Electrochemical and Electron–Electron Exchange Interactions in Binuclear Molybdenum Complexes containing the Bridging Ligand 4-(Imidazol-1-yl)phenol

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A series of mono- and bi-nuclear complexes containing {M(NO)LX} [M = Mo or W, X = Cl or I, L = tris(3,5-dimethylpyrazol-1-yl)hydroborate] groups attached to either or both ends of the potentially bridging ligand 4-(imidazol-1-yl)phenol (HL^1) have been prepared, in order to examine both electrochemical and electron–electron exchange interactions across the bridging ligand. Electrochemical studies have shown that the imidazolyl ligand shifts the redox potentials of the {Mo(NO)LX} (X = Cl or I) core cathodically to the extent that the 17e–18e reductions cannot be observed. As with the similar bridging ligand 4-(4-pyridyl)phenol, the electrochemical interaction between the two 16e–17e processes in the binuclear complex is weak. The binuclear molybdenum complexes of L^1 contain one 17-electron (imidazolyl terminus) and one 16-electron (phenolate terminus) metal centre, and are clearly valence-trapped according to the EPR spectra. However one-electron reduction to the 17e–17e biradical initiates a strong electron–electron exchange interaction, whereby both of the unpaired electrons are coupled equally to both molybdenum nuclei, despite the weak electrochemical interaction.

In pursuing our interest in the design and synthesis of molecular wires,[1] we have developed an extensive chemistry of binuclear molybdenum nitrosyl species in which the redox-active metal centres are connected by poly-aryl or -ethene conjugated bridges containing terminal pyridyl or phenolic groups as ligands.[2–4] We have obtained species which contain symmetric bridges based on biphenols, *e.g.* [{Mo(NO)LCl}$_2$(OC$_6$H$_4$–Q–C$_6$H$_4$O)] [L = tris(3,5-dimethylpyrazol-1-yl)hydroborate; Q = nothing, CO *etc.*]; the two metal centres have 16 valence electrons (16e) and may be reduced in two one-electron steps generating a valence-trapped paramagnetic monoanion (16e–17e) and a paramagnetic dianion (17e–17e).[2] We have also prepared similar paramagnetic (17e–17e) binuclear complexes [{Mo(NO)LCl}$_2$(C$_5$H$_4$N–Q–C$_5$H$_4$N)] (Q = C$_6$H$_4$, N=N or CH=CH *etc.*; C$_5$H$_4$N = 4-pyridyl) with 'extended' analogues of 4,4′-bipyridine as bridging ligands,[3] and asymmetrically bridged species [{Mo(NO)LCl}$_2$(OC$_6$H$_4$–Q–C$_5$H$_4$N)] which contain a 16-electron metal centre at the phenolate terminus of the bridge and a 17-electron metal centre at the pyridyl terminus. These asymmetric 16e–17e species are also valence trapped, but reduction to a 17e–17e species initiates exchange between the two inequivalent metal centres.[4]

The extent to which the metal centres can 'communicate' has been examined by a combination of electrochemical and EPR studies. The communication manifests itself in two distinct ways: an electrochemical interaction, whereby the potentials of the redox processes associated with the metal centres at each end of the bridge are separated; and an exchange interaction between the two unpaired electrons of the 17e–17e diradicals which can be seen by EPR spectroscopy. It is clear that the extent of electrochemical interaction is controlled by three different features of the bridging ligand: the length of the bridge (*i.e.* the separation between the redox centres);[2–4] the planarity of the bridge;[3] and, for the asymmetric ligands OC$_6$H$_4$–Q–C$_5$H$_4$N, the extent to which the bridging ligand can form a planar, delocalised quinonoid structure by charge transfer from the phenolate terminus (electron donor) to the pyridyl terminus (electron acceptor).[4] The electrochemical interactions are particularly strong, and hence easy to measure, when they involve redox orbitals that are partially delocalised on to a π-accepting bridging ligand; in [{Mo(NO)LCl}$_2$(μ-4,4′-bipy)] (4,4′-bipy = 4,4′-bipyridine) the separation between the one-electron reductions (formally a 17e–18e couple at each metal centre) is 765 mV, whereas in [{Ru(NH$_3$)$_5$}$_2$(μ-4,4′-bipy)]$^{4+}$ the two Ru^{II}–Ru^{III} couples are separated by 76 mV and cannot be resolved by cyclic voltammetry. However the predominantly metal-centred *oxidations* (17e–16e couples) in [{Mo(NO)LCl}$_2$(μ-4,4′-bipy)] and related complexes are virtually coincident.

