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REDOX-ACTIVE BIMETALLIC COMPLEXES AND REDOX-RESPONSIVE MACROCYCLES*

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Air- and moisture-stable diamagnetic alkoxides, amides and thiolates of the type [*ML**(NO)*XY*] (*M* = Mo or W; *L** = *tris*(3,5-dimethylpyrazolyl)-borate; *X* = halide, *Y* = *OR* (alkyl or aryl), NH*R* (alkyl or aryl), S*R* (alkyl or aryl), or *X* = *Y*) are redox-active, undergoing a one-electron reduction to paramagnetic species. Bimetallic complexes containing the redox-active moieties {*ML**(NO) *X*} can be constructed using bridging ligands such as $[OC_6H_4O]^{2-}$, $[NHC_6H_4CH_2C_6H_4NH]^{2-}$ or $[Fe(\eta\text{-}C_5H_3S)_2]^{2-}$. These species undergo two one-electron reductions and an analysis of the electrochemical data shows that the two redox centres may be strongly, intermediately or very weakly coupled. The redox-active unit {Mo*L**(NO) *X*} may be bound to the periphery of or directly into crown-ether rings, and addition of Na^+ to these redox-active guest macrocycles causes significant shifts in $E_{1/2}$-values.

Key Words : Bimetallic Complexes; Macrocycles; Redox-Activity

INTRODUCTION

PYRAZOLYLBORATES, as a class of ligands, were discovered more than twenty-five years ago by Trofimenko.[1] In developing the coordination chemistry of these ligands he noted the strong analogies between the behaviour of metal complexes containing *tris*-pyrazolylborato anions and those containing the η^5-cyclopentadienyl ligand. The analogy is based on the occupancy by the ligands of, formally, three coordination sites at the metal, and the existence of a single negative charge on each ligand.

RESULTS AND DISCUSSION

Of specific relevance to the work of our laboratories has been Trofimenko's synthesis of [Mo {HB ($Me_2pyz)_3$} (No) ($CO)_2$] (HB ($Me_2pyz)_3$ = *tris*-(3,5-dimethyl-pyrazolyl) borate henceforward referred to as *L**) from Mo $(CO)_6$ *via* a route[2] entirely analogous to that Piper and Wilkinson used to make [Mo (η-C_5H_5) (NO) $(CO)_2$].[3] Our interest had originally been in the chemistry of molybdenum complexes of hydrazido (1–) and (2–) groups, but containing an ancillary ligand which was more sterically demanding than C_5H_5.[4] We established that [Mo*L**(NO) I_2] reacted with hydra-

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zines in a manner similar to [Mo-(η-C_5H_5) (NO) I_2]$_2$, but obtained compounds that were structurally different.[5]

However, during our investigation of the general chemistry of [Mo*L**(NO) I_2], we established that the species was monomeric in solution[6] and in the solid state[7] and, therefore, that the metal was coordinatively unsaturated (16e^- species). The di-iodide, and its chloride and tungsten analogue [M*L**(NO)Cl_2] reacted readily with alcohols, primary and secondary aliphatic amines, arylamines, phenols and thiophenols of the type [*ML**(NO) *X*Q] and [*ML**(NO) Q_2] (*M* = Mo or W; *X* = F, Cl, Br, I; Q = O*R*, OAr, NH*R*, NR_2, NHAr, S*R*, SAr, NH*RR'*).[8]

In contrast to many other alkoxides and amido complexes, these species were monomeric, air- and moisture-stable. The fact that oligomerisation did not occur was clearly related to the steric bulk of the *L** ligand. The unexpected robustness towards oxygen and water must also be attributed, at least in part, to the strongly protective nature of *L**. At first sight, these alkoxides, amides, etc. appear to be coordinatively unsaturated, like their halide precursors. However, reperesentative and extensive crystallographic studies have revealed that there is significant multiplicity in the bond between Mo and Q (Table I). This can be explained in terms of p_π or d_π bonding from O, N or S *to* the metal atom which, in addition to causing bond shortening, also causes widening of the *M*–O–*R*, *M*–NH–*R* or *M*–S–*R* bond angles. By this donation of charge from the "hetero" ligand, the metal seeks to relieve its severe "electron deficiency", occasioned not just by the system's coordinative unsaturation, but also by the presence of the powerful π-acceptor NO and electronegative halogen ligands. The chemistry of these *tris* (pyrazolyl)-borato nitrosylspecies is therefore governed by a combination of steric and electronic effects.

