

## REDOX, PHOTOCHEMICAL AND OPTICAL ACTIVITY IN MOLYBDENUM CHEMISTRY: TOWARDS MOLECULAR ELECTRONICS

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### Abstract

Compounds containing the group  $[\text{Mo}(\text{NO})]^{3+}$  are redox-active. Incorporation into tris(3,5-dimethylpyrazolyl)borato  $\text{L}^*$  systems, eg.  $[\text{MoL}^*(\text{NO})\text{XY}]$  where X, Y = halide, alkoxide, aryloxy, amide anilide, thiolate, etc. affords a variety of species which undergo one-electron reduction. The factors influencing this behaviour are described. Attachment of the molybdenum redox centre to macrocyclic polyethers and the effect of added cation is discussed. The group  $\{\text{MoL}^*(\text{NO})\text{X}\}$  can be attached to the periphery of tetra-aryl porphyrins, and the electrochemistry and photochemistry of the extra-ring metallated species is reported. A series of ferrocenyl compounds,  $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}_6\text{H}_4\text{E}\{\text{ML}^*(\text{NO})\text{X}\}))];$  *trans*- $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}_6\text{H}_4\text{Z}=\text{ZC}_6\text{H}_4\text{E}\{\text{ML}^*(\text{NO})\text{X}\}))]$ , where Z = CH or H, E = O or NH, M = Mo or W; X = Cl or I) have been prepared, their electrochemistry investigated and several compounds identified as having non-linear optical (Secondary Harmonic Generation) properties.

In general, compounds containing the  $[\text{Mo}(\text{NO})]^{4+}$  or  $[\text{Mo}(\text{NO})]^{3+}$  groups are redox-active, readily undergoing one-electron reduction to  $[\text{Mo}(\text{NO})]^{5+}$  or  $[\text{Mo}(\text{NO})]^{2+}$  species. This is true of the tris(3,5-dimethylpyrazolyl)borato nitrosyl complexes of molybdenum  $[\text{MoL}^*(\text{NO})\text{XY}]$ , where X, Y = halide, or pseudo-halide, alkoxide, aryloxy, alkyl- or aryl-amide, alkane or arene thiolate, hydrazide or related species. The most carefully studied of this group of compounds have been the halides, where Y = Cl and I<sup>1</sup>. The dichloride  $[\text{MoL}^*(\text{NO})\text{Cl}_2]$  is readily reduced electrochemically to the monoanion  $[\text{MoL}^*(\text{NO})\text{Cl}_2]^-$ , which is stable in solution and can be isolated by chemical reduction of the neutral precursor using trifluoroethylhydrazine and triethylamine. The diiodide, in contrast, exhibits much more complex behaviour. In scrupulously dry THF,  $[\text{MoL}^*(\text{NO})\text{I}_2]$  is reversibly reduced to the corresponding monoanion at a relatively anodic potential. The e.s.r. spectrum of this species ( $\langle g \rangle = 2.027$ ) is characteristic and consistent with a paramagnetic  $[\text{Mo}(\text{NO})]^{5+}$  system in which the unique electron is in an orbital predominantly located on the metal. However, if moisture is allowed to enter the system, or if the neutral diiodide is exposed to water even in the absence of formally reducing conditions, reduction to  $[\text{MoL}^*(\text{NO})\text{I}_2]^-$  is rapidly superseded by formation of a new reduced species, identified as  $[\text{MoL}^*(\text{NO})\text{I}(\text{solvent})_n]$ , resulting from dissociation of I<sup>-</sup> from  $[\text{MoL}^*(\text{NO})\text{I}_2]^-$ . Iodide ion was readily detected in 'wet' solutions of  $[\text{MoL}^*(\text{NO})\text{I}_2]$ .

