Metal–Metal Interactions Across Symmetrical Bipyridyl Bridging Ligands in Binuclear Seventeen-electron Molybdenum Complexes

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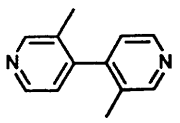
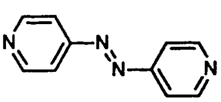
A series of 17-electron mononuclear complexes [Mo(NO)L(Cl)X] and their binuclear counterparts [{Mo(NO)LCl}$_2$(μ-X)] [L = tris(3,5-dimethylpyrazolyl)hydroborate; X = 3,3′-dimethyl-4,4′-bipyridine (3,3′-dmbipy), 1,2-bis(4-pyridyl)acetylene (bpac), 4,4′-azopyridine (azpy), 1,4-bis[2-(4-pyridyl)ethenyl]-benzene (bpeb) or 1,4-bis(4-pyridyl)benzene (bpb)] have been prepared. Electrochemical studies show that the reduction potentials of the mononuclear complexes are sensitive to the degree of unsaturation in the monodentate ligand X, whereas the oxidation potentials are virtually constant. This suggests that the redox orbital involved in the reductions have considerable ligand-based character whereas the oxidations are more strongly metal-centred. This is supported by the electrochemical properties of the binuclear complexes, where the oxidation potentials are in every case coincident but the splitting between the reduction potentials of the equivalent molybdenum centres varies from 0.16 V (X = bpeb) to 0.56 V (X = bpac). By contrast the splitting of the redox potentials of pentaammineruthenium(II) fragments at either end of 'extended' 4,4′-bipyridine analogues of this type is an order of magnitude smaller. This strong interaction between [Mo(NO)LCl] moieties is in part due to a planar conformation of the bridging ligands, even when they are in principle capable of free rotation, since changing the bridging ligand from 4,4′-bipyridine to 3,3′-dmbipy (which cannot be planar due to the steric effects of the methyl groups) results in a decrease in the splitting of the reduction potentials from 0.77 to 0.38 V. The EPR spectra of the binuclear complexes all show that the two unpaired electrons (one at each 17-electron molybdenum centre) are in fast exchange across the bridging ligand at room temperature.

The study of binuclear metal complexes in which the metals are linked by an unsaturated bridging ligand is of particular interest with regard to the study of electron transfer in mixed-valence systems.[1-3] The archetypal example is the Creutz–Taube ion, the theoretical study of which has received a great deal of attention and thereby contributed considerably to our understanding of electron-transfer theory.[4] A particularly popular bridging ligand which has long been the focus of much attention is 4,4′-bipyridine (4,4′-bipy), and a very large number of binuclear complexes containing 4,4′-bipyridine or a derivative as a link have been prepared with a view to studying metal–metal interactions across the bridging ligand.[5,6] Studies have also been performed on 'extended' analogues of 4,4′-bipyridine (the α,ω-dipyridyl polyenes) with up to five *trans* double bonds between two 4-pyridyl groups, in order to determine the effects of the length of the 'molecular wire' on electron-transfer and metal–metal interactions.[7]

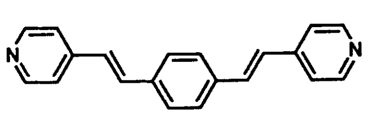


3,3′-dmbipy

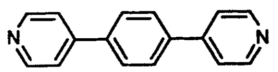
bpac



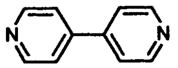
azpy



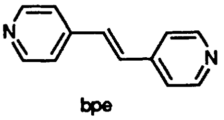
bpeb



bpb



4,4′-bipy



bpe

We recently described the preparation and properties of [{Mo(NO)LCl}$_2$(μ-4,4′-bipy)] [L = tris(3,5-dimethylpyrazolyl)hydroborate], a symmetrical binuclear complex in which EPR spectroscopy showed fast exchange of the two unpaired electrons between the two 17-electron molybdenum centres and an unprecedented large separation of 765 mV between the two (formally metal-centred) one-electron reductions.[8] We now wish to report an extension of this study to mono- and binuclear molybdenum complexes with the known bridging ligands 3,3′-dimethyl-4,4′-bipyridine (3,3′-dmbipy), 1,2-bis(4-pyridyl)acetylene (bpac), 4,4′-azopyridine (azpy) and the new bridging ligands 1,4-bis(4-pyridyl)benzene (bpb) and 1,4-bis[2-(4-pyridyl)ethenyl]benzene (bpeb), to examine the effects of metal–metal separation and ligand conformation on the magnitude of interactions mediated by the bridging ligand.

