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Syntheses and electrochemistry of bimetallic complexes containing cyclohexanediolate or cyclopentanediolate bridges

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The bimetallic complexes [{ML(NO)Cl}$_2$ (1,x-$O_2C_nH_{2n-2}$)] [L = HB(3,5-$Me_2C_3HN_2$)$_3$; n = 6, x = 2–4, M = Mo; n = 5, x = 3, M = Mo or W], in which parts of cyclohexyl or cyclopentyl groups link two redox-active {O–ML(NO)} moieties, have been synthesized and found to exhibit two one-electron reduction processes separated by a potential difference, ΔE_f, which increases with decreasing through-bond metal–metal separation. The value ΔE_f for [{MoL(NO)Cl}$_2$(1,3-$O_2C_6H_{10}$)] is only slightly less (67 mV) than that of its aryl-bridged counterpart, [{MoL(NO)Cl}$_2$(1,3-$O_2C_6H_4$)]. However, ΔE_f for [{MoL(NO)Cl}$_2$(1,4-$O_2C_6H_{10}$)] is *ca.* 300 mV smaller than for [{MoL(NO)Cl}$_2$(1,4-$O_2C_6H_4$)] which contains a mesomeric link between the metal centres.

The ability of hydrocarbyl bridges to support metal–metal interactions has been a topic of theoretical and experimental interest since the early work on mixed-valence compounds by Robin and Day, Hush, Taube and others.[1] More recently such studies have found new importance because of their relevance to the design and study of metal–organic compounds which may form new materials of interest in molecular electronics applications.[2] Experimental measurements of metal–metal interactions in such systems provide useful data for comparison with theoretical models and electronic spectral data are frequently used to provide such information. Usually the intervalence charge-transfer band associated with electron transfer between the metal centres in a mixed-oxidation-state bimetallic molecule is used to estimate the magnitude of the interaction betweeen the metallic centres. However, electrochemical measurements can give a more direct measure of metal–metal interaction.[3] Unfortunately, in bimetallic compounds with saturated polyatomic bridging groups, interactions between the metal centres are often insufficiently large to give accurately measureable ΔE_f values. Consequently, electrochemical data have not been widely used for measuring interactions in such systems. The six-co-ordinate complexes [MoL(NO)X(OR)] [L = HB(3,5-$Me_2C_3HN_2$)$_3$, X = halide, R = hydrocarbyl] formally contain 16-electron molybdenum(II) centres (assuming that the nitric oxide binds formally as NO^+) and undergo reduction to 17-electron species formally containing Mo^I.[4] Electrochemical studies of bimetallic complexes containing bifunctional aryloxo ligands reveal strong metal–metal interactions through the aryl bridge. Thus, rather than one two-electron reduction process, these complexes exhibit two one-electron processes separated by a potential difference which reflects the extent of metal–metal interaction. For [{MoL(NO)Cl}$_2$(1,4-$O_2C_6H_4$)] this separation was found to be 460 mV while for the 1,3-substituted compound in which the sites of substitution on the aryl ligand are not mesomerically linked this value falls to 260 mV.[5] These findings, coupled with the ability of the {MoL(NO)X}$^+$ moiety to form stable alkoxide complexes,[4] render it a promising candidate for an electrochemical evaluation of metal–metal interactions through saturated bridges. In the work described here we have sought to evaluate the effect of intermetallic distance, and other structural features, on metal–metal interactions mediated by saturated cycloalkanediolate bridges.

Discussion

Synthetic studies

The reactions between [ML(NO)Cl_2] (M = Mo or W) and cyclopentanol or cyclopentane-1,3-diol were carried out following well established precedents for the formation of monoalkoxides, [MoL(NO)X(OR)] (R = hydrocarbyl).[4] Similar reactions were carried out using [MoL(NO)X_2] (X = Cl or I) and cyclohexane-1,2-, -1,3- and -1,4-diol. When an excess of diol was used monometallic species were produced, but these could not usually be isolated in a pure form. Consequently cyclopentanol was used to produce monometallic models for comparison with the bimetallic systems. The reactions with the cyclohexanediols were characterised by low yields of the bimetallic complexes. Elemental analyses are summarised in Table 1.

The separation and purification of the bi- and mono-metallic complexes is complicated by the presence of a number of isomers which are difficult to separate. Cyclohexane-1,2-diol is available as the *trans* isomer but cyclopentane-1,3-diol, cyclohexane-1,4 and -1,3-diols are supplied as mixtures of the *cis* and *trans* isomers (Fig. 1). The mixture of *cis*- and *trans*-cyclopentane-1,3-diol or cyclohexane-1,3-diol contains a full set of four diastereomers, *trans*-cyclohexane-1,2-diol has two enantiomers and cyclohexane-1,4-diol has two structural isomers. In addition to the presence of chirality in the diol ligands, the metal centre in [MoL(NO)X(OR)] is also chiral, so that the bimetallic species can contain up to four chiral centres (Fig. 2). Whilst the presence of such isomers was not expected to have a substantial effect on the electrochemical results, it did present problems in the compound purification process. Enantiomerically related compounds will not be separable by normal chromatography but, under favourable circumstances, it may be possible to separate diastereoisomers by this means.[6]

The reaction between [MoL(NO)Cl_2] and cyclopentane-1,3-diol afforded three fractions which could be separated by column chromatography. The spectroscopic data from the first

