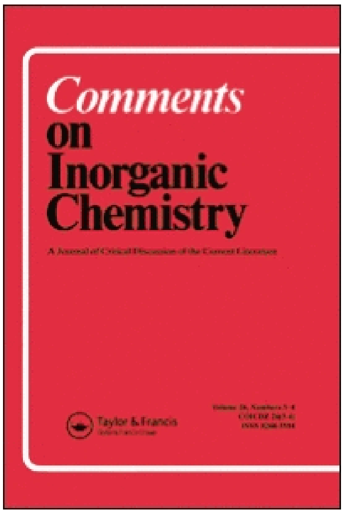

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

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To cite this Article McCleverty, Jon A. , Ward, Michael D. and Jones, Christopher J.(2001) 'Redox-Activity in Complexes with Mo(NO) and Mo(O) Cores: Facts and Consequences', Comments on Inorganic Chemistry, 22: 5, 293 — 326
To link to this Article: DOI: 10.1080/02603590108050873
URL: http://dx.doi.org/10.1080/02603590108050873

Redox-Activity in Complexes with Mo(NO) and Mo(O) Cores: Facts and Consequences

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(Received September 25, 2000)

A series of mono, di-, tri- and tetranuclear nitrosyl and oxo molybdenum complexes containing the tris(3,5-dimethylpyrazolyl)borato ligand exhibit a range of redox processes which are controlled mainly by the ligands and by the extent of oligonucleation. Homo- and hetero-dinuclear complexes have a range of properties dependent on this redox behaviour, and linear (electrochromism in the near infrared) and non-linear (second harmonic generation) properties are described.

Keywords: *molybdenum nitrosyl; oxomolybdenum(V); redox behaviour; mixed valency; non-linear optics; photochromism*

In the 1960s and 1970s coordination chemists were intrigued by the rôle which molybdenum might play in the enzyme nitrogenase. Before high resolution crystallographic information was available about the active

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Comments Inorg. Chem.
2001, Vol. 22, No. 5, pp. 293-326
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site of the enzyme, and in particular the structure of the Mo-containing cofactor, many models were developed to mimic the conversion of dinitrogen to ammonia and hydrazines. Many of these models were unrealistic in terms of their biological relevance but they illuminated an area of dinitrogen chemistry which, until then, had been little explored. Notwithstanding the relevance or otherwise of the model systems, the challenge of trying to unravel the mechanism of how N_2 could be converted under mild conditions to NH_3 led to the development of very exciting, interesting and unexpected coordination and organometallic chemistry of both molybdenum and tungsten.

Early developments involved the syntheses of a variety of low-valent tertiary phosphine complexes, and led to the discovery of novel dinitrogen, diazenido, hydrazido and imido compounds. Once the structure of the cofactor, which contained a complex cluster composed of two Fe_3Mo cores bound together by sulphide ions, became clear research moved away from phosphine chemistry towards sulphide-stabilised cubane-like systems bound by more 'conventional' N/O/S ligands.

Parallel to these developments had been the steady search for appropriate molybdenum or tungsten-based models for a variety of O-atom transfer enzymes, including oxidases (xanthine, CO, aldehyde, sulphite) and reductases (formate dehydrogenase, nitrate), all of which seemingly involve interconversion of the $MoO^{2+/3+}$ and $MoO_2{}^{2+}$groups.[1] This work has blossomed with the discovery of dithiolene-like metal binding groups in several enzymes and their characterisation, *inter alia*, by EXAFS and related structural techniques.[2]

During this period, nitrosyl chemistry of molybdenum and tungsten also developed, although it has not yet been identified with any particular enzymatic process. Most of the early interest was fundamental and although some catalytic potential was detected, most research concentrated on η^5-cyclopentadienyl complexes. Some of these provided unusual hydrazido(1-) and (2-) compounds of potential relevance to the mechanism of N_2-fixation, and the first proof of κ^2-binding of hydrazines to transition metals. This 'Comment' focuses on more recent work with the {Mo(NO)) group which has led to unexpected and potentially applicable chemistry, particularly in the area of linear and non-linear optics, and also draws out some of the remarkable parallels between the chemical and physical properties of particular complexes containing the $\{Mo(NO)\}^{1+,2+,3+}$ and $\{Mo(O)\}^{2+,3+,4+}$ cores stabilised by the tris(3,5-dimethylpyrazolyl)borato ligand, Tp*.[3]

MONONITROSYL COMPLEXES CONTAINING $\{MO(NO)Tp^*\}^{1+,2+}$

Entry to complexes containing the $\{Mo(NO)Tp^*\}^{2+}$ core is via the halogenation of the easily-made dicarbonyl $[\{Mo(NO)Tp^*(CO)_2]$, giving $[Mo(NO)Tp^*X_2]$ (X = Cl, Br or I).[4,5] These dihalides react smoothly with alcohols, phenols, alkyl- and aryl-amides, alkane- and arene-thiols affording mono- or di-substituted products, $[Mo(NO)Tp^*XY]$ [X = halide, Y = OR, OAr, NHR (R = H or alkyl), NHAr, NHNRR' or NHNRAr, SR or SAr] and $[Mo(NO)Tp^*Y_2]$.

The considerable stability of these molybdenum alkoxides, amides and hydrazides towards air and, particularly, water was remarkable and in dramatic contrast to binary alkoxides and amides of molybdenum and tungsten in oxidation states III-VI. This stability is believed to be due mainly to the protective nature of the Tp^* ligand, the methyl groups adjacent to the metal (at the 3-positions on the pyrazolyl rings) providing a "screen" over the metal, as shown by many crystallographic studies. This "screen" effectively maintains 6-coordination at the metal centre by preventing the approach of a seventh *ligand* which would make up the more regular 3:4 coordination so typical of isoelectronic molybdenum cyclopentadienyl nitrosyls. It also prevents oligomerisation or polymerisation, particularly in those complexes containing NHR. The prevalence of six-coordination is further enhanced by the ability of the Tp^* ligand to hybridise the frontier orbitals of the molybdenum and tungsten nitrosyls in an octahedral array.[6]

The determination of the oxidation state of the metal in nitrosyl complexes can be almost a matter of theology! Formally, it depends on whether the nitrosyl group is regarded as coordinated as NO^+ or NO^-. If the M-N-O bond is linear and ν_{NO} is above *ca.* 1600 cm^{-1}, it is conventional to regard the nitrosyl group formally bound as NO^+. This is the situation in all complexes containing the $\{Mo(NO)Tp^*\}^{2+}$core, and the metal is formally in oxidation state II (d^4). One-electron reduction therefore generates $\{Mo(NO)Tp^*\}^+$, a Mo(I) species (d^5).

The metal atom in $[M(NO)Tp^*XY]$ may also be thought of as formally coordinatively unsaturated, having a 16 valence electron (ve) configuration. This, when combined with coordination of the strong π-acceptor NO, means that the metal is relatively "electron deficient". The Tp^* ligand is a good σ-donor but an indifferent π-acceptor and the halides are electronegative (π-donation is possible). The overall effect of this particular ligand grouping around the molybdenum makes the $\{Mo(NO)Tp^*\}^{2+}$ group strongly electronegative. If the co-ligands are polarisable, there should be significant $p_\pi \rightarrow d_\pi$ donation from the heteroatom E (O, N, S) to the metal in $[Mo(NO)Tp^*X(ER)]$, and this has been confirmed crystallographically.[7] The Mo-E bond distances in 16 ve complexes are significantly shorter than those predicted for a single bond, even when taking into account the difficulties of calculating covalent radii for the $Mo(NO)^{3+}$ group. Typical Mo-E bond lengths are 1.90Å for Mo-O, 1.95Å for Mo-NHR, 2.31Å for Mo-SR and 2.20Å for Mo-py. The $p_\pi \rightarrow d_\pi$ donation also requires some rehybridisation of the E atom leading to an expansion of the Mo-E-C(R) bond angle, which was also found.

The charge-transfer implicit in $p_\pi \rightarrow d_\pi$ donation from E to the metal is also evident in the strong colours of the complexes. For example, $[Mo(NO)Tp^*Cl(OR)]$ is blue, $[Mo(NO)Tp^*I(OR)]$ green, $[W(NO)Tp^*Cl(OR)]$ purple, $[Mo(NO)Tp^*(OR)_2]$ red, and $[Mo(NO)Tp^*I(NHR)]$ orange or red, depending on whether R = alkyl or aryl. These LMCT absorptions occur typically in the range 430–600 nm in $[Mo(NO)Tp^*Cl(OAr)]$ and $[Mo(NO)Tp^*Cl(NHAr)]$.[8,9] In contrast, red or brown $[Mo(NO)Tp^*X(pyR)]$, which contains the reduced 17 ve $\{Mo(NO)\}^+$group, exhibits an MLCT band, typically in the region 480–600 nm.[10,11]