Experimental

Elemental analyses were performed by the Microanalytical Department at the School of Chemistry, Bristol University. NMR spectra were recorded on JEOL GX270 or GX400 spectrometers, electron-impact (EI) mass spectra on a Kratos MS9 instrument, fast-atom bombardment (FAB) mass spectra on a VG-ZAB instrument and UV/VIS spectra on a Perkin-Elmer Lambda 2 spectrophotometer. EPR spectra were recorded at both room temperature and 77 K on a Bruker ESP-300E spectrometer. Electrochemical measurements 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 dichloromethane, purified by distillation twice from CaH_2, and the base electrolyte was $[NBu_4][PF_6]$ (0.1 mol dm^{-3}). All reagents and starting materials were purchased from Aldrich. 3-Methylpyridine, 4-methylpyridine and pyridine were distilled from CaH_2 under N_2 before use; all other reagents were used as received. All solvents were dried by standard methods before use. 4,4'-Azopyridine[2] and 1,2-bis(4-pyridyl)acetylene[3] were prepared by published methods.

Preparations.—3,3'-*Dimethyl*-4,4'-*bipyridine.* A nitrogen-purged, 250 cm^3 three-neck flask was charged with finely divided Na (50% dispersion in paraffin wax, 10 g, 0.21 mol) and toluene (25 cm^3). The solvent was allowed to dissolve the paraffin wax and then carefully removed by syringe. The residual sodium was washed with two more portions of toluene (25 cm^3) in the same way to ensure complete removal of the wax. The flask was cooled to −30 °C, and a solution of 3-methylpyridine (8.00 g, 0.086 mol) in tetrahydrofuran (thf, 80 cm^3) added slowly, maintaining the internal temperature below −20 °C. After stirring the mixture overnight at room temperature, dry SO_2 gas was passed slowly through the flask whilst cooling to −20 °C; a deep blue colour developed. After 4 h ethanol was added and the mixture stirred for 30 min to destroy any excess sodium. Water (100 cm^3) was then added and the pH adjusted to 5; the mixture was filtered through Celite to remove any solid impurities, and the product was then precipitated by making the solution basic (pH > 9). After extraction into CH_2Cl_2, washing the organic extract with brine and drying ($MgSO_4$), removal of the solvent *in vacuo* afforded crude 3,3'-dimethyl-4,4'-bipyridine which was purified by chromatography on alumina with CH_2Cl_2 as eluent. The final yield was 70%. EI MS: *m/z* 184 (M^+) and 169 ($M^+ - CH_3$). The ^1H NMR spectrum was identical to that described in the literature.[9]

1,4-*Bis*(4-*pyridylethenyl*)*benzene.* To an ice-cold solution of 4-methylpyridine (3.72 g, 0.04 mol) in thf (10 cm^3) under N_2 was added dropwise a solution of lithium diisopropylamide (0.04 mol) in thf (20 cm^3). The mixture was stirred for 1 h after which terephthalaldehyde (2.68 g, 0.02 mol) in thf (10 cm^3) was added dropwise whilst maintaining the temperature below 0 °C. The mixture was allowed to attain room temperature and stirred overnight under N_2, and was then quenched with water and evaporated to dryness *in vacuo*. The crude material (the dialcohol) was dissolved in dry pyridine (50 cm^3) and a solution of $POCl_3$ (7.6 g, 0.05 mol) in pyridine (20 cm^3) was added dropwise at room temperature. After stirring for 1 h, ice was added and the mixture left until the excess $POCl_3$ was destroyed. After evaporation to dryness, distilled water (100 cm^3) was added and the pH adjusted to 3 with HCl; organic impurities were removed by washing the acidic solution with CH_2Cl_2. The product precipitated on neutralisation and was recrystallised from hot ethanol to give 1,4-bis(4-pyridylethenyl)-benzene in 60% yield. EI MS: *m/z* 284 (M^+). ^1H NMR [270 MHz, $(CD_3)_2SO$]: δ 8.41 (4 H, m, pyridyl H^2, H^6), 7.71 (4 H, m, aryl), 7.28 (4 H, m, pyridyl H^3, H^5), 6.93 (2 H, m, ethenyl) and 6.67 (2 H, m, ethenyl) (Found: C, 85.0; H, 5.4; N, 9.6. Calc. for $C_{20}H_{16}N_2$: C, 84.5; H, 5.6; N, 9.9%).

