Second Harmonic Generation by Bimetallic Complexes containing Ferrocenyl and Molybdenum or Tungsten Mononitrosyl Redox Centres

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Several new molybdenum and tungsten mononitrosyl complexes have been synthesised and their non-linear optic properties investigated using the Kurtz powder test; although complexes containing chiral ligands and, in three examples, resolved chiral molybdenum or tungsten mononitrosyl centres, have been found to give second harmonic generation intensities of less than 0.3 times urea, three complexes containing polarisable ligands, namely $[Mo(NO)LCl(NHC_6H_4\text{-}4\text{-}N{=}N\text{-}C_6H_4\text{-}4'\text{-}Fc)]$ $\{Fc = [(\eta)^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{–})], L = HB(3,5\text{-}Me_2C_3N_2H)_3\}$, $[W(NO)LCl(NHC_6H_3\text{-}(3\text{-}Me)\text{-}4\text{-}N{=}N\text{-}C_6H_4\text{-}4'\text{-}Fc)]$ and $[Mo(NO)LCl(NHC_6H_3\text{-}(3\text{-}Me)\text{-}4\text{-}N{=}N\text{-}C_6H_4\text{-}4'\text{-}Fc)]$, gave respective intensities of 59, 53 and 123 times urea.

The emergence of optical data transmission and processing technologies has generated considerable interest in materials which exhibit non-liner optic (NLO) properties. The necessary, but not sufficient, criteria for a material to exhibit large second order optical non-linearity are that it should consist of polarisable dipolar molecules which crystallise in a non-centrosymmetric space group. Using such guidelines, a number of organic materials have been synthesised which exhibit substantial NLO properties.[1,2] The incorporation of d-block metals into molecular NLO materials is of interest because it offers the potential for combining magnetic and electron transfer properties with optic properties. However, reports of molecular compounds with substantial NLO properties which contain d-block elements are rare with the first report of such a material, *cis*-$[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}CH{=}CHC_6H_4\text{-}4\text{-}NO_2]$, appearing in 1987.[3] This material exhibited a relative harmonic intensity for Second Harmonic Generation (SHG) of 62 times that of the urea standard used at 1906 nm.

In our laboratory we have been studying the chemistry of complexes containing the redox active $\{M(NO)L\}^n$ [$L = HB(3,5\text{-}Me_2C_3N_2H)_3$; M = Mo and n = 2+ or 1+; M = W and n = 2+] cores. This work has indicated[4—10] that the 16-electron $\{M(NO)LClZ\}$ (Z = O or NH) moiety (**1**) can act as an electron withdrawing substituent while the 17-electron $\{M(NO)LClZ\}^-$ moiety can act as an electron donating substituent. Furthermore, the metal centres in these molecules constitute chiral centres so that, if resolved,[11,12] they must form materials which crystallise in non-centrosymmetric space groups.

These observations suggested that compounds containing the $\{M(NO)LCl\}$ moiety, as a substituent on a polarisable molecule which also contained an electron releasing group, might meet the molecular requirements for NLO properties. The isolation of resolved materials containing chiral metal centres might also meet the solid state structural requirements for NLO activity. In order to test these proposals we have investigated the properties of several complexes containing chiral $\{M(NO)LX\}$ (M = Mo, X = Cl or I and M = W, X = Cl) groups linked to chiral ligands. We have also synthesised a number of complexes in which this group is linked to polarisable molecules containing a ferrocenyl electron donor substituent, although these compounds have not been resolved.†

The NLO properties of these new materials, and some previously synthesised compounds,[11—13] were assessed qualitatively using the Kurtz powder test to determine the relative harmonic intensity for SHG relative to a urea standard at 1906 nm. The results obtained along with nitrosyl stretching

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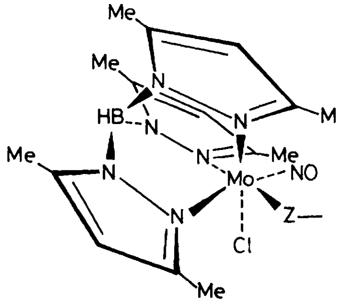
† All the new compounds have been fully characterised by i.r. mass and 270 MHz ^1H n.m.r. spectroscopy and by elemental analyses. Their electrochemical properties have also been determined and the reduction potentials for the $\{M(NO)LX\}$ moieties are in accord with the formulations given.

