Syntheses and Electrochemistry of [Mo(NO){HB(mppz)$_3$}-Cl(ER)] (mppz = 3-*p*-methoxyphenylpyrazol-1-yl; E = O or NH; R = Ph or C_6H_4Me-2) and the Crystal Structures of [Mo(NO){HB(mppz)$_3$}Cl(OPh)] and [Mo(NO){HB(mppz)$_3$}Cl(NHC$_6$H$_4$Me-2)]†

Mercedes Cano,[a] **Jose V. Heras,**[a] **Angeles Monge,**[b] **Elena Pinilla,**[a,b] **Christopher J. Jones**[c] **and Jon A. McCleverty** *[,d]

[a] *Departamento de Quimica Inorganica, Facultad Quimicas, Universidad Complutense, Madrid 28040, Spain*

[b] *Insto. de Ciencias de los Materiales sede D.C.S.I.C., Serrano 113, Laboratorio de Diffracion de Rayos-X, Facultad Quimicas, Universidad Complutense, Madrid 28040, Spain*

[c] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

[d] *School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

The new complexes [Mo(NO){HB(mppz)$_3$}Cl(ER)] (mppz = 3-*p*-methoxyphenylpyrazol-1-yl; E = O or NH; R = Ph or C_6H_4Me-2) have been prepared and the structures when E = O, R = Ph and E = NH, R = C_6H_4Me-2 determined by X-ray crystallographic methods. The reduction potentials of the new complexes are similar to those of their counterparts containing the tris(3,5-dimethylpyrazolyl)hydroborate ligand. A comparison of the structures of 24 molybdenum mononitrosyl complexes containing tris(pyrazolyl)borate ligands variously substituted in the 3 position indicates that variations in the steric demands of the ligand set are primarily accommodated by changes in the angles made at the molybdenum atom by the coligands rather than those made by the tris(pyrazolyl)borate ligand.

Allosteric effects are important in many enzyme–substrate interactions. Reactions taking place at d-block metal centres within enzymes provide a particular example where the orientation imposed on an approaching substrate by the surrounding superstructure in which the metal ion is bound might affect the reactivity of the system. However, although the steric properties of bulky ligands have been exploited in the synthesis of models for a variety of metalloenzymes,[1–8] the role of interligand interactions in modifying the redox properties of metal centres is less well explored. The suggestion that interligand interactions which affect ligand orientation could thereby influence the redox properties of a metal centre is supported by the work of Ashby and Enemark[9] which showed that the orientation of the SPh ligands in [Mo(NO)(η^5-C_5H_5)(SPh)$_2$] affects the energy of the lowest unoccupied molecular orbital (LUMO) of the complex and thus its reduction potential. This is in accord with our previous finding[10] that the reduction potential of [Mo(NO){HB-(dmpz)$_3$}(3,4-$S_2C_6H_3$Me)] (dmpz = 3,5-dimethylpyrazol-1-yl) is shifted anodically compared to its non-chelated counterpart [Mo(NO){HB(dmpz)$_3$}(SPh)$_2$] in which the orientation of the S-aryl moiety is less constrained. Other evidence that interligand interactions can affect redox potentials is provided by the oxidation potential of Fe^{II} in [Fe{HB(ppz)$_3$}$_2$] (ppz = 3-phenylpyrazol-1-yl) which is some 600 mV more anodic than in [Fe{HB(pz)$_3$}$_2$].[11] Structural studies indicate that this is associated with the presence of unusually long Fe–N distances attributed to interligand interactions. In [Mo(NO)-{HB(mppz)$_3$}(CO)$_2$] (mppz = 3-*p*-methoxyphenylpyrazol-1-yl) structural studies indicate that the sterically bulky tripodal ligand induces some steric compression of the Mo(NO)(CO)$_2$ moiety and in [Mo(NO){HB(mppz)$_3$}Cl$_2$] the reduction potential is shifted cathodically by 60 mV[12] compared to that found for [Mo(NO){HB(dmpz)$_3$}Cl$_2$]. In order further to explore the possibility that intramolecular interligand interactions might affect the redox potentials of metal centres bound to tris(pyrazolyl)borate ligand systems, we have synthesised four derivatives of [Mo(NO){HB(mppz)$_3$}Cl$_2$] to examine their electrochemical properties. In two cases the solid-state structures of the compounds have been determined by single-crystal X-ray diffraction studies.

Experimental

All commercial reagents were used as supplied; [Mo(NO)-{HB(mppz)$_3$}Cl$_2$] was prepared according to previously described methods.[12] Toluene used as the reaction medium was dried and freed of oxygen before use by distillation from sodium–benzophenone under nitrogen. Reactions were carried out under nitrogen but purification procedures were carried out in air. Silica gel 60 (70–230 mesh) was used as the stationary phase for column chromatography. Elemental analyses were carried out by the Microanalytical Laboratory at the Complutense University of Madrid.

Infrared spectra were recorded using KBr pellets and a Phillips 9U 9712 spectrometer, 300 MHz ^{1}H NMR spectra from solutions in CDCl$_3$ using a Varian XL300 spectrometer and mass spectra using a Kratos MS80RF spectrometer. Cyclic voltammetric measurements were made using a platinum-bead electrode with a PAR 174A polarograph and 10^{-3} mol dm^{-3} solutions of complex in CH$_2$Cl$_2$ containing 0.2 mol dm^{-3} [NBu$_4$][BF$_4$] as base electrolyte. Values are referred to the saturated calomel electrode (SCE) but ferrocene was used as an internal standard.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Synthetic Studies.—$[Mo(NO)\{HB(mppz)_3\}Cl(OPh)]$. The complex $[Mo(NO)\{HB(mppz)_3\}Cl_2]$ (122 mg, 0.168 mmol) and phenol (16 mg, 0.17 mmol) were added to dry toluene (20 cm^3). The mixture was heated under reflux for 20 h after which time it was cooled, filtered and the solvent removed from the filtrate by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane as the eluent. The major purple band contained the product which was further purified by recrystallisation from diethyl ether–hexane (1:1) (yield 85 mg, 65%) (Found: C, 53.0; H, 4.1; N, 12.0. $C_{36}H_{33}BClMoN_7O_5 \cdot 0.5CH_2Cl_2$ requires C, 52.9; H, 4.1; N, 11.8%); ν_{max} 2450 (BH) and 1665 cm^{-1} (NO); δ_H($CDCl_3$, 300 MHz) 6.26, 6.37, 6.41, 7.76, 7.88, 7.94 [1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2, $C_3N_2H_2$], 6.28, 6.42, 6.54, 6.82, 7.30, 7.41 [2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9, C_6H_4OMe], 6.95, 7.00, 7.10 [1 H, t, *J*(HH) 8; 2 H, d, *J*(HH) 8; 2 H, t, *J*(HH) 8 Hz, OC_6H_5], 3.49, 3.55, 3.80 (3 H, s; 3 H, s; 3 H, s, OCH_3). E_f(CH_2Cl_2, *vs.* SCE) = −0.39 V, ΔE_p = 127 mV, $E_f\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = +0.58 V, $\Delta E_p\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = 98 mV.