1,4-*Bis*(4-*pyridyl*)*benzene.* To a stirred mixture of dry pyridine (0.7 g, 8.8 mmol), anhydrous CuI (0.05 g, 0.26 mmol) and methyl chloroformate (0.6 g, 6.3 mmol) in dry thf (50 cm^3) at −30 °C under N_2 was slowly added a solution of the bis-Grignard reagent of 1,4-dibromobenzene [8.5 mmol, from 1,4-dibromobenzene (2 g)].[10] The mixture was stirred for 10 min at −30 °C and then allowed to warm to room temperature over 3 h and finally quenched with a mixture of saturated aqueous NH_4Cl (40 cm^3), concentrated NH_3 (2 cm^3) and water (40 cm^3). After stirring for 30 min the aqueous layer was separated and further extracted with thf (2 × 20 cm^3), and the combined thf layers were concentrated to *ca.* 5 cm^3 and then partitioned between Et_2O and aqueous NaCl. The ether layer was separated, dried (Na_2SO_4) and the solvent removed to give a yellow oil. The oil was dissolved in acetone–water (100 cm^3, 85 : 15 v/v), cooled in an ice bath and $KMnO_4$ (2 g, excess) added. After stirring overnight at room temperature the mixture was filtered through Celite to remove MnO_2 and concentrated to give an aqueous suspension of a white solid which was collected by filtration and dried *in vacuo*. The yield of 1,4-bis(4-pyridyl)-benzene was 0.21 g (11%). EI MS: *m/z* 232 (M^+). ^1H NMR (270 MHz, $CDCl_3$): δ 8.72 (4 H, br s, pyridyl H^2, H^6), 7.78 (4 H, s, aryl) and 7.57 (4 H, d, *J* = 4.8 Hz, pyridyl H^3, H^5) (Found: C, 82.9; H, 5.4; N, 11.9. Calc. for $C_{16}H_{12}N_2$: C, 82.7; H, 5.2; N, 12.1%).

Molybdenum complexes. The mononuclear complexes [Mo(NO)L(Cl)X] (X = 3,3'-dmbipy **1**, bpac **3**, azpy **5**, bpeb **7** or bpb **9**) were prepared by reaction of $[Mo(NO)LCl_2]$ (0.2 g, 0.4 mmol) with the appropriate ligand X (0.8 mmol) and NEt_3 (1 cm^3) in toluene–dichloromethane (40 cm^3, 2 : 1 v/v) at reflux under N_2 for 4–6 h. After cooling the mixture and evaporating to dryness, the residue was chromatographed on SiO_2. On initial elution with CH_2Cl_2–hexane (9 : 1, v/v) a green by-product (a μ-oxo binuclear molybdenum species) eluted rapidly in every case. On increasing the polarity by elution with CH_2Cl_2 containing thf (3% v/v for the reaction with azpy; 1% v/v for all others) the binuclear complex [{Mo(NO)LCl}$_2$(μ-X)] (X = 3,3'-dmbipy **2**, bpac **4**, azpy **6**, bpeb **8** or bpb **10**) was then eluted and obtained in about 20% yield in each case. The second major fraction—the desired mononuclear complex—could then be eluted by increasing the polarity with 2% thf in CH_2Cl_2 (except for the azpy complex which required 6% thf); these were obtained in 30–35% yield. If necessary trace impurities in the fractions could be completely removed by preparative-scale thin-layer chromatography on 2 mm thick silica plates (Merck, article 5717). Complexes **5** and **6** are green; **3** and **4** are blue-purple; the others are brown.

