J. CHEM. SOC. DALTON TRANS. 1989 127

Synthesis, Electrochemistry, and Electron Spin Resonance Spectra of Some Seventeen-electron Complexes containing the $\{Mo(NO)\}^{2+}$ Core and the Molecular Structure of $[Mo(NO)\{HB(Me_2pz)_3\}(pyr)_2]$ †

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The reactions between $[Mo(NO)LI_2]$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate] and several neutral, unsaturated nitrogen-heterocyclic ligands have been investigated in order to establish the nature of the paramagnetic species produced. The complexes $[Mo(NO)L(A)_2]^+$ (A = imidazole, *N*-methylimidazole, pyrazole, 3,5-dimethylpyrazole, or pyridine) have been isolated as their $[BPh_4]^-$ salts from such reactions with an excess of A. These complexes are paramagnetic and exhibit room-temperature e.s.r. signals in which hyperfine coupling to molybdenum isotopes is apparent. In the cases where A = pyridine or *N*-methylimidazole the complexes exhibited a reversible one-electron reduction process in their cyclic voltammograms. However, where an exchangeable proton was bound to a nitrogen atom in A, irreversible reduction was observed. The neutral diamagnetic complex $[Mo(NO)L(pyr)_2]$ (pyr = pyrrol-1-yl) was also prepared, and was found to undergo a reversible one-electron reduction at more anodic potentials than its cationic counterparts. An *X*-ray diffraction study of $[Mo(NO)L(pyr)_2]$ revealed a linear nitrosyl ligand and an average Mo–N(pyrrolyl) distance of 2.040 Å.

The co-ordinatively unsaturated complex $[Mo(NO)LI_2]$ (**1**) [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate] reacts with alcohols, amines, or thiols to produce air-stable, diamagnetic, formally 16-electron alkoxy, amido, or thiolato derivatives respectively.[1–3] These compounds have the general formula $[Mo(NO)L(X)(Y)]$ (X and/or Y = halide, alkoxide, phenoxide, thiolate, or organoamide) and are redox active, undergoing one-electron reductions at potentials which depend upon the nature of X and Y.[4] The complex (**1**) itself is also redox active[5] and its one-electron reduction product has been isolated in the form of $[Mo(NO)L(\mu\text{-}I)_2Li(OEt_2)_2]$.[6] Surprisingly the reaction of (**1**) with Ag^+ in MeCN, thought to be a potential oxidant, led to the reduction of the molybdenum–nitrosyl core[7] and formation of the 17-electron complex $[Mo(NO)L(MeCN)_2]^+$, (**2**). The reaction between (**1**) and pyridine in tetrahydrofuran (thf) was also found[6] to produce 17-electron species, even in the absence of Ag^+. In order to establish the nature of the paramagnetic compound formed with pyridine, and further to explore the chemistry of the Mo(NO)L moiety bound to neutral rather than anionic ligands, the reactions of (**1**) with several unsaturated nitrogen heterocycles have been investigated. In order to provide an example of a compound containing an anionic unsaturated nitrogen heterocyclic ligand for comparison, a complex containing pyrrol-1-yl ligands was also prepared. The molecular structure of this species was determined by a single-crystal *X*-ray diffraction study.

Results and Discussion

Synthetic Studies.—When present in excess, the neutral heterocycles pyridine (py), imidazole (Him), pyrazole (Hpz), *N*-methylimidazole (mim), and 3,5-dimethylpyrazole (Me_2pz) all reacted smoothly over a period of hours with (**1**) in thf or dichloromethane solutions at reflux. The green 17-electron complexes $[Mo(NO)L(A)_2]^+$ [(**3**), A = py, Him, Hpz, mim, or Me_2pz] were formed and could be precipitated from ethanolic solution by the addition of $NaBPh_4$. These salts were all air stable and soluble in dichloromethane, acetonitrile, or thf, but insoluble in hexane or diethyl ether. In contrast to the behaviour of these heterocyclic substrates, which contained an unprotonated nitrogen atom, pyrrole failed to react with (**1**) under similar conditions. However, when the reaction was carried out using an excess of sodium pyrrolide the neutral green diamagnetic, formally 16-electron complex $[Mo(NO)L(pyr)_2]$ [(**4**), pyr = pyrrol-1-yl] was obtained in high yield.[8] This complex was also air stable and could be crystallised, whereas the $[BPh_4]^-$ salts of (**3**) were obtained as powders and were 1:1 electrolytes in acetonitrile solution.[9] The yields, elemental analyses, and solution conductivities of these new compounds are presented in Table 1.

