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Oxo-bridged binuclear molybdenum nitrosyl halides: structural and redox studies, mixed-valence behaviour, and characterisation of mononuclear hydroxo precursors

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The binuclear μ-oxo compounds $[\{Mo(NO)[HB(dmpz)_3]X\}_2(\mu\text{-}O)]$ (dmpz = 3,5-dimethylpyrazol-1-yl; X = I or Cl) have been prepared. These can occur as enantiomers, one of which (X = I) has been characterised previously, and a single-crystal X-ray diffraction study of the other enantiomer (X = I) established that the molecule has a slightly asymmetric Mo–O–Mo link. The binuclear complexes undergo two one-electron reductions (E_f^1 and E_f^2) and one one-electron oxidation, established by cyclic voltammetry, the separation between E_f^1 and E_f^2 being *ca.* 1000 mV indicating that there is extremely strong interaction between the metal-containing redox centres. The EPR, IR and electronic spectra of the reduced monoanionic species $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(\mu\text{-}O)]^-$ ($S = \frac{1}{2}$) are consistent with valence-trapped (Class I) behaviour which is unusual in compounds with such short bridges. Formation of $[\{Mo(NO)[HB(dmpz)_3]X\}_2(\mu\text{-}O)]$ involves prior generation of $[Mo(NO)\{HB(dmpz)_3\}X(OH)]$ (X = Cl or I) by hydrolysis of $[Mo(NO)\{HB(dmpz)_3\}X_2]$ and reaction of the monohydroxide with $[Mo(NO)\{HB(dmpz)_3\}X_2]$. The compound $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$ is also formed by reaction of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ with water in solution and on contact with silica gel in dichloromethane. Its structure has been determined crystallographically, and it can be dehydrated on silica gel into $[\{Mo(NO)[HB(dmpz)_3](\mu\text{-}O)\}_2]$ which appears to contain a symmetrical $\{Mo(\mu\text{-}O)_2Mo\}$ bridging system.

Compounds containing the redox-active sterically hindered tris(3,5-dimethylpyrazolyl)borato molybdenum nitrosyl group $[Mo(NO)\{HB(dmpz)_3\}]^{2+}$ have found uses as Group I cation sensors,[1] as components of materials having non-linear optical properties[2] and as building blocks for oligonuclear compounds exhibiting novel magnetic behaviour.[3] The key precursors to these interesting and potentially useful materials are the dihalides $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ and $[Mo(NO)\{HB(dmpz)_3\}I_2]$, the purification of which is essential to subsequent chemistry employing them. During the preparation of these dihalides, which involves iodination of $[Mo(CO)_2(NO)\{HB(dmpz)_3\}]$ with (X = Cl) or without (X = I) subsequent addition of benzyl chloride, the bimetallic species $[\{Mo(NO)[HB(dmpz)_3]X\}_2O]$ are invariably formed, which reduces the yields of the required dihalides, and which must be removed by careful chromatography on silica gel. The ways in which these μ-oxo species are formed have not been clearly established, although the presence of water and/or oxygen in the reaction mixture containing $[Mo(NO)\{HB(dmpz)_3\}X_2]$, and the use of silica gel columns used during the work-up procedure, appear to be significant factors.[4] Regarding the formation of the oxobimetallics, there are three important questions: (*i*) whether these μ-oxo species are formed somehow by direct reaction between $[Mo(NO)\{HB(dmpz)_3\}X_2]$ and water and/or oxygen; (*ii*) whether they are generated before and/or after addition to a chromatography column and (*iii*) whether species such as $[Mo(NO)\{HB(dmpz)_3\}X(OH)]$ could be intermediates.

We have previously determined the crystal and molecular structure of an enantiomer of $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ (Fig. 1, **A**)[4] in which one NO group and an I atom are in a mutually *cis* configuration in the linkage (ON)–Mo–O–Mo–I and the other NO group and I atom are mutually *trans*. According to the Cahn–Ingold–Prelog rules the relative configurations at the metal atoms are *R*–*S*† (the absolute configuration of this molecule was not determined).[5] Other isomers **B**–**D** can, in principle, exist assuming that there is no rotation about the Mo–O–Mo bond and are shown in Fig. 1, and **B** is the enantiomer of **A** but **C** and **D** are not chiral. A further set of molecules with *R*–*R* (or *S*–*S*) configurations are also possible, **E**–**H** in Fig. 1. Thus a total of twelve possible isomers is possible for $[\{Mo(NO)[HB(dmpz)_3]X\}_2O]$ although the steric repulsion exerted by the $HB(dmpz)_3$ ligands and iodine atoms in $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ would suggest that only **A** and **B** are likely to be stable. We have earlier observed that two spectroscopically distinct forms of the corresponding dichloro species, $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2O]$, can be isolated and have suggested that these may be isomers.[6] Since the Cl atoms in this complex are significantly smaller than iodine there is likely to be less steric crowding and other isomers are possible. These must presumably be diastereomers rather than enantiomers (probably *R*–*S* and *R*–*R*/*S*–*S*). The electrochemical properties of the two 'isomers' are significantly different, although the possibility that one of them is actually $[Cl\{HB(dmpz)_3\}(NO)Mo–O–Mo-$

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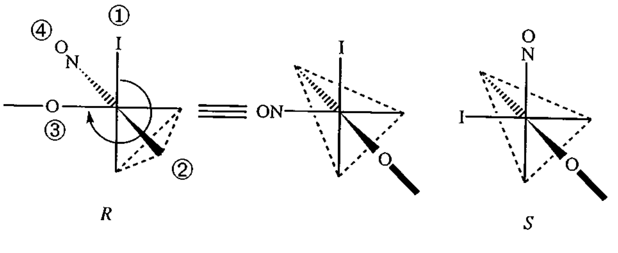
† According to the Cahn–Ingold–Prelog rules, the relative configurations of the metal fragments are assigned as shown:



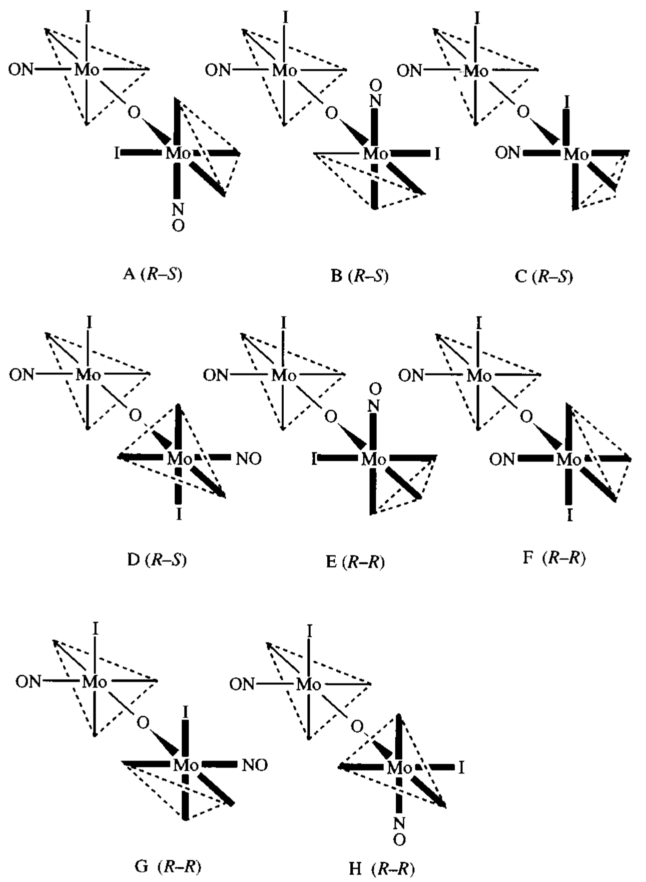


Fig. 1 **A**, Idealised structure of an enantiomer of [{Mo(NO){HB(dmpz)$_3$}I}$_2$(μ-O)] as determined in ref. 4, **B**; the other enantiomer reported in this paper; the dashed triangles represent the HB(dmpz)$_3$ ligand; **C** and **D** are other non-chiral isomers with *R–S* configurations; **E**–**H** are *R–R* isomers (corresponding *S–S* enantiomers are mirror images of these)