The binuclear complexes **2**, **4**, **6**, **8** and **10** were likewise prepared by reaction of the appropriate ligand X (0.2 mmol) with > 2 equivalents of $[Mo(NO)LCl_2]$ (0.23 g, 0.46 mmol) and NEt_3 (1 cm^3) in toluene (50 cm^3) under N_2 for 6 h. Chromatographic purification as before yielded initially the binuclear complexes (about 40% yield) followed by the mononuclear complexes (about 20%).

Elemental analyses, IR and mass spectrometric data for the complexes are given in Table 1.

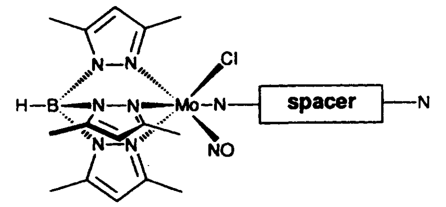
Results and Discussion

Syntheses of Ligands and Complexes.—Of the ligands used in this study, 3,3'-dmbipy, bpac and azpy are known compounds; bpac and azpy were prepared according to the literature methods.[2,3] We found that the literature methods[9] for the preparation of 3,3'-dmbipy gave rather low yields, and accordingly have found a simpler, high-yield route based on a recently published procedure[11] (reductive coupling of 3-methylpyridine with a sodium suspension in thf, followed by oxidation of the intermediate tetrahydrobipyridine with SO_2) which has been used for the preparation of other substituted derivatives of 4,4'-bipyridines; this afforded a 70% yield of 3,3'-dmbipy after purification. The new ligand bpeb was prepared by reaction of 2 equivalents of deprotonated 4-methylpyridine with terephthalaldehyde, followed by dehydration of the intermediate dialcohol with $POCl_3$; this is also based on a published method.[12] The new ligand bpb was prepared in low yield by reaction of the bis-Grignard reagent from 1,4-dibromobenzene with 2 equivalents of pyridine, which was activated to nucleophilic attack by *N*-acylation with methyl chloroformate. The presence of a catalytic amount of copper(I) iodide ensures that attack occurs at the 4

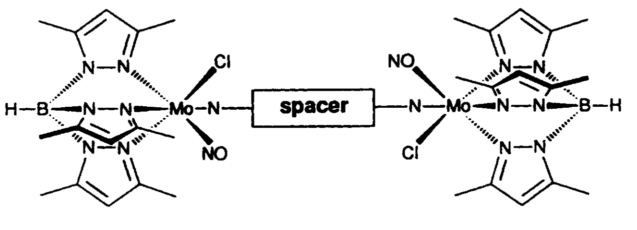
Table 1 Analytical and spectroscopic data for the new complexes

Complex	Analysis[a] C	H	N	M^+(FAB)[b]	ν_{NO}/cm^{-1}	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})[c]
1	51.0 (50.4)	5.4 (5.3)	19.2 (19.6)	640 (644)	1610	275 (11), 326 (sh), 421 (1.4), 484 (1.5)
2	45.2 (45.8)	5.0 (5.1)	20.1 (20.3)	1101 (1104)	1610	277 (17), 315 (sh), 429 (3.0), 497 (2.4)
3	51.2 (50.8)	4.6 (4.7)	19.3 (19.7)	639 (640)	1607	285 (28), 345 (sh), 425 (sh), 558 (2.4)
4	46.5 (46.0)	4.9 (4.8)	20.2 (20.4)	1101 (1100)	1611	276 (23), 340 (sh), 416 (sh), 570 (1.0)
5	46.3 (46.7)	4.6 (4.7)	23.7 (24.0)	644 (644)	1615	284 (19), 421 (2.8), 634 (1.7)
6	43.1 (43.6)	4.9 (4.8)	22.6 (22.9)	1103 (1104)	1616	283 (13), 307 (sh), 420 (4.0), 632 (1.0)
7	56.3 (56.6)	5.0 (5.2)	16.6 (17.0)	744 (744)	1607	289 (13), 368 (42), 430 (sh), 512 (3.1)
8	49.8 (50.0)	5.1 (5.0)	19.0 (18.7)	1204 (1204)	1608	281 (16), 374 (51), 437 (sh), 519 (7.3)
9	53.3 (53.9)	4.9 (4.6)	18.6 (18.3)	690 (692)	1612	284 (19), 417 (1.5), 522 (1.2)
10	48.2 (48.1)	4.5 (4.9)	19.4 (19.5)	1150 (1152)	1610	284 (12), 419 (3.3), 532 (1.0)

