Structure–Redox Potential Relations of Metal Complexes. Part 1. Organodiazenido-complexes of Molybdenum: Neighbouring-group Influence on Redox Potential

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Aryldiazenido-complexes, $[Mo(N_2C_6H_4X)(S_2CNMe_2)_3]$ (X = a range of *ortho-*, *meta-*, and *para*-substituents), undergo reversible one-electron oxidation to stable cations in non-aqueous electrolytes at platinum or vitreous carbon electrodes. E.s.r. spectra indicate that the highest occupied molecular orbital (h.o.m.o.) is essentially metal in character, and plots of $E_{\frac{1}{2}}$ against Hammett constants show that the influence of X on the h.o.m.o. *via* the –N=N– linkage is primarily through an inductive rather than a resonance mechanism.

EMPIRICAL observations relating the structure and electrochemical behaviour of metal complexes, mainly those having closed shells, have been discussed by several workers.[1-6] In this and subsequent papers[7] we shall consider the influence of co-ordinated ligands on the redox behaviour of metal complexes which may be relevant to nitrogen fixation,[8] and the transmission of electronic effects to the redox orbitals of these complexes.

The metal–ligand systems of interest to us in this context contain formal $M\leftarrow N_2$, $M–N_2R$, $M=N_2R_2$, $M–N_2R_3$, $M\leftarrow N_2R_4$, $M–NR_2$, $M=NR$, and $M\equiv N$ functions (M = metal; R = H, alkyl, or aryl). Structure–redox relations for series of complexes with co-ordinated dinitrogen ligands have been discussed elsewhere.[9,10] In this paper we have focused our attention on the N_2R group co-ordinated to molybdenum in a series of complexes of the type $[Mo(N_2R)(S_2CNMe_2)_3]$;[11] such complexes can be regarded as *derivatives* of the, as yet unknown, molybdenum(II) dinitrogen complex $[Mo(N_2)(S_2CNMe_2)_3]^-$.*

RESULTS AND DISCUSSION

The Primary Redox Process.—The complex $[Mo(N_2Ph)(S_2CNMe_2)_3]$ was examined by cyclic voltammetry at a platinum-wire electrode in dimethylformamide (dmf)–0.2 mol dm^{-3} $[NBu_4][BF_4]$. The primary oxidation process meets the criteria for a diffusion-controlled reversible one-electron oxidation (Table). In solvents such as methylene chloride or acetonitrile a further *irreversible* one-electron oxidation was observed at more positive potentials (Figure 1). The secondary oxidation remained irreversible, even at scan rates up to 30 V s^{-1}, indicating a fast following chemical reaction of the dication. These oxidation processes are summarised by the scheme (1). Cyclic voltammetry and double-potential-step experiments in the dmf electrolyte suggested that the monocation is stable for at least 30 s.

$$[Mo(N_2Ph)(S_2CNMe_2)_3] \underset{+\,1e}{\overset{-\,1e}{\rightleftharpoons}} \underset{\text{stable}}{[Mo(N_2Ph)(S_2CNMe_2)_3]^+} \xrightarrow{-\,1e} \underset{\text{unstable}}{[Mo(N_2Ph)(S_2CNMe_2)_3]^{2+}} \quad (1)$$

Controlled-potential electrolysis of a *ca.* 5×10^{-3} mol dm^{-3} solution of $[Mo(N_2Ph)(S_2CNMe_2)_3]$ in dmf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ was carried out at a potential 100 mV positive of the peak oxidation potential, E_p, of the complex. The anolyte changed in colour during the electrolysis from red-brown to purple and the current, j, decayed linearly with the charge passed, q F mol^{-1}. Figure 2 shows a plot of j against q; the intercept on the q axis corresponds to a 1 F mol^{-1} oxidation of the complex. Examination by cyclic voltammetry of the anolyte *before* and *after* the electro-oxidation showed that essentially quantitative conversion of the neutral complex into the *stable* cation, $[Mo(N_2Ph)(S_2CNMe_2)_3]^+$, had occurred. In contrast, *chemical* oxidation in various solvents with $Ag[BF_4]$, I_2, Br_2, Cl_2, or $FeCl_3$ failed to give the desired cation.