Unlike (**1**), $[Mo(NO)LCl_2]$ failed to react with the heterocycles A under similar conditions. This observation implicated the iodide ligand as the reducing agent in the formation of (**3**), and in the formation of (**2**) from (**1**) in acetonitrile. The following reactions may be proposed to account for the formation of (**3**) from (**1**) and A.

$$\begin{gathered}
[Mo(NO)LI_2] + A \longrightarrow [Mo(NO)LI(A)]^+ + I^- \\
[Mo(NO)LI_2] + I^- \longrightarrow [Mo(NO)LI_2]^- + \tfrac{1}{2}I_2 \\
[Mo(NO)LI_2]^- + A \longrightarrow [Mo(NO)LI(A)] + I^- \\
[Mo(NO)LI(A)]^+ + I^- \longrightarrow [Mo(NO)LI(A)] + \tfrac{1}{2}I_2 \\
[Mo(NO)LI(A)] + A \longrightarrow [Mo(NO)L(A)_2]^+ + I^-
\end{gathered}$$

The reduction of (**1**) by I^- has been noted previously,[6] and I_2 was detected as a by-product from the reaction of (**1**) with pyridine. Although we have been unable to isolate the proposed intermediates $[Mo(NO)LI(A)]$, in these reactions, $[Mo(NO)LI(Me_2pz)]$ has been isolated from an unrelated reaction in which some degradation of L^- had occurred. This compound

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† [Hydrotris(3,5-dimethylpyrazol-1-yl)borato]nitrosylbis(pyrrol-1-yl)-molybdenum(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Yields, elemental analyses, and conductivities for the complexes

Complex	Yield (%)	Molar conductance[a]/ ohm^{-1} cm^2 mol^{-1}	Analyses[b] (%) C	H	N
(3) (A = py)	45	137	64.6 (65.4)	5.4 (5.8)	14.0 (14.0)
(3) (A = Him)	64	127	61.5 (61.5)	5.9 (5.7)	17.3 (17.5)
(3) (A = Hpz)	58	157	61.8 (61.8)	6.3 (5.6)	17.2 (17.6)
(3) (A = mim)	64	129	62.6 (62.4)	6.5 (6.1)	17.4 (17.1)
(3) (A = Me$_2$pz)	35	128	62.8 (63.1)	6.2 (6.0)	16.4 (16.5)
(4)	88		49.9 (49.8)	5.5 (5.4)	22.3 (22.7)

[a] In acetonitrile solution at room temperature with all complexes as their [BPh$_4$]$^-$ salts. Typical values for a 1:1 electrolyte in MeCN are 120—160 ohm^{-1} cm^2 mol^{-1}.[9] [b] Calculated values in parentheses, for [BPh$_4$]$^-$ salts in the case of (3).

Table 2. Magnetic and spectroscopic data

Compound	ν_{NO}[a]/cm^{-1}	$\lambda_{max.}$[b]/nm	ε[b]/dm^3 mol^{-1} cm^{-1}	g_{iso}[c]	10^4A_{iso}[c]/cm^{-1}	$g_{\parallel}$[c]	$g_{\perp}$[c]	$10^4A_{\parallel}$[d]/cm^{-1}	$10^4A_{\perp}$[d]/cm^{-1}
(3) (A = py)	1 630	630	94	1.977	43.8	1.921	2.004	67.2	32.7
		450	145						
(3) (A = Him)	1 632	615	80	1.976	45.4	1.924	2.003	71.6	37.1
		420	185						
(3) (A = mim)	1 612	610	88	1.975	45.2	1.922	2.002	71.7	37.1
		426	175						
(3) (A = Hpz)	1 633	620	95	1.975	45.5	1.920	2.001	68.0	33.6
		426	(sh)						
(3) (A = Me$_2$pz)	1 625	615		1.973	46.0	1.917	2.006	69.8	33.2
		436							
(4)	1 682	680	315						
		420	1 590						

[a] As KBr disc. [b] In dichloromethane at room temperature. [c] Estimated errors in g are ±0.001. [d] Estimated errors in A are $\pm0.5 \times 10^{-4}$ cm^{-1}.

was structurally characterised by an *X*-ray diffraction study[10] and proved to be a paramagnetic 17-electron complex. Its electrochemical properties indicated that the species [Mo(NO)LI(A)]$^+$ should be capable of oxidising I$^-$. On one occasion a complex thought to be [Mo(NO)LI(py)] was isolated from the reaction between (**1**) and sodium dihydronaphthylide in the presence of one molar equivalent of pyridine. However, this material was very reactive and defied characterisation. It appeared to undergo facile substitution or disproportionation reactions to produce, ultimately, [Mo(NO)L(py)$_2$]$^+$. This observation suggests that the disproportionation reactions may also play a role in the formation of (**3**).

Whatever the detailed mechanism of reaction, the results we have obtained strongly implicate I$^-$ as the reducing agent responsible for the formation of 17-electron complexes, such as (**3**), from the formally 16-electron complex (**1**). Furthermore it is apparent that the substitution of I$^-$ in (**1**) by amide ligands such as NHPh$^-$ or pyr$^-$ leads to air-stable, formally 16-electron complexes,[1,8,11] while substitution with neutral ligands such as py or MeCN leads to air-stable 17-electron products.[7,8]

Spectral Studies.—The infrared spectra of (**3**) and (**4**) contained ν_{BH} at 2 500 cm^{-1} along with other bands attributable to the presence of the ligand L. In addition the complexes (**3**) (A = Him, Hpz, or Me$_2$pz) exhibited ν_{NH} in the region 3 330—3 380 cm^{-1}. Values of ν_{NO} are presented in Table 2 and were some 50 cm^{-1} lower in the 17-electron complexes, (**3**), than in their formally 16-electron counterpart, (**4**), in accord with the increased electron density associated with the molybdenum centre in (**3**). The electronic spectra of the new compounds are also presented in Table 2 and were generally similar in appearance. The absorption coefficient of both observed bands in the derivatives (**3**) suggest that they are *d–d* in character. The band in the range 600—700 nm showed a bathochromic shift of *ca.* 50 nm in (**4**) as compared to (**3**).