[a] Calcualted values in parentheses. [b] Position of most intense peak given. The theoretically calculated values (*m*/*z*) based on the most abundant isotopes are given in parentheses. [c] Spectra recorded in CH_2Cl_2.



	Bridging ligand X
1	3, 3′-dmbipy
3	bpac
5	azpy
7	bpeb
9	bpb
11	4, 4′-bipy
13	bpe



	Bridging ligand X
2	3, 3′-dmbipy
4	bpac
6	azpy
8	bpeb
10	bpb
12	4, 4′-bipy
14	bpe

Fig. 1 Structures of the complexes

position of the pyridyl ring rather than the 2 position.[13] The resulting bis(1,4-dihydropyridine) intermediate was re-aromatised to give bpb with $KMnO_4$ in aqueous acetone.

Complexes were prepared by reaction of the appropriate free ligand with [Mo(NO)LCl_2] in the presence of NEt_3 in toluene at reflux. We attempted to obtain mononuclear complexes specifically by use of a large excess of ligand, and to obtain binuclear complexes specifically by use of more than 2 equivalents of [Mo(NO)LCl_2], but in each case a mixture of both products was obtained although in a different ratio. Separation of the mononuclear complexes from their binuclear counterparts could be effected simply and efficiently by column chromatography on silica using gradient elution. The structures of complexes **1**–**10** are depicted in Fig. 1. All of the metal centres contain 17 valence electrons; attachment of a pyridyl residue to [Mo(NO)LCl_2] (a 16-electron species) is accompanied by one-electron reduction, probably by the NEt_3 which is known to have the ability to act as a hydridic reducing agent.[14]

Electrochemical Properties.—The electrochemical properties of complexes **1**–**10** are summarised in Table 2. The corresponding results for mono- and bi-nuclear complexes with the bridging ligands 4,4′-bipyridine (4,4′-bipy, complexes **11** and **12** respectively) and 1,2-bis(4-pyridyl)ethene (bpe, complexes **13** and **14** respectively) (taken from ref. 8) are also included for comparison.

For all of the mononuclear complexes the position of the formally metal-based (17e–18e) reduction is quite strongly dependent on the degree of unsaturation of the pyridyl ligand. For example, with the monodentate ligands 4,4′-bipy, bpe and bpac (complexes **11**, **13** and **3**) the reduction potentials are −1.70, −1.65 and −1.54 V *vs.* the ferrocene–ferrocenium couple respectively, indicating that the redox orbitals must be significantly delocalised onto the pyridyl ligand. This goes some way towards explaining the large splitting of the reduction potentials in **12**,[8] since two redox orbitals delocalised onto the same bridging ligand might be expected to interact strongly. However this is not a complete explanation, since interactions between the ruthenium centres in $[\{Ru(NH_3)_5\}(\mu\text{-}X)]^{4+}$ [X = 4,4′-bipy[6] or an α,ω-di(4-pyridyl)polyene[7]] are an order of magnitude smaller even though the pentaammineruthenium(II) fragment is an excellent π donor whose redox orbitals are also expected to be strongly delocalised onto the π-acidic pyridyl ligands. The oxidation potentials (17e–16e) by contrast are relatively insensitivite to the nature of the substituents on the pyridyl ligand; they only vary over a range of 50 mV, whereas the reductions vary over a range of more than 300 mV for the same set of ligands. This suggests that, compared to the reductions, they are much more metal-localised and therefore less sensitive to the nature of remote ligand substituents. A further example of the extent to which changes in ligand conjugation can affect electrochemical properties may be seen by comparing the reduction potentials of the mononuclear complexes with 4,4′-bipy (**11**) and with 3,3′-dmbipy (**1**). In the latter case the steric influence of the methyl groups will prevent the ligand from adopting a planar conformation, thereby partially decoupling the π overlap between the two pyridyl rings, and in fact the reduction potential of **1** (−1.88 V *vs.* ferrocene–ferrocenium) is nearer that of the complex with a simple, unsubstituted pyridyl ligand (−2.01 V)[8] than that of **11** (−1.70 V, Table 2).