(NO){HB(dmpz)$_3$}(OH)] cannot be entirely dismissed. We have also isolated one asymmetrically substituted species, [Cl{HB(dmpz)$_3$}(NO)Mo–O–Mo(NO){HB(dmpz)$_3$}I], from a reaction between [Mo(NO){HB(dmpz)$_3$}Cl(NH$_2$)] and [Mo(NO){HB(dmpz)$_3$}I$_2$].[6]

The μ-oxo compounds are redox-active and we have already reported on the spectroelectrochemical behaviour of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O]$^-$.[6] Somewhat to our surprise, cyclic voltammetry (CV) of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] appeared to exhibit only one reversible fast one-electron reduction process. From our considerable knowledge of the electrochemical behaviour of a wide range of bimetallic molybdenum nitrosyl species we would have expected two reduction processes, corresponding to the generation of a mono- and a di-anion.[7] However, we have observed that the separation between reduction potentials E_f^1 and E_f^2 (ΔE_f) increases substantially as the distance between the two {Mo(NO)[HB(dmpz)$_3$]X(Y)} redox centres decreases and, up till now, we have rationalised the appearance of only one wave in the CV of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] in terms of a very large value of ΔE_f (>1000 mV), so that the second reduction occurs within, or at more cathodic potentials than, the decomposition wave of the medium (CH$_2$Cl$_2$–[NBu$_4$][PF$_6$]).

In this paper we address the questions and issues posed above, report (*a*) on the nature of precursors of these μ-oxo species and on the structure of one of these, [Mo(NO){HB(dmpz)$_3$}(OH)$_2$], and on the structure of another enantiomer of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$O], (*b*) on the EPR, IR and electronic spectra, and hence the possible electronic structure, of the reduced monoanionic species [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O]$^-$ (X = Cl or I), and (*c*) on possible mechanisms of formation of the μ-oxo species.

Experimental

All reagents were used as purchased without further purification, except the species [Mo(NO){HB(dmpz)$_3$}X$_2$] (X = CO and I), which were prepared as described.[8,9] Solvents were specially purified by distillation over sodium wire, calcium chloride and/or molecular sieves as appropriate, dried in the most appropriate way and degassed with air- and water-free dinitrogen (BOC Whitespot), except for the toluene used in the preparation of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$O] which was used directly from the container (BDH Analar grade). All yields are based on the starting molybdenum-containing compound.

Proton NMR spectra were recorded on a JEOL GX270 instrument, FAB mass spectra using a VG-Autospec of the SERC Mass Spectrometry Service Centre, Swansea, and a similar instrument in the School of Chemistry in Bristol, with 3-nitrobenzyl alcohol as matrix and IR spectra in dichloromethane solutions using a PE1600 FTIR spectrophotometer. Microanalyses were determined by the Microanalytical Laboratory of the School of Chemistry, University of Bristol. Electrochemical measurements were made using an EG & PAR model 273A potentiostat. Dichloromethane, purified by distillation from CaH$_2$, was used as solvent and [NBu$^n_4$][PF$_6$] or [NBu$^n_4$][BF$_4$] (10^{-3} M) as base electrolyte. A standard three-electrode configuration was used, with a platinum-bead working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. Ferrocene was added at the end of each experiment as an internal standard; all potentials are quoted *vs.* the ferrocene–ferrocenium couple. The EPR spectra were recorded using a Bruker ESP-300E spectrometer.

Syntheses

[Mo(NO){HB(dmpz)$_3$}I$_2$]. A mixture of [Mo(CO)$_2$(NO){HB(dmpz)$_3$}] (6.0 g) and iodine (3.5 g, a slight excess) in toluene (BDH Analar grade) which had not been specially purified (not more than 300 cm^3) was refluxed under nitrogen for 12 h. The mixture was then cooled to room temperature and after 24 h the product was filtered off as black crystals. These were washed with hexane to remove the excess of I$_2$, and the product dried for 2 h at 150 °C (yields virtually quantitative). To effect more efficient removal of unreacted iodine the product was suspended in a large volume of hexane and boiled for 15 min after which time the product, as a brown-black powder, was filtered off, the iodine remaining in the filtrate. Further purification was effected by dissolving the product in the minimum volume of dichloromethane and chromatographing on silica gel using dichloromethane as eluent. Four bands were formed: the first is [{Mo(NO)[HB(dmpz)$_3$]I}$_2$O] (see below), the second the desired compound, the third [Mo(NO){HB(dmpz)$_3$}I(OH)] and the fourth (on the top of the column) [Mo(NO){HB(dmpz)$_3$}(OH)$_2$] (see below).

[{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)]. *Method* 1. A mixture of [Mo(CO)$_2$(NO){HB(dmpz)$_3$}] (3 g, 6.3 mmol), iodine (1.5 g, 11.8 mmol) and water (0.5 cm^3) in toluene (200 cm^3) was stirred and refluxed under oxygen gas or air for 15 h. The reaction mixture was evaporated *in vacuo* and the residue refluxed with hexane (300 cm^3) for 0.5 h to extract unreacted iodine. The mixture was then filtered and the residue washed with pentane to remove any remaining traces of free iodine. The products were then dissolved in the minimum volume of dichloromethane, and chromatographed on silica gel using dichloromethane as eluent to remove the main fraction, identified as [{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)]. A further fraction, identified as [I{HB(dmpz)$_3$}(NO)Mo–O–Mo(NO){HB(dmpz)$_3$}(OH)] was eluted using a tetrahydrofuran (thf) (25% v/v)–dichloromethane mixture. The metal-containing fractions were evaporated *in vacuo*, and the products recrystallised from dichloromethane–hexane giving dark green microcrystals of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)] (1.2 g, 17%) and brown microcrystals of $[I\{HB(dmpz)_3\}(NO)Mo{-}O{-}Mo(NO)\{HB(dmpz)_3\}(OH)]$ (0.3 g, 5%). For $[\{Mo(NO)[HB(dmpz)_3]I\}_2(\mu\text{-O})]$ (Found: C, 33.1; H, 4.1; N, 17.5. $C_{30}H_{44}B_2I_2Mo_2N_{14}O_3$ requires C, 32.3; H, 4.0; N, 17.6%); *M* (FAB mass spectrum) 1115 (calc. 1116); ν_{max} 1682 (NO), 1663 (NO), 744 cm^{-1} (MoOMo); $\delta_H(CDCl_3)$ 6.02, 5.92, 5.78, 5.71, 5.58, 5.45 (1 H, s; 1 H, s; 1 H, s; 1 H, s; 1 H, s; 1 H, s; $Me_2C_3\mathit{H}N_2$); 3.12, 3.08, 2.48, 2.44, 2.40, 2.38, 2.37, 2.27, 0.98, 0.96 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; $(C\mathit{H}_3)_3C_3HN_2$].‡ The compound $[\{Mo(NO)[HB(dmpz)_3]I\}_2(\mu\text{-O})]$ could also be recrystallised from carbon tetrachloride to afford crystals suitable for X-ray crystallography (see below).

Method 2. A mixture of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ (3 g, 4.4 mmol), iodine (0.5 g) and water (0.5 cm^3) in toluene (200 cm^3) was stirred and refluxed for 48 h while oxygen gas was bubbled through the mixture. The species $[\{Mo(NO)[HB(dmpz)_3]I\}_2(\mu\text{-O})]$ was separated and purified as described above, and only the starting materials and one other fraction were collected, the yield of μ-oxo diiodide being always less than 10%.