Table 1. Reduction potentials and relative harmonic intensities for second harmonic generation by [M(NO)LXY].

M	X[a]	Y[a]	ν_{NO}[b] /cm^{-1}		E_f[c]/V (SCE)	SHG[d] urea = 1
Mo	I	2-(−)-$OCH_2CH(Me)C_{10}H_6$-6-OMe	1670		−0.55	0.007
Mo	Cl	2-(−)-$OCH_2CH(Me)C_{10}H_6$-6-OMe	1670		−0.62	0.004
Mo	I	3-*O*-1,2:5,6-$(CMe_2)_2$-α-D-glucofuranose				0.245[e]
Mo	I	(1*S*,2*R*,5*S*)-(+)-mentholate				0.074[e]
W	Cl	(*R*)-(+)-NHCH(Me)Ph				n.d.[e,f]
Mo	(+)-NHCH(Me)Ph	OTPP[g]			−0.35	n.d.[f]
Mo	Cl	OTPP[g]			−0.35	1.93
Mo	I	OC_6H_4-F-Fc	1677	+0.57	−0.35	0.009
Mo	I	NHC_6H_4-4-Fc	1655	+0.59	−0.78	1.15
Mo	X = Y	OC_6H_4-4-Fc	1661	+0.53	−0.70	0.02
W	Cl	OC_6H_4-4-Fc	1640	+0.56	−0.86	n.d.[f]
W	Cl	NHC_6H_4-4-Fc	1625	+0.56	−1.23	n.d.[f]
W	X = Y	OC_6H_4-F-Fc	1620	+0.53	−1.21	n.d.[f]
Mo	I	OC_6H_4-4-N_2-C_6H_4-4′-Fc	1680	+0.60	−0.15	0.06
Mo	Cl	OC_6H_4-4-N_2-C_6H_4-4′-Fc	1682	+0.61	−0.21	0.02
Mo	Cl	NHC_6H_4-4-N_2-C_6H_4-4′-Fc	1660	+0.63	−0.57	59
Mo	I	NHC_6H_3-(3-Me)-4-N_2-C_6H_4-4′-Fc	1663	+0.60	−0.54	0.12
Mo	Cl	NHC_6H_3-(3-Me)-4-N_2-C_6H_4-4′-Fc	1663	+0.60	−0.58	123
W	Cl	NHC_6H_3-(3-Me)-4-N_2-C_6H_4-4′-Fc	1630	+0.62	−1.01	53

[a] Racemic complex [M(NO)LXY] unless otherwise stated. Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{–})$, $C_{10}H_6$ = naphthyl. [b] As KBr discs. [c] Quoted *vs.* standard calomel electrode (SCE) at 20 °C in CH_2Cl_2 containing 0.2 mol dm^{-3} Bu_4NBF_4. Ferrocene used as an internal standard typically gave $E_f = +0.56$ V with $\Delta E_P = 80$ mV. [d] Relative harmonic intensity for second harmonic generation measured with an Nd YAG laser at 1906 nm using a urea standard. [e] Measurements made on pure single enantiomers (refs. 11, 12). [f] n.d. = no SHG detected. [g] OTPP = 4-oxotetraphenylporphyrin, only the reduction potential associated with the {Mo(NO)} redox centre is given (ref. 13).



(**1**)

frequencies and electrochemical data for the new compounds, are summarised in Table 1.