The 100-MHz ^{1}H n.m.r. spectrum of (**4**) was consistent with the presence of a plane of symmetry in the molecule. The pyrazolyl methyl proton resonances appeared as four singlets with an area ratio of 3:6:6:3 at δ (relative to SiMe$_4$) = 1.44, 1.90, 2.41, and 2.49 p.p.m. The pyrazolyl CH protons appeared as two resonances of relative intensity 2:1 at δ = 5.76 and 5.82 p.p.m. Four resonances, each of relative area 2, were observed in the region δ = 5.92—8.02 p.p.m. and attributed to the pyrrol-1-yl protons. The mass spectrum of (**4**) was also recorded and exhibited a molecular-ion envelope based at *m/e* 557 (^{98}Mo, ^{11}B).

E.s.r. spectra from solutions in dichloromethane–toluene mixtures were obtained at both *X*- and *Q*-band frequencies at room temperature, and from frozen solutions at 77 K (*X*-band) and at 150 K (*Q*-band). The spin-Hamiltonian parameters were obtained by computer simulation of the spectra using methods reported previously.[12,13] The mean values of g and A (^{95,97}Mo) obtained at the two frequencies are given in Table 2. We have been unable to detect any ligand hyperfine splittings. The e.s.r. spectra, particularly those at *Q*-band frequencies, show that both g and A are axially symmetric. This is in marked contrast to [Mo(O)LX$_2$], where X = Cl, SEt, OMe, or NCS. In these latter compounds there is complete anisotropy in the g[14] and A tensors[15] as well as non-coincidence between two of the principal axes of these tensors.[15] The compounds, (**3**), are characterised by $g_{\parallel} \approx 1.92$, $A_{\parallel} \approx 70 \times 10^{-4}$ cm^{-1}, $g_{\perp} \approx 2.00$, and $A_{\perp} \approx 35 \times 10^{-4}$ cm^{-1}, with very little variation throughout the series of compounds. Similarly, the electronic absorption spectra show little variation, with two bands at approximately 630 and 430 nm which we attribute to *d–d* transitions.

The e.s.r. data, and the assignment of the electronic absorption spectra above, are compatible with a tetragonally distorted octahedral ligand field. The only way in which two *d–d* bands could arise in a trigonal ligand field is for the separation

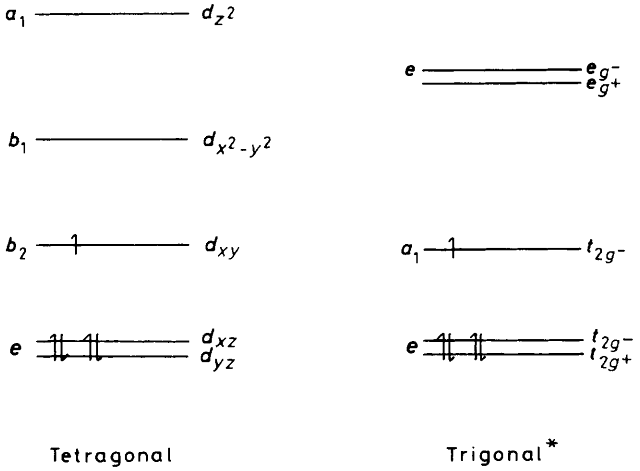


Figure 1. Orbital splitting diagrams for tetragonally distorted and trigonally[16] distorted octahedra (* orbitals defined as in ref. 16)

Table 3. Electrochemical data

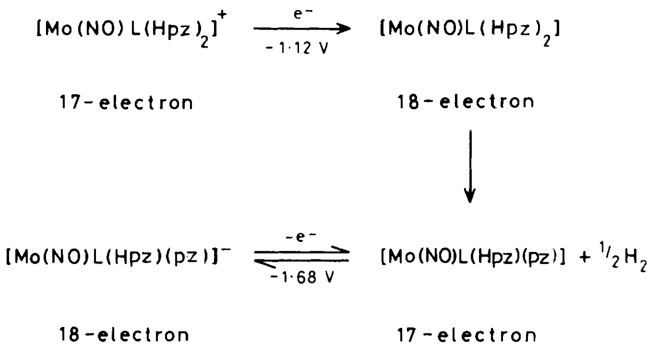
Compound	$E_{\frac{1}{2}}$ (V)[a]	ΔE_p (mV)[b]	n[c]
(3) (A = py)	-1.00	60	1.10
(3) (A = Him)	-1.54[d]		1.05
(3) (A = mim)	-1.56	70	0.94
(3) (A = Hpz)	-1.12[d]		
	-1.68	90	1.13
(3) (A = Me_2pz)	-1.40[d]		1.5
	-1.44[d,e]		1.04
	-1.86[e]	80	1.00
(4)	-0.46	80	0.95

