

# Characterisation of two different mixed-valence states in a strongly interacting dimolybdenum complex

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**The pyrazine-bridged bimetallic complex  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{Br}\}_2(\mu\text{-pz})^z [\text{HB}(\text{dmpz})_3] = \text{tris}(3,5\text{-dimethylpyrazolyl)borate}$  exists within a five-membered electron-transfer chain where  $z = -2, -1, 0, +1$  and  $+2$ ; the mixed-valence species with  $z = -1$  is delocalised on the EPR and IR spectroscopic timescales whereas that with  $z = +1$  is valence-trapped.**

The most celebrated dimetallic mixed-valence compound is the so-called Creutz-Taube ion,  $[\{\text{Ru}(\text{NH}_3)_5\}_2(\mu\text{-pz})]^{5+}$ , derived by coupling two  $\text{Ru}^{\text{II}}$  pentammine fragments by pyrazine followed by one-electron oxidation of the product.<sup>1</sup> It is now generally accepted that this ion exhibits class III mixed-valence behaviour, namely that the unpaired electron is delocalised over the metal ions and the bridging ligand.<sup>2</sup> Many other examples of such mixed-valence species have been described, showing a wide range of behaviour from fully delocalised to valence-trapped.<sup>2</sup> The majority of these species are usually assembled by coupling diamagnetic monometallic fragments using bridging ligands of varying lengths, geometries and delocalisation. In all but a few cases, these precursors are oxidised in a one-electron process to generate the mixed-valence ion, although two types of molybdenum complex,  $[\{\text{Mo}(\text{CO})_3(\text{PR}_3)_2(1,4\text{-pz})\}^-]$  (ref. 3) and  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{X}\}_2\{\text{C}_6\text{H}_4(\text{NH})_2\text{-1,4}\}^-]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),<sup>4</sup> are generated by reduction of the diamagnetic precursors, the former being described as a radical anionic ligand stabilised by metal carbonyl fragments,<sup>†</sup> whereas the latter is fully delocalised on the EPR timescale.

For a number of years we have been studying a series of binuclear molybdenum nitrosyls containing bridging dipyridine ligands. These complexes contain two metal-based redox centres whose interaction, determined electrochemically, is mediated significantly by the bridging ligand.<sup>5</sup> Furthermore, these compounds are paramagnetic (one unpaired electron on each metal atom), the unpaired spins being coupled either ferro- or antiferro-magnetically depending on bridging ligand geometry, and their EPR spectra reveal spin-spin correlation over remarkably long distances.<sup>6</sup> Our preceding work on molybdenum nitrosyl complexes of 4,4'-dipyridyl and its analogues,  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{Cl}\}_2(\text{NC}_5\text{H}_4\text{EC}_5\text{H}_4\text{N})]$  [ $\text{E} = \text{nothing}, (\text{CH}=\text{CH})_n, (\text{C}_6\text{H}_4)_n$ ] has shown that the metal-metal interactions gradually diminish with increasing length of  $\text{E}$ . Conversely we expected that a dimetallic species containing 1,4-pyrazine as bridge should reveal very substantial electrochemical and magnetic interactions, at least twice as large as those in the Creutz-Taube ion ( $\Delta E_p$ , the separation between the redox potentials, is *ca.* 390 mV).

Our early attempts to make species of the type  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{X}\}_2(1,4\text{-pz})]$  ( $\text{X} = \text{Cl}$  or  $\text{I}$ ) were partially successful, revealing unexpectedly rich electrochemical behaviour,<sup>7</sup> although the species were difficult to purify and also appeared to decompose readily. However, we have now obtained pure samples of the bromo complex,  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{Br}\}_2(1,4\text{-pz})]$ .<sup>‡</sup> In contrast to the behaviour of  $[\{\text{Ru}(\text{NH}_3)_5\}_2(1,4\text{-pz})]^{5+}$  in aqueous media, this species exhibits two reversible one-electron reductions (established coulometrically) as well as two reversible one-electron oxidations. The former occur at  $-0.95$  and  $-2.39$  V in

