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Effects of Systematic Variation in Bridging Ligand Structure on the Electrochemical and Magnetic Properties of a Series of Dinuclear Molybdenum Complexes

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Introduction

Magnetic interactions in polynuclear complexes are of particular current interest because of the possibility of preparing useful magnetic materials.[1,2] Central to this work is control of the magnetic exchange interaction *J* between a pair of paramagnetic centers. Often this is outside the control of the synthetic chemist, because the sign and magnitude of *J* can be sensitive to small structural variations in the bridge linking the metal centers: this is well-known, for example, in oxygen-bridged dinuclear copper(II) complexes.[3] Recently, however, Kahn and co-workers have shown that the sign of *J* for an interaction between two metal centers which are close together may be controlled according to the way in which the magnetic orbitals interact. Thus, overlapping magnetic orbitals of the same symmetry [e.g. d(*xy*) and d(*xy*) in a Cu(II)/Cu(II) system where the local axes are parallel] result in a strong antiferromagnetic exchange with a singlet ground state; magnetic orbitals which have extensive spatial overlap but are orthogonal [e.g. d(*xy*) and d($x^2 - y^2$) in a Cu(II)/V(IV) system] result in ferromagnetic exchange with a triplet ground state.[2] This observation has been the basis of the preparation of many magnetic chains and bulk ferromagnets with "designable" (and desirable) magnetic properties.[1,2]

In complexes of extended bridging ligands where the metals are too far apart for their magnetic orbitals to overlap directly, the exchange interaction is instead transmitted through the bridging ligand, and the sign and magnitude of *J* depend on the nature of the pathway linking the interacting centers. The McConnell spin-polarization mechanism describes how an unpaired electron on one atom polarizes the electron cloud on the adjacent atom in the opposite sense.[4] This would result in an alternation of the spin density of atoms in the bridge, and consequently the sign of *J* should alternate as additional atoms appear in the bridging pathway.

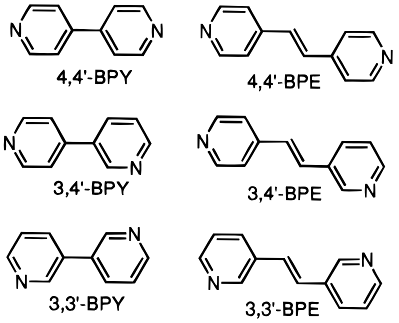

Figure 1. Structural formulas of the complexes used in this study.

We describe here the results of magnetic studies on a series of dinuclear complexes in which paramagnetic, 17-electron {Mo(NO)(Tp*)Cl} (**Mo**) fragments [Tp* = tris(3,5-dimethylpyrazolyl)hydroborate] are linked *via* extended polypyridyl-type bridging ligands (Figure 1). The two sets of dinucleating bridging ligands [4,4′-, 3,4′-, and 3,3′-BPY; 4,4′-, 3,4′-, and 3,3′-BPE] are designed to test the spin-polarization mechanism by providing bridging pathways in which the number of atoms varies by one at a time. We have shown in many EPR spectroscopic studies that the paramagnetic {Mo(NO)(Tp*)Cl} fragments in complexes of this type undergo magnetic exchange interactions over long distances and across saturated bridges.[5] However the EPR spectra of exchange-coupled species do not directly give the *sign* of *J*, but only indicate the presence of an interaction, so the quantitative results in this paper indicate how both the sign and magnitude of the magnetic interactions vary as a function of the bridging pathway.

Experimental Section

Complexes **Mo**$_2$−(4,4′-BPY), **Mo**$_2$−(3,3′-BPY), **Mo**$_2$−(4,4′-BPE) have been described before.[5a] 3,4′-BPY was prepared according to the published method.[6] 3,3′-BPE is in the literature,[7] but we used an improved one-step procedure based on the Wittig reaction of triphenyl(3-picolyl)phosphonium bromide[8] with pyridine-3-carboxaldehyde using sodium methoxide in DMSO; full details will be published separately.[9] 3,4′-BPE was prepared by condensation of deprotonated 4-methylpyridine with pyridine-3-carboxaldehyde according to the general method used for similar ligands;[5c,10] again, full details will be published separately.[9] The new complexes **Mo**$_2$−(3,3′-BPE), **Mo**$_2$−(3,4′-BPE) and **Mo**$_2$−(3,4′-BPY) were prepared by reaction of the appopriate bridging ligand with >2 equiv of [Mo(NO)Tp*Cl$_2$] in toluene/Et$_3$N, followed by chromatography on silica gel with CH$_2$Cl$_2$/thf mixtures, in exactly the same way as described for the other dinuclear complexes.[5] Characterization data for these new complexes are in Table 1.