However, the strongest indicator of the "electron deficiency" of the $\{Mo(NO)Tp^*\}^{2+}$ core is its ability to undergo a one-electron reduction. Electrochemical data obtained from $[M(NO)Tp^*XY]$ (M = Mo and W), using a variety of voltammetric techniques and coulometry, showed that this reduction process was occasionally thermodynamically reversible, more often quasi-reversible or irreversible, but was almost invariably chemically reversible except when a co-ligand was I (irreversible dissociation of I^- from the reduced species).[7,12] The formation potentials for the generation of 17 ve $[Mo(NO)Tp^*XY]^-$ were dependent on the donor/acceptor properties of X and Y, and the substituents attached to them, becoming more negative in the order I < Br < Cl,[9] and Cl < NC_4H_4 (pyrollide) < SPh < OPh < NHPh.[13,14] Reduction potentials of $[Mo(NO)Tp^*X(EC_6H_4Z)$ could be fine-tuned by altering the geometrical position and electronic nature of Z so that, for example, as Z in the *para* position became more electron-releasing (for inductive or mesomeric reasons), the value of E_f became more negative. Although the data are limited, *para* isomers reduced at potentials *ca.* 70 mV more negative than their *meta* analogues. By far the biggest effect on E_f was caused by substituting molybdenum by tungsten, the reduction potentials of the W complexes being 450–510 mV more negative than their Mo analogues.[13,14,15] In contrast, substituents at the 3-, 4- or 5-positions on the pyrazolyl ring in Tp* had little effect.[16]

We had found that [Mo(NO)Tp*Cl$_2$] did not react with pyridine to give [Mo(NO)Tp*Cl(py)], whereas [Mo(NO)Tp*I$_2$] did, also giving the cationic [Mo(NO)Tp*(py)$_2$]$^+$.[17] However, from our detailed electrochemical studies of [Mo(NO)Tp*I$_2$], which showed that labile [Mo(NO)Tp*I$_2$]$^-$ was easily formed under mild conditions,[12] we reasoned that perhaps the key to substitution by pyridine of one halide in the chloro and bromo species [Mo(NO)Tp*X$_2$] would be prior generation of [Mo(NO)Tp*X$_2$]$^-$which, hopefully, would be reactive. This turned out to be the case, and using NEt$_3$ as reducing agent, we were able to prepare a wide range of 17 ve complexes containing pyridine derivatives, [Mo(NO)Tp*X(L)].[10,18]

These 17 ve complexes not only undergo a one-electron reduction to the 18 ve [Mo(NO)Tp*X(L)]$^-$, but can also be oxidised in a one-electron process giving 16 ve [Mo(NO)Tp*X(L)]$^+$. The potentials for the reduction are dependent on the nature of L and its substituents, and are generally significantly more negative than 16 ve complexes of the type discussed above, but those of the oxidation process are generally not affected by L or its substituents.[11,19] Reduction potentials of monocationic [Mo(NO)Tp*(pyR)$_2$]$^+$ were *ca.* 400 mV more positive than [Mo(NO)Tp*X(pyR)], as expected.[17,20].

The electron transfer behaviour of those nitrosyls complexes containing the {Mo(NO)Tp*}$^{1+,2+}$ core is summarised in the relationship:

$$[\mathrm{Mo(NO)Tp^{*}X(L)}]^{-} \underset{+e^{-}}{\overset{-e^{-}}{\rightleftharpoons}} [\mathrm{Mo(NO)Tp^{*}X(L)}] \underset{+e^{-}}{\overset{-e^{-}}{\rightleftharpoons}} [\mathrm{Mo(NO)Tp^{*}X(L)}]^{+}$$

where L may be formally anionic, *e.g.* OR, NHR, SR or neutral, *e.g.* pyridines, etc. All three members of this electron transfer chain are easily detected when L is neutral, but when it is anionic, the generation of the monocation is rarely observed probably because the formation potential is very positive and beyond the solvent/base electrolyte breakdown. Because of the relatively easy synthesis, rich chemistry and physical properties of molybdenum complexes, their tungsten analogues have been somewhat ignored. Of these, there are a few 16 ve complexes of the type $[W(NO)Tp^*XY]$ and $[W(NO)Tp^*Y_2]$ but, as yet, no examples of 17 ve electron species comparable to $[Mo(NO)Tp^*XL]$ and $[Mo(NO)Tp^*L_2]^+$. It is much harder to generate $[W(NO)Tp^*X_2]^-$, but it is only a matter of time before this problem is dealt with.

The range for the reduction potentials of the generic species $[M(NO)Tp^*XY]$ (M = Mo and W) is *ca.* 2000 mV, probably the biggest range for a single electro-active metal-based system. By careful selection of metal, co-ligands, donor atoms and substituents, a particular reduction potential can be designed into the complex, and the reduced and oxidised members of the three-membered electron transfer chain for this group can easily be generated electrochemically and, sometimes, by chemical methods.

MONO-OXOMOLYBDENUM(V) COMPLEXES CONTAINING $\{MoO\}^{3+}$ CORES

The precursor for $\{Mo(O)Tp^*\}^{2+}$ chemistry is $[Mo(O)Tp^*Cl_2]$, conveniently prepared by reaction of Tp^{*-} with $Mo(O)Cl_3$, although some complexes may be formed by de-oxygenation of $[Mo^{VI}(O)_2Tp^*Cl]$ by PPh_3 in a chlorinated solvent. Enemark and his coworkers have prepared a variety of derivatives from this dichloride, not as extensive as the nitrosyl series, but of particular interest are $[Mo(O)Tp^*Cl(OR)]$, $[Mo(O)Tp^*Cl(SR)]$, $[Mo(O)Tp^*\{E(CH_2)_nE\}]$ (E = O or S) and $[Mo(O)Tp^*(cat)]$ (cat represents the dianion of a range of catechols, 1,2-dihydroxybenzenes).[21,22,23]

Although fewer compounds in this group have been studied electrochemically, the trends are largely similar to the nitrosyls. The electron transfer behaviour is summarised as:

$$[Mo(O)Tp^*Cl(ER)]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Mo(O)Tp^*Cl(ER)] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Mo(O)Tp^*Cl(ER)]^+$$

Reduction potentials for the reduction of $[Mo(O)Tp^*Cl(ER)]$ become progressively negative in the order ER = Cl < SPh < OPh < OMe.[23] and with $[Mo(O)Tp^*(OR)_2]$, the reduction potentials are, on average, 470 mV more negative than their monoalkoxide analogues.[21] In contrast to the nitrosyl series, no oxidation state ambiguities exist with the oxomolybdenum complexes. The formal oxidation state of the metal in [Mo(O)Tp*Cl(OR)] is V (d^1), and one-electron reduction and oxidation leads to Mo^{IV} (d^2) and Mo^{VI} (d^0), respectively. Only a few well-characterised Mo^{IV} complexes have so far been reported: [Mo(O)Tp*Cl(py)] and [Mo(O)Tp*(SR)(py)] (R = Ph, alkyl), obtained by reduction of [Mo(O)$_2$Tp*X] (X = Cl or SPh) in pyridine solution.[24] They may be oxidised reversibly to Mo^V species.

COMPARISON OF THE {Mo(NO)TP*}^{Z} AND {Mo(O)TP*}^{Z} FRAGMENTS

Conventional wisdom based on formal oxidation state arguments would suggest that it should be easier to oxidise a metal in a low oxidation state (Mo^{II}) species than one in a high oxidation state (Mo^V), However, photoelectron spectroscopic studies (PES) of [Mo(NO)Tp*(OR)$_2$] and [Mo(O)Tp*(OR)$_2$] showed unequivocally that the reverse is true in these cases.[25] It is *ca.* 0.8 eV *more difficult* to oxidise the Mo^{II} nitrosyl species than its Mo^V analogue. To explain this, it is first necessary to define the Mo-NO and Mo=O bonds as the z-axis in a six-coordinate framework, the three pyrazolyl N atoms, Cl and the remaining ligand's donor atom occupying the x- and y- axes.[26] The d_{z^2} and $d_{x^2-y^2}$ orbitals, therefore, are involved in σ bonding and need no longer be considered. In the *nitrosyl* system, the two empty NO π^* orbitals overlap significantly with the d_{xz} and d_{yz} metal orbitals, thereby lowering their energy, but leaving the non-bonding d_{xy} orbital virtually unperturbed (Fig. 1a).[26] The electronic configuration of the metal in the {Mo(NO)Tp*}$^{2+}$ fragment is thus $d_{xz}{}^2d_{yz}{}^2d_{xy}{}^0$, and in the [Mo(NO)Tp*}$^+$ fragment $d_{xz}{}^2d_{yz}{}^2d_{xy}{}^1$. In the *oxo* system, by contrast, the filled oxygen $2p_x$ and $2p_y$ orbitals interact with the metal d_{xz} and d_{yz} orbitals, thereby raising their energy, but again leaving the energy of the half-filled d_{yx} orbital relatively unchanged (Fig. 1b). The electronic configuration of the metal in the {Mo(O)Tp*}$^{2+}$ is therefore $d_{xy}{}^1d_{xz}{}^0d_{yz}{}^0$. The PES data confirmed that, as expected, the nitrosyl group acts as a powerful π acceptor whereas the oxo group functions as a strong π donor and further showed that the actual electron density at the metal centre in {Mo(NO)Tp*}$^+$ is comparable to that in {Mo(O)Tp*}$^{2+}$(both have $d_{xy}{}^1$ configurations).