The exchange interaction in the 17e–17e diradicals appears to be persistent even in binuclear complexes where the electrochemical interaction is very weak, *e.g.* when the bridging ligand is long or contains a saturated group which breaks the conjugation. This is in part due to the fact that delocalisation of both electrons over both metal centres, which may be viewed as a pairwise exchange process, is not impeded by an energy barrier due to solvent reorganisation, since both metal centres retain their 17-electron configuration throughout. However we have recently observed that with very long biphenol bridging ligands such as OC$_6$H$_4$C(O)C$_6$H$_4$C$_6$H$_4$C(O)C$_6$H$_4$O between two 17-electron molybdenum centres, the EPR spectra indicate that the exchange interaction is much weaker than in complexes with shorter bridging ligands, so we are starting to see a dependency of the exchange interaction on intermetal separation.[2]

In order to clarify further the structural parameters of the bridging ligand relevant to maximisation of metal–metal interactions, we have prepared a series of mono- and bi-nuclear complexes based on the asymmetric bridging ligand 4-(imidazol-1-yl)phenol (HL^1). In contrast to bridging ligands such as 4-(4-pyridyl)phenol (HL^2), HL^1 cannot so easily adopt a delocalised quinonoidal structure by charge transfer between the ends, and the electrochemical characteristics of its bimetallic complexes may reflect this. It is also of interest to examine the effect of the different type of bridging ligand on the exchange process between the paramagnetic centres in the 17e–17e complexes.

Experimental

The ^1H NMR spectra were recorded on a JEOL GX270 instrument and fast-atom bombardment (FAB) mass spectra on a VG-Autospec at the SERC Mass Spectrometry Service Centre, Swansea, with 3-nitrobenzyl alcohol as matrix. IR spectra were measured in compressed KBr discs with a Perkin Elmer 1600 FTIR spectrophotometer. EPR spectra were recorded at room temperature on a Bruker ESP-300E spectrometer. Electrochemical experiments were performed using an EG&G PAR model 273A potentiostat. A standard three-electrode configuration was used, with platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted *vs.* the ferrocene–ferrocenium couple. The solvent was CH_2Cl_2, purified by distillation from CaH_2, containing 0.1 mol dm^{-3} $[NBu_4][PF_6]$ as the base electrolyte.

4-(Imidazol-1-yl)phenol was purchased from Aldrich. All reagents were used as purchased without further purification, except for $[Mo(NO)LX_2]$ (X = Cl or I) and $[W(NO)LCl_2]$ which were prepared according to literature methods.[5] Reaction solvents were distilled under N_2 prior to use.

Preparations.—$[Mo(NO)L(OC_6H_4–NC_3H_3N)Cl]$ **1** *and* $[Mo(NO)L(NC_3H_3N–C_6H_4OH)Cl]$ **2**. A mixture of $[Mo(NO)LCl_2]$ (0.2 g; 0.41 mmol) and NEt_3 (0.5 cm^3) in dry tetrahydrofuran (thf) (30 cm^3) was heated to reflux with stirring for 0.5 h under N_2. Then a solution of HL^1 (0.16 g, 1.0 mmol) in hot thf (70 cm^3) was added and the reaction mixture heated to reflux for a further 2 h. It was then cooled and filtered, and the filtrate evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel by gradient elution using CH_2Cl_2, 9:1 CH_2Cl_2–thf and finally pure thf as eluents. Those fractions containing only pure **1** or **2** (checked by ν_{NO}) were combined, evaporated to dryness and recrystallised from CH_2Cl_2–hexane. Yields: **1**, 0.074 g (29%); **2**, 0.056 g (22%). The yields were not optimised as some mixed fractions were not used.