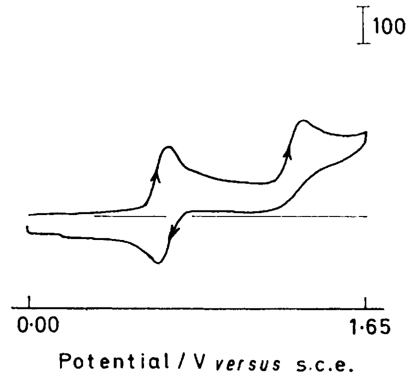

FIGURE 1 Typical cyclic voltammogram of an $[Mo(N_2R)(S_2CNMe_2)_3]$ complex (R = aryl) (in this case R = $C_6H_4NO_2$-*m*). Sweep rate 0.35 V s^{-1} at a platinum electrode in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–MeCN

At the end of a 1 F mol^{-1} *electro-oxidation*, e.s.r. spectra of the anolyte were recorded at –60 and –160 °C and these are shown in Figure 3. The spectra show that the unpaired electron is essentially located on the metal centre: molybdenum hyperfine lines observed, $\langle A_{Mo} \rangle$ =

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* Throughout, the N_2R group is named as if it were an anion in accord with present trends in I.U.P.A.C. nomenclature. This has consequences for the formal oxidation state of the metal. However, the formal oxidation state is clearly no indication of the actual charge on the metal, the bonding of the ligand, or of the electronic structure of the complexes and we have therefore refrained from defining it.

2.8 mT, are consistent with an interaction with ^{97}Mo and ^{95}Mo, spin $\frac{5}{2}$. In the solid state the *neutral* diamagnetic parent complex has a pentagonal-bipyramidal structure with the N_2Ph group occupying an axial position;[12] in the *cation* $g_x = g_y \neq g_z$ which suggests the retention of axial symmetry. The fast reversible electron transfer is also indicative of a similar geometry of the parent complex to the cation. The g values, $g_{\parallel} = 2.029$ and $g_m = 2.005$, are those expected for a 17-electron system and are typical of a d^9 configuration.[13] This is consistent with the lone pair from N^1 being involved in bonding to the cationic molybdenum centre as in the *parent* complex, which has the linear MN^{1}N^2 group with a short M–N^1 bond length of 1.718(4) Å.[12] From a simulated e.s.r. spectrum $g_{\perp}$ was estimated to be 2.001.

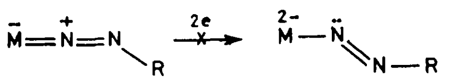
Electrochemical and electronic parameters of molybdenum diazenido- and related complexes

(*a*) Aryldiazenido-complexes

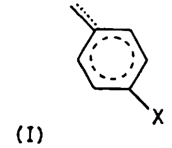
Substituent X	$E_{\frac{1}{2}}^{ox}$ [a] V *versus* s.c.e. ±0.01	$E_p^{ox} - E_p^{red}$ mV ±5	(j_p^{red}/j_p^{ox}) [b] ±0.2	λ nm ±2	ε $dm^3\ mol^{-1}\ cm^{-1}$ (±10)
H	0.52	68	1.0	411	9 310
o-Cl	0.59	59	1.0	414	10 950
o-NO_2	0.76	68	1.0	392, 497	7 410, 6 710
o-Me	0.49	68	1.0	416	8 330
o-OMe	0.47	64	1.0	420	11 170
m-Cl	0.61	75	1.0	413	14 020
m-NO_2	0.63	56	1.0	412	10 190
m-Me	0.49	62	1.0	412	8 690
m-OMe	0.55	64	1.0	418	8 720
p-F	0.50	65	1.0	410	8 810
p-Cl	0.58	74	1.0	413	11 800
p-NO_2	0.76	74	1.0	392, 510	*ca.* 5 000, 22 140
p-Me	0.41	66	1.0	414, 545	10 630, 1 510
p-OMe	0.41	84	1.0	416, 540	7 220, 1 990
(*b*) Other molybdenum complexes					
				E_p^{ox}	
$[Mo(N_2Me)(S_2CNMe_2)_3]$	0.24	65	1.0	0.27	
$[MoCl(S_2CNMe_2)_3]$	0.46	64	1.0	0.49	
$[Mo(NO)(S_2CNMe_2)_3]$	irreversible			1.20	
$[Mo(NS)(S_2CNMe_2)_3]$	irreversible			1.11	