Method 3. A mixture of $[Mo(CO)_2(NO)\{HB(dmpz)_3\}]$ (3 g, 6.3 mmol), iodine (1.5 g, 11.8 mmol) and water (0.5 cm^3) in toluene (200 cm^3) was stirred and refluxed under nitrogen (*i.e.* in the absence of oxygen) for 15 h. The solution was cooled, and it was observed that unreacted iodine was absent. The solvent was evaporated *in vacuo* and the residue chromatographed on silica gel using dichloromethane as eluent. Three products were separated and characterised: $[Mo(CO)_2(NO)\{HB(dmpz)_3\}]$ (0.3 g), $[\{Mo(NO)[HB(dmpz)_3]I\}_2(\mu\text{-O})]$ (1.4 g, 20%), a small amount of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ and a fourth unidentified paramagnetic molybdenum nitrosyl species (ν_{NO} 1621 cm^{-1}) (0.2 g).

$[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(\mu\text{-O})]$. A mixture of $[Mo(NO)\{HB(dmpz)_3\}Cl(OH)]$ (0.1 g, 0.2 mmol), $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ (0.99 g, 0.2 mmol) and NEt_3 (0.3 cm^3) in toluene (40 cm^3) was stirred and refluxed for 3 h. The solution was then cooled, pentane added (20 cm^3) to precipitate $[NEt_3H]Cl$, the mixture filtered and the filtrate evaporated *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and the product separated and purified by column chromatography on silica gel using dichloromethane as eluent. After evaporation of the solvent and recrystallisation from dichloromethane–hexane the product was obtained as dark green microcrystals (0.21 g, 11%) (Found: C, 38.9; H, 5.2; N, 20.2. $C_{30}H_{44}B_2Cl_2Mo_2N_{14}O_3$ requires C, 38.6; H, 4.8; N, 21.0%); ν_{max} 1694, 1665 cm^{-1}; $\delta_H(CDCl_3)$ 6.04, 5.86, 5.83, 5.80, 5.60, 5.39 (1 H, s; 1 H, s; 1 H, s; 1 H, s; 1 H, s; 1 H, s; $Me_2C_3\mathit{H}N_2$); 3.01, 2.90, 2.50, 2.45, 2.39, 2.36, 2.35, 2.31, 0.98, 0.86 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; $(C\mathit{H}_3)_2C_3HN_2$].

$[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$. A mixture of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ (0.55 g, 1 mmol), water (two drops) and silver acetate (0.3 g) in a mixture of dichloromethane (25 cm^3) and thf (25 cm^3) was stirred and refluxed for 6 h. The brick-red mixture was cooled to room temperature, filtered and evaporated to dryness *in vacuo*. The residue was dissolved in the minimum volume of dichloromethane and chromatographed on silica gel initially using dichloromethane as eluent to remove impurities (mainly starting material, $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$ and $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$). The main fraction was eluted with thf and was identified as the desired product. The solvent was evaporated *in vacuo* affording the compound as a pink powder (0.21 g, 46%). The complex may be recrystallised from acetone, when it is isolated as a brick-red crystalline acetone solvate (from ^1H NMR data the molecule appears to contain between 1.5 and 2 mol of acetone per formula unit of the complex). The acetone may be removed by pumping on the solid at room temperature *in vacuo*, but the crystals crumble to a powder (Found: C, 39.0; H, 5.2; N, 21.4. $C_{15}H_{24}BMoN_7O_3$ requires C, 39.4; H, 5.3; N, 21.4%); *M* (electron impact mass spectrum) 459 (calc. 457); ν_{max} 1656 (NO), 1712 cm^{-1} (CO of acetone); $\delta_H(CD_2Cl_2)$, 10.13 (2 H, s, OH); 5.89, 5.79 (2 H, s; 1 H, s; $Me_2C_3\mathit{H}N_2$); 2.49, 2.35 [6 H, s; 12 H, s; $(C\mathit{H}_3)_2C_3HN_2$]; 2.12 [6 H, s; $(CH_3)_2CO$, when present].

$[\{Mo(NO)[HB(dmpz)_3](\mu\text{-O})\}_2]$. The bis(hydroxide) described above was heated *in vacuo* [<1 mmHg (≈133 Pa)] at 150 °C for 36 h, and the compound was obtained as a pink-red solid (Found: C, 41.2; H, 5.7; N, 18.9. $C_{30}H_{44}B_2Mo_2N_{14}O_4$ requires C, 41.0; H, 5.1; N, 22.3%); *M* (FAB mass spectrum) 879 (calc. 878), (osmometric) 780; ν_{max} 1656, 1650 cm^{-1} (NO); $\delta_H(CD_2Cl_2)$ 5.89, 5.79 (2 H, s; 1 H, s; $Me_2C_3\mathit{H}N_2$); 2.49, 2.35 [6 H, s; 12 H, s; $(C\mathit{H}_3)_2C_3HN_2$].

X-Ray crystallography

Crystals of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]\cdot 2Me_2CO$ and $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]\cdot CCl_4$ suitable for X-ray work were obtained as mentioned above. All measurements were made at 150 K using a Delft Instruments FAST TV area-detector diffractometer positioned at the window of a rotating-anode generator using Mo-Kα radiation ($\lambda = 0.710\,69$ Å) by following previously described procedures.[10] The data were corrected for Lorentz-polarisation factors and also for absorption (DIFABS).[11] The structures were solved by direct methods (SHELXS)[12] and refined on F^2 by full-matrix least squares (SHELXL 93)[13] using all unique data. In both cases, the non-hydrogen atoms were anisotropic. In $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]\cdot 2Me_2CO$, the hydrogen atom attached to O(1) was located from difference maps and refined freely whilst those attached to C(4), also located from difference maps, were kept fixed; the remaining hydrogen atoms in this molecule and all hydrogens in $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]\cdot CCl_4$ were allowed to ride on their parents in idealised positions. For the hydrogen atoms the U_{iso} values were set at 1.2 (⊃CH, OH) or 1.5 (CH_3) times the U_{eq} of the parent atom. In $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]\cdot 2Me_2CO$ the two molecules of solvent (acetone) per complex refined without any problem, but in $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]\cdot CCl_4$ each complex dimer was associated with two molecules of half-occupied solvent (carbon tetrachloride), which were refined with 'ISOR' restraints 0.005 (C) and 0.015 (Cl). Sources of scattering factors were as in ref. 13. The calculations were carried out on a 486DX2/66 personal computer. The crystal data and details of data collection and structure refinement are presented in Table 2. Selected bond lengths and angles are given in Tables 3 and 4.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/562.

Results and Discussion

Syntheses

The diiodo species $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ had been previously isolated and characterised as a product of the reaction between $[Mo(NO)\{HB(dmpz)_3\}I_2]$ and refluxing 4-hydroxy-4-methylpentan-2-one.[4] At that time we believed that the formation of this μ-oxo species was probably due to the presence of water generated by the dehydration of diacetone alcohol, but we did not further clarify the reaction mechanism. However, we have subsequently noticed many times that, as mentioned in the

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‡ Spectroscopic data obtained from $[\{Mo(NO)[HB(dmpz)_3]I\}_2(\mu\text{-O})]$ described in ref. 4: ν_{max}(KBr) 1682 (NO), 1663 (NO), 744 cm^{-1} (MoOMo); δ_H(220 MHz, CD_2Cl_2) 6.02, 5.92, 5.78, 5.71, 5.58, 5.45 (1 H, s; 1 H, s; 1 H, s; 1 H, s; 1 H, s; 1 H, s; $Me_2C_3\mathit{H}N_2$); 3.23, 3.18, 2.49, 2.44, 2.40, 2.38, 2.37, 2.27, 0.99, 0.97 [3 H, s; 3 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s; $(C\mathit{H}_3)_2C_3HN_2$].