TABLE I

Bond lengths and angles obtained from [Mo*L**(NO) *XY*]

X	*Y*	Mo-hetero-atom (Å)	Bond Angle (°)
OPr^i	OPr^i	1.90–1.91	133 (Mo–O–C)
I	$O(CH_2)_3$ Br	1.89	132 (Mo–O–C)
$NHBu^n$	$NHBu^n$	1.94–1.95	130 (Mo–N–C)
I	NHC_6H_4Me-*p*	1.99	142 (Mo–N–C)
I	SC_6H_{11}	2.31	112 (Mo–S–C)

On the basis of the above thoughts, it occurred to us that the mechanism of substitution of I^- in [Mo*L**(NO) I_2] by alkoxide; amide, etc. could be *via* a dissociative process. Normally, substitution reactions in transition metal nitrosyls occur *via* associative pathways. However, this could be ruled out in [*ML** (NO) X_2] on steric grounds. In order to establish if this was the case, we investigated[7] the electrochemical behaviour of [Mo*L** (NO) I_2] with a view to establishing the occurrence of dissociated I^- in THF or MeCN solution. Cyclic voltammetry revealed that

TABLE II

Paramagnetic species obtained from [MoL^*(NO) I_2]

Reagent	Solvent	$< g >$	Assignment
Electrolyte reduction (1F mol^{-1})	dry THF	2.027	[MoL^*(NO) I_2]$^-$
Water	dry THF	1.998	[MoL^*(NO) I(Solvent)$_n$]
[Bu^n_4N]I	dry THF	2.029	[MoL^*(NO) I_2]$^-$

[MoL^* (NO) I_2] underwent a remarkably facile reversible one-electron reduction ($E_{1/2}$ = + 0.2ι V in MeCN *vs* SCE). If traces of moisture were present, then dissociation of I^- occurred very readily, causing the formation of a paramagnetic species (Table II), and it was further established that [MoL^* (NO) I_2] could be reduced under extremely mild conditions, e.g. by addition of I^-. The solution behaviour of the di-iodide is shown in Scheme 1.

$$[MoL^* (NO)\ I_2] + e^- \rightleftharpoons [MoL^*(NO)\ I_2]^-$$
$$[MoL^* (NO)\ I_2]^- + \text{moisture} \rightarrow [MoL^*(NO)\ I\ (\text{solvent})_x] + I^-$$
$$[MoL^* (NO)\ I\ (\text{solvent})_x] \rightleftharpoons [MoL^*(NO)\ I\ (\text{solvent})_x]^+ + e^-$$

SCHEME 1

It has not been possible to isolate[7] salts of [MoL^* (NO) I_2]$^-$ although we did obtain the reduced μ-iodo species [MoL^*(NO) μ-$I)_2$ Li-$(OEt_2)_2$] on treatment of the di-iodide with Li (C_6H_4Me-*p*) in ether.

The observation of electrochemical activity in [MoL^* (NO) I_2] prompted a wider investigation of the cyclic voltammetric properties of all the complexes we had prepared.[9] It was shown that the $\{M\ (NO)\}^{3+}$ unit in these *tris* (pyrazolyl) borato systems readily undergoes a one-electron reduction to give species containing the paramagnetic $\{M\ (NO)\}^{2+}$ unit. We found that in the basic system [ML^* (NO) *X*Q], the value of $E_{1/2}$ was dependent on *M* (W complexes having $E_{1/2}$-values up to 500mV more cathodic than their Mo analogues), *X* (Cl or I) and the donor atom Q (O, N or S). Some representative data are given in Table III. Within the species [ML^*(NO) *X* (CO_6 H_4R)] and their NHC_6H_4R analogues (R = *m* or *p*-substituents; halide, NO_2, CN, CO_2Me, OMe; Me, etc.) the $E_{1/2}$ values were linearly dependent on the Hammet σ constants for the substituents, and this indicated therefore that the electrochemical behaviour was influenced primarily through the σ-bonding rather than the π-bonding system of the ligands.[9]