dichloromethane vs. the ferrocene-ferrocenium couple, and the latter at  $+1.08$  and  $+1.18$  V, respectively. The separation between the reduction potentials, a measure of the coulombic interaction between the two redox centres, is 1440 mV, the largest we have so far detected and amongst the largest known, equivalent to a comproportionation constant  $K_c = 2.2 \times 10^{24}$ . For the first time we have also detected a separation between the oxidation processes in this class of dimetallic, *viz.* 100 mV ( $K_c = 49$ ). That interaction between the reduction processes is so much larger than that between the oxidations implies that the added electrons in the reduced form are substantially delocalised over the bridge whereas the unpaired electron in the oxidised form is not. Thus  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{Br}\}_2(1,4\text{-pz})^z]$  exists within a five-membered electron-transfer chain ( $z = -2, -1, 0, +1$  and  $+2$ ), reminiscent of dithiolenes complexes,<sup>8</sup> in which the formal valence-electron configuration of the two metals may be represented as  $\{18:18\}^{2-}, \{18:17\}^-, \{17:17\}, \{17:16\}^+$  and  $\{16:16\}^{2+}$ .

The green isovalent parent species ( $z = 0; \{17:17\}$ ) is EPR 'silent' in contrast to related bipyridyl species  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{Cl}\}_2(\text{NC}_5\text{H}_4\text{EC}_5\text{H}_4\text{N})]$ .<sup>5,6</sup> We expect that the unpaired spins in this species will be quite strongly coupled antiferromagnetically, as we have observed in analogues,<sup>6</sup> and in such circumstances EPR signals are not observed. § The deep blue reduced monoanion ( $\{18:17\}^-$ ), generated by cobaltocene reduction, exhibits an EPR spectrum composed of the superimposition of one, six and eleven line multiplets derived by a single electron coupling equally to both metal nuclei (<sup>95</sup>Mo, <sup>97</sup>Mo  $I = 5/2$ ; *ca.* 25% abundance in total), ¶ with  $g = 1.979$ ,  $A_{\text{Mo}} = 2.9$  mT. The IR spectrum of the neutral precursor exhibits a single NO stretching frequency at  $1626 \text{ cm}^{-1}$  (in  $\text{CH}_2\text{Cl}_2$ ) which, on reduction, moves to  $1585 \text{ cm}^{-1}$ , but remains a single peak. Our spectral data are consistent with class III, fully delocalised mixed-valence behaviour for the  $\{18:17\}^-$  monoanion on both the EPR and the IR timescale, implying that the electron exchange rate is  $10^{13} \text{ s}^{-1}$  or faster. Our previously reported mixed-valence molybdenum complexes  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{X}\}_2\{\text{C}_6\text{H}_4(\text{NH})_2\text{-1,4}\}^-]$  are delocalised on the EPR timescale,<sup>4</sup> but localised according to their IR spectra (two  $\nu_{\text{NO}}$ ) indicating that the electron exchange rate lies between  $10^8$  and  $10^{13} \text{ s}^{-1}$ . Such behaviour is very rare although it has been detected in binuclear iron carbonyls and rhenium nitrosyls.<sup>9</sup>

Further electrochemical reduction to generate the dianion,  $\{18:18\}^{2-}$ , which we predict should be diamagnetic, is difficult because of the proximity of the reduction process to the decomposition of the electrolysis medium, but by monitoring the EPR spectrum of the monoanion while reduction was occurring, we observed that the intensity of the signal decreased significantly without qualitative change in its appearance, *i.e.* consistent with the formation of diamagnetic material.

Oxidation of the neutral precursor by controlled potential electrolysis in dichloromethane at  $+1.05$  V, afforded a brown solution of  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3]\text{Br}\}_2(1,4\text{-pz})]^+$  ( $\{17:16\}^+$ ), the EPR spectrum of which was difficult to obtain due to decomposition but appeared unlike that of the monoanion described above and contained sextet signals with  $A_{\text{Mo}}$  *ca.* 5.0 mT. However, the isoelectronic chloride,