Table 1 Cyclic voltammetric data obtained from [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O]

X	Base electrolyte	Reduction processes					Oxidation process	
		E_f^1 (ΔE_p)[a,b]	E_f^1[c]	E_f^2 (ΔE_p)[b,d]	E_f^2[c]	ΔE_f[e] ($E_f^1 - E_f^2$)	E_f^3 (ΔE_p)[b]	E_f^3[c]
I	[NBu$_4$][PF$_6$]	−0.50(76)[f]	−1.01	−1.49(170)	−2.00	990	+1.56[g]	+1.05[g]
	[NBu$_4$][BF$_4$]	−0.45(110)	−1.00	−1.43(240)	−1.98	980	*h*	—
Cl	[NBu$_4$][PF$_6$]	−0.65(72)	−1.11	−1.87[i]	−2.33[i]	(1220)[j]	+1.53(70)	+1.07

[a] First reduction wave, in V ($E_p^a - E_p^c$, in mV), scan rate 50 mV s^{-1}. [b] *vs.* SCE. [c] Ferrocene–ferrocenium couple ($\Delta E_p = E_p^a - E_p^c$ = 80–120 mV). [d] Second reduction wave; scan rate 50 mV s^{-1}. [e] In mV. [f] Quasi-reversible at scan rates >100 mV s^{-1}, irreversible at 50 mV s^{-1}. [g] E_p^a, no cathodic peak. [h] Not observed. [i] E_p^c, no anodic peak. [j] Estimate based on difference between cathodic peaks.

introduction, when [Mo(NO){HB(dmpz)$_3$}X$_2$] (X = Cl or I), or *impure* [Mo(NO){HB(dmpz)$_3$}X(Z)] (Z = alkoxide, alkylamide, *etc.*), is passed down an alumina or silica gel column [{Mo(NO)-[HB(dmpz)$_3$]X}$_2$O] is invariably detected.

Our present work establishes that [{Mo(NO)[HB(dmpz)$_3$]-I}$_2$O] can be prepared, although never in large quantities, *via* the reaction of [Mo(NO){HB(dmpz)$_3$}I$_2$] with water in refluxing toluene, and we are of the opinion that the HI probably generated on the basis of the stoichiometry of these reactions may inhibit significant conversion of [Mo(NO){HB(dmpz)$_3$}I$_2$] into the μ-oxo species. Water is *essential* for the reaction: when it is omitted, and solvents and reaction conditions are kept scrupulously dry, the μ-oxo species are absent. Oxygen/air is not essential although water can be introduced to an otherwise dry system in a moist air stream thereby giving rise to traces of μ-oxo species. Heat appears to be necessary and moist refluxing toluene is particularly convenient.

From a very careful reexamination of the behaviour of [Mo(NO){HB(dmpz)$_3$}I$_2$] in wet refluxing toluene we have discovered that the hydroxo species [Mo(NO){HB(dmpz)$_3$}I(OH)] and [Mo(NO){HB(dmpz)$_3$}(OH)$_2$], both known compounds,[14] are formed, and, furthermore that [Mo(NO){HB(dmpz)$_3$}-I(OH)] reacts with [Mo(NO){HB(dmpz)$_3$}I$_2$] forming μ-oxo species.

Our first real insights into this chemistry came from the isolation of the asymmetric species [I{HB(dmpz)$_3$}(NO)-Mo–O–Mo(NO){HB(dmpz)$_3$}(OH)] by one of the procedures (Method 1) described above and, indirectly, from the mode of formation of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$(μ-O)], by heating [Mo(NO){HB(dmpz)$_3$}Cl(OH)] with [Mo(NO){HB(dmpz)$_3$}-Cl$_2$] in refluxing toluene in the presence of NEt$_3$ (to facilitate removal of HCl). It is possible, of course, that [I{HB-(dmpz)$_3$}(NO)Mo–O–Mo(NO){HB(dmpz)$_3$}(OH)] could be obtained by partial hydrolysis of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$-(μ-O)], and the existence of this compound and of [I{HB-(dmpz)$_3$}(NO)Mo–O–Mo(NO){HB(dmpz)$_3$}Cl][6] has encouraged us to seek other more reliable routes to such asymmetric species which will be described elsewhere.[15]

Although we had previously reported the synthesis of [Mo(NO){HB(dmpz)$_3$}(OH)$_2$] by reaction of the parent diiodide with silver acetate and water, its discovery as a product arising from reaction of [Mo(NO){HB(dmpz)$_3$}I$_2$] with water or hydroxide on the silica columns prompted a reinvestigation of this compound. We have determined its molecular structure, and have found that when it is heated at 150 °C *in vacuo* it is dehydrated, apparently forming the bis(μ-oxo) species [{Mo(NO)[HB(dmpz)$_3$](μ-O)}$_2$], the formulation of which is based on its molecular weight, established by mass spectrometry and osmometry, and on spectral differences with the parent bis(hydroxide).

All complexes provide reasonably satisfactory elemental analyses, and their electron impact (EI) or FAB mass spectra exhibit molecular ions.

Spectroscopic studies

The IR spectra of the binuclear compounds contain ν_{BH} in the region 2450–2495 cm^{-1} in addition to other bands attributable to the presence of the HB(dmpz)$_3$ ligand. The binuclear compounds also exhibit two NO stretching frequencies, consistent with the general structure already established for [{Mo(NO)-[HB(dmpz)$_3$]I}$_2$O].[4] The asymmetric Mo–O–Mo stretching mode appears in the range 744–776 cm^{-1}. The spectrum of [Mo(NO){HB(dmpz)$_3$}(OH)$_2$] has already been reported,[14] ν_{NO} occurring at 1640 cm^{-1} and ν_{OH} at 3500 cm^{-1}.

The ^{1}H NMR spectra of the μ-oxo species reflect the lack of a plane or axis of symmetry in these molecules. The protons attached to the C^4 atom of the pyrazolyl rings generally resonate in the range δ 6.05–5.27. However, the signals due to the methyl groups, which appear as not less than ten singlets, occur over a range of *ca.* 2.5 ppm (δ 3.23–0.69), which is unusual since such methyl signals normally occur in the region δ 2–3. From the detailed crystal and molecular structures of the two enantiomers of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$O] (Fig. 1), it is clear that two of the pyrazolyl rings are face-to-face, and so ring-current shielding must be responsible for the extension of methyl proton chemical shifts to such high fields. However, it is not possible to determine the precise molecular structures of the new binuclear species solely on the basis of their ^{1}H NMR spectra.

The ^{1}H NMR spectrum of the diiodide [{Mo(NO)[HB-(dmpz)$_3$]I}$_2$O] prepared in this study is too similar to that of the originally reported species[4] to permit a clear decision to be made as to whether the compounds are identical, or are isomers, particularly as the spectrum of the original diiodide was obtained at a different frequency and under less ideal conditions than that of the species reprepared in this work. That isomers can apparently be sufficiently differentiated is clear from the observed spectra of the two species with formula [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] and from that of [Cl{HB(dmpz)$_3$}(NO)Mo–O–Mo(NO){HB(dmpz)$_3$}I].[5]

Electrochemical studies

The binuclear compounds [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O] (X = Cl or I) undergo *three* electrode reactions at a rotating platinum-bead electrode in dichloromethane, using either [NBu$_4$][PF$_6$] or [NBu$_4$][BF$_4$] as base electrolyte (Table 1): two one-electron reductions and one one-electron oxidation. Although we did not determine the number of electrons transferred in the electrode reactions with these new compounds directly by coulometry, from spectroscopic studies described in this paper and by comparison with our earlier work[6] it is clear that one electron is involved in each process.

The reduction processes correspond to the formation of [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O]$^{-,2-}$. The first reduction process in both halides is reversible or quasi-reversible, and the value of E_f^1 for the chloride is *ca.* 100 mV more anodic than that for the iodide, consistent with electronegativity effects. The second reduction process in each compound is irreversible, and when X = Cl we were able only to detect E_p^c since the reduction is extremely close to the decomposition wave of the medium. Only for the iodide is it possible to determine ΔE_f ($E_f^1 - E_f^2$) with precision, *vis-à-vis* 990 mV, but we would estimate ΔE_f ($E_f^1 - E_f^2$) for the chloride to be of the order of 1200 mV. Comparable values of ΔE_f have been observed in cyclic voltammograms of [{Mo(NO)[HB(dmpz)$_3$]X}$_2$(NHC$_6$H$_4$NH)]

(X = Cl or I, 850 or 1030 mV),[16] and we have recently discovered a very large interaction (>1000 mV) in [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$(pyz)] (pyz = pyrazine)[17] although the metal ions in the latter have a different electronic configuration (17 valence electrons as opposed to 16 in the μ-oxo and iodo species).