$[Mo(NO)L(NC_3H_3N–C_6H_4OH)I]$ **3**. This compound was prepared from $[Mo(NO)LI_2]$ (0.3 g, 0.44 mmol), HL^1 (0.16 g, 1.0 mmol) and NEt_3 (0.5 cm^3) in dry thf (100 cm^3) as above except that the reaction time was 1 h. Yield: 0.099 g (32%).

$[\{Mo(NO)LCl\}_2(\mu-OC_6H_4–NC_3H_3N)]$ **4**. A mixture of $[Mo(NO)LCl_2]$ (0.2 g, 0.41 mmol), HL^1 (0.08 g, 0.5 mmol) and NEt_3 (0.3 cm^3) in toluene (50 cm^3) was heated to reflux under N_2 for 4 h to give a brown solution. The reaction mixture was cooled, hexane added to precipitate inorganic salts, and then filtered. The filtrate was evaporated to dryness and chromatographed on silica gel. Dichloromethane was used as the initial eluent to remove unreacted $[Mo(NO)LCl_2]$, then the main product was eluted with 9:1 CH_2Cl_2–thf. After evaporating to dryness and recrystallisation from CH_2Cl_2–hexane, brown microcrystals of **4** were isolated. Yield: 0.11 g (24%).

$[\{Mo(NO)LI\}_2(\mu-OC_6H_4–NC_3H_3N)]$ **5**. This compound was prepared from $[Mo(NO)LI_2]$ (0.3 g, 0.44 mmol), HL^1 (0.08 g, 0.5 mmol) and NEt_3 (0.3 cm^3) in toluene (50 cm^3) as for **4**, followed by chromatographic purification as for **4**. Yield: 0.16 g (29%).

$[W(NO)L(OC_6H_4–NC_3H_3N)Cl]$ **6**. A mixture of $[W(NO)LCl_2]$ (0.23 g, 0.4 mmol), HL^1 (0.16 g, 1.0 mmol) and NEt_3 (0.3 cm^3) in toluene (50 cm^3) was heated to reflux with stirring under N_2 for 5 h. The mixture was cooled, filtered, and the filtrate evaporated to dryness. The residue was chromatographed on silica gel initially with 9:1 CH_2Cl_2–thf as eluent to remove impurities, followed by pure thf to elute the main green band. After evaporation of the main fraction to dryness, complex **6** was isolated by precipitation on dropwise addition of hexane to a concentrated CH_2Cl_2 solution of the compound. Yield: 140 mg (50%).

$[W(NO)LCl(\mu-OC_6H_4–NC_3H_3N)Mo(NO)LCl]$ **7**. A mixture of complex **6** (0.1 g, 0.14 mmol), $[Mo(NO)LCl_2]$ (0.14 g, 0.28 mmol) and NEt_3 (0.2 cm^3) in toluene (30 cm^3) was refluxed with stirring under N_2 for 10 h. The mixture was cooled and filtered, and hexane added to the filtrate to give an olive-green solid. This was filtered off and chromatographed on silica gel with 19:1 CH_2Cl_2–thf as eluent. Unreacted $[Mo(NO)LCl_2]$ was eluted first; the product then eluted and was recrystallised from thf–hexane to give green microcrystals. Yield: 0.047 g (29%).

$[W(NO)LCl(\mu-OC_6H_4–NC_3H_3N)Mo(NO)LI]$ **8**. This compound was prepared as for **7**, using **6** (0.1 g, 0.14 mmol), $[Mo(NO)LI_2]$ (0.19 g, 0.28 mmol) and NEt_3 (0.2 cm^3) in toluene (30 cm^3). The crude product was isolated and purified as above. Yield: 0.06 g (34%).

Analytical and spectroscopic data for the new complexes are in Table 1.