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The e.s.r. spectrum of  $[\text{MoL}^*(\text{NO})\text{I}(\text{solvent})_n]$  ( $\langle g \rangle = 1.988$ ) was significantly different to that of  $[\text{MoL}^*(\text{NO})\text{I}_2]^-$  and the two species could be readily identified by this technique. Attempts to isolate  $[\text{MoL}^*(\text{NO})\text{I}_2]^-$  or  $[\text{MoL}^*(\text{NO})\text{I}(\text{solvent})_n]$  were not very successful, although  $[\text{MoL}^*(\text{NO})\text{I}_2\text{Li}(\text{OEt}_2)_2]$  was obtained on treatment of  $[\text{MoL}^*(\text{NO})\text{I}_2]$  with tolyl lithium in ether. This compound could be regarded either as  $[\text{MoL}^*(\text{NO})\text{I}_2]^-$  stabilised by  $[(\text{Li}(\text{OEt}_2)_2)]^+$  or as  $[\text{MoL}^*(\text{NO})\text{I}]$  'solvated' by  $\text{LiI}(\text{OEt}_2)_2$ . E.s.r. and i.r. spectral data were most consistent with the former model. Analogues of  $[\text{MoL}^*(\text{NO})\text{I}(\text{solvent})_n]$  where the 'solvent' is amine, viz.  $[\text{MoL}^*(\text{NO})\text{X}(\text{NHC}_n\text{H}_{2n})]$  ( $\text{X} = \text{Cl}$  or  $\text{I}$ ;  $n = 4$  or  $5$ ) have, however, been isolated and characterised<sup>2</sup>. They too are paramagnetic ( $\langle g \rangle = 1.999$ ) and were very readily oxidised to the diamagnetic  $[\text{MoL}^*(\text{NO})\text{I}(\text{NC}_n\text{H}_{2n})]$ . The electrochemical behaviour was irreversible as expected ( $E_p^c = -1.04 \rightarrow 1.68\text{V}$  in  $\text{CH}_2\text{Cl}_2$  vs SCE, depending on  $\text{X}$  and  $n$ ).

The compounds  $[\text{ML}^*(\text{NO})\text{XQ}]$  ( $\text{Q} = \text{OR}, \text{OAr}, \text{NHR}, \text{NHAr}, \text{SR}, \text{SAr}$ ), like their dihalide analogues, undergo one-electron reductions, and it is not surprising that when  $\text{X} = \text{Cl}$ , the reduced species are stable to dissociation whereas  $[\text{MoL}^*(\text{NO})\text{IQ}]^-$  readily dissociates with  $\text{I}^-$  loss. This property can be very important not only for the electrochemical behaviour of this class of molybdenum and related tungsten nitrosyl complexes but also for the synthetic chemistry of this system.

Substitution of halide in  $[\text{ML}^*(\text{NO})\text{X}_2]$  ( $\text{M} = \text{Mo}$ ;  $\text{X} = \text{Cl}, \text{I}$ ;  $\text{M} = \text{W}$ ,  $\text{X} = \text{Cl}$ ) is facile. Thus, in general, mono-alkoxides and aryloxides are obtained by heating the dihalide with the alcohol or phenol, or by addition of triethylamine or sodium carbonate under milder conditions in the presence of substrate<sup>3</sup>. An alternative is to convert the dihalide to a halide acetate, eg.  $[\text{MoL}^*(\text{NO})\text{X}(\text{OCOMe})]$ ; treatment of this with  $\text{ROH}$  affording the alkoxide with elimination of acetic acid demonstrating neatly the power of acetate as a most effective leaving group<sup>4</sup>. The monoamido compounds are prepared even more easily by reaction, in many cases at room temperature, of the dihalide with two mole equivalents of diluted amine<sup>3</sup>. Formation of  $[\text{ML}^*(\text{NO})(\text{NHR})_2]$ , however, requires more vigorous conditions<sup>5</sup>. It is also possible to prepare mixed ligand species of the types  $[\text{ML}^*(\text{NO})(\text{OR})(\text{NHR})]$ ,  $[\text{ML}^*(\text{NO})(\text{OR})(\text{SR})]$ , etc.