From the $E_{1/2}$ data it was clear that complexes containing phenolato ligands could be easily reduced. Indeed, treatment of [MoL^* (NO) Cl-(OC_6H_4OMe-*p*)] with cobaltocene afforded the paramagnetic salt [CO (η-$C_5H_5)_2$] [MoL^*(NO) Cl (OC_5H_4OMe-*p*)], whose esr spectral parameters (g = 1.968, < A > (Mo) = 52.0 gauss) indicated that the unpaired electron was mainly located on the metal.[10]

During our synthetic studies of the anilido and phenolato complexes we realised that it should be possible to synthesise bimetallic species *via* appropriate para-functionalisation of the aromatic ring in the metal anilide or phenolate. The

TABLE III

$E_{1/2}$ data obtained from [Mo*L**(NO) *XY*]

M	*X*	*Y*	Solvent	$E_{1/2}$(V)[a]
Mo	I	I	THF	+ 0.22
Mo	Cl	Cl	THF	− 0.09
W	Cl	Cl	THF	− 0.46
Mo	I	$OC_6H_4N_2Ph$-*p*	MeCN	− 0.14
Mo	I	OPh	MeCN	− 0.30
Mo	NC_4H_4	NC_4H_4	MeCN	− 0.46
Mo	I	$NHC_6H_4N_2Ph$	MeCN	− 0.57
Mo	SPh	SPh	MeCN	− 0.62
Mo	I	OEt	MeCN	− 0.65[b]
Mo	I	NHPh	MeCN	− 0.83
Mo	I	NHEt	MeCN	− 1.21[b]
Mo	NHPh	NHPh	MeCN	− 1.32
Mo	OEt	OEt	MeCN	− 1.33
Mo	NHEt	NHEt	MeCN	− 1.50[b]

[a] *vs* SCE at 21 ± 2°, by cyclic voltammetry using Pt wire and $[Bu^n_4N]PF_6$ as base electrolyte; reversible unless otherwise stated.

[b] Irreversible process; $E_{1/2} = E_p$ (red).

synthetic strategy was simple: for example (*a*) treat [Me*L** (NO) I ($NHC_6H_4NH_2$-*p*)] with [Mo*L** (NO) I_2] or (*b*) react two mole equivalents of [Mo*L**(NO) Cl_2] with one mole equivalent of *p*-HOC_6H_4OH, perhaps in the presence of NaOH as a deprotonating agent.[9,11] Both routes worked reasonably well and a range of bimetallic species were produced. Further, a few related *m*-substituted complexes could be prepared. In an extension of this idea it was possible to prepared a trimetallic derivative using ferrocene dithiol.[12]

$$2\,[ML^*(NO)\,Cl_2] + F\,(\eta\text{-}C_5H_5SH)_2 \rightarrow (Fe\,\{\eta\text{-}C_5H_3SML^*(NO)\,Cl\}_2]$$

and it was observed that [M*L**(NO) *X* (NH_6H_4I-*p*)] would undergo oxidative additions with [Pt (PPh_3)$_2$ (C_2H_4)] or [Pd (PPh_3)$_4$] giving [*ML**(NO) *X* {NHC_6H_4M' (PPh_3)$_2$ I}] (*M* = Mo, *X* = I, *M'* = Pd or Pt; *M* = W, *X* = Cl, *M'* = Pt).[13]

The formation of these bi-and tri-metallic species gave us an unrivalled opportunity to study the interaction of two redox centres close but not directly attached to each other, within a readily varied but stable coordination framework. Of futher interest and significance was the possibility of reducing these bimetallic species in a one-electron step, thereby affording species possibly analogous to the Creutz-Taube ion, $[\{Ru(NH_3)_5\}_2N_2C_4O_4]^{5+}$ ($N_2C_4H_4$ = pyrazine) and related compounds.[14] In other words, would the electron in the monoanionic bimetallics be localised on one redox-centre (valence-trapped), hopping between the two centres or completely delocalised ?