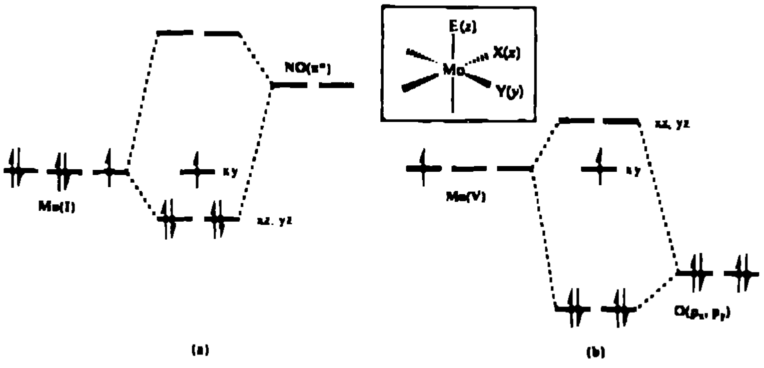

FIGURE 1 Important molecular orbitals in [Mo(E)Tp*XY]: (a), E = NO; (b) E = O

DI-, TRI- AND TETRANUCLEAR COMPLEXES CONTAINING $\{Mo(NO)TP^*\}^{N+}$ AND $\{Mo(O)Tp^*\}^{N+}$ CORES

The discovery of the controllable redox behaviour of the nitrosyl and oxo molybdenum species provided a golden opportunity to construct oligonuclear species using appropriately functionalised bridging ligands, such as benzene-1,4-diolate, 4,4'dipyridyl and benzene-1,3,5-triolate (trianion of phloroglucinol) in which the metal centres might interact electronically, but not via direct metal-metal bonds. The synthetic strategy we employed has been outlined elsewhere,[7] and the many types of bridging ligand used are shown in Fig. 2 and 3.

Dinuclear complexes

Two groups of complexes were prepared, the larger containing a single bridging ligand, $[\{Mo(Z)Tp^*X\}_2(bridge)]$ (X = halide, Z = NO or O) and the smaller *two* bridging ligands $[\{Mo(Z)Tp^*(bridge)\}_2]$. The singly bridged complexes are further sub-divided depending on whether the bridge is formally dianionic or neutral. The dianionic bridges support two diamagnetic 16 ve $\{Mo(NO)Tp^*\}^{2+}$ or paramagnetic d^1 $\{Mo(O)Tp^*\}^{2+}$ units connected either via di-substituted benzene or naphthalene rings (Fig. 2: Ia, Ib or III)[9,27,28,29] or by links containing

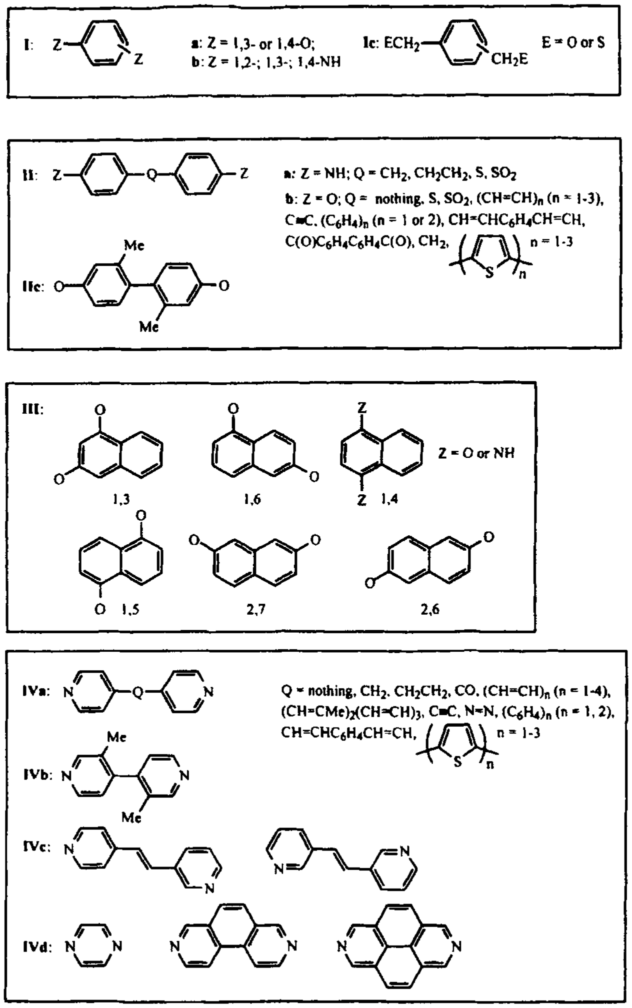

FIGURE 2 Dinucleating bridging ligands

two benzene rings separated by an atom or group of atoms (Fig. 2: IIa,b).[30,31,32] The neutral ligands, so far mainly bis-pyridine ligands or analogues, support two paramagnetic $\{Mo(NO)Tp^*\}^+$ cores

V:

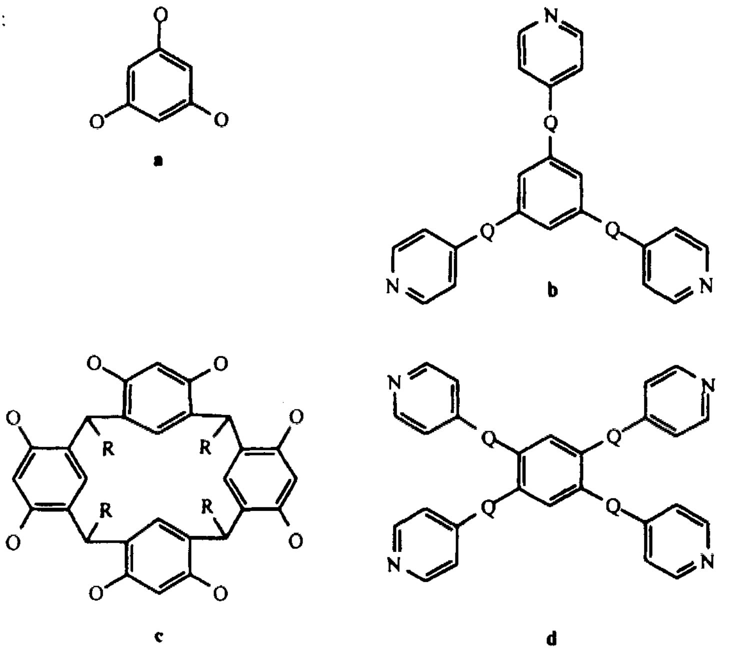

FIGURE 3 Tri- and tetra-nucleating ligands

(Fig. 2: IV),[8,10,11,33] and, of course, there are hybrids of both types in which, for example, $\{Mo(NO)Tp\}^+$ can be linked to $\{Mo(O)Tp^*\}^{2+}$.[19,34,35]

All of these dinuclear species undergo two one-electron reductions. The most interesting feature of this behaviour is the difference between the potentials of the first and second charge transfer (ΔE_f), which is a measure of the electronic interaction between the two redox centres in the ground state. This interaction, not surprisingly, decreases significantly as the distance between the redox centres increases, as can be seen from data in Table I. For example, the dipyridyl-bridged compounds $[\{Mo(NO)Tp^*Cl\}_2(IVa)]$, where Q = nothing and $(CH{=}CH)_n$, n = 1 – 4 or $(CH{=}CMe)_2(CH{=}CH)_3$,[11] show ΔE_f reducing from 765 to *ca.* 40 mV as the distance between the redox centres shortens from 20 to 12Å, so that at 20Å, the separation between the two potentials is statistical, *viz.* 36 mV.

and the two redox centres are not interacting. In comparison, however, ΔE_f for the pyrazine (pz) complex $[\{Mo(NO)Tp^*Cl\}_2(IVd)]$ is 1440 mV, one of the largest separations between coupled redox processes ever detected (equivalent to a comproportionation constant of $2.2x10^{24}$ in CH_2Cl_2).[36] A further manifestation of the bridging ligand effect on ΔE_f can be taken from $[\{Mo(NO)Tp^*Cl\}_2(IVa)]$ where $Q = C_6H_4$ (260 mV),[10] *trans* CH=CHCH=CH (390 mV),[11] and 2,5-thienyl (450 mV),[10] which shows clearly that the 2,5-thienyl link is the most efficient at transmission of charge.

The size of ΔE_f is also influenced by the donor atoms of, and positional isomerism in, for example a C_6H_4 bridge. Changing Z in $[\{Mo(NO)Tp^*I\}_2$(1,3-ZC6H4Z)] from S through O to NH causes ΔE_f to increase first by 8% and then by a huge 50% (to 390 mV).[37] Even bigger differences were observed in $[\{Mo(NO)Tp^*Cl(1,4\text{-}ZC_6H_4Z)]$ where ΔE_f doubles on going from Z = O to Z = NH.[9,28] The effect of positional isomerism is seen in the ΔE_f-values for the *ortho, meta* and *para*-isomers of $[\{Mo(NO)Tp^*Cl\}_2$(NHC6H4NH)]: 778, 371 and 917 mV, respectively.[9] A reduction of ΔE_f can be caused by the insertion of what might be regarded as insulating or part-insulating atoms or groups between two benzene rings, or a distortion between those rings. A good example of the first is shown by the $[\{Mo(NO)Tp^*Cl\}_2(OC_6H_4QC_6H_4O)]$ (II) where ΔE_f decreases in the order Q = S > nothing > CO > SO_2,[30] which is due mainly to a reducing availability of appropriate $p\pi$ orbitals in Q, although conformational effects associated with the dihedral angle between the two arene rings may also be important. An illustration of the effect of twisting about two rings can be taken from data obtained from $[\{Mo(NO)Tp^*Cl\}_2(IVa)]$ (Q = nothing) and its 2,2'-dimethyl-4,4'-dipyridyl analogue (IVb), where ΔE_f effectively halves, the methyl groups in IVb preventing the dipyridyl ligand from being planar.[10]

These data show clearly that the redox centres communicate very effectively via the π-electron system of the bridging ligands, and anything which diminishes the efficiency of that causes a reduction of ΔE_f. This explains neatly why ΔE_f in 1,3-disubstituted ligands of type I is smaller than that in their 1,4-analogues and how the variations in ΔE_f in the naphthalene diolates (III) arises. It also explains why ΔE_f in complexes containing ligands of type IIa, b and c or IVa, b and c decreases as the ligand grows longer, or the connector group has no π orbitals, or the two benzene or pyridine rings are forced to twist. All of these effects reduce opportunities for delocalisation in the bridging ligand.