Results and Discussion

Syntheses of the Complexes.—Eight new mono- and binuclear complexes were prepared; their formulations are summarised in Table 1. Reaction of HL^1 with the 16-electron complex $[Mo(NO)LCl_2]$ in the presence of NEt_3 afforded a mixture of mononuclear products in which the metal is attached to either the phenolate terminus (**1**) or the imidazolyl terminus (**2**) of HL^1. The imidazolyl-substituted complexes such as **2** appear to form more readily than the analogous pyridyl-substituted complexes, since reaction of $[Mo(NO)LCl_2]$ with 4-(4-pyridyl)phenol (HL^2) gave phenolate-substituted species as the only mononuclear products; no pyridyl complexes were detected if a phenolate complex could form preferentially.[4] Attachment of the phenol terminus to the metal involves deprotonation of HL^1 by the NEt_3, and results in a diamagnetic 16-electron species. In contrast, attachment to the imidazolyl terminus results in a paramagnetic 17-electron molybdenum centre. In this respect the imidazolyl group behaves like a pyridyl group, since attachment of a pyridyl ligand also involves one-electron reduction of the $\{Mo(NO)LX\}$ (X = Cl or I) centre, probably by NEt_3 which can act as an hydridic reducing agent.[6] The mononuclear complexes with $\{W(NO)LCl\}$ attached to the phenolate terminus (**6**) and $\{Mo(NO)LI\}$ attached to the imidazolyl terminus (**3**) of HL^1 were prepared similarly.

Homobinuclear complexes **4** and **5** were prepared by reaction of the appropriate starting complex $[Mo(NO)LX_2]$ (X = Cl or I respectively) with HL^1 under more forcing conditions (toluene at reflux) than used for the mononuclear complexes, and with a higher ratio of metal complex to bridging ligand. Finally the mixed-metal binuclear complexes **7** and **8** were prepared in a stepwise manner by reaction of the mononuclear tungsten complex **6**, containing a pendant imidazolyl group, with additional $[Mo(NO)LX_2]$ (X = Cl or I for **7** and **8** respectively). We could not isolate a complex in which a tungsten centre was attached to the imidazolyl terminus of HL^1.

All of the complexes were characterised satisfactorily by elemental analysis and FAB mass spectrometry, the latter giving a strong molecular ion cluster in each case (Table 1). The positions of the ν_{NO} stretching bands in the IR spectra are also diagnostic: for 17-electron molybdenum centres (with imidazolyl ligands) ν_{NO} appears in the range 1600–1620 cm^{-1} whereas in the 16-electron molybdenum complexes (with phenolate ligands) ν_{NO} is at approximately 1680 cm^{-1}. The 16-electron tungsten–phenolate complexes have ν_{NO} at about 1640 cm^{-1}. The two diamagnetic complexes **1** and **6** were also characterised by ^1H NMR spectroscopy in CD_2Cl_2 solution. Both displayed signals corresponding to seven protons of L between δ 7 and 8, three inequivalent pyrazolyl ring protons (H^4) between δ 5.7 and 6.1, and six inequivalent singlets of intensity 3 H each between δ 2.1 and 2.7 corresponding to the pyrazolyl methyl groups.

Electrochemical Properties.—The complexes of HL^1 were

Table 1 Analytical and spectroscopic data for the new complexes

	$Y-OC_6H_4-NC_3H_3N-Z$		Analysis* (%)				
Complex	Y	Z	C	H	N	FAB MS* M^+	$\tilde{\nu}_{NO}/cm^{-1}$
1	Mo(NO)LCl	—	46.4 (46.7)	4.9 (4.7)	19.8 (20.4)	618 (617)	1681
2	H	Mo(NO)LCl	47.4 (46.6)	5.0 (4.9)	19.8 (20.4)	618 (618)	1615
3	H	Mo(NO)LI	39.8 (40.6)	4.4 (4.1)	18.1 (17.8)	712 (710)	1617
4	Mo(NO)LCl	Mo(NO)LCl	42.8 (43.5)	5.0 (4.8)	20.5 (20.8)	1078 (1076)	1679, 1618
5	Mo(NO)LI	Mo(NO)LI	37.3 (37.2)	4.1 (4.1)	17.5 (17.8)	1259 (1259)	1682, 1621
6	W(NO)LCl	—	40.1 (40.9)	4.3 (4.1)	17.1 (17.9)	706 (705)	1633
7	W(NO)LCl	Mo(NO)LCl	40.4 (40.3)	4.5 (4.4)	19.3 (19.3)	1164 (1164)	1647, 1599
8	W(NO)LCl	Mo(NO)LI	36.7 (37.3)	4.2 (4.1)	17.5 (17.8)	1257 (1255)	1638, 1618