$[Mo(NO)\{HB(mppz)_3\}Cl(OC_6H_4Me\text{-}2)]$. This compound was prepared in a similar manner to $[Mo(NO)\{HB(mppz)_3\}Cl(OPh)]$ using $[Mo(NO)\{HB(mppz)_3\}Cl_2]$ (56 mg, 0.077 mmol) and 2-methylphenol (8.3 mg, 0.077 mmol). The major red-brown band on the chromatography column contained the product which was further purified by recrystallisation from diethyl ether–hexane (1:1) (yield 22.7 mg, 37%) (Found: C, 55.1; H, 4.2; N, 12.0. $C_{37}H_{36}BClMoN_7O_5$ requires C, 55.5; H, 4.3; N, 12.2%); ν_{max} 2495 (BH) and 1680 cm^{-1} (NO); δ_H($CDCl_3$, 300 MHz) 6.29, 6.31, 6.39, 7.77, 7.86, 7.94 [1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2, $C_3N_2H_2$], 6.28, 6.41, 6.86, 6.95, 7.31, 7.45 [2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9 Hz, C_6H_4OMe], 6.82–7.03 (4 H, m, OC_6H_4Me), 3.52, 3.57, 3.81 (3 H, s; 3 H, s; 3 H, s, OCH_3) and 1.73 (3 H, s, $OC_6H_4CH_3$). E_f(CH_2Cl_2, *vs.* SCE) = −0.43 V, ΔE_p = 110 mV, $E_f\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = +0.56 V, $\Delta E_p\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = 115 mV.

$[Mo(NO)\{HB(mppz)_3\}Cl(NHPh)]$. The complex $[Mo(NO)\{HB(mppz)_3\}Cl_2]$ (80 mg, 0.109 mmol) and aniline (35 mg, 0.329 mmol) were added to dry dichloromethane (20 cm^3) and the mixture stirred at room temperature for 36 h. After this time diethyl ether (20 cm^3) was added to precipitate the arylammonium chloride formed. This was removed by filtration through a bed of Kieselguhr and the solvent removed from the filtrate by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel using dichloromethane as the eluent. The major brown band contained the product which was further purified by recrystallisation from dichloromethane–hexane (1:1) (yield 45.6 mg, 53%) (Found: C, 54.8; H, 4.2; N, 14.0. $C_{36}H_{34}BClMoN_8O_4$ requires C, 55.0; H, 4.3; N, 14.2%); ν_{max} 2450 (BH) and 1650 cm^{-1} (NO); δ_H($CDCl_3$, 300 MHz) 6.19, 6.31, 6.33, 7.69, 7.82, 7.85 [1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2, $C_3N_2H_2$], 6.63, 6.72, 6.88, 7.24, 7.40, 7.47 [2 H, d, *J*(HH) 8; 2 H, d, *J*(HH) 8; 2 H, d, *J*(HH) 8; 2 H, d, *J*(HH) 8; 2 H, d, *J*(HH) 8; 2 H, d, *J*(HH) 8 Hz, C_6H_4OMe], 6.82–7.00 (5 H, m, NHC_6H_5), 3.74, 3.80, 3.82 (3 H, s; 3 H, s; 3 H, s, OCH_3). E_f(CH_2Cl_2, *vs.* SCE) = −0.85 V, ΔE_p = 105 mV, $E_f\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = +0.56 V, $\Delta E_p\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = 110 mV.

$[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$. This compound was prepared in a similar manner to $[Mo(NO)\{HB(mppz)_3\}Cl(NHPh)]$ using $[Mo(NO)\{HB(mppz)_3\}Cl_2]$ (75 mg, 0.103 mmol) and 2-methylaniline (33.3 mg, 0.309 mmol) with a reaction time of 30 h. The major brown band from the chromatography column contained the product (yield 32.9 mg, 40%) (Found: C, 55.3; H, 4.2; N, 14.1. $C_{37}H_{37}BClMoN_8O_4$ requires C, 55.6; H, 4.5; N, 14.0%); ν_{max} 2450 (BH) and 1655 cm^{-1} (NO); δ_H($CDCl_3$, 300 MHz) 6.28, 6.34, 6.40, 7.83 [1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 1 H, d, *J*(HH) 2; 3 H, m, $C_3N_2H_2$], 6.24, 6.54, 6.96, 6.96, 7.54, 7.88 [2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9; 2 H, d, *J*(HH) 9, C_6H_4OMe], 6.82–7.03 (4 H, m, NHC_6H_4Me), 3.52, 3.53, 3.86 (3 H, s; 3 H, s; 3 H, s, OCH_3) and 1.40 (3 H, s, $OC_6H_4CH_3$). E_f(CH_2Cl_2, *vs.* SCE) = −0.89 V, ΔE_p = 105 mV, $E_f\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = +0.56 V, $\Delta E_p\{[Fe(C_5H_5)_2]^+–[Fe(C_5H_5)_2]\}$ = 120 mV.

Structural Studies.—$[Mo(NO)\{HB(mppz)_3\}Cl(OPh)]$. Diffraction data were measured on an Enraf–Nonius CAD4 diffractometer operating in the ω–2θ mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) up to θ = 25° from a purple crystal of dimensions 0.3 × 0.3 × 0.2 mm coated with epoxy resin. Three standard reflections were monitored hourly to check the stability of the system. 6980 Unique reflections were scanned, *hkl* (−15, 0, 0) to (15, 24, 18), and 4662 [$I \geq 2\sigma(I)$] were considered observed and used in the analysis.

Crystal data. $C_{36}H_{33}BClMoN_7O_5 \cdot 0.5CH_2Cl_2$, M_r = 828.37, monoclinic, space group $P2_1/n$, a = 12.975(3), b = 20.266(5), c = 15.180(3) Å, β = 96.73(2)°, U = 3964(1) Å^3, $F(000)$ = 1692, μ = 5.04 cm^{-1}, Z = 4, D_c = 1.38 g cm^{-3}.

