Magnetic communication in acyclic mixed-valence trimolybdenum complexes mediated by redox switching

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Reversible one-electron reduction converts the 'V-shaped' $[Mo(NO)[HB(dmpz)_3]\{OC_6H_4XpyMo(NO)[HB(dmpz)_3]Cl\}_2]$ (dmpz = 3,5-dimethylpyrazolyl; X = nothing, CH=CH or CH_2CH_2; py = pyridyl) with two unpaired electrons on the peripheral metals, whose magnetic exchange properties depend on X, into a monoanion having three unpaired paired spins on each metal centre which engage in magnetic exchange in solution irrespective of X.

Molecular magnets are materials which may be derived either from organic radicals or from oligonuclear metal complexes containing at least one paramagnetic transition metal centre.[1] The construction of stable multicentre high-spin organic molecules remains a difficult synthetic challenge and the confirmation of interesting magnetic behaviour has been elusive.[2] However, the assembly of two or more transition metal components of differing spin, whose 'magnetic' orbitals are orthogonal and which are embedded in chain-like structures incorporating relatively short rigid organic bridges, has been more successful leading, for example, to solids exhibiting bulk ferromagnetic behaviour.[3]

The identification of paramagnetic transition metal components which can be easily linked within a rigid carbon-based architectural framework and which may couple magnetically is an important objective in the design and assembly of 'molecular magnets'. Central to this type of work is the control of the sign and magnitude of the magnetic exchange interaction J which depends critically on the nature of the pathway linking the interacting spins. We have recently shown that in paramagnetic isovalent dinuclear molybdenum nitrosyl complexes containing bipyridyl ligands (metal configuration 17 valence electrons), the sign of J can be predicted using a spin-polarisation mechanism,[4] and ferromagnetic behaviour has been detected in $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(3,4'\text{-bpe})]$ (bpe = bipyridylethene; J = +2.4 cm^{-1}).[5] Furthermore, we have demonstrated that antiferromagnetic coupling can occur over surprisingly long distances, as in the isovalent $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2\{py(CH{=}CH)_4py\}]$ (*ca.* 20 Å; J *ca.* −6.6 cm^{-1}).[6]‡ We have also shown that spin correlation, a manifestation in solution of magnetic coupling detected by EPR spectroscopy, occurs in the trinuclear species $[1,3,5\text{-}\{Mo(NO)[HB(dmpz)_3]Cl(pyCH{=}CH)\}_3C_6H_3]$ and $[1,3,5\text{-}\{Mo(NO)[HB(dmpz)_3]Cl(pyC{\equiv}C)\}_3C_6H_3]$ although we have not yet determined the relative signs of J.[7]

The mixed-valence/mixed donor atom species $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(OC_6H_4CH{=}CHpy)]$ which we prepared earlier contains a diamagnetic $16e^-$ and a paramagnetic $17e^-$ metal centre. The solution EPR spectrum shows A_{Mo} = 5.0 mT, consistent with valence-trapped behaviour, but on reduction to the isovalent monoanion, the EPR spectrum revealed that the two unpaired spins correlate strongly (A_{Mo} = 2.5 mT). The reduced species is isoelectronic and probably 'isomagnetic' with $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(4,4'\text{-bpe})]$ (A_{Mo} = 2.5 mT, J = −18 cm^{-1}),[5] the magnetic interaction between the two molybdenum centres being 'switched on' by reversible reduction of the molybdenum phenolate terminus from a $16e^-$ to a $17e^-$ configuration.

By substitution of both chlorides in $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ by the appropriate pyridine–phenol the diamagnetic bis-phenoxides $[Mo(NO)\{HB(dmpz)_3\}(4\text{-}OC_6H_4py)_2]$ **1**, $[Mo(NO)\{HB(dmpz)_3\}(4\text{-}OC_6H_4CH{=}CHpy)_2]$ **2** and $[Mo(NO)\{HB(dmpz)_3\}(4\text{-}OC_6H_4CH_2CH_2py)_2]$ **3**, have been obtained. Further reaction of these with $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ in the presence of NEt_3 afforded a mixture of di- and tri-metallic species which were separated by chromatography. The trimetallic species, $[Mo(NO)\{HB(dmpz)_3\}\{4\text{-}OC_6H_4pyMo(NO)[HB(dmpz)_3]Cl\}_2]$ **4**, $[Mo(NO)[HB(dmpz)_3]\{4\text{-}OC_6H_4CH{=}CHpyMo(NO)[HB(dmpz)_3]Cl\}_2]$ **5** and $[Mo(NO)[HB(dmpz)_3]\{4\text{-}OC_6H_4CH_2CH_2pyMo(NO)[HB(dmpz)_3]Cl\}_2]$ **6**, contain a mixed-valence 17 : 16 : 17e^- trimetal core in a 'V-shaped' array because of the *cis*-disposition of the phenoxide groups at the central molybdenum atom.§ Cyclic voltammetry¶ of **4**, **5** and **6** in dichloromethane revealed two synchronous one-electron oxidations of the molybdenum–pyridyl terminal groups and two reduction processes, one one-electron process associated with the central bis-phenolato molybdenum group and two synchronous one-electron reductions of the molybdenum–pyridyl termini. The formation potentials for the generation of the monoanion fall in the range −1.05 to −1.29 V *vs.* ferrocene–ferrocenium couple, entirely consistent with the reduction of $\{Mo(OC_6H_4\text{–})_2\}$ cores and with the cyclic voltammetric behaviour of **1**, **2** and **3**,[8] and are well-separated from the reduction processes of the terminal molybdenum–pyridyl groups.

