Valence-localised and Valence-delocalised Mixed-valence States; The Effect of the Substitution Pattern of 1,2-, 1,3- and 1,4-$[C_6H_4(NH)_2]^{2-}$ as Bridging Ligands

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The mixed-valence complexes $[\{MoL(NO)X\}_2\{\mu\text{-}1,n\text{-}C_6H_4(NH)_2\}]^-$ [L = tris(3,5-dimethylpyrazolyl)hydroborate; X = Cl, Br, I; n = 2,3,4] containing a 1,2-, 1,3- or 1,4-diamidobenzene bridge are prepared by electrochemical or chemical reduction of the diamagnetic neutral species; EPR spectroscopy shows that with 1,2- or 1,4-diamidobenzene as the bridge the mixed-valence state is delocalised on the EPR timescale, whereas with a 1,3-diamidobenzene bridge the mixed-valence state is valence-trapped.

Dinuclear complexes linked by a difunctional bridging ligand are of interest because of the possibility of studying intervalence charge-transfer (IVCT) processes in mixed-valence (MV) states.[1] Although there are many studies in which the length and degree of conjugation of the bridging ligand are systematically varied, studies on the effects of the substitution pattern of aromatic bridges on the properties of such binuclear complexes are much rarer. The most notable examples are described by Richardson and Taube, who used sets of bridging ligands such as 1,2-, 1,3- and 1,4-dicyanobenzene; pyrazine and pyrimidine; and various isomers of dicyanonaphthalene to link $\{Ru(NH_3)_5\}^{2+}$ fragments.[2] It was observed that 1,3-substituted bridges such as pyrimidine and 1,3-dicyanobenzene result in much weaker metal–metal interactions, with smaller K_c values and higher-energy, less intense IVCT bands.

The commonest spectroscopic technique used to study valence delocalisation in MV complexes is of course electronic spectroscopy, but IR[3–5] and Mössbauer[6] spectroscopy have been of use in certain specific instances. The use of EPR spectroscopy to characterise MV systems is also possible;[4,5] for example in *trans,mer*-$[\{Mo(PPr^i_3)_2(CO)_3\}(\mu\text{-pyrazine})]^+$ EPR spectroscopy shows that the odd electron is coupled equivalently to both metal centres.[5] We describe here the EPR spectra of a series of MV dinuclear complexes based on 1,2-, 1,3- and 1,4-diamidobenzene bridges which show that the MV states are fully delocalised on the EPR timescale for the complexes with 1,2- and 1,4-substituted bridges, but valence-localised for the complex with a 1,3-substituted bridge. This is the first demonstration of a change in the nature of an MV state from delocalised to valence-trapped according to the substitution pattern of the bridging ligand, and highlights how advantageous EPR spectroscopy can be for studying MV complexes.

We have been employing the $\{MoL(NO)X\}$ [L = tris(3,5-dimethylpyrazolyl)hydroborate] fragment (X = halide) as a probe for examining electrochemical interactions as a function of bridging ligand structure.[7] We have published[8,9] the syntheses and electrochemical properties of the isomeric complexes $[\{MoL(NO)X\}_2\{\mu\text{-}(NH)_2C_6H_4\}]$, where the bridging ligand is derived from 1,2-, 1,3- or 1,4-$C_6H_4(NH_2)_2$ and X is Cl or I. We have now also prepared the three complexes with X = Br by the same method, but using benzyl bromide at the appropriate point in the synthesis in place of the chloride or iodide: the new complexes were satisfactorily characterised by elemental analysis, electrochemistry and FAB mass spectrometry. All of these diamido-bridged complexes show very strong electrochemical interactions, with large separations between the two metal-centred one-electron reductions (Table 1); the much larger interaction for the complexes with 1,2- and 1,4-substituted bridging ligands compared to those with the 1,3-substituted bridge is consistent with the findings of Richardson and Taube.[2] The large separation between the two reductions means that chemical or electrochemical reduction by one electron to the paramagnetic MV state is relatively easy. Thus for all nine complexes, reaction with cobaltocene (in CH_2Cl_2 under N_2) can only reduce one of the two metal centres since $E_{1/2}$ for the cobaltocene–cobaltocenium couple is −1.34 V *vs.* Fc/Fc$^+$ (Table 1). We also generated the MV complexes *in situ* in an EPR flat cell by controlled potential electrolysis with a Pt grid working electrode.

Representative EPR spectra are in Fig. 1. There are two possible types of behaviour which can be envisaged for the MV species. If they are valence-trapped on the EPR timescale, the spectrum will be that of an isolated mononuclear Mo centre, *i.e.* a typical 'singlet + sextet' spectrum with a separation of *ca.* 5 mT in the sextet due to hyperfine coupling to those nuclei (*ca.* 25% natural abundance) with I = 5/2. If the MV state is delocalised on the EPR timescale, then the single electron will couple equally to both nuclei to give superimposed components consisting of 1, 6 and 11 lines with a separation of *ca.* 2.5 mT between the hyperfine components.[5,7] This could happen in a class III MV complex where the electron is fully delocalised (a single minimum in the potential-energy curve) or in a strongly interacting class II complex in which the thermal barrier between the two minima of the potential-energy curve is sufficiently small that thermal excitation is fast on the EPR timescale (*ca.* 10^{-8} s).