Thus, there are two reduction potentials in these binuclear μ-oxo species, consistent with the presence of two strongly interacting redox centres. That we failed to detect the second anodic process in earlier measurements[6] of the two forms of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] was partly due to our choice of medium and to electrochemical cell design, although, as mentioned in the introduction, we expected that there would be a large interaction between the redox centres, and that the second reduction wave could occur within, or at potentials more negative than, the reductive decomposition of the medium. Our suspicions have been borne out by the results reported here, and we note that the chloro-species described here has a reduction potential close to that of the principal isomer of [Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] reported earlier (−0.56 V).[5]

We also observed a cathodic electron transfer, at *ca.* +1.5 V (*vs.* SCE), consistent with the formation of unstable [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O]$^+$. We have not previously reported cathodic electrode processes in species of the type [Mo(NO){HB(dmpz)$_3$}X(Y)] (X, Y = anionic ligands) but they do occur in the pyridine-containing species [Mo(NO){HB(dmpz)$_3$}X(py)] and related 17-valence-electron species.[18] The oxidation process in [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] is reversible but we have been unable to generate the monocation in sufficient quantity for characterisation.

Reduction of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] and EPR spectroscopic studies of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O]$^-$

From the electrochemical data reported above, the monoanion [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O]$^-$ should be accessible by reduction of the neutral precursor using cobaltocene. We chose the chloride to test this, since our earlier experience with iodo derivatives suggested that dissociation of I$^-$ from reduced compounds might complicate spectral analysis, even though we found little evidence of this from the voltammetric studies of the iodide. Treatment of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] with cobaltocene in dichloromethane–thf (1:1 v/v) afforded the monoanion, whose EPR spectrum exhibited $g_{\text{iso}} = 1.9790$ and $A_{\text{iso}} = 5.0$ mT, consistent with a single electron coupled to a molybdenum nucleus [sextet, ^{95}Mo (15.72%) and ^{97}Mo (9.46%), $I = \frac{5}{2}$]. The EPR spectrum varies with temperature, being slightly broad at room temperature and continuing to broaden up to *ca.* 300 K, but sharpening on cooling to 230 K. In contrast, [{Mo(NO)[HB(dmpz)$_3$]I}$_2$O]$^-$, similarly prepared, did not show a temperature-variable spectrum over the range 280–310 K. The behaviour of these reduced species in a variety of solvents and over a temperature range warrants further study, which is not reported here. However, we observed that A_{Mo} remains very close to 5.0 mT throughout the temperature range investigated. If the electron was effectively *delocalised* over both metal centres we would have expected A_{Mo} to be *ca.* 2.5 mT, consistent with a situation where the electron spends an equal amount of time on each metal centre. However, in view of the observation of a 5.0 mT hyperfine coupling, and the appearance of very weakly solvatochromic absorption bands in the NIR spectrum of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O]$^-$, we are inclined to revise our earlier view that this monoanion exhibits Class III behaviour. We now think that the compound is better categorised as valence-trapped (Class I behaviour) on the EPR time-scale at or just below room temperature.[6,19]

Intuitively, one might not expect such a result, particularly in view of the very close proximity of the two metal centres. However, we can offer a reasonably satisfactory explanation for this behaviour. If the Mo–N–O bond system defines the *z* axis and the remaining donor atoms lie on the other axes, we may assume that the d_{xz} and d_{yz} orbitals are stabilised by interaction with the π*(NO) orbitals leaving the d_{xy} orbital as the uppermost empty molecular orbital (LUMO) in the complex. This view is well substantiated in six-co-ordinate transition-metal nitrosyl systems.[20] Taking into account the structures of [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O] and the assumption that the Mo–N–O group is not in the same plane, they are actually in perpendicular planes as indicated in Figs. 1 and 3, then the d_{xy} orbitals on each metal are orthogonal to each other. Thus they cannot overlap *via* the oxygen p orbitals, as we previously suggested. Hence, in [{Mo(NO)[HB(dmpz)$_3$]X}$_2$O]$^-$ the metal configuration can be represented as $\{(d_{xy})^0\text{–O–}(d_{xy})^1\}$, and must be valence-trapped.

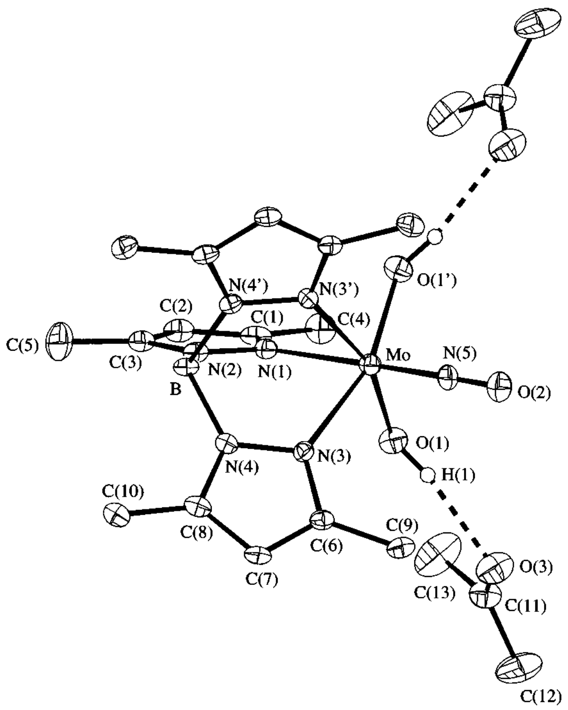


Fig. 2 Structure of [Mo(NO){HB(dmpz)$_3$}(OH)$_2$]·2Me$_2$CO

The IR spectrum of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O]$^-$ in dichloromethane exhibits two NO stretching vibrations, at 1603 and 1578 cm^{-1}, 91 and 87 cm^{-1} lower in energy than those of the precursor. The corresponding [{Mo(NO)[HB(dmpz)$_3$]I}$_2$O]$^-$ behaves similarly (ν_{NO} 1670 and 1652 cm^{-1}) although the NO stretching frequencies do not decrease in energy nearly as much as the corresponding chloride (23 and 16 cm^{-1}). We would not expect *a priori* such a big difference in these halides, and we have no really satisfactory explanation for this behaviour. It is possible, of course, that the structure of the dichloro species is different to that of its diiodo analogue, but we have been unable to obtain single crystals of [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$O] to ascertain this.

Crystal structures of [Mo(NO){HB(dmpz)$_3$}(OH)$_2$]·2Me$_2$CO and [{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)]·CCl$_4$

In the crystal structure of [Mo(NO){HB(dmpz)$_3$}(OH)$_2$]·2Me$_2$CO each molecule of acetone is bound to the bis(hydroxide) by hydrogen bonding, *e.g.* O(1)–H(1)···O(3) [O(1)–H(1) 0.87, H(1)···O(3) 2.07, O(1)···O(3) 2.93 Å; O(1)–H(1)–O(3) 169°] and van der Waals forces. The bis(hydroxide) complex, Fig. 2, possesses a mirror plane of symmetry passing through Mo, NO, B and one N$_2$C$_3$HMe$_2$ moiety of the dmpz ligand. The co-ordination sphere of the Mo atom is distorted octahedral, the deviations from ideal geometry being caused by the rigid framework of the tridentate HB(dmpz)$_3$ ligand which occupies one triangular face of the octahedron. The N–Mo–N angles involving these atoms range from 76.38(14) to 84.52(10)°. Other angles involving atoms in the *cis* positions are 83.16(10)–105.6(2)°. The *trans* angle involving the NO ligand is nearly linear [176.5(2)°], whilst those involving the OH ligands [160.62(11)°] show larger variations from linearity. Of the three Mo–N (dmpz) bonds, that lying *trans* to the NO ligand [2.238(4) Å] is significantly longer than the other two [2.210(3) Å]. The Mo–N (NO) and Mo–O (OH) bond lengths are 1.748(4) and 1.928(2) Å, respectively. The dimensions of the latter are consistent with related Mo–O (alkoxide) bond distances observed previously[8,14,21] and are consistent with significant O–Mo p_π–d_p bonding. The Mo–N(5)–O(2) angle is close to linearity [176.4(4)°], with an N–O distance of 1.223(5) Å. The bond lengths and angles of the HB(dmpz)$_3$ ligand are as expected, but the expected three-fold axis is replaced by a mirror symmetry, the dihedral angles between the pyrazole ring planes being 110.0, 125.0 and 125.0°. The N–B–N angles [105.5(4)–108.5(3)°] are slightly smaller than the ideal tetrahedral value (109.5°).