The EPR spectrum (room temp., CH_2Cl_2 solution) of **5** is typical of significant spin exchange coupling in dinuclear molybdenum nitrosyl systems (g_{iso} = 1.977, A_{Mo} = 2.4 mT), *i.e.* strong spin correlation with $|J| \gg A_{Mo}$.[5] The spectrum of **4** is different from that of **5** (Fig. 1), being probably second order and characteristic of significant reduction in the exchange interaction, $|J| \approx A_{Mo}$, perhaps brought about by twisting of the rings within the bipyridyl fragments.‖ We have observed similar effects in related molecules.[9] However, the EPR spectrum of **6** reveals no spin correlation and therefore negligible magnetic interaction between the paramagnetic termini, *i.e.* $|J| \ll A_{Mo}$; A_{Mo} = 4.9 mT. This is probably a consequence of the insertion of saturated hydrocarbon links in the bridging ligands, of the number of bonds between the peripheral Mo centres (in ligands with extensive delocalisation,

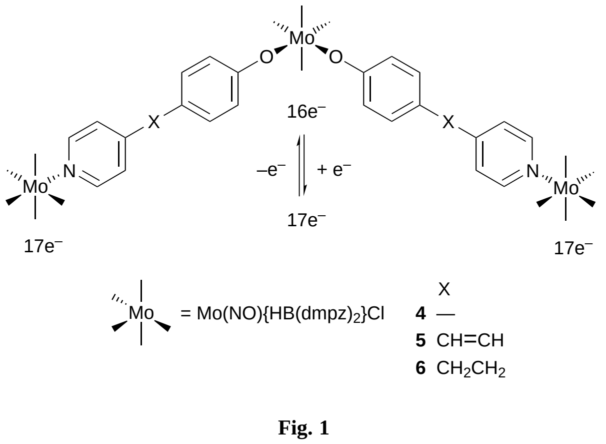

Fig. 1

strong correlation seems to persist up to about 20 atoms), and of possible twisting which degrades π-delocalisation.[10]

Reduction of the monometallic precursors **1**, **2** and **3** gave EPR spectra entirely similar to that of **6**, namely characteristic of one unpaired electron on an isolated 17-valence electron molybdenum nitrosyl group. However, the EPR spectra of $\mathbf{4}^-$ and $\mathbf{5}^-$, produced by chemical or electrochemical reduction of **4** and **5**, provided EPR spectra revealing strong correlation between all three 17-electron metal centres, $g_{iso} = 1.976$, $A_{Mo} = 1.7$ mT, very similar to the data obtained from the symmetrical $[1,3,5\text{-}\{Mo(NO)[HB(dmpz)_3]Cl(pyCH{=}CH)\}_3\text{-}C_6H_3]$. Even more remarkably, the EPR spectrum of $\mathbf{6}^-$ also revealed strong spin correlation (large $|J|$) between all three metal centres ($g_{iso} = 1.973$, $A_{Mo} = 1.7$ mT).

It appears, therefore, that reduction of the central molybdenum bis(phenoxy) moiety from a 16- to a 17-valence electron unit is essential to facilitate strong spin-correlation and so strong magnetic interaction between all three 17-electron metal centres. The EPR spectral consequences of the correlation in these 'V-shaped' molecules appear to be broadly similar to those in the more symmetrical $[1,3,5\text{-}\{Mo(NO)[HB(dmpz)_3]Cl(pyCH{=}CH)\}_3C_6H_3]$ and its analogues. Thus the reversible conversion of **6** to $\mathbf{6}^-$ can be interpreted as an example of a simple molecular magnetic or 'J switch' in that changing the redox level of the central atom increases spin correlation (*i.e.* magnetic exchange) between the terminal groups.

While the molecular components and the effects described here are of themselves small by molecular electronic standards, by elaboration of the design of these mixed phenoxy–pyridine complexes into oligomeric and polymeric species, it should be possible to build up an extended array of mixed-oxidation state metal systems which may be switched to isovalent species whose magnetic properties may be sufficiently strong to constitute useful devices.

Notes and References

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‡ Earlier magnetic susceptibility results obtained over the range 80–300 K indicated $J = -41$ cm^{-1} (ref. 6), but more recent results measured down to 2 K give $J = -6.6$ cm^{-1}; D. Moryusef, J. Boinvoisin, J.-P. Launay, J. A. McCleverty and M. D. Ward, unpublished work; D. Moryusef, DEA Thesis, Université Paul Sabatier, 1996–7.

§ All compounds analysed correctly for C, H and N; ν_{NO} (KBr discs) of **1**, **2** and **3**: 1656, 1655 and 1651, respectively; **4**, **5** and **6**: 1616, 1670; 1611, 1670 and 1617, 1656 cm^{-1}, respectively.

¶ In CH_2Cl_2, *vs.* ferrocene–ferrocenium couple, using Pt wire and $[NBu^n_4][PF_6]$ as supporting electrolyte: **1**, $E_f = -1.10$ V; **2**, $E_f = -1.14$ V; **3**, $E_f = -1.30$ V; **4**, $E_f = +0.03, -1.05, -2.11$ V; **5**, $E_f = +0.04, -1.06, -1.99$ V; **6**, $E_f = +0.05, -1.29, -2.12$ V.

‖ Typical first and second order spectra of these types of molybdenum nitrosyl complexes have been illustrated in refs. 7 and 9.

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