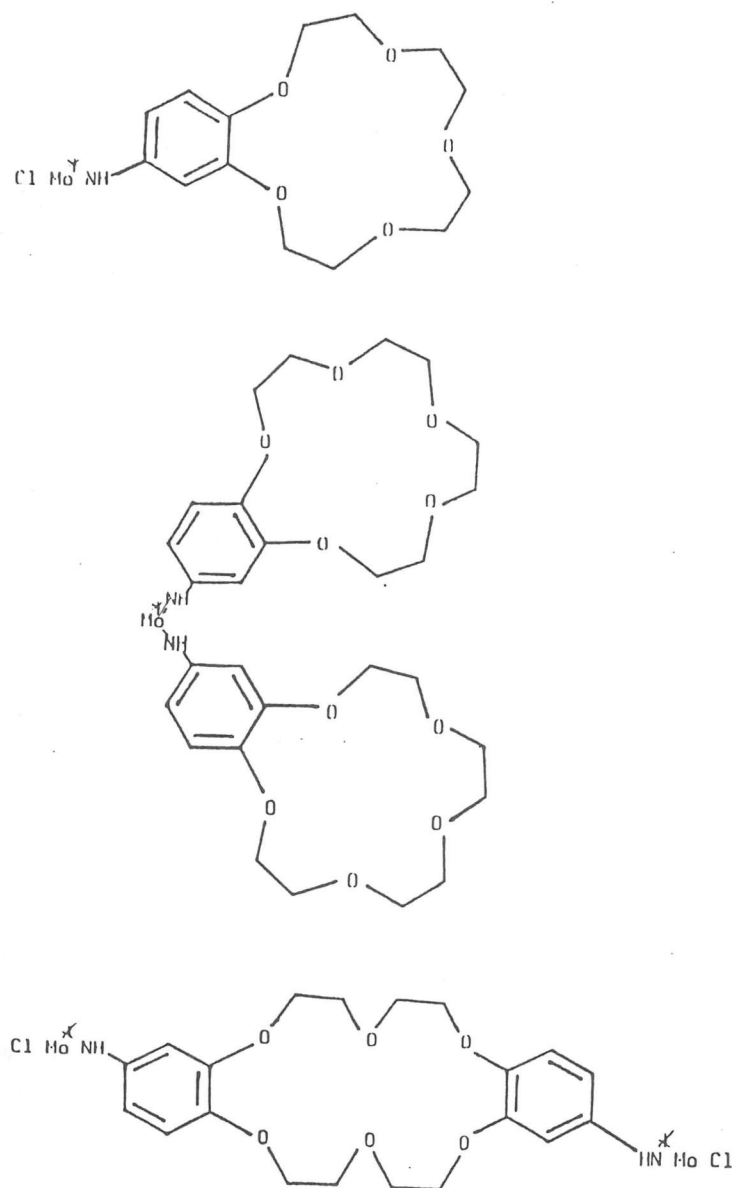
The structures of representative members of the series  $[\text{MoL}^*(\text{NO})\text{XQ}]$  have been determined crystallographically<sup>6</sup>. In all of them, the protective nature of the tris(3,5-dimethylpyrazolyl)borate ligand is evident, the 5-methyl groups hanging down over the metal atom, effectively enforcing six-coordination of these species which normally prefer seven- or eight-coordination. In addition, the bond distances between the metal and the hetero-atom of the  $\text{Q}$  group are short, indicating a substantial amount of  $p_\pi-d_\pi$  or  $d_\pi-d_\pi$  bonding between  $\text{O}, \text{N}$  or  $\text{S}$  and  $\text{Mo}$ . These factors undoubtedly contribute to the high stability of this class of compounds towards oxidative decomposition and to the

facility with which they may be reduced.

The  $E_{1/2}$ -values of the reduction potentials of  $[\text{ML}^*(\text{NO})\text{XQ}]$  are strongly influenced by the nature of  $\text{M}$ ,  $\text{X}$  and  $\text{Q}$ <sup>7</sup>. In general, potentials of tungsten compounds are usually between 300 and 500 mV more cathodic than those of their Mo analogues. There are insufficient data to state precisely how  $\text{X}$  influences the redox potential in these species, other than that the  $E_{1/2}$ -values of iodo complexes are usually significantly more anodic than those of their chloro-analogues. However, the value of redox potential is substantially affected by the hetero-atom in  $\text{Q}$ , and by the substituents attached to them. In general, for Mo complexes  $E_{1/2}$ -values fall in the ranges  $-0.50 \rightarrow -0.65\text{V}$  when  $\text{Q} = \text{OR}$ ,  $-0.10 \rightarrow -0.42\text{V}$  when  $\text{Q} = \text{OAr}$ ,  $-1.10 \rightarrow -1.22\text{V}$  when  $\text{Q} = \text{NHR}$  and  $-0.60 \rightarrow -1.10\text{V}$  when  $\text{Q} = \text{NHAr}$ . Further fine-tuning of the redox potential can be achieved by using *p*- or *m*- substitution of aryl rings in species of the type  $[\text{MoL}^*(\text{NO})\text{X}(\text{ZC}_6\text{H}_4\text{Y})]$  where  $\text{Z} = \text{O}$  or  $\text{NH}$  and  $\text{Y} = \text{H}, \text{NH}_2, \text{OMe}, \text{F}, \text{CN}$ , etc., in the *meta* or *para* positions<sup>8</sup>. Thus, in the series  $[\text{MoL}^*(\text{NO})\text{I}(\text{NCH}_2\text{CH}_2\text{Z-p})]$  ( $\text{Z} = \text{NH}_2, \text{OH}, \text{OMe}, \text{H}, \text{F}, \text{Br}, \text{Cl}, \text{I}, \text{SO}_2\text{Ph}, \text{N}_2\text{Ph}$ ) the  $E_{1/2}$ -value ranged from ca.  $-0.5$  to  $-1.0\text{V}$  and can be correlated very well with Hammett  $\sigma$  constants for these substituents.