[a] Estimated by cyclic voltammetry from $E_{\frac{1}{2}}^{ox} = (E_p^{ox} + E^{red})/2 \simeq E_p^{ox} - 29$ mV. The shape parameter $E_p^{ox} - E_{p/2}^{ox}$ lay within the range 60—80 mV for all the complexes. *iR* compensation was not employed. [b] Peak-current ratio at 0.3 V s^{-1}. j_p^{ox} is proportional to $V^{\frac{1}{2}}$ over the range 0.01—1.0 V s^{-1} for *ca.* 5×10^{-3} mol dm^{-3} solutions of the complex. j_p^{ox} was measured at concentrations (10^{-3} mol dm^{-3}), c, of 9.73, 5.01, 2.19, 1.07, and 0.53, for the X = H complex, at scan rates 0.01—1.0 V s^{-1}. The current function, $j_p^{ox}/cv^{\frac{1}{2}} = 0.123$ A dm^3 s$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$ mol^{-1}, was close to that observed for the ferrocene–ferrocinium couple at the same electrode (0.146 A dm^3 s$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$ mol^{-1}). The current function for the other complexes, measured at one concentration, lay within the range 0.10—0.15 A dm^3 s$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$ mol^{-1}.

We did not observe reduction of the neutral diazenido-complex at potentials up to —2.4 V *versus* a saturated calomel electrode (s.c.e.) in dmf, acetonitrile, or tetrahydrofuran. This shows that the lowest unoccupied molecular orbital (l.u.m.o.) is at least *ca.* 70 kcal higher in energy than the highest occupied molecular orbital (h.o.m.o.) of the closed-shell species.* Other molybdenum complexes having the linear M–N^1–N^2 function such as $[Mo^{II}Br(N_2Me)(dppe)_2]$ or $[Mo^{IV}Br(N_2H_2)(dppe)_2]Br$ are also electrochemically inactive toward reduction (dppe = $Ph_2PCH_2CH_2PPh_2$). The tendency for multiple M–N bond formation to give closed-shell 18-electron complexes with no low-lying unoccupied orbitals is clearly strong and the 'uncoupling' of d_{π}–p_{π} M–N^1 bonding by reduction is not a ready process, even in the higher-oxidation-state molybdenum complex:



Correlation of Redox Potential with Hammett Parameters.—Cyclic voltammograms of aryl-substituted complexes $[Mo(N_2C_6H_4X)(S_2CNMe_2)_3]$ were recorded under the same conditions as for the parent complex (X = H). Each complex showed a well defined *reversible* one-electron oxidation (Table). If we assume that changes in solvation-energy differences for the substituted series are negligible, then $E_{\frac{1}{2}}^{ox}$ can be regarded as a measure of the energy of the h.o.m.o. of each complex. The e.s.r. data for X = H have already suggested that this is primarily a metal-based orbital. The primary oxidation potentials show the expected trends: the more electron withdrawing the substituent X the more positive is the oxidation potential E_p^{ov} (or $E_{\frac{1}{2}}^{ox}$), *i.e.* the lower is the energy of the h.o.m.o. A more detailed pattern emerges from plots of the Hammett constants σ, σ$^+$, or σ$^-$ against $E_{\frac{1}{2}}^{ox}$ for the *meta*- and *para*-substituted series. Figure 4 shows that a good linear correlation for $E_{\frac{1}{2}}^{ox}$ and σ is observed whilst the correlations with σ$^+$ and σ$^-$ are significantly poorer (correlation coefficients, r = 0.99, 0.95, and 0.95 respectively). This suggests that there is restricted resonance stabilisation of the cation species by delocalisation of the charge from the aromatic ring into the diazenido-nitrogens, and the influence of the substituent X is essentially inductive. Support for this argument comes from the structure of the neutral complex with X = H. In the solid state the aryl ring is twisted out



(I)

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* Throughout this paper: 1 cal = 4.184 J.

of the N–N–C plane by 6° which suggests that π delocalisation extending from the ring to the metal [as shown in (I)] is hindered.[12,14]

The magnitude of the reaction constant ρ, which is obtained from the gradient in Figure 4 using the expression $\rho = -\Delta E/2.303RT\Delta\sigma$, has a value of 5.70.