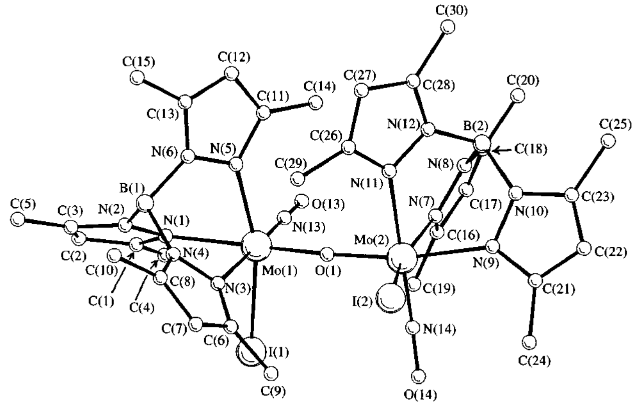


Fig. 3 Structure of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)]·CCl$_4$

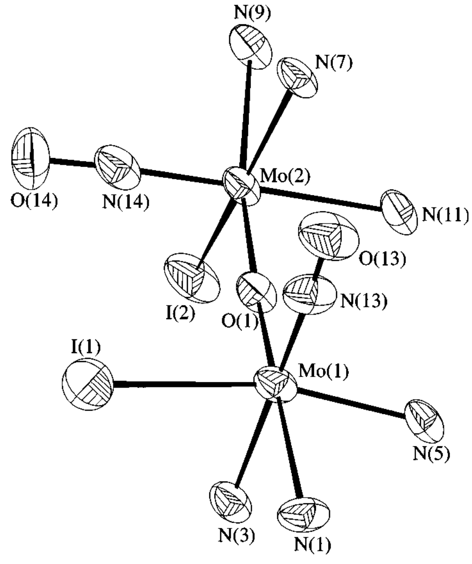
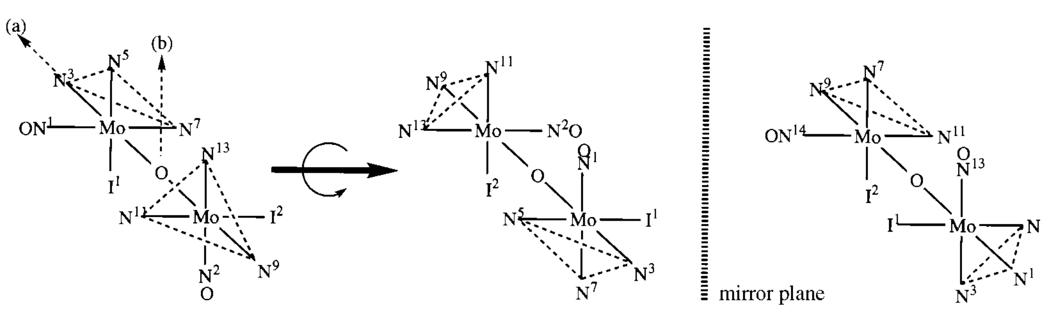


Fig. 4 Simplified representation of the metal co-ordination sphere in [{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)]·CCl$_4$

In the crystal structure of [{Mo(NO)[HB(dmpz)$_3$]I}$_2$(μ-O)]·CCl$_4$ (Fig. 3), the dinuclear molecules and carbon tetrachloride solvates (1 : 1) are held together by van der Waals forces. The complex is constructed from two {Mo(NO)[HB(dmpz)$_3$]I} units bridged by an oxo group, its overall geometry being derived from two distorted octahedra sharing a corner and having an eclipsed configuration. The geometry of the binuclear core is illustrated more clearly in Fig. 4. The distortions in the octahedral geometry are reflected in the angles 75.7(3)–104.1(3)° involving the *cis* atoms, and 161.9(2)–178.0(4)° involving the *trans* atoms. The crystallographic study clearly establishes that the present compound is the enantiomer **B** depicted in Fig. 1. The enantiomers **A** and **B** can be *notionally* constructed by rotation by 180° of the Mo′ fragment with respect to the fixed Mo fragment, but the diastereomeric relationship is more clearly illustrated in Fig. 5. The Mo–O (bridge) distances in the two diastereomers, 1.86(2) and 1.93(2) Å in **B** and 1.901(7) and 1.912(7) Å in **A**, are virtually the same within experimental error and suggest a slightly unsymmetrical Mo–O–Mo bridge system. These Mo–O bond lengths are comparable with those (1.86–1.92 Å) found in the related alkoxide complexes [Mo(NO){HB(dmpz)$_3$}X(Y)] [X = OPr^i, Y = OPr^i or OEt; X = I, Y = O(CH$_2$)$_3$Br][14,21] and [Mo(NO){HB(4-Cl-3,5-Me$_2$C$_3$N$_2$)$_3$}Cl(OPr^i)],[8] and, as observed before, the relatively short values are consistent with partial π bonding between the O and the two Mo atoms, which is also enhanced by the near-eclipsed arrangement of the two octahedra.[4] The Mo–O–Mo angle deviates significantly from linearity [171.7(4)° in **B**, 171.0(5)° in **A**], which may be explained by the steric requirements of the two bulky HB(dmpz)$_3$ ligands in the dimer. We observe that two dmpz moieties [N(5),N(6),C(11)–C(15) and N(11), N(12),C(26)–C(30)] from two ligands, which lie nearly parallel to each other (dihedral angle of only 2.2°), have quite short non-bonded contacts [C(11)···C(29) 3.324 and N(5)···C(29) 3.336 Å] reflecting the degree of steric crowding within these bimetallics. The dihedral angles between the N$_2$C$_3$ planes in the HB(dmpz)$_3$ ligands bonded to Mo(1) and Mo(2) have values of 111.0, 121.3, 126.3 and 101.2, 124.7 and 134.1°, respectively, the larger of these values involving planes that 'embrace' the oxo and iodide ligands. The Mo–N (dmpz) bond lengths vary from 2.149(9) to 2.294(9) Å which compare very well with those in the enantiomer **A** [2.13(3)–2.28(3) Å][4] and in [Mo(NO){HB(dmpz)$_3$}(OH)$_2$] [2.207(3)–2.236(4) Å], and are consistent with the π-bonding capacity of the *trans* ligand. The Mo–I and Mo–N (NO) distances of 2.766(2), 2.788(1) and 1.762(11) and 1.804(10) Å, respectively, are close to the corresponding values in **A** [2.752(5), 2.777(5) and 1.73(3) and 1.74(3) Å].[4] The Mo–N–O angles [176.2(10), 177.1(9)°] are slightly bent from linearity, with N–O distances of 1.214(11) and 1.215(11) Å. The dimensions of the HB(dmpz)$_3$ ligands are as expected with N–B–N angles close to tetrahedral [106.5(10)–110.8(9)°].