TABLE I Separation between reduction or oxidation waves (ΔE_f) in [{Mo(Z)Tp*X}$_2$Q] and [{Mo(Z)Tp*Q}$_n$], n = 3 or 4

Bridging ligand	ΔE_f *(mV) oxidation*	K_c *(ox)*	ΔE_f *(mV) reduction*	K_c *(red)*	*Ref*
[{Mo(NO)Tp*Cl}$_2$(dianionic bridge)					
O			1220	4.2×10^{20}	a
OC$_6$H$_4$(2,5-C$_4$H$_2$S)$_2$C$_6$H$_4$O			670	2.1×10^{11}	8
1,4-OC$_6$H$_4$O			460	6.0×10^{7}	37
1,3-OC$_6$H$_4$O			260	2.5×10^{4}	
1,2-O$_2$C$_6$H$_{10}$			302	1.3×10^{5}	b
1,3-O$_2$C$_6$H$_{10}$			193	1.8×10^{3}	
1,4-O$_2$C$_{10}$H$_6$			150	343	28
2,7-O$_2$C$_{10}$H$_6$			150	343	
OCH$_2$CH=CHCH$_2$O			150	343	c
OCH$_2$C≡CCH$_2$O			120	110	
OCH$_2$CH$_2$CH$_2$CH$_2$O			100	49	
OC$_6$H$_4$SC$_6$H$_4$O			138	215	30
OC$_6$H$_4$C$_6$H$_4$O			110	72	
OC$_6$H$_4$C(O)C$_6$H$_4$O			85	27	
OC$_6$H$_4$S(O)$_2$C$_6$H$_4$O			75	18.5	
OCH$_{64}$CH$_2$C$_6$H$_4$O			*ca.* 65	*ca.* 13	
OC$_6$H$_4$C(O)C$_6$H$_4$C$_6$H$_4$C(O)C$_6$H$_4$O			56	8.8	

Bridging ligand		*ΔE_f(mV) oxidation*	*K_c (ox)*	*ΔE_f(mV) reduction*	*K_c (red)*	*Ref*
1,3-SC_6H_4S				240	1.1×10^4	37
1,4-NHC_6H_4NH (as iodide)				1076	$1.5\text{x}10^{18}$	9
1,2-NHC_6H_4NH (as iodide)				[870]	$5.1\text{x}10^{14}$	
1,3-NHC_6H_4NH (as iodide)				380	$2.7\text{x}10^6$	
$N(CH_2CH_2)_2N$				[560]	$2.9\text{x}10^9$	d
$NHC_6H_4S(O)_2C_6H_4O$ (as iodide)				135	192	30
$NHC_6H_4OC_6H_4O$				111	75	
$NHC_6H_4CH_2C_6H_4NH$ (as iodide)				62	11	
$NHC_6H_4CH_2CH_2C_6H_4NH$ (as iodide)				45	5.8	
[{Mo(NO)Tp*(dianionic bridge}$_2$]						
2,7-$O_2C_{10}H_6$; *syn* isomer				174	874	41
4,4'-$OC_6H_4CH_2C_6H_4O$; *syn*, *anti* isomers				*ca.* 90	*ca*, 33	39
$OCH_2C_6H_4CH_2O$; *anti* isomer				*ca.* 85	*ca.* 27	
[{Mo(NO)Tp*Cl}$_2$(bridge)]						
pyrazine, pz		100	49	1440	$2.2\text{x}10^{24}$	36
4,4-dipyridyl, py-py				765	8.6×10^{12}	11
py(CH=CH)$_n$py;	n = 1			582	6.9×10^9	
	n = 2			390	$3.9\text{x}10^6$	
	n = 3			230	$7.7\text{x}10^3$	
	n = 4			110	72	

Bridging ligand		$\Delta E_f(mV)$ *oxidation*	K_c *(ox)*	$\Delta E_f(mV)$ *reduction*	K_c *(red)*	*Ref*
$(CH{=}CMe)_2(CH{=}CH)_3$				36	4.1	
pyC≡Cpy				560	2.9×10^9	
pyN=Npy				500	2.8×10^8	
3,3'-dimethyl-4,4'dipyridyl, IVb				380	2.7×10^6	
py-C_6H_4-py				260	2.5×10^4	
$pyCH{=}CHC_6H_4CH{=}CHpy$				160	507	
$pyCH_2CH_2py$				105	60	
py-(2,5-thienyl)$_n$-py, IVa(2,5-thienyl)$_n$	n = 1			450	4.0×10^7	8
	n = 2			220	5.2×10^3	
	n = 3			60	10	
	n = 4			n.r.		
IVd(ii)				790	2.3×10^{13}	
IVd(iii)				730	22×10^{12}	
pyC(O)py; IVa (Q = CO)						
[{Mo(O)Tp*Cl}$_2$(dianionic bridge)]						
1,4-OC_6H_4O		*ca.* 990	1.4×10^{11}	250	1.7×10^4	e
1,3-OC_6H_4O		irrev.		200	2.4×10^3	
$OC_6H_4C_6H_4O$; II,Q = nothing		480	1.3×10^8	n.r.		
$OC_6H_4(C_6H_4)_nC_6H_4O$; II,Q = C_6H_4	n = 1	180	1.1×10^3	n.r.		
	n = 2	n.r.		n.r.		

Bridging ligand		$\Delta E_f(mV)$ *oxidation*	K_c *(ox)*	$\Delta E_f(mV)$ *reduction*	K_c *(red)*	*Ref*
$OC_6H_3(Me)C_6H_3(Me)O$, IIc		230	$7.7x10^3$	n.r.		
$OC_6H_4CH_2C_6H_4O$		120	107	n.r.		31
$OC_6H_4SC_6H_4O$		430	$1.9x10^7$	n.r.		
$OC_6H_4SO_2C_6H_4O$		80	23	n.r.		
$O_2C_{10}H_6$	III; 1,3	irrev.		200	$2.4x10^3$	29
	III; 1,5	670	$2.1x10^{11}$	150	343	
	III; 1,6	irrev.		120	107	
	III; 2,6	780	$1.5x10^{13}$	140	233	29
	III; 2,7	irrev.		120	107	
[{Mo(NO)Tp*(dianionic bridge)}$_2$]						
2,7-$O_2C_{10}H_6$	III; 2,7			174	874	39
Anti-$OCH_2C_6H_4CH_2O$				*ca.* 85	*ca.* 27	
$OC_6H_4CH_2C_6H_4O$	IIa ($Q = CH_2$)			*ca.* 90	*ca.* 33	
[{Mo(O)Tp*(dianionic bridge)}$_2$]						
1,3-OC_6H_4O		n.m.		390	$2.6x10^5$	42
2,7-$O_2C_{10}H_6$	III; 2,7	n.m.		110	72	
$OC_6H_4CH_2C_6H_4O$		n.m.		n.r.		
1,3-SC_6H_4S		n.m.		160	507	
[{Mo(NO)Tp*(dianionic bridge)}$_3$]						
Syn,syn-1,4-OC_6H_4O				418	$1.2x10^7$	45

Bridging ligand	$\Delta E_f(mV)$ *oxidation*	K_c *(ox)*	$\Delta E_f(mV)$ *reduction*	K_c *(red)*	*Ref*
			321	2.7×10^5	
Anti,syn-1,3-OC_6H_4O			250	1.7×10^4	
			206	3.0×10^3	
Vc (1 >2)			*ca. 60*	*ca.* 10	
Anti,syn-1,4-OC_6H_4O; W complex; (1→2);			275	4.5×10^4	
(2→3)			264	2.9×10^4	
[{Mo(O)Tp*(dianionic bridge)}$_3$]					
1,3-OC_6H_4O (1→2)			200	2.4×10^3	42
(2→3)			230	7.7×10^3	
2,7-$O_2C_{10}H_6$ (1→2)			110	72	
(2→3)			14	1.7	
1,3-SC_6H_4S (1→2)			160	507	
[{Mo(NO)Tp*(dianionic bridge)}$_4$]					
Anti,syn,syn-1,3-OC_6H_4O (1→2)			418	1.2×10^7	45
Vc (1→2)			140	233	

Abbreviations: n.m = not reported; n.r. = not resolved by voltammetry; (1→2) = ΔEf between first and second reduction wave; (2→3) = ΔEf between second and third reduction wave; a A. Wlodarczyk, J. P. Maher, S. Coles, D. E. Hibbs, M. H. B. Hursthouse, K. M. Abdul Malik, J. Chem. Soc., Dalton Trans., 2597 (1997); b S. L. W. Mchinnie, C. J. Jones, J. A. McCleverty and L.J. Yellowlees, Polyhedron, 15, 1401 (1996).; c J. A. Thomas, C. J. Jones, J. A. McCleverty and M. G. Hutchings, Polyhedron, 15, 1409 (1996); dN. Al-Obaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, J. Chem. Soc., Dalton Trans., 2653 (1987); eV. Â. Ung, D. A. Rardwell, J. C. Jeffery, J. P. Maher, J. A. McCleverty, M. D. Ward and A. Williamson, Inorg. Chem., 35, 5290 (1996).