The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo were taken from ref. 13. The structure was solved by MULTAN and Fourier methods using the X-RAY 80 system.[14] An empirical absorption correction[15] was applied at the end of the isotropic refinement. The maximum and minimum absorption factors were 1.36 and 0.61 respectively. A slight disorder was found in the carbon and chlorine atoms of the dichloromethane molecule and consequently these were refined isotropically with a 0.5 population factor. Final mixed refinement employed fixed isotropic thermal parameters and coordinates for hydrogen atoms. In order to prevent bias on F *versus* F_o or (sin θ)/λ, the last steps of the refinement were calculated by PESOS[16] with weights $w = w_1w_2$ where $w_1 = 1/(a + b|F_o|)^2$ and $w_2 = 1/[c + d(\sin\theta)/\lambda]$ and the coefficients are shown in Table 1. Refinement led to R = 0.062 and R' = 0.072. Average shift-to-error ratios were < 0.24:1. Final difference synthesis showed no significant electron density. Final atomic parameters are presented in Table 2 and ORTEP[17] was used to generate the structure shown in Fig. 1.

$[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$. Diffraction data were measured as above from a brown crystal of dimensions 0.3 × 0.1 × 0.2 mm coated with epoxy resin. There was ≤ 15% decay in the intensity of three standard reflections monitored hourly to check the stability of the system. 6351 Unique reflections were scanned, *hkl* (−15, −15, 0) to (15, 15, 15), and 4363 [$I \geq 2\sigma(I)$] were considered observed and used in the analysis.

Crystal data. Crystals of $C_{37}H_{37}BClMoN_8O_4$, M_r = 799.85, are triclinic, space group $P\bar{1}$, a = 12.933(3), b = 13.172(3), c = 13.265(4) Å, α = 75.08(3), β = 97.90(3), γ = 60.99(3)°, U = 1815(1) Å^3, $F(000)$ = 820, μ = 4.75 cm^{-1}, Z = 2, D_c = 1.46 g cm^{-3}.

The cell dimensions were refined and intensities corrected as

Table 1 Coefficients for the weighting scheme in $[Mo(NO)\{HB(mppz)_3\}Cl(OPh)] \cdot 0.5CH_2Cl_2$

	a	*b*	*c*	*d*
$\lvert F_o \rvert < 22$	4.65	−0.14		
$22 < \lvert F_o \rvert$	0.51	0.05		
(sin θ)/λ < 0.36 Å^{-1}			6.06	−15.55
0.36 Å^{-1} < (sin θ)/λ			0.52	0.42

Table 2 Fractional atomic coordinates for $[Mo(NO)\{HB(mppz)_3\}Cl(OPh)]\cdot 0.5CH_2Cl_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Mo	0.325 72(3)	0.140 66(2)	0.110 40(3)
Cl	0.272 4(1)	0.033 40(7)	0.144 94(9)
B	0.576 2(5)	0.152 7(3)	0.103 9(4)
N(1)	0.241 4(4)	0.174 9(3)	0.181 0(3)
N(11)	0.457 4(4)	0.119 5(2)	0.216 9(3)
N(12)	0.555 9(4)	0.120 9(4)	0.191 6(3)
N(21)	0.421 1(4)	0.227 2(2)	0.106 0(3)
N(22)	0.525 5(4)	0.221 1(3)	0.101 5(3)
N(31)	0.425 3(4)	0.100 8(2)	0.010 1(3)
N(32)	0.529 6(4)	0.111 4(3)	0.025 7(3)
O(1)	0.178 3(4)	0.197 5(3)	0.223 3(3)
O(2)	0.235 6(3)	0.152 9(2)	0.003 4(3)
O(11)	0.144 6(4)	0.038 4(3)	0.505 8(4)
O(21)	−0.001 1(4)	0.373 0(3)	0.164 9(3)
O(31)	0.030 3(4)	0.019 7(3)	−0.277 9(3)
C(1)	0.133 1(5)	0.165 3(3)	−0.019 3(4)
C(2)	0.058 5(5)	0.144 9(4)	0.032 6(5)
C(3)	−0.045 7(6)	0.159 0(5)	0.006 7(7)
C(4)	−0.074 8(7)	0.191 8(5)	−0.069 6(7)
C(5)	−0.000 6(7)	0.212 5(5)	−0.123 4(6)
C(6)	0.103 6(6)	0.198 1(4)	−0.098 4(4)
C(11)	0.623 2(5)	0.094 2(4)	0.254 9(5)
C(12)	0.569 5(6)	0.074 8(5)	0.322 2(5)
C(13)	0.466 6(5)	0.092 1(3)	0.297 5(4)
C(14)	0.380 3(5)	0.079 1(3)	0.350 5(4)
C(15)	0.371 4(6)	0.016 8(4)	0.383 7(4)
C(16)	0.293 1(6)	0.000 8(4)	0.437 2(5)
C(17)	0.224 3(5)	0.049 3(4)	0.454 6(4)
C(18)	0.233 6(6)	0.112 0(4)	0.423 9(4)
C(19)	0.311 6(5)	0.127 1(3)	0.372 5(4)
C(110)	0.130 0(7)	−0.027 8(5)	0.534 3(6)
C(21)	0.569 3(5)	0.279 6(4)	0.115 1(5)
C(22)	0.494 7(6)	0.325 5(4)	0.127 3(5)
C(23)	0.402 2(5)	0.291 3(3)	0.121 3(4)
C(24)	0.296 9(5)	0.316 1(3)	0.129 2(4)
C(25)	0.274 0(6)	0.347 6(3)	0.205 9(4)
C(26)	0.175 5(6)	0.365 4(4)	0.215 5(4)
C(27)	0.095 9(5)	0.353 9(3)	0.148 1(4)
C(28)	0.117 8(5)	0.324 7(3)	0.070 0(4)
C(29)	0.217 6(5)	0.306 5(3)	0.060 8(4)
C(210)	−0.083 4(6)	0.366 5(6)	0.094 3(5)
C(31)	0.576 8(5)	0.086 7(3)	−0.040 9(4)
C(32)	0.504 3(5)	0.060 0(4)	−0.101 2(4)
C(33)	0.409 4(5)	0.069 2(3)	−0.069 0(4)
C(34)	0.307 9(5)	0.052 9(3)	−0.118 5(4)
C(35)	0.227 8(5)	0.020 7(3)	−0.083 5(4)
C(36)	0.134 8(5)	0.008 3(3)	−0.134 8(4)
C(37)	0.119 8(5)	0.027 3(3)	−0.222 3(4)
C(38)	0.200 2(5)	0.058 1(4)	−0.259 2(4)
C(39)	0.292 5(5)	0.070 6(4)	−0.207 3(4)
C(310)	−0.058 9(7)	−0.004 5(5)	−0.240 7(6)
C(7)	0.946 7(56)	0.250 6(31)	0.311 9(41)
Cl(2)	0.955 1(17)	0.208 4(12)	0.386 5(15)
Cl(3)	0.844 6(16)	0.222 6(11)	0.243 4(14)