#### Molybdenum Nitrosyls as Sensors

Benzo- and dibenzo-crown ethers may readily be functionalised to afford amino groups on the benzene rings. These 'anilines' react with  $[\text{MoL}^*(\text{NO})\text{Cl}_2]$  affording anilido derivatives of the type I, II and III<sup>9</sup>. These complexes behave electrochemically as though they are simple derivatives of the type  $[\text{MoL}^*(\text{NO})\text{Cl}(\text{NHAr})]$  or  $[\text{MoL}^*(\text{NO})(\text{NHAr})_2]$ , ie. they undergo reductions in the region of  $-0.85\text{V}$  (monoanilide) and  $-1.3\text{V}$  (bis-anilide), respectively. The bimetallic species undergo a two-electron reduction and there is no evidence of interaction between the two metal centres. On addition of one mole equivalent of  $\text{NaBPh}_4$ , the  $E_{1/2}$ -values of these species shifted anodically by between 60 and 90 mV. Similar effects are observed with  $\text{KBPh}_4$  with I, II and III, and with  $[\text{MoL}^*(\text{NO})\text{Cl}_2\text{NHC}_6\text{H}_3\text{C}_{10}\text{H}_{20}\text{O}_7\text{C}_6\text{H}_3\text{NH}]$  and  $[\text{MoL}^*(\text{NO})\text{Cl}_2\text{NHC}_6\text{H}_3\text{C}_{12}\text{H}_{24}\text{O}_8\text{C}_6\text{H}_3\text{NH}]$ . However, the potassium shifts were only of the order of 40 mV, suggesting that there is a charge-to-radius effect on the shift in  $E_{1/2}$ -values when comparing the host-guest complexes formed by the crown ethers with  $\text{Na}^+$  and  $\text{K}^+$ .