Some selected potential data for bimetallic species are given in Table IV. The results show behaviour of three kinds: (*a*) strong coupling between the redox centres

TABLE IV

$E_{1/2}$ data obtained from bimetallic complexes [M*L**(NO) *X*-*Q*-*XM'L**(NO) *Y*]

M	*M'*	*X*	*Y*	*Q*	$E_{1/2}^{1}$[a]	$E_{1/2}^{2}$[a]
Mo	Mo	Cl	Cl	OC_6H_4O	− 0.26	− 0.72
Mo	Mo	Cl	Cl	NHC_6H_4NH	− 0.61	− 1.46
Mo	Mo	I	I	NHC_6H_4NH	− 0.49	− 1.42[b]
W	W	Cl	Cl	NHC_6H_4NH	− 1.16	− 1.72[b]
Mo	W	I	Cl	NHC_6H_4NH	− 0.74	− 1.66[b]
Mo	W	I	Cl	OC_6H_4NH	− 0.28	− 1.60[b]
Mo	Mo	Cl	Cl	$OC_6H_4COC_6H_4O$	− 0.17	− 0.26
Mo	Mo	Cl	Cl	$OC_6H_4SC_6H_4O$	− 0.25	− 0.39
Mo	Mo	I	I	$NHC_6H_4OC_6H_4NH$	− 0.79	− 0.90
Mo	Mo	Cl	Cl	$OC_6H_4C_6H_4O$	− 0.19	− 0.28
Mo	Mo	I	I	$NHC_6H_4(CH_2)_2\ C_6H_4NH$	− 0.81	− 0.86

[a]*vs* SCE in MeCN, $[Bu_4^n N][PF_6]$ as base electrolyte with Pt wire; reversible unless otherwise stated.

[b]Irreversible process, $E_{1/2} = E_p$ (red).

in species having relatively compact bridging ligands, e.g. $OC_6H_4O^{2-}$, $NHC_6H_4S^{2-}$, etc.; (*b*) intermediate coupling when ligands are of the type $NHC_6H_4OC_6H_4NH^{2-}$ or $OC_6H_4COC_6H_4O^{2-}$; and (*c*) very weak, almost negligible coupling in systems containing, for example, $NHC_6H_4CH_2CH_2C_6H_4NH^{2-}$. The extent of coupling was estimated by the separation, ΔE, between the two reduction waves exhibited by all of the bimetallic complexes. Systems having ΔE values between 500 and 1000mV, fall into category (*a*), those wiht ΔE in the range 100-400mV in category (*b*), and those with ΔE 100mV in category (*c*). On the basis of simple theory,[15] those bimetallic species where there is no coupling between the redox centres, but reduction potentials should be identical, ΔE must be 36mV. It is not possible to determine such a small potential difference using cyclic volammetry; but using differential pulse techniques a single slightly broad wave is dectected whose peak width at half-height was ca. 45mV in the voltammograms of both [{Mo*L**(NO) I}$_2$ $NHC_6H_4(CH_2)_n\ C_4H_4NH$] ($n$ = 1 or 2).

The electrochemical behaviour of [Fe {η-$C_5H_4SMoL^*$(NO) Cl}$_2$] was most interesting [12] As expected, the species exhibited a reversible anodic cyclic wave corresponding to the oxidation of the ferrocene centre. The $E_{1/2}$-value for this wave was somc 200mV more anodic than that for [Fe (η-$C_5H_4SH)_2$], demonstrating the strong electron-withdrawing nature of the Mo centres. The species exhibited two reduction waves, ΔE = 20mV, suggesting that there was intermediate coupling between the two Mo centres through the ferrocene system. The ΔE-value is comparable to that observed for the bimetallic species [{Mo*L**(NO) Cl}$_2$ (m-SC_6H_4S)].

In our studies of the bimetallic systems described above we synthesised species such as [Mo*L**(NO) Cl (NHC_6H_4O) Mo*L**(NO) Cl] and [Mo*L**(NO) I (NHC_6H_4O)

WL*(NO) Cl].[11] In all of our work, we noted that when a second metal was present in systems of this type, the first reduction potential was significantly more anodic than that of the monometallic precursor. Representive data are given in Table V. This is, in our view,[9] a direct result of the strong electron withdrawing influence of the second redox centre, transmitted *via* the σ-bonding system. The second reduction potential is substantially more cathodic than the $E_{1/2}$-value for the reduction of the original monometallic. This indicates that the first reduced redox centre has a powerful electron releasing influence on the second redox centre thereby depressing the second $E_{1/2}$-value, although a cathodic shift would be expected on coulombic grounds.