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Table 1. Analytical and Mass Spectroscopic Data for the New Complexes

complex	analytical data[a] % C	% H	% N	FAB−MS data m/z (M$^+$)
Mo$_2$−(3,4′-BPY)	44.5 (44.8)	4.6 (4.9)	21.1 (20.9)	1074
Mo$_2$−(3,3′-BPE)	45.7 (45.9)	4.9 (5.0)	20.4 (20.4)	1100
Mo$_2$−(3,4′-BPE)	45.7 (45.9)	5.1 (5.0)	20.5 (20.4)	1100

[a] Expected values in parentheses

Table 2. Electrochemical Data for the Six Dinuclear Complexes

	BPY bridge		BPE bridge	
	$E_{1/2}$ for reductions[a]	$\Delta E_{1/2}$	$\Delta E_{1/2}$ for reductions[a]	$\Delta E_{1/2}$
4,4′	−1.41, −2.17[b]	0.76	−1.46, −2.04[b]	0.58
3,4′	−1.74, −2.20	0.46	−1.74, −2.23	0.49
3,3′	−1.85, −2.06[b]	0.21	−1.95, −2.14	0.19

[a] All potentials are in volts *vs* the ferrocene/ferrocenium couple. Cyclic voltammograms were recorded at a Pt-bead working electrode in CH_2Cl_2 containing 0.1−0.2 M Bu_4NPF_6 as base electrolyte. All reduction waves are chemically reversible with peak−peak separations in the range 100−150 mV at scan rates of 0.2 V s^{-1}. [b] Data taken from ref 5a.

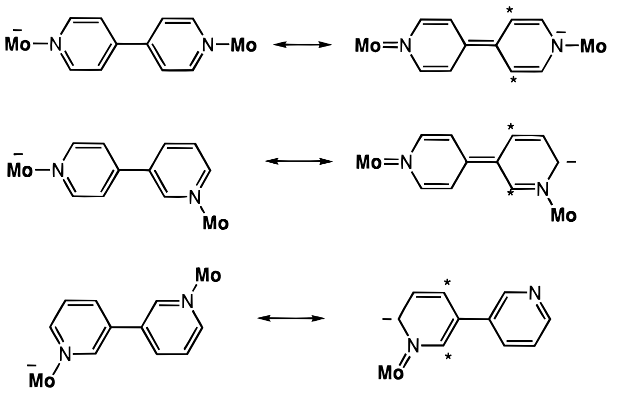
Magnetic susceptibilites were measured in the temperature range 3−270 K in an applied field of 1 T using a Mètronique Ingènièrie MS03 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.[11] Best fits to the magnetic susceptibility data were calculated using a least-squares procedure.[12]

Results and Discussion

The electrochemical data for the two sets of dinuclear complexes (with the BPY and BPE ligand series) are summarised in Table 2. As is well established for these complexes,[5] there is an exceptionally strong electrochemical interaction which results in a substantial separation between the two chemically reversible reductions, which are formally metal-centered (from 17 valence electrons to 18) although it is likely that they have significant ligand-based character. The two oxidations (from 17 valence electrons to 16) in contrast are always coincident. For each series the decrease in the electrochemical interaction—measured by the separation between the two reductions—as the substitution pattern changes from 4,4′ to 3,4′ to 3,3′ is clear, and indicates that the interaction is mediated *via* the delocalized π-system of the bridging ligand. This is a well-known phenomenon.[13] One can see that in **Mo**$_2$−4,4′-BPY, the first added electron may be delocalized across the π-system between the two metals, so there is a strong Coulombic resistance to adding the second electron (Scheme 1). In **Mo**$_2$−3,4′-BPY the first added electron may be delocalized out of the 4-pyridyl ring but only on to the C^2, C^4 and C^6 positions of the 3-pyridyl ring; the Coulombic resistance to reducing the second metal is therefore less. Finally, in **Mo**$_2$−3,3′-BPY the metal-based reduction cannot delocalize beyond the first pyridyl ring, and the Coulombic resistance to reducing the second metal is lower again. The same arguments apply to the BPE series.