Examination of the reduction potentials for the binuclear complexes is in agreement with these arguments and shows the importance of the ligand conformation in controlling the

Table 2 Electrochemical and EPR data for the new complexes

	Electrochemical data[a]				EPR data	
Complex	Ligand-based reductions	Metal-based reductions	$\Delta E_{\frac{1}{2}}$	Oxidations	g_{iso}[b]	Hyperfine splitting/mT[c]
1		−1.88 (90)		+0.12 (90)	1.978	4.85
2		−1.69 (90), −2.07 (80)	0.38	+0.16 (90)[d]	1.978	2.44
3		−1.54 (80)		+0.16 (70)	1.979	4.85
4		−1.36 (130), −1.92 (110)	0.56	+0.17 (80)[d]	1.979	2.42
5	−1.02 (70), −2.49 (150)	−1.71 (140)		+0.18 (70)	1.979	4.85
6	−1.06 (80), −2.54 (160)	−1.63 (150), −2.13 (130)	0.50	+0.18 (90)[d]	1.979	2.41
7	−2.15 (110)	−1.65 (60)		+0.12 (70)	1.979	4.86
8	−2.44 (130)	−1.59 (60), −1.75 (80)	0.16	+0.12 (70)[d]	1.979	2.44
9		−1.72 (70)		+0.14 (70)	1.978	4.84
10		−1.64 (100), −1.91 (100)	0.26	+0.13 (70)[d]	1.978	2.42
11[e]		−1.70			1.969	4.85
12[e]		−1.408, −2.173	0.765		1.971	2.45
13[e]		−1.648			1.970	4.95
14[se]		−1.453, −2.035	0.582		1.970	2.45

[a] Electrochemical measurements were made in CH_2Cl_2 at a scan rate of 0.2 V s^{-1}; potentials are quoted *vs.* the ferrocene–ferrocenium couple which was measured at the end of each experiment as an internal reference. Error in $E_{\frac{1}{2}}$ values, ± 10 mV. [b] Spectra obtained at room temperature in CH_2Cl_2–thf (1:2, v/v) solution. Error for samples **1**–**10**, ±0.001. [c] Error ±0.05 mT. [d] Two-electron process arising from simultaneous oxidation of both metal centres. [e] Results from ref. 8 included for comparison purposes. The slight difference in *g* values may be ascribed to the different solvent and instrumentation used for the measurements.

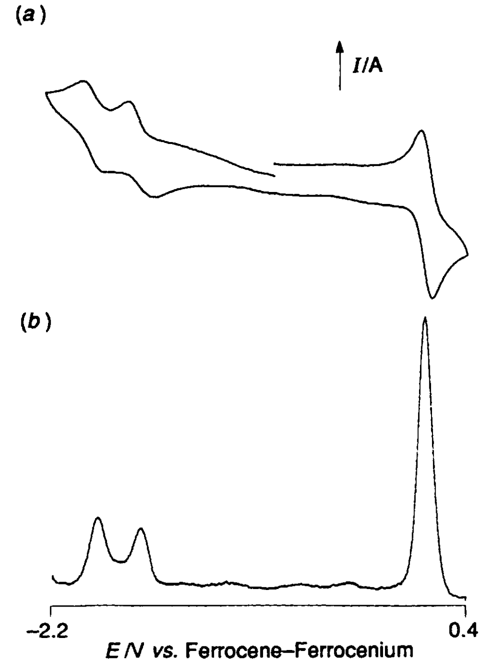


Fig. 2 Cyclic voltammogram (*a*) and square-wave voltammogram (*b*) for complex **10** in CH_4Cl_2 at a scan rate of 200 mV s^{-1}