For all three series of complexes (X = Cl, Br, I) the room-temperature solution spectra show that, on the EPR timescale, with the 1,2- and 1,4-$[NHC_6H_4NH]^{2-}$ bridge the MV state is delocalised whereas with 1,3-$[NHC_6H_4NH]^{2-}$ as the bridge the MV state is localised (Fig. 1). In the 'delocalised' spectrum [Fig. 1(*b*)] only the first two components of the undecet are apparent on the low-field side of the spectrum—the high-field side of these spectra always suffer from anisotropic line-broadening—but the presence of two sets of hyperfine signals of different intensity, and the halved hyperfine coupling compared to the spectrum of Fig. 1(*a*), clearly confirms the delocalised nature of the complex.[5] For the complexes with X = I, decomposition of the reduced species was observed after a few minutes but the spectra of the initially generated MV

Table 1 Summary of the electrochemical properties of $[\{MoL(NO)X\}_2\{\mu\text{-}1,n\text{-}C_6H_4(NH)_2\}]$ as a function of halide (X = Cl, Br, I) and the bridging ligand structure (n = 2,3,4)

	1,2-bridge[a,b]			1,3-bridge[a,b]			1,4-bridge[a,b]		
X	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$
Cl	−1.14	−1.92	0.78	−1.35	−1.72	0.37	−1.10	−2.03	0.92
Br	−1.09	−1.89	0.80	−1.30	−1.67	0.37	−1.07	−2.00	0.93
I	−1.03[c]	−1.88[c]	0.85	−1.28[c]	−1.65[c]	0.37	−1.04[c]	−1.99[c]	0.95

[a] All potentials are in volts *vs.* the ferrocene–ferrocenium couple. [b] $E_{1/2}$ for the cobaltocene–cobaltocenium couple is −1.34 V *vs.* Fc/Fc$^+$ under the conditions employed. [c] This process is not fully reversible on the voltammetric timescale; the peak potential from square-wave voltammogram is given.

species are in agreement with those of the X = Cl and X = Br series. The results are the same whether chemical or electrochemical reduction was employed. Freezing the MV species to 77 K confirms the results: the 1,3-bridged complexes give typical axial spectra for an isolated mononuclear molybdenum centre with three *g*-values, whereas the 1,2- and 1,4-bridged complexes give completely different broad, featureless spectra. A few points should be made:

(1) We assume that the unpaired electron is largely metal-based, in view of the similarity of these spectra to those of related isoelectronic {MoL(NO)X} complexes where the sixth ligand has no π-acceptor character (*e.g.* phenolate),[10] and the obviously different spectra that arise in other cases when a Mo centre is coordinated to a ligand radical anion.[11]

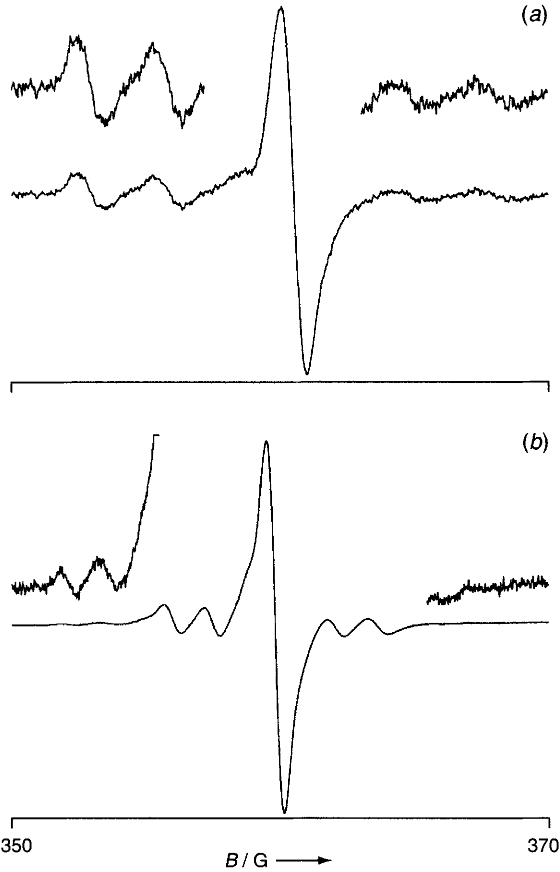

Fig. 1 Solution EPR spectra (CH_2Cl_2, room temperature) of the electrochemically generated mixed-valence complexes $[\{MoL(NO)X\}_2\{\mu\text{-}1,n\text{-}C_6H_4(NH)_2\}]^-$: (*a*) with X = Br and $1,3\text{-}[C_6H_4(NH)_2]^{2-}$ as the bridge; (*b*) with X = Cl and $1,2\text{-}[C_6H_4(NH)_2]^{2-}$ as the bridge. Spectrum (*a*) is representative of all those complexes with the 1,3-substituted bridge; (*b*) is representative of all those complexes with 1,2- or 1,4-substituted bridges.

(2) The results for the 1,4-bridged complexes are in interesting contrast to those for the similar MV complex $[\{MoL(NO)Cl\}_2(\mu\text{-}1,4\text{-}OC_6H_4O)]^-$ which was shown to be valence-trapped by EPR spectroscopy.[11] The better delocalisation—and much larger electrochemical interaction—observed in $[\{MoL(NO)Cl\}_2(\mu\text{-}1,4\text{-}NHC_6H_4NH)]^-$ compared to its phenolic counterpart may be ascribed to the formal sp^2 hybridisation of the amido N atoms, which affords continuous $d_\pi\text{–}p_\pi\text{–}p_\pi$ overlap throughout the Mo–NH–phenyl fragment.[9]

(3) For these complexes, UV–VIS spectra of the MV species are of little use as intense and broad ligand-to-metal charge-transfer bands often extend into the region where IVCT bands might be expected.

(4) The spectra of the MV species do not vary significantly with temperature in the range 180–300 K: thus the IVCT process cannot be 'frozen out' for the delocalised MV complexes, nor can it be initiated for the localised MV complexes by heating, within this range.

In summary, these complexes are the first in which a change in the nature of the mixed-valence state from localised to delocalised has been demonstrated as the substitution pattern of the bridging ligand is varied.

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