TABLE V

Comparative $E_{1/2}$-data for mono- and bi-metallic species [MoL*(NO)X(YC$_6$H$_4$$Z$)]

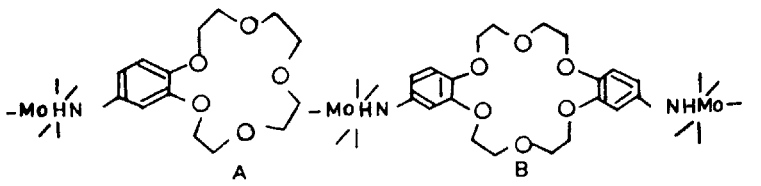
			Bimetallic[a]			Monometallic			
X	Y	Z	E_1	E_2	E	Z	E_m	E_m-E_1	E_m-E_2
Cl	NH	NHMoL*(NO) Cl	− 0.61	− 1.46	850	NH_2	− 1.05	4.0	410
Cl	O	OMoL*(NO) Cl	− 0.26	− 0.72	460	OMe	− 0.42	160	300
Cl	NH	OMoL*(NO) Cl	− 0.24			OMe	− 0.42		180
				− 1.24		OMe	− 0.96		280
I	NH	OC_6H_4NHMoL*(NO) I	− 0.79	− 0.90	112	(NH_2)[b]	− 0.86	70	40
I	NH	$(CH_2)_2$ C_6H_4NHMoL* (NO) I	− 0.81	− 0.86	46	(NH_2)[b]	− 0.85	40	10

[a] $E_{1/2}$ values (m.v.) obtained *vs* SCE in MeCN, $\Delta E = E_2 - E_1$, in mV.
[b] Monometallic species contains ligands $NHC_6H_4OC_6H_4NH_2$, or $NHC_6H_4(CH_2)_2$ $C_6H_4NH_2$.

In certain cases it has been possible to reduce the bimetallic species both chemically and electrochemically.[10] In general, compounds of the type [MoL*(NO) Cl (OAr)] are the best-behaved in terms of redox stability. Treatment of [{MoL* (NO) Cl}$_2$ OC_6H_4O] with cobaltocene afforded both [Co (η-C_5H_5)$_2$] [{MoL*(NO) Cl}$_2$ OC_6H_4O] and [Co (η-C_5H_5)$_2$]$_2$ [{MoL*(NO) Cl}$_2$ OC_6H_4O]. ESR spectral examination of the former, monoreduced species gives evidence for the localised nature of the electron, i.e. the species is probably a valence-trapped compound. Very preliminary and somewhat inclusive studies of the di-reduced species suggest that it is diamagnetic, but as it is extremely sensitive to oxidation and decomposition, this result must be treated with caution.

The way in which the two redox centres could interact with each other raised other interesting possibilities. Would it be possible, for example, to attach one or two redox centres to a crown ether, *via* anilido or phenolato linkages? If it was, would the presence of a guest cation in this redox-active host have an influence on the $E_{1/2}$-values? Could such a system form the basis of a redox sensor?

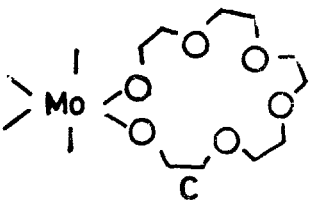
It was possible to prepare the species A and B shown below.[16] Both species exhibited a single redox wave, that of B being a two-electron process associated with two negligibly interacting redox sites in the molecule. Addition of Na^+ to solutions



A B

containing these complexes in anodic shift of $E_{1/2}$ by 60–70mV. Addition of Na^+ to solutions of the molybdenum complex derived from 3,4-dimethoxyaniline caused on significant change in $E_{1/2}$. There was no evidence for an increase in coupling between the two redox sites in B on addition of Na^+.

A more dramatic observation was made with species of the C. Here, a redox centre is directly fused into a polyether system *via* alkoxide linkages. These species,



C

like their more simple analogues $[MoL^*(NO)(OR)_2]$,[17] are air- and moisture-stable, and undergo a discrete one-electron reduction. On addition of one mole equivalent of Na^+, there is a substantial anodic shift of $E_{1/2}$-value, being 180mV ($n = 5$), 280mV ($n = 4$) and 320mV ($n = 3$). Although only preliminary studies have taken place, there is a predictable element of selectivity in complexation of other alkali metal cations by these redox-active crown ethers. The development of these systems is being extended to the formation of guests containing two redox centres, e.g. $[ML^*(NO)\text{-}\{O(CH_2CH_2O)_n CH_2CH_2O\}_2 ML^*(NO)]$, and the use of organic cations as guests. These prototype compounds suggest the promise of future reagents which may effect stereospecific electron transfer reactions on bound organic substrates.

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