$[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3\text{Cl}]_2(1,4\text{-pz})\}^+]$  (generated similarly), was more stable, exhibiting an EPR spectrum with  $g = 1.979$  and  $A_{\text{Mo}} = 4.8$  mT, having a one and six line superimposed pattern,<sup>¶</sup> which shows that the unpaired electron is coupled with only one Mo atom. The IR spectrum of the bromo monocation exhibited two NO stretching frequencies, at 1720 and 1606  $\text{cm}^{-1}$  (the chloro species was similar,  $\nu_{\text{NO}} = 1717, 1608$   $\text{cm}^{-1}$ ). The fully oxidised brown dication  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3\text{Br}]_2(1,4\text{-pz})\}^{2+}]$  ( $\{16:16\}^{2+}$ ) was prepared by oxidation of the neutral parent by acetylferrocenium ion. It was EPR 'silent' and therefore probably diamagnetic, and exhibited only one  $\nu_{\text{NO}}$  (1703  $\text{cm}^{-1}$ ). On the basis of these spectral data we conclude that the partially oxidised monocations  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3\text{X}]_2(1,4\text{-pz})\}^+]$  ( $\text{X} = \text{Cl}, \text{Br}$ ) are valence-trapped.

While the isoivalent  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3\text{Br}]_2(1,4\text{-pz})\}(\{17:17\})]$  behaves in a way reminiscent of its ruthenium analogue, it exhibits more extensive electron-transfer capability. This is partly a function of solvent, base electrolyte, *etc.*, and the original Creutz-Taube ion was characterised electrochemically in aqueous media which has a more limited voltage window. Nevertheless, the dinuclear molybdenum nitrosyl described here is one of the very few compounds in which mixed-valence behaviour is generated by oxidation and reduction and it is unique in giving rise, reversibly, to two different classes of mixed-valence states without significant structural modification. The electrochemical data nicely complement the EPR spectral results, since the character of the mixed-valence states is related to the comproportionation constants for the mixed-valence species, a large value of  $K_c$  implying substantial delocalisation while a small  $K_c$  implies significantly less interaction.

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#### Footnotes

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† This system cannot be defined as a genuine mixed-valence species, since the metal-based orbitals are formally occupied (each metal centre has 18 valence electrons prior to reduction) and the LUMO must be predominantly bridging ligand based.

‡ Both  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3\text{Br}]_2(1,4\text{-pz})\}]$  and  $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\text{Br}(1,4\text{-pz})\}]$  are prepared by refluxing  $[\text{Mo}(\text{NO})\{\text{HB}(\text{dmpz})_3\text{Br}_2\}]$  with pyrazine in toluene containing triethyl-

amine and are separated chromatographically on silica gel using dichloromethane-thf as eluent. FABMS: 1087 ( $\text{M}^+$ ). (Found C, 38.1; H, 4.4; N, 20.4.  $\text{C}_{22}\text{H}_{52}\text{B}_2\text{Br}_2\text{Mo}_2\text{N}_{16}\text{O}_2$  requires C, 37.6; H, 4.5; N, 20.6%). Cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$ , using Pt bead electrode, ferrocene as reference,  $[\text{NBu}^n_4]\text{PF}_6$  as base electrolyte, scan rate 50 and 100  $\text{mV s}^{-1}$ .

§ Preliminary magnetic susceptibility measurements in the range 80–300 K show that  $[\{\text{Mo}(\text{NO})[\text{HB}(\text{dmpz})_3\text{Cl}]_2(1,4\text{-pz})\}]$  exhibits antiferromagnetic behaviour ( $J$  ca.  $-180$   $\text{cm}^{-1}$ ) consistent with our recently reported findings regarding the sign and magnitude of  $J$  (ref. 6).

¶  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$  have  $I = 5/2$ , a relative overall abundance of ca. 25% and similar nuclear magnetic moments. For an electron coupled to one Mo atom, the signal consists of a singlet (ca. 75% of Mo nuclei,  $I = 0$ ) and a sextet (ca. 25% of Mo nuclei,  $I = 5/2$ ). For an electron coupled to two Mo atoms, the signal appears as a singlet ( $I = 0, I = 0$ ), 1:1:1:1:1:1 sextet ( $I = 5/2, I = 0$ ), and 1:2:3:4:5:6:5:4:3:2:1 11-fold multiplet ( $I = 5/2, I = 5/2$ ) nuclear spin combinations. From previous data, we expect  $A_{\text{Mo}}$  to be 4.5–5.0 mT for one electron coupled to one Mo centre and 2.4–2.5 mT for one coupled to two Mo centres (refs. 4, 5).

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