Table 3 Fractional atomic coordinates for $[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	0.358 24(6)	0.340 34(6)	0.726 99(5)
Cl	0.162 3(2)	0.435 3(2)	0.758 4(2)
B	0.406 4(9)	0.148 3(9)	0.597 1(7)
N(1)	0.439 6(6)	0.306 3(6)	0.860 6(5)
N(2)	0.350 1(6)	0.495 4(7)	0.661 1(6)
N(11)	0.345 1(6)	0.170 4(6)	0.766 7(5)
N(12)	0.357 7(6)	0.115 3(6)	0.689 9(5)
N(21)	0.532 0(6)	0.206 3(6)	0.705 1(5)
N(22)	0.528 6(6)	0.135 0(6)	0.647 4(6)
N(31)	0.265 1(6)	0.382 2(6)	0.547 3(5)
N(32)	0.314 4(7)	0.281 5(7)	0.515 9(5)
O(1)	0.495 8(7)	0.284 5(7)	0.951 5(5)
O(11)	0.194 1(6)	0.254 3(7)	1.196 0(5)
O(21)	0.821 1(6)	0.363 7(8)	1.007 5(6)
O(31)	−0.101 5(8)	0.983 7(7)	0.416 3(7)
C(1)	0.371 3(8)	0.574 9(8)	0.703 2(7)
C(2)	0.408 9(9)	0.647 5(9)	0.644 9(8)
C(3)	0.437 0(10)	0.716 9(9)	0.693 3(9)
C(4)	0.427 0(10)	0.714 9(9)	0.795 6(9)
C(5)	0.387 9(10)	0.646 3(10)	0.852 2(8)
C(6)	0.360 9(10)	0.575 0(9)	0.806 2(8)
C(7)	0.424 2(13)	0.650 4(11)	0.534 7(9)
C(11)	0.324 8(8)	0.031 8(8)	0.714 8(8)
C(12)	0.291 1(9)	0.032 3(9)	0.806 9(8)
C(13)	0.304 0(7)	0.119 2(7)	0.837 7(6)
C(14)	0.276 8(8)	0.153 0(8)	0.931 9(7)
C(15)	0.364 6(8)	0.141 1(8)	1.015 5(7)
C(16)	0.335 1(8)	0.175 0(8)	1.102 2(7)
C(17)	0.215 4(8)	0.221 8(8)	1.107 7(7)
C(18)	0.126 2(8)	0.233 9(9)	1.026 1(7)
C(19)	0.157 5(8)	0.199 0(9)	0.939 7(7)
C(110)	0.070 9(11)	0.312 9(14)	1.198 8(11)
C(21)	0.644 2(9)	0.045 4(8)	0.661 0(8)
C(22)	0.726 0(9)	0.057 2(9)	0.725 4(8)
C(23)	0.653 5(8)	0.159 7(8)	0.752 3(6)
C(24)	0.697 6(8)	0.211 9(9)	0.818 3(7)
C(25)	0.789 4(9)	0.137 3(9)	0.920 6(8)
C(26)	0.829 4(10)	0.190 5(11)	0.981 4(9)
C(27)	0.780 2(9)	0.318 1(10)	0.940 4(8)
C(28)	0.692 2(9)	0.392 6(10)	0.837 7(8)
C(29)	0.653 0(8)	0.338 1(9)	0.777 1(7)
C(210)	0.770 0(11)	0.494 0(11)	0.971 4(11)
C(31)	0.267 0(10)	0.321 4(10)	0.406 1(7)
C(32)	0.187 8(10)	0.446 5(10)	0.365 2(8)
C(33)	0.186 3(8)	0.483 4(8)	0.455 5(8)
C(34)	0.114 1(8)	0.614 6(8)	0.448 5(7)
C(35)	0.031 1(10)	0.653 8(9)	0.504 6(8)
C(36)	−0.038 4(10)	0.778 0(11)	0.492 6(9)
C(37)	−0.027 0(9)	0.865 5(9)	0.420 7(9)
C(38)	0.052 5(10)	0.827 8(10)	0.362 2(10)
C(39)	0.121 1(10)	0.705 0(9)	0.373 9(9)
C(310)	−0.090 6(14)	1.079 7(12)	0.344 2(12)

above. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo and Cl were taken from ref. 13. The structure was solved by Patterson and Fourier methods using the X-ray 80 system.[14] An empirical absorption correction[15] was applied at the end of the isotropic refinement. The maximum and minimum absorption factors were 1.56 and 0.53 respectively. Final refinement employed fixed isotropic thermal parameters and coordinates for hydrogen atoms, except for H(1), H(2) and the hydrogen atoms on the B atom and on the N(2) atom which have been located in a final difference synthesis and refined. No trend in F *versus* F_o or $(\sin\theta)/\lambda$ was observed. Refinement led to $R = 0.080$ and $R' = 0.093$ and average shift-to-error ratios were $< 0.31:1$. Final atomic parameters are presented in Table 3; ORTEP was used to generate the structure shown in Fig. 2.

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

Results and Discussion

Synthesis and Electrochemistry.—The complexes $[Mo(NO)\{HB(mppz)_3\}Cl(ER)]$ (E = O or NH; R = Ph or C_6H_4Me-2) were prepared from the reaction of $[MoNO\{HB(mppz)_3\}Cl_2]$

with REH. The Ir spectra of the products contained ν_{BH} in the region 2450–2495 cm^{-1} in addition to other bands attributable to the presence of the HB(mppz)$_3$ ligand. The arylamide complexes exhibited ν_{NO} at 1650 (R = Ph) and 1655 cm^{-1} (R = C_6H_4Me-2), values close to that found for [Mo(NO){HB(dmpz)$_3$}Cl(NHPh)]. However, the aryloxo compound [Mo(NO){HB(mppz)$_3$}Cl(OPh)] is anomalous in that ν_{NO} is observed at 1665 cm^{-1} (ER = OPh) compared to the value of 1680 cm^{-1} found for both [Mo(NO){HB(mppz)$_3$}Cl(OC_6H_4Me-2)] and [Mo(NO){HB(dmpz)$_3$}Cl(OPh)].[17] The 270 MHz ^{1}H NMR spectra of [Mo(NO){HB(mppz)$_3$}Cl(ER)] are consistent with the absence of a plane of symmetry in the molecules. Generally three doublets of relative area 1:1:1 are observed in the range δ_H 7.69–7.94 due to the pyrazolyl H^5 protons, although in the case of [Mo(NO){HB(mppz)$_3$}Cl(NHC_6H_4Me-2)] these are not fully resolved. A further set of three doublets of relative area 1:1:1 is observed in the range δ_H 6.19–6.41 due to the pyrazolyl H^4 protons. The MeOC_6H_4 aryl protons appear as two sets of three doublets in the ranges δ 6.28–6.88 and 6.82–7.88; the three signals in each set having the relative areas 2:2:2. This finding indicates that rotations about the aryl–pyrazolyl bonds in the HB(mppz)$_3$ ligands in the complexes are sufficiently unhindered to be rapid on the NMR time-scale at ambient temperature. The MeOC_6H_4 methyl protons appear as three singlets of relative areas 3:3:3 in the region δ 3.49–3.86. Signals attributable to the phenyl or 2-methylphenyl aryl protons are also observed and for [Mo(NO){HB(mppz)$_3$}Cl(OC_6H_4Me-2)] the methyl protons of the aryloxide ligand appear as a singlet of relative area 3 at δ 1.73 while for [Mo(NO){HB(mppz)$_3$}Cl(NHC_6H_4Me-2)] this signal appears at δ 1.40.