In contrast to the nitrosyl complexes, the redox behaviour of the oxomolybdenum arene diolato species [{Mo(O)Tp*Cl}$_2$(Ia,b/II/III)] is relatively uninteresting, the two reduction processes being coincident ($\Delta E_f \approx$ 36 mV) showing that there is little interaction between the metal centres.[38] The only exception is [{Mo(O)Tp*Cl}$_2$(1,4-OC$_6$H$_4$O)], where ΔE_f = 250 mV. The corresponding 1,3-isomer showed only one reduction wave (2x 1 e^-).

But what about oxidation behaviour? Two groups of complexes exhibit this: the bis-pyridine and related complexes [{Mo(NO)Tp*Cl}$_2$(IV)] and the oxomolybdenum(V) species [{Mo(O)Tp*Cl}$_2${Ia,b/II/III}]. The CVs of the former, with one exception, show two coincident waves due to synchronous electron transfers whose potentials are separated statistically by 36 mV. The exception is the pyrazine complex (IVd) which showed two discrete oxidative electron transfer processes separated by 100 mV and, in fact, this complex is part of a five-membered electron-transfer chain [{Mo(NO)Tp*Cl}$_2$(pz)]^z with charge z = +2, +1, 0, −1 and −2.[36] In contrast, the oxomolybdenum complexes show significant splittings of the two oxidation waves, ΔE_f reducing because of factors much the same as those identified with the nitrosyl complexes.

How can the fact that there is a large interaction between the {Mo(NO)Tp*}$^{2+/+}$ and {Mo(O)Tp*}$^{2+/3+}$ couples and an extremely small one between the {Mo(O)Tp*}$^{2+/+}$ couple be explained. Perhaps the most plausible approach is that illustrated in Fig. 4a.[26] The relatively high-energy d_{xy} orbitals are not far below the low-lying π^* orbitals of the bis-pyridine bridging ligand over which delocalisation can occur. Addition of a second electron to each d_{xy} orbital, generating two {Mo(NO)Tp*}^{0} centres, will raise them in energy nearer to the π^* level, such that on reduction the d_{xy} electrons are delocalised even more effectively over the bridge. One can therefore represent the two extreme forms of the doubly-reduced species as {[Mo(NO)Tp*]^0-[IV]^0-[Mo(NO}Tp*]^0} and {[Mo(NO)Tp*]$^+$-[IV]$^{2-}$-[[Mo(NO)Tp*]$^+$}. Such representations are consistent with the known ability of polypyridine ligands to be reduced easily. Since the two additional electrons are brought together by this process the electrostatic repulsion between them will be strong, making addition of the second electron much more difficult than addition of the first – hence the large ΔE_f values. In contrast, oxidation of the metals, with the resulting positive charge, will lower the d_{xy} orbitals away from the π^* levels such that the d_{xy} electrons are more metal-localised. Also, the HOMO of the bridging ligand is much lower than the d_{xy}orbitals and therefore cannot participate in stabilising the oxidised species: *i.e.* the doubly-oxidised form $\{[Mo(NO)Tp^*]^{2+}$-$[IV]^0$-$[Mo(NO)Tp^*]^{2+}\}$ will not have any significant contribution from the $\{[Mo(NO)Tp^*]^+$-$[IV]^{2+}$-$[Mo(NO)Tp^*]^+\}$ form in which the oxidations are partly ligand-centred.

The contrary behaviour of the oxomolybdenum species which contain two Mo(V) centres may be rationalised using Fig. 4b. The d_{xy} orbital, being the lowest in energy of the metal *d*-orbitals, is not far above the HOMO of the phenolate bridging ligand, which is relatively high in energy because of the double negative charge. Oxidation will lower the d_{xy} orbitals further, and the positive charges will therefore be partly delocalised onto the bridging ligand. In contrast, reduction to Mo(IV) will raise the d_{xy} orbitals away from the bridging ligand HOMO such that delocalisation is decreased, and the bridging ligand LUMO is too high in energy to participate, so the reductions are metal-localised. Thus for the doubly-oxidised species it is possible to visualise $\{Mo(VI)$-$[I/II/III]^{2-}$-$Mo(VI)\}$ and $\{Mo(V)$-$[I/II/III]^0$-$Mo(V)\}$ as extreme canonical forms. The known tendency of *para*-substituted phenols to be oxidised to quinones encourages the thought that oxidation of the bridging ligand in these complexes may be very important. It is significant that with the *meta*-substituted bridge (I, Z = O), in which no quinonoidal form is possible, only a single totally irreversible oxidation occurs. However, recent ZINDO calculations and spectroelectrochemical studies of this group of complexes has led to the conclusion that the oxidation behaviour is largely metal-centred, *i.e.* [Mo(V)/Mo(VI)], albeit with some delocalisation onto the bridging ligand via a suitable π-symmetry orbital.[31]

Metallomacrocycles

The X groups in octahedral $[Mo(Z)Tp^*X_2]$ (Z = NO or O) are mutually cis, a situation maintained by the rigidity of the tripodal Tp* ligand and when both are replaced by relatively rigid bridging or ditopic ligands, metallomacrocycles should be formed. Schematised examples of di-, tri- and tetranuclear species are shown in Fig. 5–7.

The macrocyclic *dimetallics* $[\{Mo(NO)Tp^*(bridge)\}_2]$ (bridge = Ic, E = O[39] or S;[40]; IIb, Q = CH_2;[39]; 2,7-III;[41]) and $[\{Mo(O)Tp^*(bridge\}_2]$

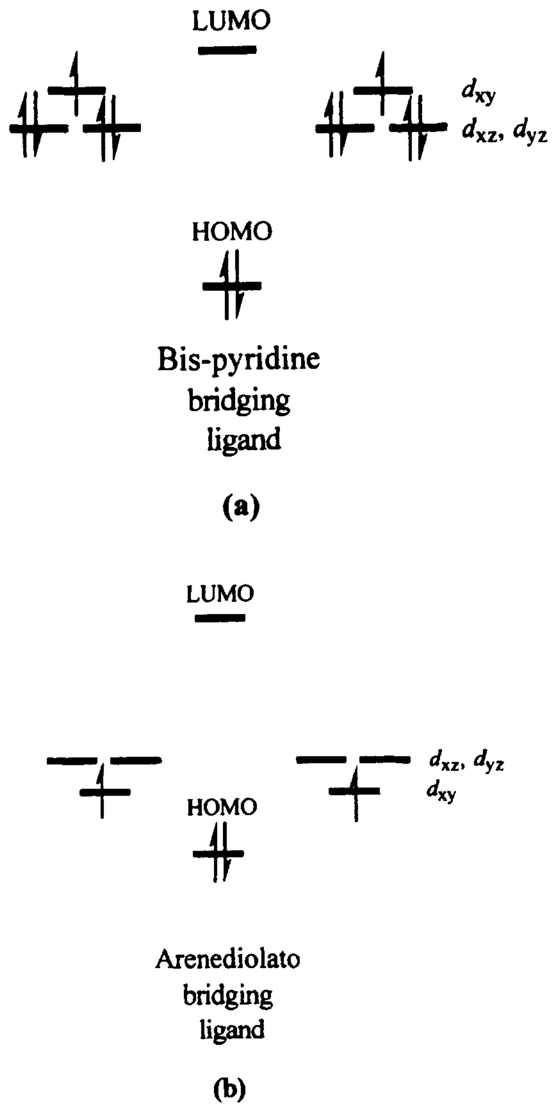

FIGURE 4 Qualitative MO scheme for dinuclear complexes (a) [{Mo(NO)Tp*Cl}$_2$(IV)] and (b) [{Mo(O)Tp*Cl}$_2${I/II/III}]

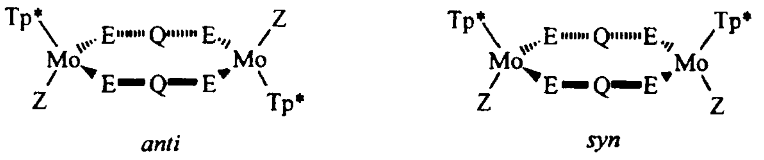

FIGURE 5 Isomers of dinuclear macrocycles where M may be Mo or W and Z = NO or O, E = O or S

(bridge = 1,3-O/SC$_6$H$_4$O/S, 2,7-III; IIb, Q = CH$_2$[42]) present an interesting contrast to the singly-bridged complexes described above. First, they can and do form stable *anti* and *syn* isomers, defined by the {Mo(E-Q-E)$_2$Mo} pseudo plane, as shown in Fig. 5. Examples of both have been characterised crystallographically. Second, two delocalising ligands and the accompanying greater rigidity inherent in the macrocycle framework have a noticeable effect on the electrochemical properties of these species when compared to their singly-bridged analogues.