The electrochemical interaction across 4,4′-BPY is larger than that across 4,4′-BPE, and likewise the interaction across 3,3′-BPY is larger than that across 3,3′-BPE. This may be ascribed simply to the shorter metal−metal separation (both through space and through the bridging network) in the BPY complexes compared to their BPE counterparts. In contrast, the interaction across 3,4′-BPY is smaller than that across 3,4-BPE; i.e., the interaction in **Mo**$_2$-3,4′-BPY is somewhat smaller than might be expected solely on the grounds of metal−metal separation. Since all of the BPE ligands are of necessity essentially planar, this implies that the bridging ligand in **Mo**$_2$-3,4′-BPY is more substantially twisted than in the 3,3′-BPY and 4,4′-BPY complexes, thereby reducing the π-overlap. Calculation of the minimum-energy structures of the three BPY-based complexes using the molecular mechanics method with standard MM2 parameters[14] gave the following torsion angles between the two pyridyl rings of the BPY ligand: 26° for **Mo**$_2$−4,4′-BPY, 35° for **Mo**$_2$−3,4′-BPY, and 31° for **Mo**$_2$−3,3′-BPY. The steric interaction between the bulky **Mo** fragments in **Mo**$_2$−3,3′-BPY is alleviated by a *transoid* ligand conformation, so the most sterically hindered complex—with the largest dihedral twist in the bridging ligand—is indeed expected to be **Mo**$_2$−3,4′-BPY, in agreement with the electrochemical results.

Scheme 1. Delocalization of the Negative Charge in Monoreduced Dinuclear Complexes[a]



[a] The alternative sites of localization for the negative charge are labeled with an asterisk.

Table 3. Summary of the Magnetic Properties of the Molybdenum Complexes

	BPY bridge			BPE bridge		
	J/cm^{-1}	Θ/K	C/emu·K·mol^{-1}	J/cm^{-1}	Θ/K	C/emu·K·mol^{-1}
4,4′	−33	−33	0.66	−18	−9.54	0.65
3,4′	+0.8	+0.37	0.68	+2.4	+1.09	0.60
3,3′	−1.5	−0.69	0.71	−1.5	−2.38	0.72

The magnetic susceptibilities of the complexes were measured down to 3 K (Table 3); the data were analysed using the spin Hamiltonian of the form

$$H = -J\mathbf{S_1}\cdot\mathbf{S_2}$$

(i.e. ferromagnetic interactions have positive J, antiferromagnetic interactions have negative J). At high temperatures for all of the complexes the χT values are close to those expected for non-interacting spins. For **Mo**$_2$−4,4′-BPY and **Mo**$_2$−4,4′-BPE the χ *vs* T curves show maxima at about 20 K which is characteristic of a strong antiferromagnetic interaction (Figure 2): in agreement with this, the coupling constants were found to be −33 and −18 cm^{-1} respectively. In contrast, **Mo**$_2$−3,4′-BPY and **Mo**$_2$−3,4′-BPE show weak ferromagnetic interactions

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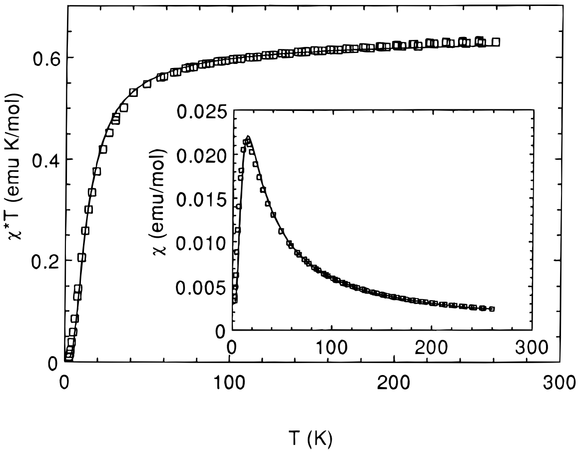

Figure 2. Temperature dependence of χT for **Mo**$_2$−4,4′-BPE. The insert shows χ *vs* T.

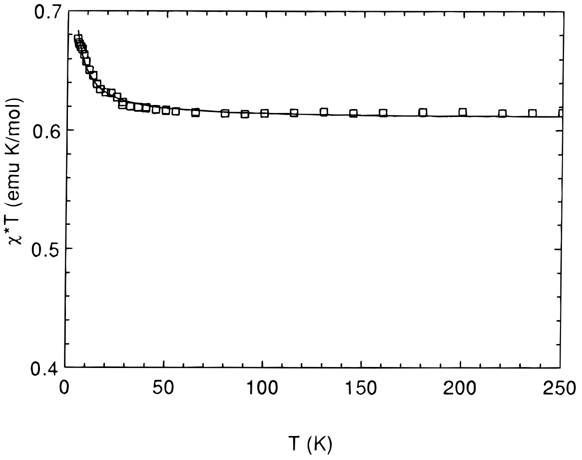

Figure 3. Temperature dependence of χT for **Mo**$_2$−3,4′-BPE.