Recognising that the bis-alkoxides  $[\text{MoL}^*(\text{NO})(\text{OR})_2]$  could be readily prepared from  $[\text{MoL}^*(\text{NO})\text{X}_2]$ , the formation of chelated species, ie.  $[\text{MoL}^*(\text{NO})\{\text{O}(\text{CH}_2)_n\text{O}\}]$  ( $n = 2, 3, 4, 5, 6$ ) seemed possible. We have prepared a variety of species from  $\alpha, \omega$ -alkane diols, eg.  $[\text{MoL}^*(\text{NO})\text{X}\{\text{O}(\text{CH}_2)_n\text{OH}\}]$ ,  $[\text{MoL}^*(\text{NO})\{\text{O}(\text{CH}_2)_n(\text{OH})\}_2]_m$   $[\text{MoL}^*(\text{NO})\{\text{O}(\text{CH}_2)_n\text{O}\}]$  and  $[\{\text{MoL}^*(\text{NO})\}\{\text{O}(\text{CH}_2)_n\}_2\{\text{MoL}^*(\text{NO})\}]$ , by appropriate manipulation of the reaction conditions for mixtures of  $[\text{MoL}^*(\text{NO})\text{X}_2]$  and  $\text{HO}(\text{CH}_2)_n\text{OH}$ <sup>10</sup>. However, reaction of  $[\text{MoL}^*(\text{NO})\text{X}_2]$  with a series of polyethylene glycols in the presence of triethylamine afforded cyclic polyethers in which the redox-active  $\{\text{MoL}^*(\text{NO})\}$  was incorporated within the macrocycle<sup>9</sup>. The structure of one of these metallated macrocycles,  $[\text{MoL}^*(\text{NO})\{\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{O}\}]$  has been determined crystallographically. It is clear that the steric effect of the tris(3,5-dimethylpyrazolyl)borate group is such as to protect one side of the macrocycle, effectively inserting one 5-methyl group into the rear of the  $\text{O}_5$  ring system, and forcing the polyether ring to adopt a conformation in which all five O atoms project outwards from the front of the macrocycle. Further, the NO group is also aligned with the other O atoms, thereby presenting a highly nucleophilic environment to any potential electrophilic guests. Addition to  $\text{NaBPh}_4$  to these metallo-macrocycles afforded 1:1 complexes, whose reduction potentials revealed substantial anodic shifts in  $E_{1/2}$ -values. Thus, for the species where  $n = 5, 6$  and  $7$ ,  $\Delta E$  ( $\Delta E$  is defined as the difference between  $E_{1/2}$  (guest-host species) -  $E_{1/2}$  (macrocycle)) was 320, 280 and 180 mV respectively. These anodic shifts also parallel very closely the known stability of adducts formed between  $\text{O}_5$ ,  $\text{O}_6$  and  $\text{O}_7$ -polyether macrocycles and  $\text{Na}^+$ . It should be noted that these effects have been observed in acetonitrile solution, in the presence of large amounts of  $[\text{Bu}^n_4\text{N}]\text{BF}_4$  (ca. 0.2M) and that in electrochemical titrations, the value of  $\Delta E$  was maximised at a 1:1 ratio of guest and host. Furthermore, addition of aliquots of  $\text{NaBPh}_4$  to solutions containing  $[\text{MoL}^*(\text{NO})\text{Cl}\{\text{NHC}_6\text{H}_3(\text{OMe})_2-3,4\}]$  resulted in shifts in reduction potential of no more than 10 mV. Thus, there is a clear unambiguous relationship between the shifts in  $E_{1/2}$  of these polyether compounds and the polarising power of the cationic guest. Guest-host compounds have been isolated and characterised, confirming the 1:1 relationship, but so far no material suitable for X-ray crystallographic examination has been obtained.

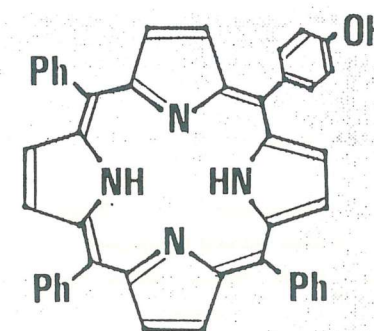
#### Photochemically-Active Redox Systems

As a development of our interest in the electrochemical and electronic properties of bimetallic redox systems<sup>11</sup>, where the two electrochemically-active centres are adjacent but not attached by metal-metal bonds or single atom bridges, we have attempted to prepare bi-redox centres containing a metal and an organic electron-transfer centre. Porphyrins are well-established redox systems in their own right, and we have succeeded in modifying the periphery of tetraphenylporphyrin to create mono- and tetra-phenolic functionality, IV.

Treatment of  $[\text{MoL}^*(\text{NO})\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{I}, \text{OH}, \text{NHCMePh}$ ) with  $(\text{HOC}_6\text{H}_4)\text{Ph}_3\text{PorphH}_2$  afforded the extra-ring metallated species  $[\text{MoL}^*(\text{NO})\text{X}\{(\text{OC}_6\text{H}_4)\text{Ph}_3\text{PorphH}_2\}]^{12}$ . These species are electrochemically rich, a total of five electron transfer processes being detected by cyclic voltammetry and differential pulse techniques. However, from the accumulated data, it is quite clear that there is very little interaction between the porphyrin and molybdenum redox centres in the ground state. Thus, the unmetallated porphyrin (ie.  $(\text{HOC}_6\text{H}_4)\text{Ph}_3\text{PorphH}_2$ ) exhibits two oxidation and two reduction processes, all one-electron transfers, and the potentials are virtually unaffected by the nature of the molybdenum species when they are attached. The  $E_{1/2}$ -values of the molybdenum moiety are influenced only by the nature of  $\text{X}$  in  $[\text{MoL}^*(\text{NO})\text{X}\{(\text{OC}_6\text{H}_4)\text{Ph}_3\text{PorphH}_2\}]$ . Similar results have been obtained from related metalloporphyrins,  $[\text{MoL}^*(\text{NO})\text{X}\{(\text{OC}_6\text{H}_4)\text{Ph}_3\text{PorphM}'\}]$  ( $\text{M}' = \text{Zn}, \text{Ni}, \text{Pt}, \text{FeCl}$ ).