A, as shown in ref. 4

A, rotated by 90° clockwise about axis (a), and 180° clockwise about axis (b)

B, as shown in Fig. 4

Fig. 5 Relationship between enantiomers **A** and **B**; the atom labelling of **A** is that used in ref. 4 and that of **B** is that shown in Fig. 4

Table 2 Crystal data and details of data collection and refinement for $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]\cdot 2Me_2CO$ **1** and $[\{Mo(NO)[HB(dmpz)_3]I\}_2(\mu\text{-}O)]\cdot CCl_4$ **2** [a]

	1	**2**
Formula	$C_{15}H_{24}BMoN_7O_3\cdot 2C_3H_6O$	$C_{30}H_{44}B_2I_2Mo_2N_{14}O_3\cdot CCl_4$
M	573.32	1269.90
Crystal system	Orthorhombic	Triclinic
Space group	*Pnma* (no. 62)	$P\bar{1}$ (no. 2)
a/Å	16.136(1)	10.958(2)
b/Å	18.336(2)	13.336(3)
c/Å	8.9980(9)	18.602(2)
α/°	—	100.95(1)
β/°	—	100.80(1)
γ/°	—	99.03(1)
U/Å^3	2662.2(4)	2569.1(7)
Z	4	2
D_c/g cm^{-3}	1.430	1.642
F(000)	1192	1240
μ(Mo-Kα)/cm^{-1}	5.36	19.42
Crystal size/mm	0.18 × 0.16 × 0.16	0.30 × 0.18 × 0.15
θ Range for data collection/°	2.22–25.01	1.93–25.08
hkl Ranges	−13 to 17, −15 to 20, −10 to 10	−12 to 12, −15 to 15, −20 to 19
Total data measured	9546	10 327
Total unique (R_{int})	2159 (0.0532)	6799 (0.0629)
Absorption correction factors: minimum, maximum	0.921, 1.038	0.848, 1.154
No. parameters, data	182, 2159	577, 6799
ρ_{min}, ρ_{max}/e Å^{-3}	−0.451, +0.652	−0.651, +1.434
$(\Delta/\sigma)_{max}$	0.001	0.003
Goodness of fit	0.950	1.010
$R1$	0.0575 (0.0340) [b]	0.0883 (0.0613) [b]
$wR2$	0.0792 (0.0768) [b]	0.1695 (0.1626) [b]

[a] Details in common: cell parameters from 250 reflections, $T = 150(2)$ K. [b] The $R1$ and $wR2$ values for data with $F_o > 4\sigma(F_o)$ are given in parentheses. $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = [F_o^2 + 2F_c^2]/3$ and $a = 0.0341$ for complex **1** and 0.0750 for **2**.

Table 3 Selected bond lengths (Å) and angles (°) for $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]\cdot 2Me_2CO$

Mo–N(5)	1.748(4)	Mo–O(1)	1.928(2)
Mo–N(3)	2.210(3)	Mo–N(1)	2.238(4)
N(5)–Mo–O(1)	98.73(11)	O(1)–Mo–O(1′)*	105.4(2)
N(5)–Mo–N(3)	92.71(12)	O(1)–Mo–N(3)	87.76(10)
O(1)–Mo–N(3′)*	160.87(11)	N(3)–Mo–N(3′)*	76.38(14)
N(5)–Mo–N(1)	176.5(2)	O(1)–Mo–N(1)	83.37(10)
N(3)–Mo–N(1)	84.52(10)		

The primed atoms belong to one and the same molecule and are generated by the symmetry operation $x, \frac{1}{2} - y, z$.

By constructing space-filling models of enantiomers **A** and **B** it is relatively easy to see that the steric arrangements in these two forms are particularly comfortable. There is no major steric hindrance, but it is clear that interconversion by rotation about the O–Mo′ bond is likely to be difficult because of mutual interference of the methyl groups on the face-to-face pyrazolyl rings of the adjacent $HB(dmpz)_3$ ligands. We have failed to detect any change in the ^{1}H NMR spectrum of diastereomer **B** on heating to *ca.* 120° which confirms the difficulty of rotation about either of the Mo–O bonds. From the same space-filling considerations, isomers **C**–**H** appear to be sterically very crowded, and we have so far obtained no evidence to substantiate their existence.

Mechanism of formation of binuclear μ-oxo compounds

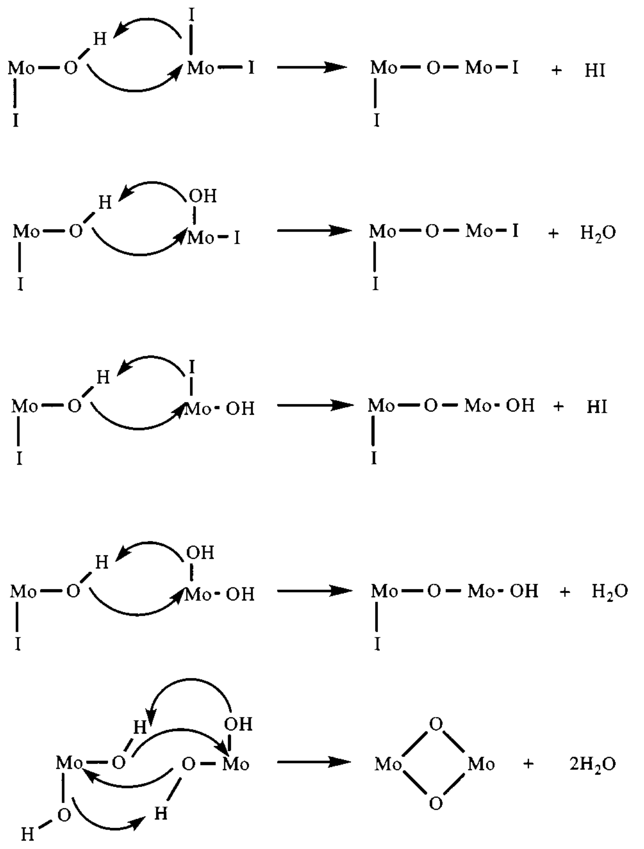
Our mechanistic investigations have been carried out using mainly the iodo precursor $[Mo(NO)\{HB(dmpz)_3\}I_2]$. From the experimental information presented above, and from additional observations summarised below, we believe that the formation of μ-oxo species in this system is due to the intermediacy of $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$, and probably $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$, in reaction systems using the diiodide as precursor. The following observations support these particular conclusions.

Table 4 Selected bond lengths (Å) and angles (°) for $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]\cdot CCl_4$

I(1)–Mo(1)	2.766(2)	I(2)–Mo(2)	2.7878(13)
Mo(1)–N(13)	1.804(10)	Mo(2)–N(14)	1.762(11)
Mo(1)–O(1)	1.912(7)	Mo(2)–O(1)	1.901(7)
Mo(1)–N(1)	2.248(9)	Mo(2)–N(7)	2.202(9)
Mo(1)–N(3)	2.294(9)	Mo(2)–N(9)	2.218(9)
Mo(1)–N(5)	2.149(9)	Mo(2)–N(11)	2.279(9)
N(13)–Mo(1)–O(1)	95.8(4)	N(14)–Mo(2)–O(1)	93.7(4)
N(13)–Mo(1)–N(5)	94.0(4)	N(14)–Mo(2)–N(7)	95.2(4)
O(1)–Mo(1)–N(5)	96.4(3)	O(1)–Mo(2)–N(7)	92.4(3)
N(13)–Mo(1)–N(1)	94.9(4)	N(14)–Mo(2)–N(9)	92.8(4)
O(1)–Mo(1)–N(1)	168.3(3)	O(1)–Mo(2)–N(9)	166.9(3)
N(5)–Mo(1)–N(1)	78.0(4)	N(7)–Mo(2)–N(9)	75.7(3)
N(13)–Mo(1)–N(3)	178.0(4)	N(14)–Mo(2)–N(11)	176.4(4)
O(1)–Mo(1)–N(3)	85.9(3)	O(1)–Mo(2)–N(11)	88.1(3)
N(5)–Mo(1)–N(3)	86.8(3)	N(7)–Mo(2)–N(11)	87.9(3)
N(1)–Mo(1)–N(3)	83.5(3)	N(9)–Mo(2)–N(11)	86.1(3)
N(13)–Mo(1)–I(1)	89.1(3)	N(14)–Mo(2)–I(2)	91.3(3)
O(1)–Mo(1)–I(1)	98.6(2)	O(1)–Mo(2)–I(2)	104.1(2)
N(5)–Mo(1)–I(1)	164.3(2)	N(7)–Mo(2)–I(2)	161.9(2)
N(1)–Mo(1)–I(1)	86.4(3)	N(9)–Mo(2)–I(2)	87.1(2)
N(3)–Mo(1)–I(1)	89.6(2)	N(11)–Mo(2)–I(2)	85.2(2)
Mo(2)–O(1)–Mo(1)	171.7(4)		

(*a*) After refluxing freshly prepared, spectroscopically pure, $[Mo(NO)\{HB(dmpz)_3\}I_2]$ under argon in *dry* toluene for not less than 48 h, there is *no* IR spectral evidence for $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ in the reaction mixture prior to chromatography on silica gel.