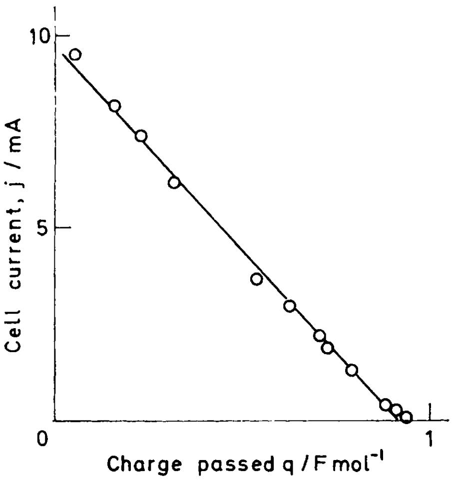


FIGURE 2 Controlled-potential electrolysis of $[Mo(N_2Ph)(S_2CNMe_2)_3]$ at a 1-cm^2 platinum-gauze electrode in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–dmf

A similar $E_{\frac{1}{2}}$ correlation for a series of complexes of the type $[Cr(CNC_6H_4X)_6]$ has been reported with a reaction constant $\rho = -0.085$ V which gives a conventional value of $\rho = 0.43$ per isocyanide ligand.[15] Although the same number of atoms separate the metal centre from the substituent X in both series, a rationale for the more effective transmission of the electronic influence of X in the diazenido-series would be unwise in view of the disparate nature of the two series of complexes.

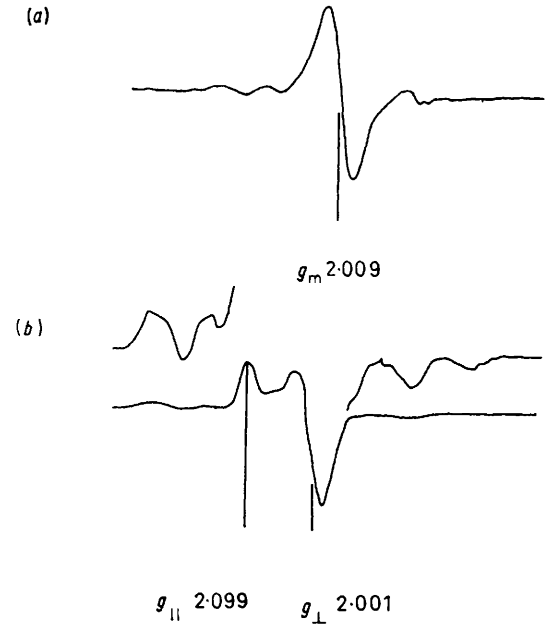


FIGURE 3 E.s.r. spectra of $[Mo(N_2Ph)(S_2CNMe_2)_3]^+$ in a dmf electrolyte: (a) solution spectrum at −60 °C; (b) frozen-solution spectrum at −160 °C. Spectra recorded after thawing and then refreezing are identical to (a) and (b) respectively

Included in the Table are the redox parameters of some other isostructural complexes of the type $[MoY(S_2CNMe_2)_3]$ (Y = a one- or three-electron donor ligand). The relative ease of oxidation of the methyldiazenido-complex is consistent with the stronger inductive influence of alkyl compared to aryl groups. Whereas the reversible oxidation of the chloro-complex is similar to the oxidation of the aryldiazenido-complexes, the three-electron donor-ligand complexes $[Mo(NS)(S_2CNMe_2)_3]$ and $[Mo(NO)(S_2CNMe_2)_3]$ are more difficult to oxidise and the oxidation process is irreversible in each case. The relative σ-donor and/or π-acceptor properties of NO and N_2Ph ligands have been the subject of some debate.[14,16] The M–N–S and M–N–O groups are linear in the dithiocarbamato-complexes and the relative, albeit irreversible, oxidation potential of the NO (or NS) complex compared with the N_2Ph complex (Table) suggests that N_2Ph is the better σ-donor and/or weaker π-acceptor ligand.