magnitude of electrochemical interactions across it. The 0.765 V splitting between the reduction potentials of the two chemically equivalent molybdenum centres in **12** is reduced to 0.38 V in **2**. This must mean that in the former case the bipy bridge is essentially planar, with the stabilisation provided by electron delocalisation and exchange overcoming the steric barrier of *ca.* 6 kJ mol^{-1} [15] to ligand planarity, whereas in the latter case the bulky methyl groups inhibit ligand planarity and decrease the coupling. If the 4,4′-bipy ligand were not planar in **12** but rotating freely, the presence of the methyl substituents in **2** would not have such a strong effect. We have recently shown that an asymmetric binuclear molybdenum complex with 4-(4-hydroxyphenyl)pyridine as a bridging ligand also shows strong electrochemical interactions between the metal centres, because a quinonoidal contribution to the structure of the bridging ligand constrains it to be planar.[16]

A dependence of the electrochemical interaction on inter-metal separation may also be seen. The 0.765 V splitting of the reduction potentials in **12** drops to 0.582 V with bpe as the bridging ligand, 0.56 V with bpac and 0.50 V with azpy (complexes **14**, **4** and **6** respectively, which all have similar inter-metal separations); introduction of successively longer spacers between the pyridyl termini in complexes with bpb (**10**) and bpeb (**8**) decreases the splitting to 0.26 and 0.16 V respectively. By contrast in the bis[pentaammineruthenium(II)] complex of 1,8-bis(4-pyridyl)octatetra-1,3,5,7-ene, which is comparable to bpeb in length and degree of unsaturation, the metal centres oxidise at the same potential.[7] (In **5** and **6**, the metal-based reductions occur after the first ligand-based reduction of azpy and are therefore shifted to a more negative potential than might have been expected by comparison with complexes of bpe and bpac. Assignment of reductions as molybdenum- or azpy-centred in **5** and **6** was possible by comparison with the known literature values for the reduction potentials of azpy in other complexes.[3])

Despite the large splittings between the reductive processes in all of the binuclear complexes, the oxidations are in every case coincident. In all five new binuclear complexes a single symmetric oxidation wave was observed of twice the intensity of the separate reductions; the two processes could not be resolved even by square-wave voltammetry or differential pulse polarography. A typical example (complex **10**) is shown in Fig. 2. This behaviour is rather similar to (although more extreme than) the behaviour of complexes which contain two $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) and two $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) groups linked 'back-to-back' *via* a 4,4′-bipyridyl bridge.[17] In each case the two oxidations (predominantly metal-centred) are only *ca.* 56 mV apart, whereas the first two reductions (predominantly centred on the bridging ligand) are *ca.* 300 mV apart.

UV/VIS Properties.—The UV/VIS spectra are summarised in Table 1. All contain a broad absorption in the visible region, which we assign to a metal-to-ligand charge transfer (m.l.c.t.) process for two reasons. Firstly, the wide variation in λ_{max} with the nature of the linking group between the two pyridyl rings suggests the involvement of the bipyridyl ligand in the transitions; it is inconsistent with the presence of d–d character in the transitions since the ligand field would not be substantially perturbed by remote substituents on the pyridyl ligands. Secondly, the partly ligand-based character of the lowest

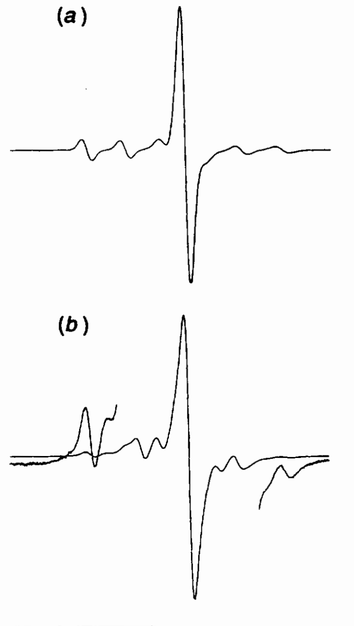


Fig. 3 EPR spectra of complex **5** (*a*) and complex **6** (*b*) at room temperature, G = 10^{-4} T

unoccupied molecular orbital (LUMO) is confirmed by the wide variation in the $E_{\frac{1}{2}}$ values for the reductions with the nature of the bridging ligand. The spectra also all contain a transition near 430 nm, whose constancy suggests a d–d transition, possibly enhanced by intensity borrowing from adjacent charge-transfer bands. Finally in the UV region are ligand-based π–π^* transitions. In general the spectra of the binuclear species are qualitatively similar to those of their mononuclear counterparts, although the changes in intensity are unpredictable.