[a] Obtained at a Pt bead electrode in acetonitrile solutions containing 0.1 mol dm^{-3} [NBu^n_4]BF_4 as supporting electrolyte with an s.c.e. reference electrode and at scan rate 0.3 V s^{-1}. The [BPh_4]$^-$ salts of (3) were generally used. [b] Separation between anodic and cathodic peak potentials. [c] Number of electrons estimated from the cathodic peak diffusion current as compared to [Mo(NO)LCl_2] and confirmed by coulometry for cases (3) (A = py) and (4). [d] Cathodic peak potential for an irreversible process exhibiting no anodic peak. [e] Data for the I$^-$ salt of (3); A = Me_2pz.

between the a_1 and $e(t_{2g\pm})$ orbitals (Figure 1) to be very much greater than the spin–orbit coupling constant for molybdenum.[16] However, the consequence of this would be that $g_{\parallel}$ is either 2.0023 or approximately 4 depending upon whether the odd electron is in the a_1 or $e(t_{2g\pm})$ orbitals respectively. This is not compatible with the experimental observations.

Electrochemical Studies.—Since the complexes [Mo(NO)L(X)(Y)] and [Mo(NO)L$(Y)_2$] (Y = arylamide, X = I or Cl) were known to undergo one-electron reduction reactions to produce 17-electron complexes, we had anticipated that the complexes (3) might exhibit the converse behaviour and be electrochemically oxidised to 16-electron complexes. However, in acetonitrile solution cyclic voltammetry (c.v.) revealed only irreversible multi-electron oxidations in the region 0.8—1.0 V. Similar behaviour was found in dichloromethane solution for (3) (A = Him). The reduction behaviour of (3) (A = py or mim) was better defined and both complexes underwent reversible one-electron reductions as shown in Table 3. These processes correspond with the formation of the 18-electron species [Mo(NO)L$(A)_2$] (A = py or mim) which are analogues of [Mo(NO)$(CO)_2$L], but occurred at rather more cathodic potentials than the 0.81 V reported[7] for the reduction of [Mo(NO)L$(MeCN)_2$]$^+$. This reflects the more basic character of the heterocyclic compounds as compared to MeCN.

In the complexes (3) (A = Him, Hpz, or Me_2pz) which contained ionisable protons in A, an irreversible reduction process was observed in the region -1.1 to -1.6 V. In the cases where A = Hpz or Me_2pz a second, reversible reduction was also observed at more cathodic potentials. This was not observed for (3) (A = Him) but may have been obscured by the rising background current near -2.0 V. If the c.v. of (3) (A = Hpz) was scanned from 0 to -2 V and held for 30 s before carrying out the anodic scan and a second cathodic scan, the irreversible cathodic peak at -1.12 V was all but eliminated in the second scan, while the peak at -1.68 V remained. This behaviour may be rationalised in terms of a reaction sequence involving reduction and hydrogen elimination to produce [Mo(NO)L(Hpz)(pz)] which then undergoes a reversible one-electron reduction as shown in the Scheme. The possibility also exists that prior dissociation of H$^+$ may occur to produce [Mo(NO)L(Hpz)(pz)], and that the wave at -1.12 V corresponds to the reduction of free protons. However, this would not be in accord with the observed difference in potentials between (3) (A = Hpz) and (3) (A = Me_2pz) for this process (Table 3). Attempts to prepare and isolate [Mo(NO)L(Him)(im)] to provide some chemical support for such a Scheme were not fully successful. Treatment of (3) (A = Him) with NaH did produce a red product which was highly reactive. Unfortunately attempts to isolate and purify this material have thus far only afforded the green starting complex.



Scheme.

The formally 16-electron complex (4) was also investigated by cyclic voltammetry and exhibited a multi-electron irreversible oxidation at 1.10 V, along with a reversible one-electron reduction at -0.46 V. This may be compared with the value of 1.32 V for the reduction of a related bis(amide) derivative,[11] [Mo(NO)L$(NHPh)_2$]. The pyrrol-1-yl ligand would thus appear to have an effect on the electronic properties of the {Mo(NO)L}$^{2+}$ unit which is intermediate between those of pyridine and anilide. In the former case reduction of the 16-electron molybdenum core is facilitated to such an extent that only the 17-electron species [Mo(NO)L$(py)_2$]$^+$ can be isolated, while in the latter case the 16-electron complex is isolated and may only be reduced at rather cathodic potentials. In the presence of the pyrrol-1-yl ligand it is the 16-electron {Mo(NO)L}$^{2+}$ complex which is isolated, but its reduction to a 17-electron complex is facilitated by 860 mV compared to that of the bis(anilide) derivative.