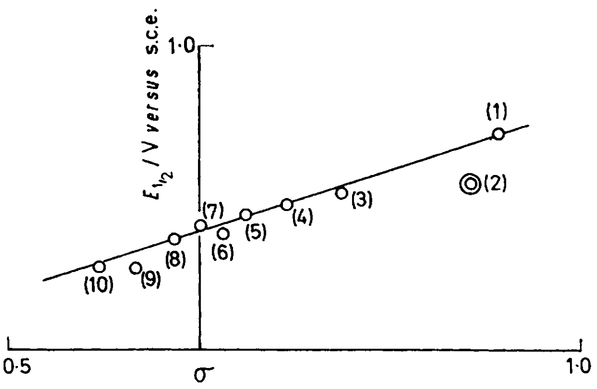
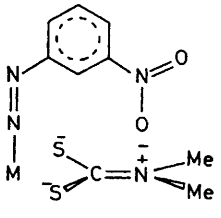


FIGURE 4 Hammett plot of $E_{\frac{1}{2}}^{ox}$ against σ for complexes of the type $[Mo(N_2C_6H_4X)(S_2CNMe_2)_3]$ where X = *p*-NO_2 (1), *m*-NO_2 (2), *m*-Cl (3), *p*-Cl (4), *m*-OMe (5), H (6), *p*-F (7), *m*-Me (8), *p*-Me (9), and *p*-OMe (10). The best straight line was calculated using a least-mean squares program

The data in the Table show that the lowest-energy transition in the visible–u.v. spectra of the aryldiazenido-complexes is a charge-transfer (c.t.) band, since $\varepsilon > 8\,000$ dm^3 mol^{-1} cm^{-1}. This is an intramolecular process, and the position of the band is independent of solvent (CH_2Cl_2, MeCN, dmf, or $PhNO_2$). In contrast to $E_{\frac{1}{2}}$, λ is not sensitive to the ring substituent X for all the complexes, which exhibit peak absorptions at *ca.* 415 nm. For some of the complexes an additional band is observed at lower energies which is generally much weaker, although for the $N_2C_6H_4NO_2$-*p* complex this band is the most intense. Whereas the molybdenum(IV) complex $[MoCl(S_2CNMe_2)_3]$ ($E_{\frac{1}{2}}^{ox}$ 0.46) is yellow-green and shows no c.t. band in the 300—600 nm region, the $[Mo(N_2R)(S_2CNMe_2)_3]$ complexes are intensely red-brown. This suggests that the c.t. transition is located within the

M–N=N–R chromophore (R = aryl). Clearly, either *both* the orbitals associated with the c.t. band are insensitive to a change in X, or a *compensating* effect is operative, *i.e.* both donor and acceptor orbitals are shifted in energy to a similar extent when X is changed. The former insensitivity would preclude the h.o.m.o. as the donor orbital and this appears unlikely.

Neighbouring-group Influence on Oxidation Potential.—The Hammett plot in Figure 4 shows that the *meta*-substituted diazenido-complex is anomalous: it is substantially easier to oxidise than would be expected from purely inductive considerations. *X*-Ray structure analysis has shown that the $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$ complex has the same basic geometry as $[Mo(N_2Ph)(S_2CNMe_2)_3]$ but with the aryl ring twisted with respect to the Mo–N–N axis such that an oxygen atom of the nitro-group is now within contact distance [3.259(22) Å] of the positive nitrogen atom of a dithiocarbamate ligand in the pentagonal plane (II).[12] If such an interaction persists in solution the basicity of the coordinated sulphur atoms should be increased, thereby raising the energy of the h.o.m.o., consistent with the observed redox potentials.



(II)

EXPERIMENTAL

Electrochemical measurements were made using a Hi-Tek Instruments Ltd. type DT2101 potentiostat and a Chemical Electronics Ltd. type RB1 waveform generator and electronic integrator, and were recorded on a Bryans type 2100A X-Y recorder or Hewlett-Packard type 1201A oscilloscope. The purification of solvents, the preparation of the supporting electrolyte, the electrochemical cells, and the methods of cyclic voltammetry and controlled-potential electrolyses have been described previously.[17] Electronic spectra were recorded on a Unicam SP 1800 u.v. spectrophotometer, the e.s.r. spectra on a Varian Associates Ltd. type E9 spectrometer. The preparation of the diazenido- and related complexes used have been described elsewhere.[11]

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