In general, the two reduction potentials of the doubly-bridged species were more negative than those of the single-bridge acyclic analogues, as expected by comparison with redox behaviour of [Mo(NO)Tp*X(OR)] and [Mo(NO)Tp*(OR)$_2$], and their CVs exhibited a single wave due to two near-synchronous one electron additions whose ΔE_f values were determined by differential pulse voltammetry. The ΔE_f value for the *syn* isomer of [{Mo(NO)Tp*(2,7-III)}$_2$] (174 mV) was 9% larger than that in the acyclic analogue [{Mo(NO)Tp*Cl}$_2$(2,7-III)],[41] suggesting that the interaction in the macrocycle was slightly greater than in the singly-bridged analogue. This may occur because the macrocycle has two delocalising ligands and/or that the redox centres are closer in a macrocyclic ring. A similar situation was detected with the *syn* and *anti* isomers of [{Mo(NO)Tp*(IIb,Q=CH$_2$}$_2$], where ΔE_f was estimated to be 38% larger than that of the acyclic analogue [{Mo(NO)Tp*Cl}$_2${IIb,Q=CH$_2$}].[39] However, ΔE_f in [{Mo(NO)Tp*(1,4-Ic,E=O)}$_2$] was comparable to that in the acyclic analogue, but this ligand system is not particularly effective in delocalising charge.[39] *Syn* and *anti* isomers of 1,3- and 1,4-xylene dithiolates [{Mo(NO)Tp*(Ic,E=S}$_2$] were isolated but specific structures could not be assigned. Each of the four isomers exhibited unresolved two-electron reduction processes, consistent with very weak interaction between the redox centres, but the potentials of the *syn*

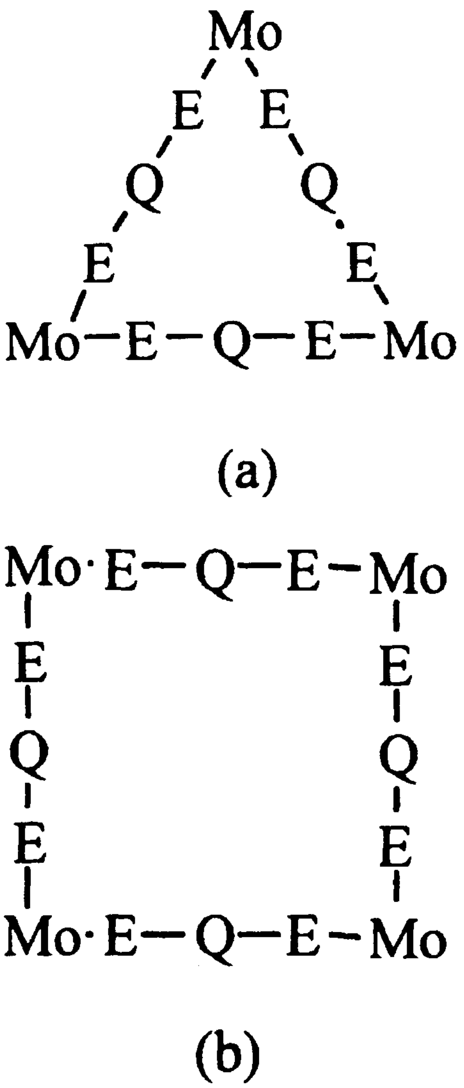

FIGURE 6 Schematised structures of (a) tri- and (b) tetranuclear metallomacrocycles. M = Mo(NO)Tp* and/or W(NO)Tp*, or Mo(O)Tp; Q may be 1,3- or 1,4-C_6H_4, 1,4′-$C_6H_4C_6H_4$, 1,4′-$C_6H_4CH_2C_6H_4$, 2,7-$C_{10}H_6$, 1,3- or 1,4- $CH_2C_6H_4CH_2S$; E = O or S

and *anti* forms of the 1,3- and 1,4- dithiolates were detectably different, by 32 mV for the former and 64 mV for the latter. Although these are small differences they are significant and provide a rare example of isomer effects on redox potentials. The reasons for this may be due to conformational demands within the macrocycle ring which could impose different (ON)Mo-Mo-S-C(H_2) torsion angles in the different isomers. This would influence the orientation of the filled sulphur $p\pi$ donor orbitals with respect to the Mo d_{xy} acceptor orbital, leading to better or worse overlap, an effect which has been commented on regarding the redox behaviour of $[Mo(NO)(\eta^5\text{-}C_5H_5)(SPh)_2]$[43] and $[Mo(NO)Tp^*(SPh)_2]$.[14]

The redox behaviour of the oxomolybdenum macrocycles $[\{Mo(O)Tp^*(bridge)\}_2]$ is consistent with medium interaction between the redox centres.[42] All complexes, except that containing Ic(E = O), exhibited two well-defined one-electron reductions (no oxidation behaviour was reported, but it is expected), ΔE_f for $[\{Mo(O)Tp^*(1,3\text{-}OC_6H_4O)\}_2]$ being 60% larger than that for the corresponding acyclic complex $[\{Mo(O)Tp^*Cl\}_2(1,3\text{-}OC_6H_4O)]$. The corresponding values for the macrocyclic and acyclic $2,7\text{-}O_2C_{10}H_6$ derivatives were virtually identical, but this may have been due to solvent effects. The reduction potentials of $[\{Mo(O)Tp^*(1,3\text{-}SC_6H_4S)\}_2]$ were more positive than those of the benzene diolato analogue, as expected,[23] and ΔE_f was 40 mV smaller, presumably once again reflecting a poorer overlap between the S $p\pi$, ligand π and Mo d_{xy} orbitals.

Tri- and tetranuclear species, like the dinuclear species described previously, can also form isomers and examples have been characterised crystallographically.[40,44,45] The isomer possibilities, which are best defined by indicating the M-Z vector, are shown in Fig. 7.

Within the trinuclear series, those complexes containing 1,3- or $1,4\text{-}OC_6H_4O$ as the bridging ligand exhibit three distinct negative one-electron transfers, corresponding to the processes outlined in Fig. 8.[45] The reduction potentials of the tungsten species were more negative than their molybdenum analogues, as expected.[13,14,15] Consistent with earlier observations, the ΔE_f values for the oxomolydenum(V) analogues are much smaller than their nitrosyl counterparts.[42] Similar results were obtained from the trimetallocycles containing $\{Mo(O)Tp^*\}^{2+}$ and $2,7\text{-}[O_2C_{10}H_6]^{2-}$ or $[OC_6H_4CH_2C_6H_4O]^{2-}$,[42] although the values of ΔE_f were smaller because of the greater separation between the redox centres. The individual electron transfer processes could not be resolved in the CVs of those species derived from

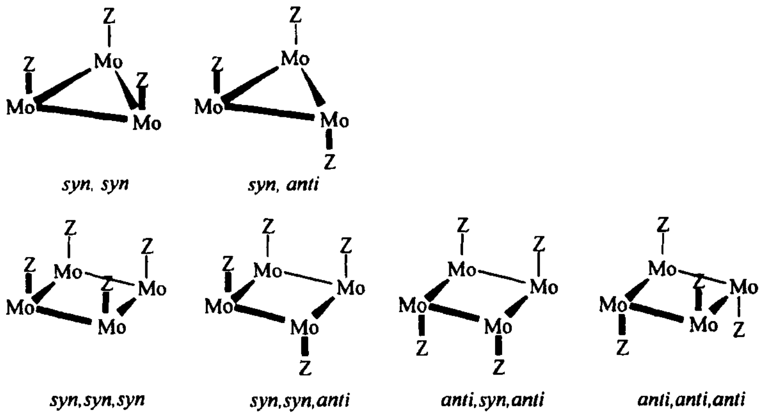

FIGURE 7 Isomers possible for tri and tetranuclear metallomacrocycles where $M = MoTp^*$ or WTp^* and $Z = NO$ or O

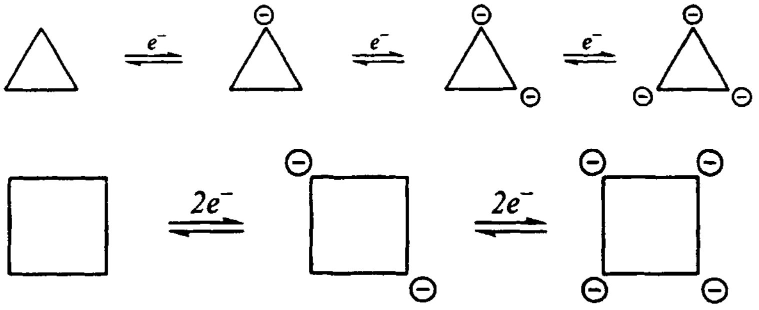

FIGURE 8 Pattern of electron additions to metallomacrocycles (a) One-electron addition to trinuclear macrocycles (b) Electron addition to tetranuclear macrocycles

$\{Mo(NO)Tp^*\}^{2+}$and $[OC_6H_4C_6H_4O]^{2-}$, where the distance between the metal centres is significant and there is probably a twist about the diphenyl linkage.[46]

It was also impossible to resolve all four of the possible reduction waves in the CVs of the tetranuclear species. Instead, two separate two-electron transfers were detected, corresponding to generation of a dianionic and a tetra-anionic species, as shown in Fig. 8.[42,45,46] Each of these processes should correspond to the reduction of two diagonally opposed redox centres. Although each of these centres would be expected to be non-interacting, there was evidence of weak communication. The ΔE_f value for the cyclic tetramers is larger than that observed for corresponding trimers, in accord with the presence of two reduced metal centres, one on each side of the remaining unreduced centre, following the first reduction process.