* Calculated values in parentheses.

Table 2 Electrochemical, EPR and UV/VIS data for the new complexes

	$Y-OC_6H_4-NC_3H_3N-Z$				UV/VIS spectra^b
Complex	Y	Z	$E_{\frac{1}{2}}/V$ (ΔE_p/mV)	g_{iso} (A_{iso}/G)^a	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})
1	Mo(NO)LCl	—	−0.85 (100)	—	308 (6.0), 472 (2.8)
2	H	Mo(NO)LCl	−0.08 (100)	1.980 (50)	438 (0.6)
3	H	Mo(NO)LI	−0.03 (80)	2.007 (46)	367 (5.2)
4	Mo(NO)LCl	Mo(NO)LCl	−0.07 (80), −0.83 (120)	1.979 (50)	315 (8.8), 434 (7.3), 475 (sh)
5	Mo(NO)LI	Mo(NO)LI	−0.03 (70), −0.76 (90)	2.005 (47)	360 (11), 454 (9.5)
6	W(NO)LCl	—	+1.11 (130), −1.39 (170)	—	392 (8.2), 588 (0.4)
7	W(NO)LCl	Mo(NO)LCl	+1.10 (110), −0.07 (80), −1.38 (150)	1.977 (50)	368 (8.1), 585 (0.3)
8	W(NO)LCl	Mo(NO)LI	+1.11 (100), −0.03 (80), −1.35 (130)	2.005 (46)	356 (12), 587 (0.4)

^{a} Recorded in CH_2Cl_2 at room temperature. Error in g_{iso} ± 0.001. Error in A_{iso} ± 1 G. ^{b} Recorded in CH_2Cl_2.

studied by cyclic and square-wave voltammetry in CH_2Cl_2 solution; the results are summarised in Table 2, and are of particular interest in comparison with the analogous complexes of HL^2.[4] The {$Mo(NO)LCl(OC_6H_4-NC_3H_3N)$} ($NC_3H_3N$ = imidazolyl) group of **1** undergoes a metal-centred 16e–17e reduction at −0.85 V *vs.* ferrocene–ferrocenium. With an unsubstituted phenolate ligand the analogous reduction potential is −0.94 V;[7] the imidazolyl substituent therefore makes the reduction easier by 90 mV, suggesting that it acts as an electron-accepting substituent on the phenolate ligand. In contrast the 16e–17e reduction of compound **6**, at −1.39 V, is similar to that of [W(NO)L(OPh)Cl] (−1.38 V), although in **6** we also observe a 16e–15e oxidation which is not present for [W(NO)L(OPh)Cl]. The substituent effect of the pendant imidazolyl group in **1** and **6** is, therefore, substantially less than that of a 4-pyridyl group; the reduction potential of [$Mo(NO)L(OC_6H_4-C_5H_4N)Cl$] ($C_5H_4N$ = 4-pyridyl) is −0.70 V,[4] an anodic shift of 240 mV compared to [Mo(NO)L(OPh)Cl], and the tungsten analogue reduces at −1.22 V, with the pendant 4-pyridyl group causing an anodic shift of 170 mV. This is because charge transfer from the phenolate terminus of L^2 to the pyridyl terminus is easy, *via* formation of a quinonoidal structure, resulting in substantial loss of electron density at the metal centre which facilitates reduction [Fig. 1(*a*)]. Although such charge transfer may still occur in L^1 as every atom in the ligand is trigonally hybridised, the adoption of a quinonoidal structure involves contributions from the canonical forms in which negative charges are adjacent to one another [Fig. 1(*b*)], and may therefore be regarded as less favourable.