The electrochemistry of the new complexes was investigated using cyclic voltammetry. All exhibit a single reduction process with well defined cathodic and anodic peaks and peak current ratios $i_{pc}:i_{pa}$ close to 1:1. The reduction potentials of the arylamide complexes [Mo(NO){HB(mppz)$_3$}Cl(NHR)] (−0.85 and −0.89 V *vs.* SCE respectively for R = Ph and C_6H_4Me-2) are comparable with the value of −0.85 V found[18] for [Mo(NO){HB(dmpz)$_3$}Cl(NHPh)]. The slightly more cathodic potential of the compound with R = C_6H_4Me-2 is in accord with the presence of the electron-releasing methyl group in the *ortho* position of the aryl group. Similarly, the reduction potentials found for [Mo(NO){HB(mppz)$_3$}Cl(OR)] (−0.39 and −0.43 V *vs.* SCE respectively for R = Ph and C_6H_4Me-2) are comparable with that of −0.42 V reported for [Mo(NO){HB(dmpz)$_3$}Cl(OPh)]. Thus the electrochemical data provide no evidence for strong interligand interactions between HB(mppz)$_3$ and ER in these complexes.

Structural Studies.—In order to determine whether any anomalous structural features might arise from interligand interactions between the ER groups and the HB(mppz)$_3$ ligands in [Mo(NO){HB(mppz)$_3$}Cl(ER)] the crystal structures of [Mo(NO){HB(mppz)$_3$}Cl(OPh)] **1** and [Mo(NO){HB(mppz)$_3$}Cl(NHC_6H_4Me-2)] **2** were determined. The molecular structures are shown in Figs. 1 and 2.[17] Selected bond distances and angles are presented in Table 4. Both complexes exhibit distorted-octahedral co-ordination geometries around the formally 16-electron molybdenum centres. The Mo–O bond distance of 1.903(4) Å in **1** is comparable with those 1.863(7) and 1.886(12) Å found respectively in the alkoxide complexes [Mo(NO){HB(cdmpz)$_3$}Cl(OPr^i)] (cdmpz = 4-chloro-3,5-dimethylpyrazolyl)[19] and [Mo(NO){HB(mppz)$_3$}I(OC_3H_6Br)].[20] Similarly the Mo–N(amide) bond distance of 1.948(9) Å in **2** is comparable with those of 1.932(14) and 1.945(10) Å found respectively in the arylamide complexes [Mo(NO){HB(dmpz)$_3$}Cl(NHC_6H_4{N=NC_6H_3(Me-3)[(η^5-C_5H_4)Fe(η^5-C_5H_5)-4]}-*p*)][21] and [Mo(NO){HB(dmpz)$_3$}I(NHC_6H_4OMe-4)].[22] This bond distance is also similar to those of 1.954(23) and 1.964(13) Å found in the alkylamide complex [Mo(NO){HB(dmpz)$_3$}I(NHEt)].[23]

The bond angles within the molecule are the feature most

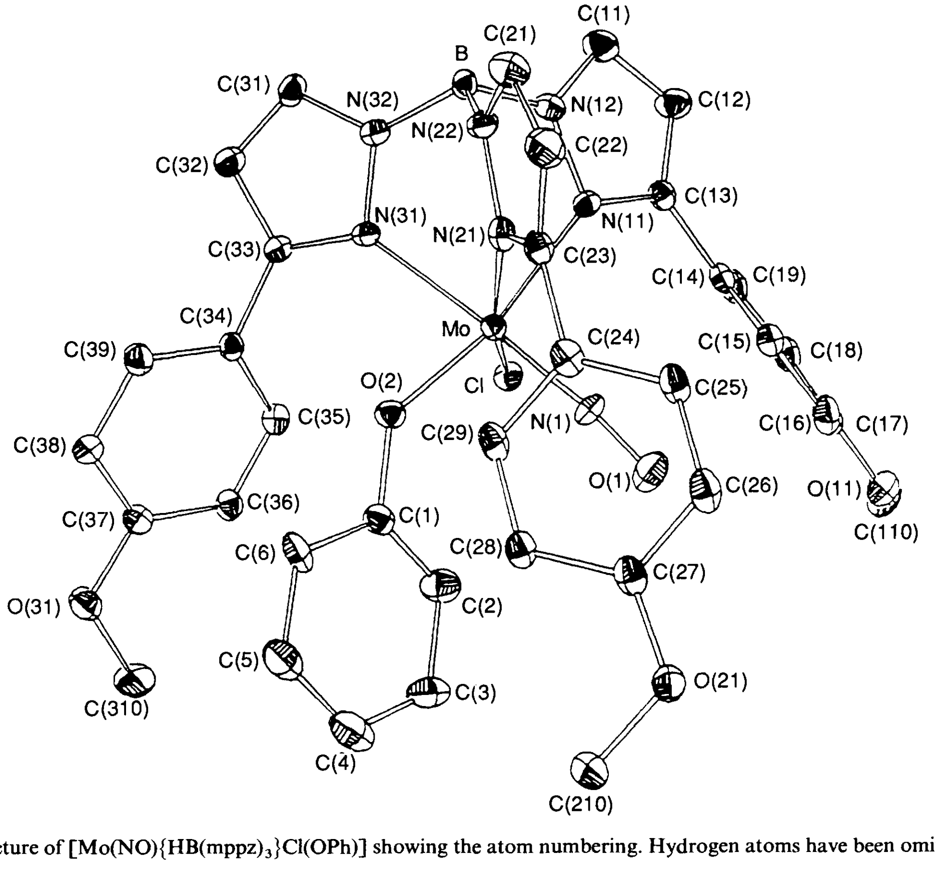

Fig. 1 The crystal structure of [Mo(NO){HB(mppz)$_3$}Cl(OPh)] showing the atom numbering. Hydrogen atoms have been omitted for clarity