The complexes {Mo(NO)LX[(−)-$OCH_2CH(Me)$-$C_{10}H_6OMe$]} (X = Cl or I; $C_{10}H_6$ = naphthyl) contain a chiral ligand but the diastereoisomers resulting from the presence of the second chiral centre at the metal were not separated. Both materials exhibited only very weak SHG. The resolved complexes [Mo(NO)LCl(3-*O*-1,2:5,6-di-isopropylidene-α-D-glucofuranoate)], {Mo(NO)LCl[(1*S*,2*R*,5*S*)-(+)-mentholate]} and {W(NO)LCl[(*R*)-(+)-methylbenzamide]} contain chiral ligands and chiral metal centres, and were tested in the form of single pure diastereoisomers.[11,12] Again these materials only exhibited weak if any SHG. The saturated nature of the parts of these ligands bound to the metal centre may account for these disappointing results in that the molecules are not highly polarisable in the region of the acceptor substituent. However, there may also be structural reasons for the low SHG intensities observed. A single crystal *X*-ray diffraction study of [Mo(NO)LCl(3-*O*-1,2:5,6-di-isopropylidene-α-D-glucofuranoate)] shows that this molecule crystallises in the monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit. The findings of the Joint Opto Electronic Research Scheme[14] indicate that, under these circumstances, it is possible for the molecular hyperpolarisability, β, of one molecule in the unit cell to be oriented so as to oppose that of the other molecule. This produces a pseudo-centrosymmetric situation with respect to the hyperpolarisability, resulting in low SHG intensities despite the presence of a chiral molecule. It is apparent from these results that merely placing the {M(NO)L} moiety in a chiral molecule is insufficient to produce a material exhibiting strong SHG.

Much larger SHG intensities were obtained with some of the compounds containing polarisable ligands attached to the electron withdrawing {M(NO)LClZ} (Z = O or NH) moiety. Thus [Mo(NO)LCl(NHC_6H_4-4-N=N-C_6H_4-4′-Fc)] {Fc = [$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{–})$]}, [W(NO)LCl($NHC_6H_3$-(3-Me)-4-N=N-$C_6H_4$-4′-Fc)] and {Mo(NO)LCl[$NHC_6H_3$-(3-Me)-4-N=N-$C_6H_4$-4′-Fc]}, in which the Fc substituent was present as an electron releasing group on the polarisable -NHC_6H_3-(3-R)-4-N=N-C_6H_4– (R = H or Me) bridge, gave respective SHG intensities of 59, 53 and 123 times urea. Since these complexes were not resolved these findings depend upon the compounds fortuitously crystallising in non-centrosymmetric space groups; possibly through each enantiomer forming discrete crystals which exclude the other. It is noteworthy that neither $NO_2C_6H_4$-4-N=N-C_6H_4-4′-Fc nor $NO_2C_6H_3$-(3-Me)-4-N=N-C_6H_4-4′-Fc, in which a nitro group replaces the metal mononitrosyl acceptor moiety, exhibit measurable SHG intensities. Furthermore, the compounds [Mo(NO)LX-(NHC_6H_4-4-$CHCHC_6H_4$-4′-Z)] (X = Cl or I; Z = OMe or NMe_2), in which the diaza link and the Fc terminus have been replaced respectively by *trans*-1,2-ethenyl and OMe or NMe_2, exhibit little or no SHG. It appears, therefore, that both the {M(NO)LCl} and the $FcC_6H_4N_2C_6H_4$– moieties are necessary for large SHG intensities to be obtained in this type of compound.

At this stage it is not clear to what extent the ability of the {M(NO)L} moiety to act as an electron acceptor is contributing to the observed SHG results. It may be that the primary function of this group arises from its steric bulk and that this induces a favourable packing of the dipolar polarisable $-C_6H_3$-(3-R)-4-N=N-C_6H_4-4′-Fc (R = H or Me) moiety. However, a comparison of the results for [Mo(NO)LCl(OC_6H_4-4-N=N-C_6H_4-4′-Fc)] and [Mo(NO)LCl(NHC_6H_4-4-N=N-C_6H_4-4′-Fc)], in which O is replaced by NH, and for {Mo(NO)LI[NHC_6H_3-(3-Me)-4-N=N-C_6H_4-4′-Fc]} and {Mo(NO)LCl[NHC_6H_3-(3-Me)-4-N=N-C_6H_4-4′-Fc]}, in which I is replaced by Cl, shows that large changes in SHG intensity may result from compositional changes which might be expected to have only minor structural consequences.[15—18] Thus it appears likely that the electronic properties of the {M(NO)LXY-} (X = I or Cl and Y = O or NH) moiety play some role in determining the NLO properties of the compound. Further synthetic, structural, and electro-optic studies of the new type of NLO material described here are under way to more fully establish the molecular basis for their observed SHG properties.

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