Structural Studies.—The molecular structure of [Mo(NO)L$(pyr)_2$], (4), is presented in Figure 2, which also shows the

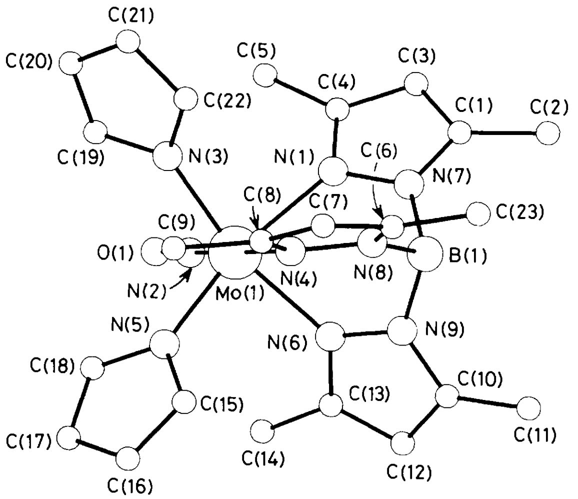


Figure 2. The molecular structure of [Mo(NO){HB(Me$_2$pz)$_3$}(pyr)$_2$] (**4**) showing the atom numbering scheme

atom labelling. Bond lengths and angles are presented in Table 4. The molybdenum atom is in a nearly octahedral co-ordination environment and the geometry of the complex is broadly similar to that found[11] in [Mo(NO)L(NHBu^n)$_2$] and (**2**), which also contain the MoN$_6$ co-ordination shell. The nitrosyl ligand is effectively linear, but with an N–O distance some 0.02 Å shorter than that of 1.213 Å found in (**2**). This is in accord with the lower oxidation state and value for ν_{NO} (1 652 cm^{-1}) found in (**2**). The N–O bond distance in (**4**) was also significantly shorter than those found in [Mo(NO)L(OR)$_2$], R = Et or Pr^i, and [Mo(NO)L(NHBu^n)$_2$],[11] and reflects a lower electron density on the {Mo(NO)}$^{3+}$ centre in (**4**).

The average Mo–N(pyrrolyl) distance in (**4**) is 2.040 Å and is shorter than the average Mo–N(acetonitrile) distance of 2.142 Å found in (**2**). However, it is longer than the average Mo–N-(amide) distances of 1.959 and 1.940 Å found in [Mo(NO)LI-(NHEt)] and [Mo(NO)L(NHBu^n)$_n$] respectively.[1,11] The two pyrrol-1-yl ligands are oriented to fit between the methyl substituents of the pyrazole rings in L and the steric interactions produced result in an average opening of the ligand 'bite' between N(4) and N(6) or N(1) and N(4) to 2.993 Å compared to 2.793 Å for N(1) to N(6) which straddle the NO ligand. Similar distortions have been observed in the structures of [Mo(NO)L(NHBu^n)$_2$], [Mo(NO)L(OEt)$_2$] and [Mo(NO)L-(OPr^i)$_2$],[1,11] and may be contrasted with the more symmetrical arrangement of the pyrazole ring planes found in (**1**).[1,7,11] There are no intermolecular contacts between non-hydrogen atoms of less than 3.4 Å.

Table 4. Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Co-ordination sphere and nitrosyl ligand			
Mo(1)–N(1)	2.206(2)	Mo(1)–N(2)	1.761(2)
Mo(1)–N(3)	2.047(2)	Mo(1)–N(4)	2.246(2)
Mo(1)–N(5)	2.034(2)	Mo(1)–N(6)	2.179(2)
N(2)–O(1)	1.190(3)		
N(1)–Mo(1)–N(2)	95.3(1)	N(2)–Mo(1)–N(3)	90.2(1)
N(2)–Mo(1)–N(5)	91.2(1)	N(2)–Mo(1)–N(6)	96.8(1)
N(1)–Mo(1)–N(3)	88.7(1)	N(3)–Mo(1)–N(5)	102.2(1)
N(5)–Mo(1)–N(6)	89.3(1)	N(1)–Mo(1)–N(6)	79.1(1)
N(1)–Mo(1)–N(4)	85.1(1)	N(4)–Mo(1)–N(6)	84.4(1)
N(3)–Mo(1)–N(4)	88.6(1)	N(4)–Mo(1)–N(5)	88.6(1)
Mo(1)–N(2)–O(1)	176.4(3)		
(*b*) Hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand			
N(1)–N(7)	1.367(3)	B(1)–N(7)	1.554(4)
N(4)–N(8)	1.377(3)	B(1)–N(8)	1.533(4)
N(6)–N(9)	1.370(4)	B(1)–N(9)	1.533(4)
min. C–N	1.335(4)	max. C–N	1.358(4)
mean C–N	1.342(4)	min. C–C(ring)	1.362(5)
max. C–C(ring)	1.387(4)	mean C–C(ring)	1.375(5)
min. C–C(subst.)	1.482(5)	max. C–C(subst.)	1.512(5)
mean C–C(subst.)	1.500(5)		
Mo(1)–N(1)–N(7)	120.1(2)	Mo(1)–N(4)–N(8)	118.2(2)
Mo(1)–N(6)–N(9)	119.3(2)	N(7)–B(1)–N(8)	108.9(2)
N(8)–B(1)–N(9)	109.7(2)	N(7)–B(1)–N(9)	107.3(3)
N(1)–N(7)–C(1)	110.0(2)	N(4)–N(8)–C(6)	109.4(2)
N(6)–N(9)–C(10)	109.6(3)	N(7)–N(1)–C(4)	106.5(2)
N(8)–N(4)–C(8)	106.4(2)	N(9)–N(6)–C(13)	107.0(3)
C(1)–C(3)–C(4)	106.6(3)	C(6)–C(7)–C(8)	106.5(3)
C(10)–C(12)–C(13)	107.3(3)	min. C(subst.)–C–C	127.2(3)
max. C(subst.)–C–C	130.1(3)	mean C(subst.)–C–C	128.8(3)
(*c*) Pyrrol-1-yl ligands			
min. C–N	1.369(4)	max. C–N	1.402(4)
mean C–N	1.386(4)	min. C–C	1.344(5)
max. C–C	1.417(6)	mean C–C	1.374(6)
C(19)–N(3)–C(22)	105.8(3)	C(15)–N(5)–C(18)	105.6(3)
min. C–C–C	106.8(3)	max. C–C–C	107.9(4)
mean C–C–C	107.2(3)	min. C–C–N	109.4(4)
max. C–C–N	110.7(3)	mean C–C–N	110.0(3)
min. Mo–N–C	125.8(2)	max. Mo–N–C	128.2(2)
mean Mo–N–C	127.0(2)		