However, it was noticed that the normal fluorescence of the tetra-arylporphyrins was quenched on attachment of the  $\{\text{OMoL}^*(\text{NO})\text{X}\}$  fragment. Thus the emission at 645 nm was (caused by excitation at 510 nm) of  $[\text{MoL}^*(\text{NO})\text{Cl}\{(\text{OC}_6\text{H}_4)\text{Ph}_3\text{PorphH}_2\}]$  is reduced to 7% of that in  $\text{Ph}_4\text{PorphH}_2$  and that in the species where  $\text{X} = \text{OH}$  and  $\text{NHCMePh}$  to 15% and 25%, respectively. That the observed quenching process is apparently intramolecular has been demonstrated by dilution studies. There is a broad correlation between the efficiency of quenching and the  $E_{1/2}$ -values for the reduction of the molybdenum fragment in the porphyrin species ( $\text{X} = \text{Cl}$ ,  $E_{1/2} -0.29\text{V}$ ;  $\text{X} = \text{OH}$ ,  $E_{1/2} = 0.81\text{V}$ ;  $\text{X} = \text{NHCMePh}$ ,  $E_{1/2} = -1.12\text{V}$ ). The energy of the first excited state in the porphyrin fragment is 0.85 eV, and this is sufficient to effect reduction of the molybdenum fragment, at least when  $\text{X} = \text{Cl}$ , and  $\text{OH}$ . A possible explanation for the quenching effect is that, on photo-excitation of the porphyrin centre, electron transfer occurs from the macrocycle's first excited state to the LUMO of the  $\{\text{MoL}^*(\text{NO})\text{X}\}$  moiety, thereby preventing normal relaxation processes in the porphyrin which lead to fluorescence. Such behaviour in porphyrins to which quinonoidal groups are attached (the so-called diad, triad and tetrad centres) is well-established and is central to biological photosynthesis<sup>13</sup>.

The extra-ring metallated porphyrins are diamagnetic, at least in the ground state, and





thus are e.s.r. 'silent'. On irradiation (visible light) of dichloromethane-toluene (75:25v/v) glasses of  $[\text{MoL}^*(\text{NO})\text{Cl}\{(\text{OC}_6\text{H}_4)_3\text{PorphH}_2\}]$  the system is still e.s.r. 'silent'<sup>14</sup>. It was hoped that signals due to the porphyrin radical cation and  $\{\text{OMoL}^*(\text{NO})\text{Cl}\}^-$  centres would be observed. Reduction of  $[\text{MoL}^*(\text{NO})\text{Cl}\{(\text{OC}_6\text{H}_4)_3\text{PorphH}_2\}]$  with cobaltocene did indeed afford a paramagnetic ( $S = 1/2$ ) species whose e.s.r. spectrum is entirely consistent with a reduced molybdenum phenoxide centre to which a virtually unperturbed porphyrin ring was attached. Interestingly, this system also exhibits extremely efficient fluorescence quenching<sup>12</sup>.

The behaviour of this system has been further complicated by the observation of apparent photochemically-stimulated intermolecular electron transfer between  $(\text{HOC}_6\text{H}_4)_3\text{PorphH}_2$  and  $[\text{MoL}^*(\text{NO})\text{Cl}_2]$  or species closely related to this dichloride. Solutions of  $[\text{MoL}^*(\text{NO})\text{Cl}_2]$  show weak e.s.r. signals associated with a paramagnetic  $\{\text{MoL}^*(\text{NO})\text{Cl}\}$  ( $S = 1/2$ ) centre. It is not clear whether this is  $[\text{MoL}^*(\text{NO})\text{Cl}_2]^-$  or a closely related species or decomposition product. However, when dichloromethane-toluene glasses containing a mixture of  $(\text{HOC}_6\text{H}_4)_3\text{PorphH}_2$  and this  $[\text{MoL}^*(\text{NO})\text{Cl}_2]$  are irradiated by visible light, the weak e.s.r. signal is significantly enhanced. In our view, photo-electron transfer must be occurring between the excited porphyrin and a molybdenum-based acceptor.

