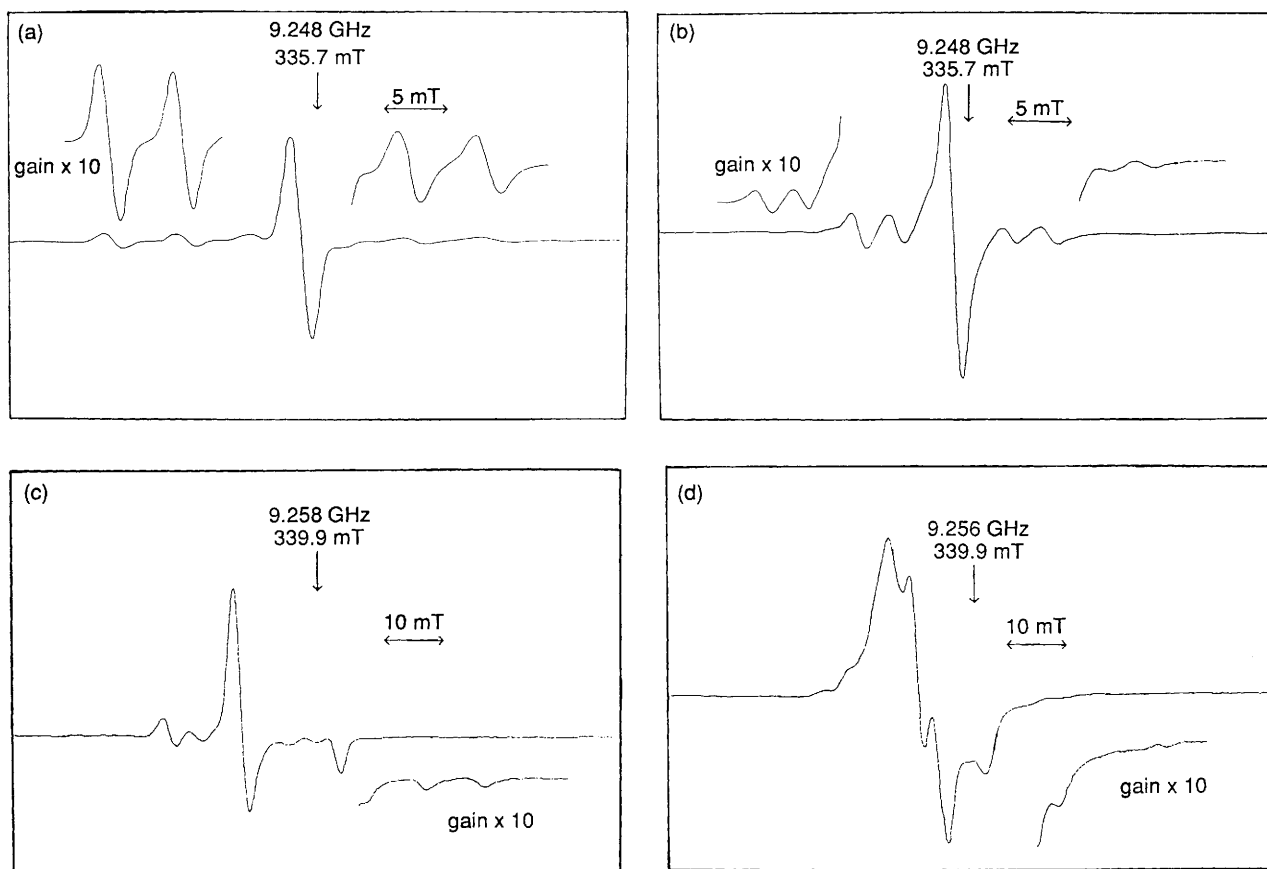


Figure 2. EPR spectra of $[\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}(3,3'\text{-bipy})]$: (a) at room temperature, (c) at 77 K; $[\{\text{Mo}(\text{NO})\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Cl}\}_2(\mu\text{-}3,3'\text{-bipy})]$: (b) at room temperature, (d) at 77 K.

The EPR spectral data presented in Table 1 show that all the new molybdenum complexes exhibit g_{iso} values of *ca.* 1.970 in $\text{CH}_2\text{Cl}_2/\text{toluene}$ solution at 300 K. The hyperfine coupling constants for the monometallic complexes are all in the range $45.7 (\pm 0.5) \times 10^{-4} \text{ cm}^{-1}$. The bimetallic complexes, on the other hand, all exhibit hyperfine splitting of approximately half the magnitude found in their monometallic counterparts. Furthermore, all the components expected from a dimer with equivalent molybdenum sites and the metals in natural abundance were observed, see Figure 2(b). This implies rapid site exchange of the unpaired electrons at room temperature. Solid solution spectra were also obtained at 77 K in the same solvents. The monometallic species displayed axial symmetry, but the bimetallics all gave broad featureless spectra, in which no half-field line was apparent.

The EPR spectra of the bimetallic species are consistent with $|J| \gg A_0$ (where J is the exchange integral and A_0 is the hyperfine interaction).⁶ The hyperfine splitting in the predicted spectrum for the case where $|J| \gg A_0$ is $1/2 a$ ($a = A_0/g\beta$), that is, half the value found in the spectrum of a radical containing a single unpaired electron in an identical monomeric fragment. In the solid state, additional terms, which average to zero in solution, affect the bimetallic spectra giving the broad featureless traces observed. Failure to observe a half-field transition may be due to the large metal-metal distances involved. The intensity of the half-field transition decreases as the distance between the electron sites increases and the metal-metal distances in the present systems are at least double that in $[(\text{C}_5\text{H}_5)\text{V}(\mu\text{-C}_{12}\text{H}_{10})\text{V}(\text{C}_5\text{H}_5)]$ described by Elschenbroich and Hack for which a half-field line was observed.⁷

Since the bimetallic 17-electron molybdenum complexes are symmetric the electron exchange process involves no net reorganisation of the primary or secondary metal co-ordination spheres so that a very small barrier to electron exchange would be expected. Studies of triplet transfer rates across saturated cyclohexyl or decalyl⁸ bridges show electron transfer rates in the region of 10^6 to 10^9 s^{-1} . The higher of these rates is of sufficient magnitude to produce EPR spectra consistent with our findings.

These new bimetallic molybdenum complexes represent a new type of strongly coupled system in which the coupling is an order of magnitude larger than in the widely studied ruthenium systems. Further EPR, low temperature magnetic susceptibility, and spectroelectrochemical studies are in progress to explore more fully the properties of these new strongly interacting systems.

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