The electrochemical behaviour of tetranuclear complexes containing 1,3-$[SC_6H_4S]^{2-}$ and Ic, E = S was similar to that of their oxygenated analogues. The potentials for reduction of $[\{Mo(O)Tp^*(SC_6H_4S)\}_3]$ were somewhat more positive than its benzene diolato counterpart,[42] again consistent with earlier observations.[21,23] However, the CVs of the molybdenum nitrosyl complexes containing xylene dithiolato bridges exhibited broad reduction waves, consistent with the addition of three electrons to very weakly interacting or non-interacting redox centres.[40]

Tri- and tetra-nuclear complexes can be formed from tris- and tetra-substituted ligands such as those shown in Fig. 3, V. Both the nitrosyl and oxo molybdenum complexes of the phloroglucinate ion (Va) exhibited three well-separated reduction processes ($0 \rightarrow -1$, $-1 \rightarrow -2$, $-2 \rightarrow -3$), ΔE_f being 220 and 360 mV for the oxo species, indicating medium interaction between the metal centres, comparable to that in $[\{Mo(Z)Tp^*(1,3\text{-}OC_6H_4O)\}_3]$.[47] The CVs of the tetranuclear nitrosyl molybdenum complex of deprotonated tetrahexylcalix[4]resorcinarene (Vc), like comparable macrocyclic species described above, showed two broad reduction waves separated by 140 mV, both corresponding to the addition of two electrons to diagonally-related pairs of metal centres.[45] The interactions between the metals was therefore very weak.

MIXED VALENCY IN DIMETALLIC COMPLEXES

The potential separations in several of the singly-bridged dinuclear complexes $[\{Mo(Z)Tp^*X\}_2(bridge)]$ were such that we could conveniently generate monoanionic 16:17 ve mixed-valence species, either electrochemically or, in some cases, by one-electron reduction with cobaltocene. The partially reduced complexes are paramagnetic ($S = 1/2$ per dinuclear species) and exhibit characteristic epr spectra. Useful information about the electronic state of the metal centres may also be obtained from NO stretching frequencies. By these techniques, we showed that both isomers of $[\{Mo(NO)Tp^*Cl\}_2(OC_6H_4O)]^-$ were valence-trapped on the epr timescale.[27,28,48] In contrast, the 1,2- and 1,4-isomers of $[\{Mo(NO)Tp^*Cl\}_2(NHC_6H_4NH)]^-$ appeared to exhibit Class II or III mixed valency behaviour, the unique electron interacting with both Mo centres.[9] On reduction of these two isomers the single NO stretching frequency observed in the neutral species was replaced by two ν_{NO}, showing that the unpaired electron is delocalised on the EPR timescale but trapped on the IR timescale, placing the intramolecular electron exchange rate in the range 10^8 to 10^{13} per second. We were unable to obtain satisfactory IR spectral data from the reduced 1,3-isomer but it was clear that the monoanion is valence-trapped on the EPR timescale. These data are generally compatible with empirical rules devised by Richardson and Taube to explain the mediating effect of bridging ligands on metal-metal interactions. These interactions are greatly enhanced when the metal centres are close together and when there is extensive conjugation in the bridging ligands: clearly the case with 1,2- and 1,4-NHC_6H_4NH but not with the 1,3-isomer, and consistent with our electrochemical findings discussed above.

Spectroelectrochemical studies of $[\{Mo(O)Tp^*Cl\}_2(1,4\text{-}OC_6H_4O)]$, as it was progressively reduced through the monoanion to the dianion, showed that the LMCT (phenolato → Mo^V) absorption at 660 nm gradually reduced in intensity while new strong absorptions at 1127 and 1700 nm evolved as $[\{Mo(O)Tp^*Cl\}_2(1,4\text{-}OC_6H_4O)]^-$ was generated.[31] These new absorptions were assigned to intervalence charge transfer (IVCT) bands and this was confirmed by their disappearance on formation of $[\{Mo(O)Tp^*Cl\}_2(OC_6H_4O)]^{2-}$.[31] It was concluded that the monoanion $[\{Mo(O)Tp^*Cl\}_2(1,4\text{-}OC_6H_4O)]^-$ could be classified as a class II mixed valence species. In contrast, the corresponding 1,3-isomer did not exhibit IVCT bands on progressive reduction, although the LMCT absorptions present in the neutral precursor did diminish on reduction. Broadly similar behaviour was observed in the 1,5- and 2,6-naphthalene diolato complexes $[\{Mo(O)Tp^*Cl\}_2(III)]^-$, where the former had an IVCT absorption at *ca.* 1250 nm and the latter at *ca.* 1150 nm.[29] These monoanions also appeared to show weak class II behaviour.

However, the most remarkable mixed-valence behaviour in this group of compounds has been that of the pyrazine-bridged complexes $[\{Mo(NO)Tp^*X\}_2(pz)]^z$ (X = Cl, Br; Fig 2: IVd). This species is a member of a five-membered electron transfer chain where z = −2, −1, 0, +1 and +2.[36] The separation between the reduction potentials (z = 0 → −1 and z = −1 → −2) of the bromo complexes is 1440 mV, the largest yet detected with this class of compounds. The EPR spectrum of deep blue $[\{Mo(NO)Tp^*X\}_2(pz)]^{-1}$, (17:18 ve), in contrast to its neutral precursor (z = 0, 17:17 ve) which was "epr silent" and suggestive of significant antiferromagnetic coupling between the unpaired electrons (later confirmed), is consistent with delocalised behaviour of the unpaired electron. The NO stretching frequency of the monoanion was 40 cm^{-1} lower than that of its neutral precursor, but both complexes exhibited only one absorption. This behaviour showed that the unpaired electron in $[\{Mo(NO)Tp^*Cl\}_2(pz)]^{-1}$ was fully delocalised on both the EPR and IR spectral timescales, implying that the electron exchange rate is 10^{13} s^{-1} or faster. This result may be compared with that reported for $[\{Mo(NO)Tp^*Cl\}_2\{1,4\text{-}NHC_6H_4NH\}]^{-1}$ above. Similar behaviour has been observed in dinuclear mixed valence iron carbonyls and rhenium nitrosyls,[49] but it is quite rare. Further reduction of the pyrazine complex affords the dianion, which should be diamagnetic (18:18 ve), and the reduction of the intensity of the EPR signal from the monoanion as the second reduction proceeded was consistent with this prediction. As was mentioned above, these pyrazine derivatives are the only species of type IV (Fig. 2), to exhibit two distinct one-electron oxidation processes, these separated by only 100 mV. Oxidation of $[\{Mo(NO)Tp^*X\}_2(pz)]$ gave a rather unstable brown monocation (17:16) whose EPR spectrum indicated that the unpaired electron is coupled with only one metal centre and whose IR spectrum had two ν_{NO}. These results indicate that the monocation is valence-trapped. Further oxidation afforded $[\{Mo(NO)Tp^*X\}_2(pz)]^{2+}$ which is "EPR silent" and therefore probably diamagnetic and exhibits only one NO stretching frequency.

The behaviour of $[\{Mo(NO)Tp^*X\}_2(pz)]$ is, of course, reminiscent of the Creutz-Taube ion, $[\{Ru_2(NH_3)_{10}(pz)]^z$, in which z = +4, +5 and +6. The mixed-valent +5 complex also exhibits delocalised behaviour, like that of $[\{Mo(NO)Tp^*X\}_2(pz)]^{-1}$, but was at the lower end of Class III behaviour. The nitrosyl complex, however, has more extensive redox behaviour, allowing detection of a second mixed-valence species, and the observation of two types of such behaviour within the same structural framework is extremely unusual, if not unprecedented.

NON-LINEAR OPTICAL BEHAVIOUR

The growth of optical data transmission and processing technologies in the last 25 years has led to an explosion of interest in new types of processable non-linear optical materials. Although a number of purely inorganic substances (*e.g.* KH_2PO_4, $LiNbO_3$) have long been known to exhibit frequency doubling as well as other second-order non-linear optical effects, *molecular* organic materials aroused considerable interest because of the expectation that their non-linear optical properties could be optimised through manipulation of their electronic and structural properties. A wide variety of molecular and polymeric organic non-linear optical materials have been characterised, but materials based on metal-organic compounds have been less extensively studied. Owing to the special properties that transition metal centres might impart to molecular materials (*e.g.* redox and magnetic behaviour with the potential for on/off or other forms of switching), interest in the non-linear optical properties of such compounds has grown significantly in recent years.[50]

The general criteria for obtaining organic molecules with large first hyperpolarisability (β) values are now well-established and these have been applied in the search for molecular metal-organic non-linear optical materials. In particular, the ferrocenyl group has been successfully used as a donor function in donor-acceptor molecules which exhibit second harmonic generation (SHG), and theoretical studies showed that in $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}CHC_6H_4NO_2\text{-}4]$ the metal-organic fragment acts as a π-donor primarily through a metal-to-ligand (MLCT) – ligand-to-ligand charge transfer (LLCT) state.