The {$Mo(NO)LCl(NC_3H_3N)$} fragment of complex **2** undergoes a metal-centred 17e–16e oxidation at −0.08 V. This is more cathodic than the analogous pyridyl complexes which typically oxidise at +0.11 V,[4] and may be ascribed to the greater electron density at the metal centre because imidazolyl ligands are less effective π acceptors than pyridine ligands (for example, substitution of imidazole for pyridine in ruthenium complexes likewise decreases the $Ru^{II}-Ru^{III}$ potential).[8] The 17e–18e reduction, which occurs at −2.00 V in [Mo(NO)L(py)Cl] (py = pyridine),[9] is not visible for **2** presumably because it has been cathodically shifted to a potential more negative than the limit of the solvent–base electrolyte combination.

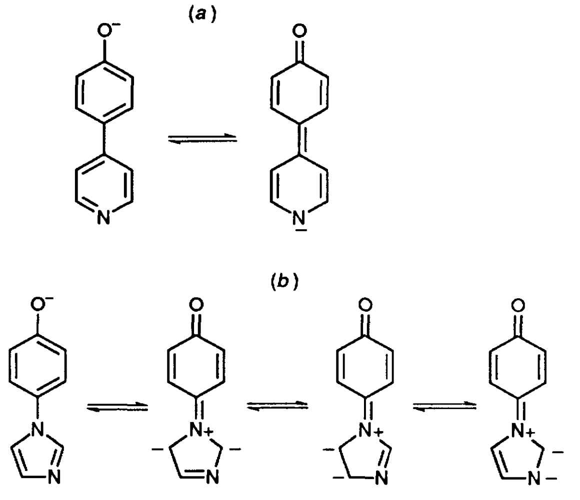

Fig. 1 Depiction of the quinonoidal contributions to (*a*) HL^2 and (*b*) HL^1

The redox potentials of the binuclear complex **4**, at −0.07 and −0.83 V, are essentially unchanged from those of the mononuclear components **1** and **2**. These two 16e–17e couples are therefore electrochemically non-interacting. This is similar to the behaviour of complexes [{$Mo(NO)LCl$}$_2$(μ-$OC_6H_4-C_5H_4N$)], where the 16e–17e redox potentials are at +0.11 and −0.70 V as compared to +0.12 and −0.65 V in the appropriate mononuclear components,[4] and also to the behaviour of symmetrically bridged complexes such as [{Mo(NO)LCl}$_2$(μ-4,4′-bipy)] and its extended analogues, which show well separated 17e–18e reductions but coincident 17e–16e oxidations. We have suggested that this behaviour is primarily due to the fact that the 17e–16e redox processes are primarily metal centred, so the communicative abilities of the bridging ligands are irrelevant.[3] A similar lack of interaction may be seen by comparison with the 16e–17e redox potentials of complex **5** with those of its mononuclear components **3** and [Mo(NO)L(OPh)I];[7] by comparison of **7** (Fig. 2) with **2** and **6**; and by comparison of **8** with **3** and **6**. In all cases the electrochemical properties of the binuclear complexes are essentially the sum of those of the mononuclear components with very little perturbation.

To make a better comparison of the relative abilities of HL^1 and HL^2 to mediate electrochemical interactions we should compare the 17e–18e redox potentials of the {Mo(NO)LCl(NC_3H_3N)} fragment in its mono- and bi-nuclear complexes, since (by analogy with the pyridyl-substituted complexes) it is these processes in binuclear complexes which are most likely to be separated *via* interaction across the bridging ligand. Unfortunately we could not observe these processes in any cases as the potentials are too negative for the solvent–base electrolyte combination we employed.