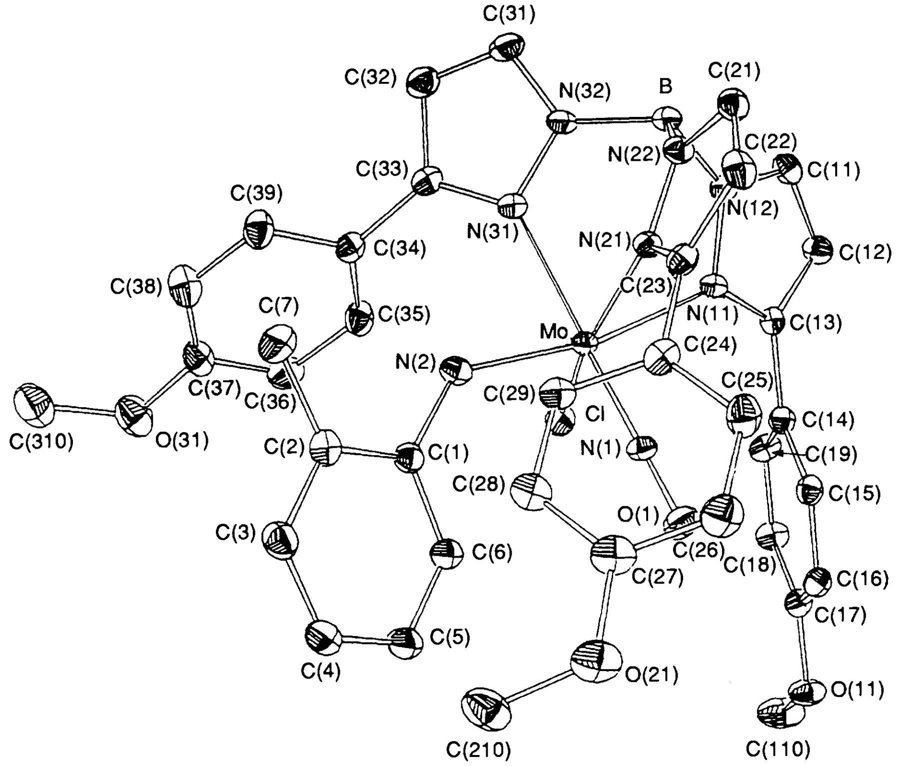

Fig. 2 The crystal structure of $[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$ showing the atom numbering. Hydrogen atoms have been omitted for clarity

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

	$[Mo(NO)\{HB(mppz)_3\}$-$Cl(OPh)]$[a]	$[Mo(NO)\{HB(mppz)_3\}$-$Cl(NHC_6H_4$-Me-$2)]$[b]
Mo–Cl	2.359(2)	2.375(3)
Mo–N(1)	1.761(5)	1.752(7)
Mo–N(11)	2.252(4)	2.259(9)
Mo–N(21)	2.156(5)	2.201(7)
Mo–N(31)	2.259(5)	2.308(7)
Mo–Z(2)	1.903(4)	1.948(9)
N(1)–O(1)	1.190(8)	1.20(1)
C(1)–Z(2)	1.358(7)	1.42(2)
Cl–Mo–N(1)	90.5(2)	93.0(3)
Cl–Mo–N(11)	83.2(1)	83.4(2)
Cl–Mo–N(21)	160.5(1)	163.1(2)
Cl–Mo–N(31)	91.5(1)	91.4(2)
Cl–Mo–Z(2)	98.2(1)	95.9(3)
N(1)–Mo–N(11)	96.4(2)	96.8(3)
N(1)–Mo–N(21)	95.7(2)	90.4(4)
N(1)–Mo–N(31)	175.1(2)	175.4(4)
N(1)–Mo–Z(2)	96.0(2)	95.5(4)
Z(2)–Mo–N(11)	167.5(2)	167.8(3)
Z(2)–Mo–N(21)	99.5(2)	100.2(4)
Z(2)–Mo–N(31)	79.3(2)	82.9(3)
N(11)–Mo–N(21)	77.7(2)	79.8(3)
N(11)–Mo–N(31)	88.3(2)	85.0(3)
N(21)–Mo–N(31)	83.9(2)	85.8(3)
Mo–N(1)–O(1)	174.8(5)	178.9(8)
Mo–Z(2)–C(1)	136.6(4)	134.4(6)
C(1)–C(2)–C(7)		122(1)
C(3)–C(2)–C(7)		119(1)

[a] Z = O. [b] *Z* = N.

likely to reveal the presence of significant interligand interactions in complexes of the type [Mo(NO)L(X)(EY)] (L = a tris(pyrazolyl)borate ligand; E = O, N or NH; Y = a hydrocarbyl or hydrocarbylamide; X = halide or EY). In an ideal octahedron the sum (Σ^{L}) of the three angles made at the Mo atom by the three nitrogen-donor atoms of L should be 270°. Similarly the sum (Σ^{E}) of the angles made by the donor atoms [N(O), X, E(Y)] of the coligands at the Mo atom should also be 270°. Deviations from this feature reveal distortions from ideal octahedral co-ordination and may be used as a basis for comparing the structures of different complexes. The results of such calculations on 24 complexes of the type [Mo(NO)L(X)(EY)] are summarised in Table 5.[24–36] The first point to emerge from these features is the remarkable consistency of the N(pz)–Mo–N(pz) angle sum, Σ^{L}. Over a range of coligand sets X/E(Y) involving O, N, S, I or Cl donor atoms and with examples of four types of L Σ^{L} varies over a range of only 5.2°, from 245.1° in $[Mo(NO)\{HB(dmpz)_3\}(OPr^{i})_2]$ to 250.8° in $[Mo(NO)\{HB(dmpz)_3\}(NHC_6H_4Me\text{-}4)]$. The values of Σ^{L} in structures involving $HB(mppz)_3$, $HB(impz)_3$ (impz = 3-isopropyl-5-methylpyrazolyl) and $HB(pz)_3$ all fall within this range. As might be expected a larger variation is found in the angle sum at Mo arising from the E(Y),X,N(O) donor-atom set. This is most pronounced for the two 18-electron complexes $[Mo(NO)L(CO)_2]$ [L = $HB(pz)_3$ or $HB(mppz)_3$] where the difference in Σ^{L} is only 1° but the difference in Σ^{E} is 16.5° reflecting the presence of the sterically bulky $MeOC_6H_4$ substituents in the 3 positions of the pyrazolyl rings of $HB(mppz)_3$.