The strong polarisability and electrochemical behaviour of the $\{Mo(NO)Tp^*\}^{3+}$ group suggested that it would be an excellent acceptor which, when linked via a polarisable bridging group to a donor such as ferrocene, could form a heterobimetallic dipolar species capable of exhibiting second order non-linear optical behaviour. This turned out to be correct, since powder SHG efficiencies (Kurtz test, 1907 nm laser fundamental) of molecules of the type shown in Fig. 9, were significant.[51,52] While powder SHG efficiencies are only semiquantitative guides as to the effectiveness of materials in frequency doubling, it was observed that the tungsten complexes were significantly less active than their molybdenum analogues. This could imply that alterations in the energy of the acceptor's LUMO with respect to the donor's HOMO might influence SHG efficiency. These efficiencies parallel the trends in our electrochemical data which showed that the $\{W(NO)Tp^*\}^{2+}$ core was harder to reduce than its Mo analogue. There was no evidence that these major changes in SHG efficiencies were related to structural differences in these complexes. However, more recent studies of these compounds in thin films have indicated that magnitude of χ_2 (second order susceptibility) and probably β in these molybdenum complexes was not as large as that in $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH{=}CHC_6H_4NO_2\text{-}4]$.[53] Analogous complexes in which Tp* is replaced by Tp^{An} (An = 3-anisyl) do, however, exhibit significant third order non-linear susceptibilities, χ_3.[54]

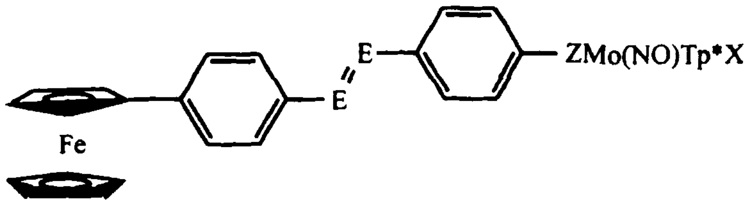

FIGURE 9 Polarisable molecules exhibiting SHG: E = N or CH, Z = NH or O, X = Cl, Br or I

However, the most intriguing information which the SHG efficiency tests revealed was the apparent dependence of SHG on the energy of the LUMO of the nitrosyl centre which, as has been described above, can be "tuned", by changes of the metal centre, the halide and the components of the bridging ligand. The correlation may be wholly fortuitous, but there is a clear implication that electronic, rather than structural, effects control the efficiency of SHG, but until first-order hyperpolarisability (β) data are obtained, this cannot be confirmed.

Redox behaviour is incorporated in the design of these SHG-active heterobimetallics: the ferrocenyl fragment can be oxidised and, obviously, the metal nitrosyl acceptor can be reduced. In further explorations of the optical properties of these unusual compounds, we have begun to investigate what happens to second order optical properties when the acceptor is pre-reduced (population of the LUMO) or the donor pre-oxidised (depopulation of the HOMO) before laser excitation. In either case the energies of the ground and excited states of the molecules will be drastically altered and this could lead to interesting switching effects.

Preliminary experiments designed to determine β before and after reduction of selected complexes were somewhat ambiguous. The intensity of SHG observed before and after reduction of [Mo(NO)Tp*Cl(NHC$_6$H$_4$Fc)] reduced by 94%, and that observed from [{Mo(NO)Tp*Cl-(NHC$_6$H$_4$N=NC$_6$H$_4$Fc)] decreased to 0. These results were encouraging but the fact that one response did not disappear altogether suggested that our initial expectations of switching behaviour were naive and a more in-depth examination of this behaviour was necessary. However, we concluded that if we were to make an electrochemically-operated on-off SHG switch, it would make more sense to construct a molecular system incorporating an acceptor with a half-filled LUMO (SOMO) which, on reduction, could become fully occupied and therefore incapable of being involved in the photochemically-promoted electron transfer from the donor. Alternatively, oxidation of the donor should result in total loss of SHG capabilities, and preliminary studies reveal that this is likely.

We had available two types of compounds to develop these ideas: [Mo(NO)Tp*Cl(pyQFc)], having a 17 ve metal nitrosyl centre (Q could be N=N, CH=CH or C≡C), and the d^1 oxomolybdenum complex [Mo(O)Tp*Cl(OC$_6$H$_4$QFc)]. The NLO activity of these complexes has not yet been reported, but during their characterisation we discovered that both exhibited unexpected and extremely interesting *linear* optical behaviour associated with their redox behaviour; the former with reduction and the latter with oxidation.

SWITCHABLE ELECTROCHROMIC NIR DYES

CVs of [MoOTp*Cl(OC$_6$H$_4$QFc)] (Q = N=N or C≡C) showed that the molecule is reversibly reduced in a one-electron process giving a Mo^{IV}/Fc species, and reversibly oxidised in two steps, Fc → Fc$^+$ and then Mo^V → Mo^{VI}.[55] Spectroelectrochemical investigation of this species as the monocation was generated showed that the ArO → Mo LMCT band at *ca.* 600 nm was slightly blue-shifted, while a ferrocenium LMCT band evolved at *ca.* 900 nm, behaviour characteristic of removal of an electron from the ferrocenyl fragment. However, unexpectedly, the second oxidation process, predominantly associated with the {MoOTp*Cl} group, led to the evolution of a very intense new transition in the region between 800 and 950 nm, depending on Q. This behaviour was consistent with some admixture of metal and ligand character in the HOMO of $[MoOTp^{*}Cl(OC_6H_4QFc)]^{2+}$ which permits the introduction of a new low-energy fully allowed $\pi \rightarrow \pi^{*}$ transfer in this condition.

Broadly similar observations were made with $[\{Mo(O)Tp^{*}Cl\}_2\{Ia,b,Z=0]$ and $[\{Mo(O)Tp^{*}Cl\}_2(IIb)]$ $(Q = C_6H_4$, N=N, CH=CH, thienyl, etc.).[31] Spectroelectrochemical studies on the mono- and di-oxidised complexes showed that both cations had very intense absorptions in the NIR region, that in the monoxidised species being replaced by a blue-shifted transition of significantly greater intensity on generation of the dication. For example when $z = 0$ in $[\{Mo(O)Tp^{*}Cl\}_2(IIb,Q=C_6H_4)]^{z}$ there are no absorptions in the visible and NIR region between 600 and 2000 nm, but when $z = +1$ and $+2$, absorptions at 1131 nm ($\varepsilon = 25000\ M^{-1}\ cm^{-1}$) and 1015 nm ($\varepsilon = 62000\ M^{-1}\ cm^{-1}$) are prominent. By a combination of spectroelectrochemical studies on mononuclear complexes and by molecular orbital (ZINDO) calculations, we showed that these NIR transitions were due primarily to phenolate → Mo^{VI}charge transfer, in contrast to the ferrocenyl species described above, where bridging ligand oxidation may play more important rôle. By appropriate choice of Q, the NIR absorption could be moved as far down as 1600 nm.

The oxidation of these dinuclear species is electrochemically and chemically reversible, indicating that compounds may have potential as variable optical attenuators.[56] This has been demonstrated with $[\{Mo(O)Tp^{*}Cl\}_2(IIb,Q=(thienyl)_2)]$ which, on one-electron electrochemical oxidation, exhibited a strong NIR absorption band at 1340 nm (ε 23000 $M^{-1}\ cm^{-1}$) and a slightly weaker transition at 752 nm, both of which were assigned to phenolate → Mo(VI) LMCT transitions. The transition at 1340 nm provides a strong and fully switchable absorbance within the 1300 nm window of silica fibres. On further oxidation to the dication, this transition moves to higher energy, with λ_{max} at *ca.* 1200 nm, but this dication is too unstable to be practically useful. The dianion $[\{Mo(O)Tp^{*}Cl\}_2(IIb,Q=(thienyl)_2)]^{2-}$ is transparent at wavelengths above 950 nm. Preliminary experiments using electrochemically generated $[\{Mo(NO)Tp^{*}Cl\}_2(IIb,Q=(thienyl)_2)]^{-}$ indicate that reversible optical switching could be sustained for several thousand cycles by repeated stepping between an applied potential of 0 and 1.5V. Further experiments suggest that this material can attenuate NIR laser light to a degree comparable to the best that is currently available from alternative attenuator technologies, and at a low voltage.

Spectroelectrochemical studies of [Mo(NO)Tp*Cl(pyR)], where R = 3- or 4-Ph, COMe, COPh, CN, Cl) showed that, on reduction to the 18 ve monoanion, those complexes having 4-substituents evolved an intense low-energy m.l.c.t. transition from the electron rich 18 ve metal centre to the LUMO of the pyridine ligands, usually at the red end of the visible spectrum.[57] However, those complexes having electron withdrawing substituents at the 3-position in the pyridine ligand showed a second m.l.c.t. absorption which is well into the NIR region of the spectrum. For example, when R = 3-COPh, λ_{max} = 1514 nm, offering the possibility of electro-optic switching in a reductive regime as opposed to the oxidative regime which operates for [{Mo(O)Tp*Cl}$_2$(II)].

CONCLUSION

The redox abilities of the {Mo(NO)Tp*}$^{2+,+}$ and {Mo(O)Tp*}$^{2+}$ cores afford a remarkable degree of control over the polarisability, electronic and magnetic properties of any compound that contains them. This has led to materials having interesting and potentially applicable optical properties and to formation of complexes exhibiting unusual mixed valence properties. There are many other ways in which these molybdenum species can be exploited and, although we have not described them in this article, information about the magnetic properties, including redox switching effects, of di- and trinuclear complexes containing {Mo(NO)Tp*}$^+$ and {Mo(O)Tp*}$^{2+}$cores has been described elsewhere.[26,58] Furthermore, attachment of {Mo(NO)Tp*}$^{2+}$ and {Mo(O)Tp*}$^{2+}$groups to porphyrins and their metal derivatives gives compounds which exhibit photoelectron transfer[59,60] and which are good models for sulphite oxidase in which there are weak magnetic interactions between intraporphyrin iron and peripheral molybdenum centres.[61] It is highly likely that these core units will find other interesting uses in the future.

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