(*b*) *Direct* treatment of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ with water in toluene affords $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$ and only very small amounts of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$, both detected spectroscopically prior to chromatography. While the bis(hydroxide) is *not* formed in significant amounts in the reaction of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ with water in toluene, it can be produced in reasonable yields by reaction of $[Mo(NO)\{HB(dmpz)_3\}I_2]$ with water and silver acetate, only small amounts of other green compounds, possibly $[Mo(NO)\{HB(dmpz)_3\}$-



Scheme 1 Some possible mechanisms for the formation of µ-oxo molybdenum complexes [NO and $HB(dmpz)_3$ ligands omitted for clarity]

$I(OH)]$ or $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$, being produced as by-products.

(*c*) On passing freshly prepared, spectroscopically pure (dry), $[Mo(NO)\{HB(dmpz)_3\}I_2]$ down a silica gel column using dry dichloromethane as eluent, there is clear visual evidence for $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$ (olive green) and $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ (light green), in addition to starting material, on the column, and both species can be isolated in spectroscopically characterisable yields; there are traces of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$ (red-brown) and possibly $[\{Mo(NO)[HB(dmpz)_3](\mu\text{-}O)\}_2]$ (red-pink) at the top of the column.

(*d*) After refluxing freshly prepared, spectroscopically pure, $[Mo(NO)\{HB(dmpz)_3\}I_2]$ under argon in thoroughly degassed (*i.e.* containing minimum amounts of O_2) toluene *containing water* followed by chromatography on silica gel using dichloromethane as eluent, there is clear spectroscopic (and visual) evidence for the starting material $[Mo(NO)\{HB(dmpz)_3\}I_2]$ (grey-black), $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$ (olive green), $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ (green) and traces of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$ (red-brown, mainly at the top of the column).

(*e*) The compound $[\{Mo(NO)[HB(dmpz)_3](\mu\text{-}O)\}_2]$ can be formed by heating $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$ *in vacuo*, and is sometimes formed at the top of chromatography columns down which $[Mo(NO)\{HB(dmpz)_3\}I_2]$ in dichloromethane has been passed and from which $[Mo(NO)\{HB(dmpz)_3\}I_2]$, $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$ and $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ have been extracted. Low yields of this compound can be eluted using acetone.

From this body of evidence, we conclude that the monohydroxide $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$, which is generated by reaction of the diiodide with water in toluene solution, is the precursor of the µ-oxo species $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$. This monohydroxo species reacts with additional $[Mo(NO)\{HB(dmpz)_3\}I_2]$ giving $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$. We have emulated this reaction using stoichiometric mixtures of the hydroxoiodide and diiodide, and although we were not able to separate and characterise each component of the mixture of products formed we obtained clear and unequivocal evidence for the occurrence of $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ in the reaction products. Further, we have shown that $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2O]$ is formed by heating 1:1 molar equivalents of $[Mo(NO)\{HB(dmpz)_3\}Cl(OH)]$ and $[Mo(NO)\{HB(dmpz)_3\}Cl_2]$ in toluene, in the presence of NEt_3. The amine assists in the elimination of HCl from this reaction and may also be involved in deprotonation of the hydroxo group, thereby generating the nucleophilic intermediate $[Mo(NO)\{HB(dmpz)_3\}Cl(O^-)]$.

The discovery that both $[Mo(NO)\{HB(dmpz)_3\}I(OH)]$ and $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$ are generated from the pure diiodide in the absence of added water on a silica gel column is initially surprising. However, although the silica gel had been oven-dried under nitrogen maintained in a dry nitrogen atmosphere, it is impossible to prevent some adsorption of water when the columns are being prepared. We think that it is this adsorbed water which reacts with $[Mo(NO)\{HB(dmpz)_3\}I_2]$ on the column, forming the mono- and the bis-hydroxides. The monohydroxide could then react with the diiodide, as suggested above, giving $[\{Mo(NO)[HB(dmpz)_3]I\}_2O]$. We suggest also that $[\{Mo(NO)[HB(dmpz)_3](\mu\text{-}O)\}_2]$ can be formed by dehydration of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$ on the column and it is also generated by simple thermal dehydration of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$. Possible mechanisms are illustrated in Scheme 1.

Conclusion

In addressing questions (*i*)–(*iii*) posed in the introduction we interpret our synthetic results, coupled to the mechanistic rationalisation, as revealing that $[\{Mo(NO)[HB(dmpz)_3]X\}_2O]$ is formed from $[Mo(NO)\{HB(dmpz)_3\}X(OH)]$ and, to a lesser extent $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$. The species $[Mo(NO)\{HB(dmpz)_3\}X(OH)]$ is the key intermediate and is formed in toluene solution directly from the reaction of the dihalide with water. Hydroxylation of dry $[Mo(NO)\{HB(dmpz)_3\}X_2]$ can also occur on silica gel columns. Dehydrohalogenation of 2 mole equivalents of $[Mo(NO)\{HB(dmpz)_3\}X(OH)]$, giving $[\{Mo(NO)[HB(dmpz)_3]X\}_2O]$, or dehydration of $[Mo(NO)\{HB(dmpz)_3\}(OH)_2]$, giving $[\{Mo(NO)[HB(dmpz)_3](\mu\text{-}O)\}_2]$, occurs on heating and/or on silica gel columns. From our synthetic and ^1H NMR spectral work it appears that the formation of the µ-oxo dinuclear species is stereospecific under the conditions reported here, giving a racemic mixture of enantiomers **A** and **B** only since we have been unable to detect any other species of identical stoichiometry. We were perhaps lucky to extract crystals of enantiomer **A** on the previous occasion,[4] while under the crystallisation conditions used in this work we obtained **B**.

The binuclear species $[\{Mo(NO)[HB(dmpz)_3]X\}_2O]$ behave electrochemically in the same way as other related binuclear species having longer bridging groups in undergoing two one-electron reduction processes. The EPR spectral analysis of the mixed-valence species $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2O]^-$ is consistent with valence-trapped behaviour.[19] This is a very rare example of valence trapping in a system with such a short bridge, and may be contrasted with the behaviour of $[\{Ru(NH_3)_5\}_2(\mu\text{-}O)]^{5+}$ in which the unpaired electron is delocalised over the Ru–O–Ru framework.[22] There is a formal electronic difference here, however, since the dimolybdenum µ-oxo species is generated by reduction and therefore *addition* of an electron to a M–O–M framework non-bonding orbital, whereas $[\{Ru(NH_3)_5\}_2(\mu\text{-}O)]^{5+}$ is generated by oxidation of $[\{Ru(NH_3)_5\}_2(\mu\text{-}O)]^{4+}$, causing *removal* of an electron from a bonding orbital (see Fig. 2), which occurs without loss of delocalisation over the M–O–M framework. The electronic situation in $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2O]^-$ may be compared with that in $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(OC_6H_4O\text{-}p)]^-$ in which the unpaired electron is also apparently valence trapped at room temperature,[23] in direct contrast to $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(NHC_6H_4NH\text{-}p)]^-$ in which it is delocalised.[24]

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