EPR Properties.—The 17-electron molybdenum centres of **2** and **3** have characteristic EPR signals at $g = 1.980$ (± 0.001) and 2.007 (± 0.001) respectively, the differing g values being attributable to the different spin-orbit coupling constants of the co-ordinated halogens.[10] Because of the isotopic distribution of molybdenum (approximately 75% has $S = 0$ and 25% has $S = \frac{5}{2}$) these signals consist of a sextet ($A_{Mo} = 4.6$–5.0 mT) superimposed on a central singlet [Fig. 3(*a*)].[2-4] The 16-electron complex **1** could be reduced to the 17-electron species $\mathbf{1}^-$ by reduction with cobaltocene *in situ* in the EPR tube, since the cobaltocene–cobaltocenium couple is sufficiently cathodic (-1.37 V *vs.* ferrocene–ferrocenium) to reduce the metal centre completely. Its EPR spectrum has the same sextet-plus-singlet appearance as the others but a lower g value of 1.969 (± 0.001), which is typical of a $[Mo(NO)L(OR)Cl]^-$ (R = aryl) core.[2,4] The spectra of complexes **5** and **8** are identical to that of **3**, and those of **4** and **7** are identical to that of **2**, which confirms that in the binuclear complexes containing one 16-electron diamagnetic centre and one 17-electron paramagnetic centre the odd electron is localised and the complex is valence trapped. This is to be expected considering the large difference in redox potential between the two ends of these complexes.

The diradical $\mathbf{4}^-$ could be prepared by chemical reduction of the 16-electron molybdenum–phenolate terminus with cobaltocene. This now contains two inequivalent 17-electron centres and its EPR spectrum [Fig. 3(*b*)] shows, as we have come to expect for diradicals of this type, that *both* unpaired electrons are coupled to *both* nuclei.[2-4] This is clear from three features of the spectrum: (*a*) the spectrum is a single signal with a g value (1.973) approximately midway between the g values of the component parts $\mathbf{1}^-$ and **2** (1.969 and 1.980 respectively); (*b*) the spectrum comprises a superposition of a central singlet, a 1:1:1:1:1:1 sextet, and a 1:2:3:4:5:6:5:4:3:2:1 eleven-fold multiplet which would be expected from coupling to both metal centres in a binuclear Mo complex with the appropriate isotopomer combinations (two $S = 0$ nuclei; one $S = 0$ and one $S = \frac{5}{2}$; two $S = \frac{5}{2}$ nuclei, respectively); and (*c*) the separation between the hyperfine components has halved to approximately 2.5 mT; if an electron has a hyperfine interaction of A_{Mo} with each of two nuclei, the apparent splitting on the spectrum is predicted to be $A_{Mo}/2g\beta$ (half that for a mononuclear complex) provided the exchange interaction $|J|$ between the two electrons is much greater than A_{Mo}.[11]

This behaviour, *i.e.* a change from fully localised in the mixed-valence complex **4** to 'delocalised' in the homovalent, reduced complex $\mathbf{4}^-$, is identical to that observed using L^2 as a bridging ligand.[4] It is a moot point as to whether the behaviour of a diradical such as $\mathbf{4}^-$ is best considered as a rapid, pairwise intramolecular exchange with the two electrons hopping between the metal centres, or as a delocalised system with the two unpaired electrons in separate molecular orbitals which span both metal centres. In the former case $|J|$ may be interpreted as an electron-transfer rate which must be substantially greater than about 10^7 Hz to give the observed spectrum.[4] In the latter case $|J|$ may be interpreted as an electron–electron interaction energy analogous to an antiferromagnetic coupling constant, of the order of at least 10^{-3} cm^{-1}.