#### Towards Molecular Electronics: Non-Linear Optical Properties and Secondary Harmonic Generation in Ferrocenyl Molybdenum Nitrosyl Compounds.

There is currently great interest in the general field of 'molecular electronics'. This has stimulated a search for new liquid crystalline compounds, for 'organic' metals and semiconductors, for materials exhibiting non-linear optical, photochromic or electrochromic properties and for molecular species exhibiting bulk piezo- or pyro-electric phenomena.

Non-linear optical properties are extremely important in optical information processing, viz. in the switching, amplification and modulation of optical signals. According to the Pockels effect, the refractive index of a material varies with an applied electric field, and this permits the switching or modulation of light signals which are passing through that material in response to the applied field. To a first approximation, the polarisation  $P$  of a material (ie. the induced dipole per unit volume) is proportional to an applied electric field (produced by the oscillating electric ( $E$ ) of the radiation) and the linear electrical susceptibility ( $\chi$ ).

However, a more exact description of this relationship includes higher powers of  $E$ :

$$\chi = \epsilon_0(\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \chi_4 E^4 + \dots)$$

where  $\chi_2, \chi_3, \chi_4$  are higher order electric susceptibilities and  $\epsilon_0$  is a universal constant. It should be noted that for materials which crystallise in centrosymmetric space groups

(which includes the majority of non-chiral coordination and organometallic compounds) the even terms,  $\chi_2$  and  $\chi_4$  must be zero. In linear optics, the refractive index,  $\eta$ , of a substance is related to the electric susceptibility by the relationship  $\eta^2 = 1 + \chi_1$ . In non-linear optics, if terms beyond second order are ignored,  $P = \epsilon_0(\chi_1 E + \chi_2 E^2)$  which can be simplified to  $P = \epsilon_0 \chi_{\text{eff}} E$  where  $\chi_{\text{eff}} = (\chi_1 + \chi_2 E)$ . Thus

$$\eta^2 = 1 + \chi_{\text{eff}}$$

Since  $\chi_{\text{eff}}$  is dependent on the field  $E$ , the refractive index is also field dependent. Having established these relationships for materials exhibiting non-linear optical behaviour, similar considerations are needed for molecular species. The molecular dipole moment,  $\mu$ , which is induced by an applied electric field,  $E$ , obeys a relationship very similar to that in solids, viz:

$$\mu = \alpha E + \beta E^2 + \gamma E^3 + \dots$$

where  $\alpha$  is the molecular polarisability, and  $\beta$  and  $\gamma$  are the first and second hyperpolarisabilities. To obtain large values for  $\chi_2$ , large values of  $\beta$  are needed.

The necessary requirements to obtain large values of  $\beta$  in molecules are that they must have (a) excited states close in energy to the ground state, (b) large oscillator strengths for electronic transitions from ground to excited states, and (c) a large difference between ground and excited state dipole moments. The means, in effect, that suitable molecules must be dipolar and highly polarisable. If the molecule as a solid material is to have NLO properties, however, it must crystallise in a non-centrosymmetric space group. This may be achieved adventitiously, but can be guaranteed if a chiral species is isolated as a pure enantiomer or diastereomer. Demonstration of potentially interesting  $\beta$  values is obtained by the Kurtz powder test in which Secondary Harmonic Generation (SHG) is measured by irradiating a powdered or microcrystalline sample with a laser frequency  $\nu$  (typically 1907 or 1064 nm) and observation of emission at  $2\nu$ . The efficiency of the material as a Secondary Harmonic Generator is referred to that of urea, taken as unity ( $\Xi = 1$ ).

In constructing compounds with potentially non-linear optical properties, design usually requires a powerful donor and separate strong acceptor functions connected by a polarisable bridge. Typical donor groups are  $\text{NMe}_2$ ,  $\text{OMe}$  or 4-pyridyl and acceptors can be  $\text{NO}_2$ ,  $\text{CO}_2\text{R}$  or 4-pyridinium salts. The bridging group may be a benzene ring or *trans*- $-\text{C}_6\text{H}_4\text{Z}=\text{ZC}_6\text{H}_4-$ , where  $\text{Z} = \text{CH}$  or  $\text{N}$ . Some simple organic materials which exhibit SHG are 3-nitroaniline ( $\Xi = 8$ ) and 2-methyl-4-nitroaniline ( $\Xi = 22$ )<sup>15</sup> and certain types of polyacetylenic compounds have  $\Xi$ -values in the hundreds. Coordination and organometallic species can have donor or acceptor properties at least as powerful as

amines or cyano group, and the ability of organometallics to exhibit non-linear optical properties was elegantly demonstrated by the ferrocenyl species *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{CH=CHC}_6\text{H}_4\text{NO}_2\text{-p}\}]^{16}$  where the SHG efficiency,  $\Xi$ , was 62 (excitation at 1907 nm).