Conclusions

The results described here have shown that the 16-electron complex (**1**) reacts with neutral, unsaturated nitrogen heterocycles to produce cationic 17-electron complexes by displacement of both iodide ligands. The iodide liberated during the reaction is able to effect the reduction of the molybdenum–nitrosyl core and this finding accounts for the formation of [Mo(NO)L-(MeCN)$_2$]$^+$ from (**1**) in MeCN, despite the presence of Ag$^+$. When the anionic, unsaturated nitrogen-heterocyclic ligand pyrrol-1-yl is present it is the 16-electron complex which is isolated. However, this material undergoes reduction to a 17-electron species at substantially more anodic potentials than its arylamide counterpart, [Mo(NO)L(NHPh)$_2$]. The absence of ligand hyperfine couplings in the e.s.r. spectra of the 17-electron compounds indicates that the unpaired electron is largely localised on the molybdenum atom in these species.

A theoretical model[17] of the related monomeric 16-electron complex [Mo(NO)(η^5-C$_5$H$_5$)(SPh)$_2$] provides a basis for understanding the differences in the relative stabilities of the 16- and 17-electron complexes described here. An *X*-ray diffraction study of this molecule indicates that the orientation of the phenyl rings attached to sulphur is such as to optimise the overlap between a filled *p* orbital on sulphur and the unfilled d_{xy} orbital on molybdenum. This results in destabilisation of the lowest unoccupied molecular orbital (l.u.m.o.), which is primarily Mo(d_{xy}) in character, and thus reduces the ability of this orbital to act as an acceptor. The failure of this complex to dimerise, despite the apparent lack of steric interactions to prevent this, could thus be explained in terms of the destabilisation of the l.u.m.o. by p_π–d_π donation from S to Mo.

In the complexes [Mo(NO)L(Y)$_2$] similar p_π–d_π charge donation has been proposed to account for the short Mo–N or

Mo–O bond lengths found in the alkoxide or amide derivatives.[1–3,11] This π-donation was also manifest in the reduced value of ν_{NO} in the alkoxide or amide derivatives, as compared to the halide complexes. The principal mode of π donation was proposed to involve the filled *p* orbital on oxygen or nitrogen which lay in the Mo–O–R, or Mo–NH–R, plane and the empty A_{1g} orbital (principally d_{z^2}) associated with the molybdenum centre.[1] In the case of the pyrrol-1-yl complex, (**4**), this orbital is unavailable for π bonding to molybdenum. Thus, although (**4**) is a 16-electron bis(amide) analogue of $[Mo(NO)L(NHBu^n)_2]$, its nitrosyl stretching frequency is some 50 cm^{-1} higher, its nitrosyl N–O bond distance 0.04 Å shorter, and its Mo–N(amide) distance 0.07 Å longer. These structural differences are associated with a substantially more anodic reduction potential and, by analogy with the Ashby and Enemark model,[17] this would seem to reflect the failure of the pyrrol-1-yl ligand to destabilise the l.u.m.o. by π donation to the extent found in alkoxide, thiolate, or amide analogues.

The situation becomes even more extreme in the case of less basic neutral ligands such as pyridine, imidazole, and pyrazole. Here, the absence of a formal charge on the ligand, combined with the reduced availability of a filled *p* orbital of the appropriate symmetry, results in a net stabilisation of the l.u.m.o. compared to the halide complexes $[Mo(NO)LX_2]$, X = I or Cl. As a consequence it is the 17-electron species containing an $\{Mo(NO)\}^{2+}$ core which is isolated as the stable product. Although *X*-ray quality crystals of (**3**) have not yet been obtained, the structural effects of the additional electron are evident in the molecular structure of (**2**). In this compound both the nitrosyl N–O and the Mo–N(MeCN) distances are elongated in comparison with their counterparts in (**4**) or $[Mo(NO)L(NHBu^n)_2]$.[6,11]