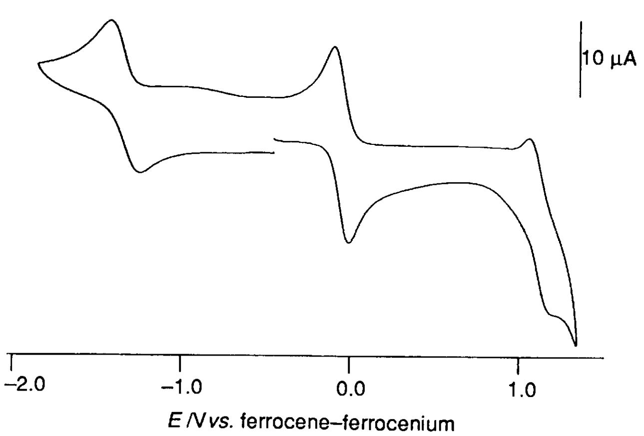

Fig. 2 Cyclic voltammogram of complex **7** in CH_2Cl_2 with a platinum-bead working electrode at a scan rate of 0.2 V s^{-1} showing (from left to right): 17e–16e couple of the tungsten centre; 17e–16e couple of the molybdenum centre; 16e–15e couple of the tungsten centre

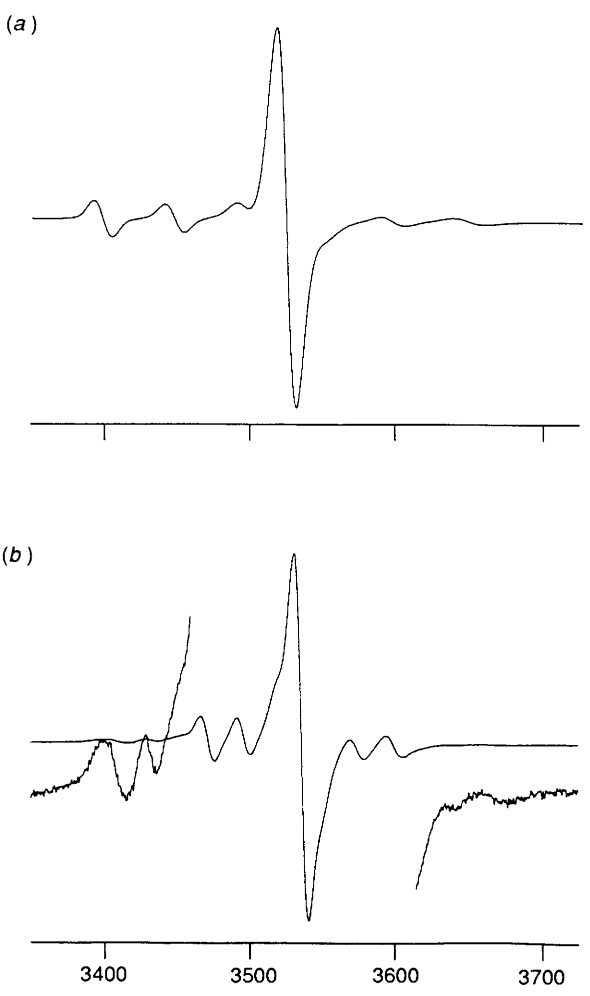

Fig. 3 EPR spectra of (*a*) **2**, a characteristic 17-electron mononuclear molybdenum complex, and (*b*) $\mathbf{4}^-$, a characteristic 17e–17e dimolybdenum diradical

We also attempted to reduce the tungsten centre of complex **8** electrochemically (the potential is too cathodic for cobaltocene) *in situ* in the EPR cavity, to generate a diradical with different metal centres and see if exchange of the two electrons occurred. However this was not successful, as prolonged reduction at the appropriate potential led to decomposition and gave a spectrum with a signal at $g = 1.969$. This is only consistent with rearrangement of the complex to give a reduced species in which the molybdenum group had detached from the imidazolyl terminus of L^1 and attached to the phenolate terminus.

Conclusion

We have prepared a series of mono- and bi-nuclear molybdenum and tungsten complexes of HL^1 in which either or both of the phenol and imidazolyl termini are involved. Electrochemical interactions between the 16e–17e redox couples at each end are very weak, as they are with the analogous pyridyl–phenol bridging ligand HL^2. We were unable to examine the extent of interaction of the 17e–18e couples. In diradical complexes with a 17-electron molybdenum centre at each terminus, EPR spectroscopy shows the presence of a strong exchange interaction between the unpaired electrons.

Acknowledgements

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