Recognising that  $\{\text{MoL}^*(\text{NO})\text{X}\}$  is extremely electron - withdrawing (electron 'deficient' metal, electronegative X and powerful  $\pi$ -acceptor NO), compounds incorporating this functionality and ferrocenyl residues have been prepared<sup>17</sup>. Three basic types of complexes have been prepared: (i)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}_6\text{H}_4\text{E}\{\text{ML}^*(\text{NO})\text{X}\})]$ , (ii)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}_6\text{H}_4\text{N=NC}_6\text{H}_3\text{RE}\{\text{ML}^*(\text{NO})\text{X}\})]$  and (iii)  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{C}_6\text{H}_4\text{CH=CHC}_6\text{H}_4\text{E}\{\text{ML}^*(\text{NO})\text{X}\})]$  where E = O or NH, M = Mo or W, X = Cl or I and R = H or Me. In the species (ii) and (iii) the alkene diazo bridges adopt the *trans*- configuration, but as yet no crystallographic data are available. These compounds are, of course, electroactive, and ferrocenyl moiety undergoing a reversible one-electron oxidation at  $E_{1/2}$ -values in the region of +0.58V. The oxidation potential is very little influenced by the nature of the attached groups, in contrast to the behaviour of the chelating dithio-ferrocenyl species  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_3\text{S}_2\{\text{MoL}^*(\text{NO})\})]$  where there is close contact between the Fe and the nitrosyl group on the molybdenum, and  $E_{1/2}(\text{ferrocenyl})$  is shifted cathodically by 90mV relative to dithioferrocene<sup>18</sup>. In a comparable way, the reduction potentials of the  $\{\text{ML}^*(\text{NO})\text{X}\}$  fragment in the ferrocene-containing systems is little influenced by the metallocene but follows the normal trends as influenced by M, X and E. In testing these materials for SHG behaviour, we have found that iodides are readily decomposed by laser light at 1064 nm, but this is not too surprising in view of the facile reductive elimination of  $\text{I}^-$  in solution, referred to above. Many of the compounds investigated exhibit negligible or very low values of  $\Xi$ , but a number have been found which give rise to  $\Xi$ -values up to 125.

In attempting to design compounds NLO properties, we have resolved the chiral species  $[\text{ML}^*(\text{NO})\text{X}(\text{OR})]$  and  $[\text{ML}^*(\text{NO})\text{X}(\text{HNR})]$ <sup>19</sup>. These species are enantiomeric and resolution was effected by forming alkoxides with optically pure mono-saccharides and with resolved  $\text{NH}_2\text{CHMePh}$ . It appears that the prochiral  $[\text{ML}^*(\text{NO})\text{X}_2]$  reacts with (+)-sugar or (+)- or (-)- $\text{NH}_2\text{CHMePh}$  to form two diastereomers, one of which rapidly converts into the thermodynamically stable form. A crystal structure of one diastereomer,  $[\text{MoL}^*(\text{NO})\text{I}(\text{C}_{12}\text{H}_{19}\text{O}_6)]$  where  $\text{C}_{12}\text{H}_{19}\text{O}_6\text{H}$  is 1,2,5,6-di-*O*-isopropylidene-*D*-glucofuranose, has established that the absolute configuration at the metal is S. The conformations of all related compounds were then established by CD measurements. The iodo-glucofuranose does not exhibit SHG and, so far, incorporation of enantiomerically pure  $\{\text{MoL}^*(\text{NO})\text{X}\}$  fragments into other simple systems has not yielded compounds with significant  $\Xi$ -values.

## Conclusion

The effectiveness and versatility of the redox centres based on  $\{\text{ML}^*(\text{NO})\}$  has been demonstrated. That these have useful and applicable properties is clear, and the design of molecules which have unusual and even specific electronic properties is already possible. The creation of liquid crystalline species and polymers containing  $\{\text{ML}^*(\text{NO})\}$  is in progress.

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