Amongst the 16-electron complexes Σ^{E} varies by almost 20°; from 279.1° in $[Mo(NO)\{HB(dmpz)_3\}I(NC_4H_8)]$ to 297.7° in $[Mo(NO)\{HB(dmpz)_3\}(OPr^{i})_2]$. The values of Σ^{E} may be divided into three groups. The largest angles are found in the complexes where the E and X donor atoms are small, *i.e.* O or N. Angle sums Σ^{E} ranging from 292.9° for $[Mo(NO)\{HB(impz)_3\}(OEt)_2]$ to 297.7° for $[Mo(NO)\{HB(dmpz)_3\}(OPr^{i})_2]$ are found for this group. One exception is the low value of 283.6° found for the bis(pyrrolyl) complex $[Mo(NO)\{HB(dmpz)_3\}(NC_4H_4)_2]$. Otherwise the smallest angle sums arise when the large iodide ion is present in the X, E(Y), N(O) donor atom set. Thus for such compounds Σ^{E} ranges from 280.9° in $[Mo(NO)\{HB(dmpz)_3\}I(NHEt)]$ to 284.6° in

Table 5 Angle sums at Mo for the MoL and Mo(NO)X(EY) moieties in $[Mo(NO)L(X)(EY)]$

Compound	Ref.	$\Sigma^E/°$ for Mo–E,X,N(O)[a]	$\Sigma^L/°$ for N(pz)–Mo–N(pz)[b]	Mo–E–Y angle/°
$[Mo(NO)\{HB(mppz)_3\}Cl(OPh)]$	This work	284.7	249.9	136.6(4)
$[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$	This work	284.4	250.6	134.4(6)
$[Mo(NO)\{HB(dmpz)_3\}Cl(NHR)]$[c]	21	288.4	250.6	134.8(10)
$[Mo(NO)\{HB(dmpz)_3\}Cl(L')]$[d]	35	287.5	250.2	132.6(7)
$[\{Mo(NO)\{HB(dmpz)_3\}Cl[N(CH_2)_2]\}_2]$	24	287.6	250.6	
$[Mo(NO)\{HB(cdmpz)_3\}Cl(OPr^i)]$	19	290.1	248.4	132.4(6)
$[Mo(NO)\{HB(dmpz)_3\}I(NHC_6H_4Me\text{-}4)]$	22	282.9	250.8	141.7(17)
$[Mo(NO)\{HB(dmpz)_3\}I(NHC_6H_4OMe\text{-}4)]$	22	284.1	250.0	137.5(8)
$[Mo(NO)\{HB(dmpz)_3\}I(NHEt)]$	23	283.3	250.0	146.9(18)
		280.9	249.8	136.2(12)
$[Mo(NO)\{HB(dmpz)_3\}I(NHNMePh)]$	25	283.5	250.6	
$[Mo(NO)\{HB(dmpz)_3\}I(NHNMe_2)]$	25	281.8	249.6	
$[Mo(NO)\{HB(dmpz)_3\}I(NC_4H_8)]$	26	279.1	250.6	
$[Mo(NO)\{HB(dmpz)_3\}I\{O(CH_2)_3Br\}]$	20	284.6	249.8	131.8(13)
$[Mo(NO)\{HB(dmpz)_3\}I(SC_6H_{11})]$	27	283.5	250.2	
$[Mo(NO)\{HB(dmpz)_3\}(SPh)_2]$	28	284.1	249.2	
$[Mo(NO\{HB(dmpz)_3\}(O_2CMe)(NHPh)]$	29	294.8	249.8	138.3(4)
$[Mo(NO)\{HB(dmpz)_3\}(2\text{-}NHC_5H_4N)_2]$	30	295.0	247.1	135.5(2)
				135.4(2)
$[Mo(NO)\{HB(dmpz)_3\}(NHBu^n)_2]$	31	295.9	246.5	129.7(19)
				130.1(20)
$[Mo(NO)\{HB(dmpz)_3\}(NC_4H_4)_2]$	32	283.6	248.6	
$[Mo(NO)\{HB(dmpz)_3\}(OEt)(OPr^i)]$	36	295.3	245.3	129.5(4)
				129.8(4)
$[Mo(NO)\{HB(dmpz)_3\}(OPr^i)_2]$	36	297.7	245.1	133.4(4)
				133.4(4)
$[Mo(NO)\{HB(impz)_3\}(OEt)_2]$	33	292.9	247.9	129(1)
$[Mo(NO)\{HB(pz)_3\}(CO)_2]$	34	271.4	247.3	
$[Mo(NO)\{HB(mppz)_3\}(CO)_2]$	12	254.9	248.3	

[a] Sum of the angles made by the Mo–N(O), Mo–X and Mo–E(Y) bonds at Mo. [b] Sum of the angles made by the Mo–N(pyrazolyl) bonds at Mo. [c] $R = C_6H_4\{N{=}NC_6H_3(Me\text{-}3)[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\text{-}4]\}\text{-}p$. L′ = 5-*p*-oxidophenyl-10,15,20-triphenylporphyrin.

$[Mo(NO)\{HB(dmpz)_3\}I\{O(CH_2)_3Br\}]$. The chloro complexes $[Mo(NO)L(Cl)(EY)]$ form an intermediate group with Σ^E ranging from 284.4° in $[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$ to 288.4° in $[Mo(NO)\{HB(dmpz)_3\}Cl(NHC_6H_4\{N{=}NC_6H_3(Me\text{-}3)[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\text{-}4]\}\text{-}p)]$ and 290.1° in $[Mo(NO)\{HB(cdmpz)_3\}Cl(OPr^i)]$. The Σ^E values for the two complexes containing $HB(mppz)_3$ lie at the low end of the range of values for the chloro complexes and are about 4° less than in complexes containing $HB(dmpz)_3$. This difference is barely significant and, for these 16-electron complexes, indicates that the steric effects of the ligands $HB(dmpz)_3$ and $HB(mppz)_3$ on the X, E(Y), N(O) donor atom set are not significantly different. A much larger difference is apparent between the Σ^E values found in the two 18-electron complexes $[Mo(NO)L(CO)_2]$ [$L = HB(pz)_3$ or $HB(mppz)_3$]. A further structural feature which may reveal steric differences between the ligands $HB(pz)_3$ and $HB(mppz)_3$ is the Mo–E–C–C(aryl) torsion angle.[9,10,23] The Mo–N(2)–C(1)–C(2) and Mo–O(2)–C(1)–C(6) torsion angles in $[Mo(NO)\{HB(mppz)_3\}Cl(NHC_6H_4Me\text{-}2)]$ and $[Mo(NO)\{HB(mppz)_3\}Cl(OPh)]$ are respectively 152.8 and 152.5°. These values differ little from one another or from the 152.4 and 155.1° calculated for $[Mo(NO)\{HB(dmpz)_3\}(O_2CMe)(NHPh)]$ and $[Mo(NO)\{HB(dmpz)_3\}I(NHC_6H_4OMe\text{-}4)]$ respectively.