(+0.8 and +2.4 cm^{-1}, respectively); below 50 K the χT values increase with decreasing temperature (Figure 3 shows the χT *vs* T curve for **Mo**$_2$−3,4′-BPE). **Mo**$_2$−3,3′-BPE and **Mo**$_2$−3,3′-BPE display weak antiferromagnetic interactions, with $J = -1.5$ cm^{-1} in both cases. The magnetic data are summarized in Table 3.

There are three points to notice regarding these data for the dinuclear complexes.

(1) For the two sets of three dinuclear complexes (with the BPY and BPE ligand series) the magnetic interaction alternates in sign as the bridging pathway between the **Mo** groups changes in length by one atom: thus with 4,4′-BPY and 4,4′-BPE the interaction is antiferromagnetic; with 3,4′-BPY and 3,4′-BPE it is ferromagnetic; and with 3,3′-BPY and 3,3′-BPE it is antiferromagnetic again. The qualitative magnetic behaviour of the dinuclear complexes is therefore exactly in accord with the McConnell spin-polarization mechanism (Figure 4).[4]

(2) It is noteworthy that the magnitudes of J are very much lower for the 3,4′- and 3,3′-substituted ligands than for the 4,4′-substituted ligands. This cannot be attributed solely to ligand conformation effects since it occurs for the planar BPE series in which the ligands are constrained to be essentially planar, and it also does not appear to be related to metal−metal separation. A possible explanation lies in the fact that for the 3,4′- and 3,3′-substituted ligands there are two inequivalent pathways across the bridging ligand, whereas for the 4,4′-substituted ligands the two pathways are equivalent. This can give rise to “quantum interference”, whereby there is destructive interference between the two inequivalent components of the interaction transmitted along the different pathways, resulting in unexpectedly weak interactions.[15] This idea has been used to explain why electronic interactions (V_{ab}) can become unexpectedly weak when the symmetry of the bridging ligand is reduced.[15] Although electronic and magnetic interactions can be very different in energy, both are related to electronic delocalization and we suggest here that the symmetry properties of the bridging ligands might also account for the relative magnitudes of the magnetic interactions. We intend to study this possibility further with a variety of symmetric and asymmetric bridging ligands.

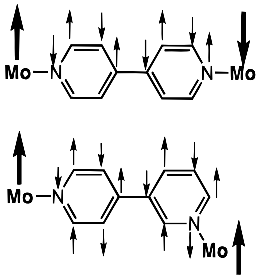

Figure 4. Schematic representation of the spin-polarization mechanism for **Mo**$_2$−4,4′-BPY and **Mo**$_2$−3,4′-BPY showing how the sign of J changes according to the bridging pathway. The two large arrows represent the unpaired spin on each molybdenum atom; the small atoms represent the direction of polarization of the electron clouds on the intervening atoms.

(3) The presence of a double bond in the bridging pathway affects the magnitudes of J in an erratic manner. Moving from **Mo**$_2$−(4,4′-BPE) to **Mo**$_2$−(4,4′-BPY) results in an increase in the magnitude of J from −18 to −33 cm^{-1}, which is to be expected due to decreased metal−metal separation. However from **Mo**$_2$−(3,3′-BPE) to **Mo**$_2$−(3,3′-BPY) the interaction does not increase but remains the same (−1.54 and −1.53 cm^{-1} respectively), implying that in **Mo**$_2$−(3,3′-BPY) the decreased metal−metal distance is offset by the twist between the two halves of the flexible bridge. Moving from **Mo**$_2$−(3,4′-BPE) to **Mo**$_2$−(3,4′-BPY) actually decreases the interaction from +2.4 to +0.81 cm^{-1}, implying that the 3,4′-BPY bridge has an even greater twist which decouples the two components. This is consistent with both the electrochemical results and the relative dihedral angles predicted from the molecular mechanics calculations.

In conclusion, we have been able to relate the magnetic properties of the complexes to various properties of the bridging ligand such as length, substitution pattern, and conformation.

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