Experimental

The complex $[Mo(NO)LI_2]$ (**1**) was prepared by a reported method[18] and other reagents were used as supplied without further purification. Solvents were dried and redistilled under dinitrogen before use. Acetonitrile for electrochemical studies was redistilled from CaH_2. All reactions were carried out under a nitrogen atmosphere. Infrared, electronic, mass, and 100-MHz n.m.r. spectra were recorded respectively on PE 297, PE M330, Kratos MS 90, and PE R34 instruments. Electron spin resonance (e.s.r.) spectra were obtained on fluid and frozen solutions at *X*- and *Q*-band frequencies using a Varian E112 spectrometer. Cooling at *X*-band was effected using an Oxford Instruments ESR9 continuous flow cryostat with liquid nitrogen as the refrigerant. Electrochemical measurements were made using a Hitek galvanostat/potentiostat and waveform generator using platinum bead electrodes with a saturated calomel reference electrode. Elemental analyses were performed by the Microanalytical Laboratory, University of Birmingham.

Synthetic Studies.—$[Mo(NO)\{HB(Me_2pz)_3\}(py)_2][BPh_4]$. A solution of $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ (1.0 g, 1.5 mmol) and pyridine (7 cm^3, 88 mmol) in tetrahydrofuran (thf) was refluxed for 2 d. After this time the solvent volume was reduced to *ca.* 5 cm^3 by evaporation *in vacuo*. Hexane (*ca.* 5 cm^3) was added and a brown oil formed. After decantation of the supernatant liquor this was redissolved in dichloromethane and hexane added to precipitate a green powder. This was collected by filtration and redissolved in ethanol. An ethanolic solution of $NaBPh_4$ was then added to precipitate the product as a pale green powder (0.6 g, 0.67 mmol). This could be further purified by recrystallisation from dichloromethane–diethyl ether mixtures.

$[Mo(NO)\{HB(Me_2pz)_3\}(Him)_2][BPh_4]$. A solution of $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ (1.5 g, 2.2 mmol) and imidazole (0.3 g, 4.4 mmol) in thf (100 cm^3) was refluxed overnight, during which time the solution became green. The reaction mixture was then cooled and the solvent volume reduced to *ca.* 5 cm^3 by evaporation *in vacuo*. Addition of hexane (*ca.* 5 cm^3) precipitated a brown oil which was purified in a similar manner to $[Mo(NO)\{HB(Me_2pz)_3\}(py)_2]^+$ to give the product $[BPh_4]^-$ salt as a pale green powder (1.24 g, 1.4 mmol). Further purification could be effected by recrystallisation from thf–hexane mixtures.

$[Mo(NO)\{HB(Me_2pz)_3\}(Hpz)_2][BPh_4]$. This complex was prepared in an identical manner to its imidazole-containing analogue using pyrazole (0.6 g, 4.4 mmol) in place of imidazole. The product was obtained as a pale green powder (1.10 g, 1.25 mmol) and could be recrystallised from thf–diethyl ether mixtures.

$[Mo(NO)\{HB(Me_2pz)_3\}(mim)_2][BPh_4]$. A solution of $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ (1.5 g, 2.2 mmol) and *N*-methylimidazole (2 cm^3, 24 mmol) in thf (100 cm^3) was refluxed overnight, during which time the solution became green. The reaction mixture was cooled and the crude product was obtained as a pale green microcrystalline solid by filtration. This was further purified and converted to its $[BPh_4]^-$ salt in a similar way to that described for the imidazole analogue, to give a pale green product (1.28 g, 1.4 mmol) which could be recrystallised from dichloromethane–diethyl ether mixtures.

$[Mo(NO)\{HB(Me_2pz)_3\}(Me_2pz)_2][BPh_4]$. This complex was prepared in an identical manner to its *N*-methylimidazole analogue using $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ (1.3 g, 1.9 mmol) and 3,5-dimethylpyrazole (0.5 g, 5.2 mmol). The product obtained as the $[BPh_4]^-$ salt was a pale green powder (0.62 g, 0.66 mmol) which could be recrystallised from dichloromethane–hexane mixtures.

$[Mo(NO)\{HB(Me_2pz)_3\}(pyr)_2]$. Sodium metal (1.0 g, 44 mmol) was added to a solution of pyrrole (5 cm^3, 77 mmol) in thf (100 cm^3) and the mixture stirred at room temperature for 4 h. The solution was then filtered under nitrogen and $[Mo(NO)\{HB(Me_2pz)_3\}I_2]$ (1.0 g, 1.5 mmol) added to the filtrate. The mixture was then refluxed overnight during which time the solution became dark green. The reaction mixture was then cooled, filtered, and the filtrate evaporated *in vacuo* to a volume of *ca.* 5 cm^3. The addition of hexane caused the product to precipitate as a dark green solid which could be recrystallised from dichloromethane–hexane mixtures (0.72 g, 1.3 mmol).

Crystal-structure Determination of $[Mo(NO)\{HB(Me_2pz)_3\}(pyr)_2]$.—Crystals were obtained as dark green blocks by the slow evaporation of a solution in dichloromethane–hexane. Unit-cell data were originally investigated photographically, and intensity data and accurate cell dimensions subsequently measured with a diffractometer.