The finding that the largest angle sums Σ^E are associated with the smallest donor atoms could be ascribed either to steric or to electronic effects, or to both. Steric effects arising from intramolecular interligand repulsions might normally be expected to produce the largest angle sums, Σ^E, with the largest ligand (EY,X). The finding that the smallest angle sums are associated with complexes containing the larger iodide ligand (X), and the largest with complexes containing the smaller N or O (E,X) donor atoms, runs counter to this expectation. However, the smaller donor atoms may be able to penetrate more deeply into the cleft between the adjacent pyrazolyl rings in the tripodal ligand than can the larger iodine atom. This would allow greater relief of steric congestion in the EY,X,NO ligand set and result in larger angle sums for the smaller donor atoms. There may also be an electronic effect favouring larger angle sums when O- or N-donor atoms are present. Other structural studies of nitrosyl complexes indicate that the non-bonded radius of this π-acid ligand may depend upon the population of the acceptor orbitals.[37] In the structures described here the larger angle sums arise with the stronger π-donor ligands. This is in accord with increased back donation to the nitrosyl ligand leading to its having a larger non-bonded radius and inducing a larger angle sum. The higher degree of back donation when two O- or N-donor atoms are present is manifest in the lower N–O stretching frequency found for such complexes, as compared to complexes with poorer π-donor ligands.[18,38] The extent of π donation to the metal centre in these complexes is also manifest in their reduction potentials, E_f,[18] but there is not a good general correlation between E_f values and Σ^E values. This suggests that electronic arguments alone cannot account for the observed structural trends in these complexes. Although it is not possible unequivocally to distinguish steric from electronic effects, it seems probable that both are contributing to the observed angle sum, Σ^E.

The electrochemical and structural results described here indicate that, in derivatives of the 16-electron $\{Mo(NO)[HB(mppz)_3]\}^{2+}$ group, the borate ligand can accommodate co-ligands of the type ER (E = O or NH, R = Ph or $2\text{-}MeC_6H_4$) without incurring large intramolecular interligand interactions. Any interactions which may be present appear insufficiently large to produce significant changes in the structures or electrochemical properties of the complexes as compared to their counterparts containing the $HB(dmpz)_3$ ligand.

Acknowledgements

We are grateful to Direccion General de Investigaccion Cientifica y Technica of the Ministry of Education and Science of Spain for the support of this work on project PB/890127.

References

1 S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.
2 S. Trofimenko, *Prog. Inorg. Chem.*, 1986, **34**, 115.
3 N. Kitajima, N. Tamura, M. Tanaka and Y. Moro-oka, *Inorg. Chem.*, 1992, **31**, 3342.
4 N. Kitajima, S. Hikichi, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1993, **115**, 5496.
5 S. A. Roberts, C. G. Young, W. E. Cleland, R. B. Ortega and J. H. Enemark, *Inorg. Chem.*, 1988, **27**, 3044.
6 S. A. Roberts, C. G. Young, C. A. Kipke, W. E. Cleland, K. Yamanouchi, M. D. Carducci and J. H. Enemark, *Inorg. Chem*, 1990, **29**, 3650.
7 W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc.*, 1984, **106**, 3653.
8 P. N. Turowski, W. H. Armstrong, M. E. Roth and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 681.
9 M. T. Ashby and J. E. Enemark, *J. Am. Chem. Soc.*, 1986, **108**, 730.
10 N. AlObaidi, C. J. Jones and J. A. McCleverty, *Polyhedron*, 1989, **8**, 1033.
11 D. M. Eichhorn and W. H. Armstrong, *Inorg. Chem.*, 1990, **29**, 3607.
12 M. Cano, J. V. Heras, A. Monge, E. Gutierrez, S. L. W. McWhinnie, C. J. Jones and J. A. McCleverty, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 2435.
13 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 72–98.
14 J. M. Stewart, The X-RAY 80 System, Computer Science Centre, University of Maryland, College Park, 1985.
15 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
16 M. Martinez-Ripoll and F. H. Cano, PESOS program, Instituto Rocasolano, Madrid, 1975.
17 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
18 N. AlObaidi, D. Clague, M. Chaudhury, C. J. Jones, J. A. McCleverty, J. C. Pearson and S. S. Salam, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1733.
19 J. A. McCleverty, D. Seddon, N. A. Bailey and N. W. Walker, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 898.
20 C. J. Jones, J. A. McCleverty, B. D. Neaves, S. J. Reynolds, H. Adams, N. A. Bailey and G. Denti, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 733.
21 B. J. Coe, S. S. Kurek, N. M. Rowley, J.-D. Foulon, T. A. Hamor, M. E. Harman, M. B. Hursthouse, C. J. Jones, J. A. McCleverty and D. Bloor, *Chemtronics*, 1991, **5**, 23.
22 J. A. McCleverty, G. Denti, S. J. Reynolds, A. S. Drane, N. ElMurr, A. E. Rae, N. A. Bailey, H. Adams and J. M. A. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 81.
23 J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 429.
24 N. AlObaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 2653.
25 J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 71.
26 N. AlObaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty, K. Paxton, A. J. Howes and M. B. Hursthouse, *Polyhedron*, 1988, **7**, 1931.
27 J. A. McCleverty, A. S. Drane, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 91.
28 J. H. Enemark and S. A. Roberts, *Acta Crystallogr.*, *Sect. C*, 1989, **45**, 1292.
29 A. Wlodarcyzk, A. J. Edwards and J. A. McCleverty, *Polyhedron*, 1988, **7**, 103.
30 N. AlObaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1063.
31 N. AlObaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty and K. Paxton, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 1525.
32 N. AlObaidi, A. J. Edwards, C. J. Jones, J. A. McCleverty, B. D. Neaves, F. E. Mabbs and D. Collison, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 127.
33 M. Cano, J. V. Heras, S. Trofimenko, A. Monge, E. Gutierrez, C. J. Jones and J. A. McCleverty, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 3577.
34 E. M. Holt, S. M. Holt, F. Cavalito and K. J. Watson, *Acta Chem. Scand.*, *Ser. A*, 1976, **30**, 225.
35 N. M. Rowley, T. A. Hamor, C. J. Jones and J. A. McCleverty, unpublished work.
36 J. A. McCleverty, A. E. Rae, I. Wolochowicz, N. A. Bailey and J. M. A. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 951.
37 F. M. Conroy-Lewis, A. D. Redhouse and S. J. Simpson, *J. Organomet. Chem.*, 1990, **399**, 307.
38 J. A. McCleverty, *Chem. Soc. Rev.*, 1983, **12**, 331.

Received 1*st December* 1993; *Paper* 3/07102B