EPR Properties.—All five mononuclear complexes show characteristic isotropic solution spectra, with g_{av} = 1.979 (±0.001) and a hyperfine splitting (coupling constant) of 4.85 mT (±0.05) to the molybdenum nucleus [Fig. 3(*a*)]. Molybdenum has two spin-active isotopes, $^{95}_{42}$Mo and $^{97}_{42}$Mo (natural abundances 15.72 and 9.46%), which have very similar nuclear magnetic moments of −0.913 and −0.933 nuclear magnetons. The hyperfine coupling constants are therefore sufficiently similar not to be able to distinguish two sets of signals, and the spectra can be adequately explained simply by considering that 25.2% of the signal intensity is split into a 1:1:1:1:1:1 sextet with the other 74.8% as a central single peak [Fig. 4(*a*)].

The EPR spectra of the five new binuclear complexes are all consistent with rapid site exchange of the unpaired electrons, as previously observed for the complexes with 4,4′-bipy and bpe bridges [Fig. 3(*b*)].[8] The hyperfine splitting is halved to 2.4 mT, which is the expected result for an electron showing hyperfine coupling to two equivalent atoms when $|J| \gg A_0$ (where $|J|$ is the exchange integral and A_0 is the hyperfine interaction).[18] In addition all of the components expected from a binuclear complex with equivalent molybdenum sites are present; we would expect a superposition of a central singlet with 56.0% of the overall intensity, a 1:1:1:1:1:1 sextet comprising 37.7% of the overall intensity and a 1:2:3:4:5:6:5:4:3:2:1 eleven-fold multiplet comprising the remaining 6.3% of the overall signal intensity [Fig. 4(*b*)]. Not all of these are resolved and the simple simulation does not take anisotropic effects into account which broaden the spectra at higher fields and perturb some of the line intensities, but enough of the weak, outlying components are present to confirm the assignment. At 77 K the mononuclear complexes all give axial spectra, but the binuclear complexes all give broad, featureless spectra in which no half-field line is apparent. In both cases these are similar to the spectra for **12** shown in ref. 8.

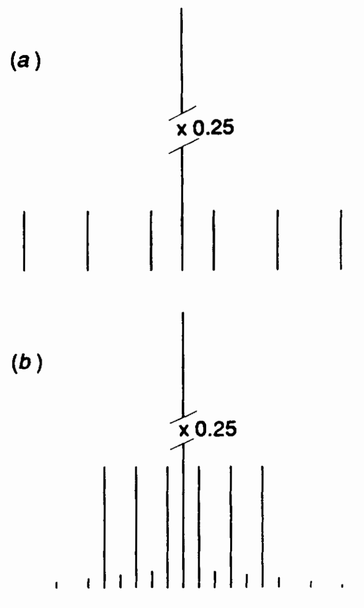


Fig. 4 Simulated 'stick' EPR spectra showing the expected line intensities arising from coupling to one (*a*) and two (*b*) molybdenum centres assuming the naturally-occurring isotopic distribution

Conclusion

We have prepared a series of symmetrical, binuclear complexes containing 17-electron molybdenum centres which show strong electrochemical interactions between reductions at the metal centres despite large internuclear separation; however there are no interactions between oxidations at the metal centres. The presence of substituents which sterically prevent the bridging ligand from adopting a planar conformation result in a substantial decrease in this electrochemical interaction. The EPR spectra show that all of the binuclear complexes undergo fast exchange of the two unpaired electrons across the bridging ligand. These results have relevance to the control of electronic communication between remote metal centres along 'molecular wires'.

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