Crystal data. $C_{23}H_{30}BMoN_9O$, *M* = 555.3, triclinic, *a* = 8.751(3), *b* = 10.260(3), *c* = 15.152(4) Å, α = 92.96(2), β = 97.81(2), γ = 101.69(2)°, *U* = 1 315 Å^3, *Z* = 2, D_c = 1.41 g cm^{-3}, *F*(000) = 572, space group $P\bar{1}$ (no. 2, C_i^1), Mo-K_α radiation (λ = 0.7107 Å, μ = 4.6 cm^{-1}).

Intensity data. The crystal was mounted on an Enraf–Nonius CAD4 diffractometer at the Crystallography Unit, Universities of Aston and Birmingham. Accurate cell dimensions and intensity data were obtained by the standard methods described previously.[19] Within the range $2 < 2\theta < 50°$, 4 183 independent reflections having $I > 2.5\sigma(I)$ were observed. Two standard reflections, measured every 2 h, showed no variation with time. Data were corrected for Lorentz and polarisation factors but not for absorption.

Structure determination. The structure was solved by conventional Patterson–Fourier techniques, and refined, using scattering factors for neutral atoms,[20] by full-matrix least-squares methods. Anisotropic thermal parameters were intro-

Table 5. Final atomic positional parameters with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	−0.002 46(2)	0.210 81(2)	0.210 57(1)
N(1)	0.098 7(3)	0.043 7(2)	0.260 6(2)
N(2)	0.120 7(3)	0.244 5(3)	0.128 1(2)
N(3)	0.161 6(3)	0.337 9(2)	0.301 8(2)
N(4)	−0.156 8(3)	0.171 9(2)	0.317 4(2)
N(5)	−0.140 9(3)	0.333 8(2)	0.158 9(2)
N(6)	−0.168 7(3)	0.040 9(3)	0.136 1(2)
N(7)	0.002 2(3)	−0.068 3(2)	0.282 9(2)
N(8)	−0.200 4(3)	0.042 7(2)	0.339 7(2)
N(9)	−0.243 3(3)	−0.058 7(2)	0.181 8(2)
O(1)	0.206 0(4)	0.274 5(3)	0.074 2(2)
B(1)	−0.177 4(4)	−0.073 8(3)	0.278 9(3)
C(1)	0.086 3(4)	−0.160 6(3)	0.304 3(2)
C(2)	0.013 3(5)	−0.296 3(4)	0.329 1(3)
C(3)	0.239 6(4)	−0.108 0(3)	0.297 0(2)
C(4)	0.244 1(3)	0.019 6(3)	0.270 0(2)
C(5)	0.385 1(4)	0.121 1(4)	0.253 5(3)
C(6)	−0.264 2(4)	0.042 7(3)	0.415 8(2)
C(7)	−0.262 7(4)	0.172 8(3)	0.442 7(2)
C(8)	−0.196 6(3)	0.249 8(3)	0.380 2(2)
C(9)	−0.172 2(5)	0.398 3(3)	0.378 4(3)
C(10)	−0.361 2(4)	−0.141 0(3)	0.125 2(2)
C(11)	−0.464 8(5)	−0.259 8(4)	0.153 2(3)
C(12)	−0.359 2(4)	−0.092 5(4)	0.042 4(3)
C(13)	−0.238 8(4)	0.019 2(4)	0.051 1(2)
C(14)	−0.186 1(5)	0.107 6(5)	−0.020 1(2)
C(15)	−0.300 9(4)	0.321 8(3)	0.161 5(2)
C(16)	−0.358 3(4)	0.410 4(4)	0.111 5(3)
C(17)	−0.231 1(5)	0.483 9(4)	0.073 9(3)
C(18)	−0.100 8(4)	0.435 2(4)	0.103 9(2)
C(19)	0.280 9(4)	0.440 6(3)	0.281 8(3)
C(20)	0.374 9(5)	0.497 8(4)	0.357 6(4)
C(21)	0.317 4(5)	0.429 9(5)	0.427 9(3)
C(22)	0.187 7(4)	0.334 3(4)	0.392 7(2)
C(23)	−0.323 0(6)	−0.084 6(4)	0.458 2(3)

duced for all non-hydrogen atoms, and hydrogen atoms in calculated positions included in the structure-factor calculations, without refinement, and with two common, isotropic thermal parameters for the methyl and non-methyl hydrogen atoms.

The refinement converged to $R = 0.034$ and $R' = 0.039$, using a final weighting scheme with $w = 1/[\sigma^2(F) + 0.002(F)^2]$. Final parameter shifts were $<0.1\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of $|F_o|$ was satisfactory. A final difference map was featureless, apart from small peaks <0.5 e Å^{-3} close to the position of the molybdenum atom. The calculations were carried out using the Honeywell Multics system at Birmingham University Computer Centre and the CDC 7600 computer at the University of Manchester Regional Computer Centre, with the programs[21] SHELX 76 and PLUTO. Final positional parameters are listed in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We are indebted to the S.E.R.C. (B. D. N. and F. E. M.), the Royal Society (D. C.), and Mustansirigh University of Iraq (N. A-O.) for their support and to Mr. T. Green for technical assistance. We thank the staff at the University of Birmingham Computer Centre for their assistance.

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Received 25*th January* 1988; *Paper* 8/00374B