Table 1 Characterisation data for the new complexes

Compound $[\{ML(NO)Cl\}_n(Q)]$		Analysis[a]/(%)			IR[b] $\tilde{\nu}_{max}$(NO)/cm^{-1}	^{1}H NMR[c] [δ (integral multiplicity)]					
Number	Q (M_n)	C	H	N		CH (pz)	Me (pz)		Ring[d]	Q	Proton[e]
1a	1,3-OC_5H_8O (Mo_2)	43.1	6.4	20.6	1672	5.85	2.52	2.36	A	7.05	1b, 3b
		(41.3)	(5.2)	(19.3)		5.84	2.49	2.37	B	2.90	2a
						5.93	2.45	2.39	C	2.50	2b
						5.91	2.41	2.39	D	2.60–2.40	4a
						5.77	2.41	2.36	E	2.60	4b
						5.76	2.40	2.36	F	1.90	5a
										2.40	5b
							Major component				
1b	1,3-OC_5H_8O (Mo_2)	43.7	5.9	19.3	1667	5.84	2.53	2.51	A	6.90	1a, 3b
		(41.3)	(5.2)	(19.3)		5.89	2.43	2.38	B	3.00	2a, 2b
						5.76	2.43	2.38	C	2.35	4a, 5b
										1.90	4b, 5a
							Minor component				
						5.86	2.38	2.33	A	6.90	1a, 3b
						5.76	2.37	2.35	B	2.30	2a, 2b
						5.84	2.35	2.35	C	2.45	4a, 5b
										2.45	4b, 5a
2a	1,3-OC_5H_8O (W_2)	35.7	4.5	17.4	1635	5.95	2.60	2.58	A	6.90	1b, 3b
		(36.2)	(4.5)	(16.9)		5.93	2.57	2.54	B	2.70	2a
						5.85	2.48	2.26	C	2.30	2b
						5.85	2.38	2.37	D	2.45	4a
						5.83	2.36	2.36	E	2.60–2.30	4b
						5.83	2.34	2.34	F	1.80	5a
										2.25	5b
2b	1,3-OC_5H_8O (W_2)	35.4	4.4	18.8	1635	5.91	2.70	2.69	A	6.85	1a, 3b
		(36.2)	(4.5)	(16.9)		5.89	2.61	2.59	B	2.73, 2.21	2a, 2b
						5.85	2.56	2.51	C	2.70, 2.35	4a, 4b
						5.85	2.48	2.46	D	2.25, 1.72	5a, 5b
						5.83	2.38	2.37	E		
						5.83	2.35	2.33	F		
3	OC_5H_9 (Mo)	44.7	5.8	17.7	1667	5.90 (1s)	2.33 (3s)			6.90 (1br)	
		(44.0)	(5.7)	(18.0)		5.84 (1s)	2.44 (3s)			2.05 (2br)	
						5.75 (1s)	2.38 (3s)			1.76 (4br)	
							2.35 (9s)				
4	OC_5H_9 (W)	37.5	5.0	15.7	1633	5.92 (2s)	2.60 (3s)			6.76 (1br)	
		(37.9)	(4.9)	(15.5)		5.85 (2s)	2.58 (3s)			2.05 (2br)	
						5.81 (2s)	2.42 (3s)			1.76 (4br)	
							2.37 (3s)				
							2.34 (3s)				
							Major component[f]				
5a	1,4-$OC_6H_{10}O$ (Mo_2)	41.8	5.4	19.3	1665	5.83	2.51	3.35	A	6.45	a
		(41.9)	(5.2)	(19.0)		5.92	2.47	2.39	B	2.05–2.40	b,c,d,e
						5.35	2.36	2.36	C		
							Minor component[f]				
						5.94	2.53	2.37	A	6.25	a
						5.79	2.45	2.42	B	3.00	b
						5.85	2.37	2.39	C	2.30	c
										1.80	d
										1.90	e
							Major component[f]				
5b	1,4-$OC_6H_{10}O$ (Mo_2)	42.5	5.9	18.5	1667	5.84	2.45	2.40	A	6.45	a
		(41.9)	(5.2)	(19.0)		5.61	2.44	3.37	B	2.50, 2.40	b,c
						5.74	2.42	2.37	C	1.95	d,e
							Minor component[f]				
							2.54	3.36	A	6.20	a
							2.44	3.38	B	3.00	b
							2.40	2.35	C	2.25	c
										1.90	d
										1.80	e
6	1,3-$OC_6H_{10}O$ (Mo_2)	42.2	5.5	18.2	1672	5.87 (2s)	2.53 (6s)			6.27 (2br)	
		(41.9)	(5.2)	(19.0)		5.84 (2s)	2.42 (6s)			2.95 (2br)	
						5.71 (2s)	2.37 (6s)			2.16 (2br)	
							2.36 (6s)			1.81 (4br)	
							2.34 (6s)				
							2.33 (6s)				

Table 1 *continued*

Compound $[\{ML(NO)Cl\}_n(Q)]$		Analysis[a]/(%)			IR[b] $\tilde{\nu}_{max}$(NO)/cm^{-1}	^{1}H NMR[c] [δ (integral multiplicity)]				
Number	Q (M_n)	C	H	N		CH (pz)	Me (pz)	Ring[d]	Q	Proton[e]
7	1,2-$OC_6H_{10}O$ (Mo_2)	43.3	5.9	17.8	1668	5.76 (2s)	2.38 (6s)		6.29 (2br)	a
		(43.3)	(6.1)	(17.8)		5.70 (2s)	2.37 (6s)		1.86 (2br)	b
						4.85 (2s)	2.36 (6s)		3.13 (2br)	c
							2.24 (6s)		0.80 (4br)	d,e
							2.21 (6s)			
							1.55 (6s)			
8a	1,2-$OC_6H_{10}OH$ (Mo)				1665	5.98 (1s)	2.52 (3s)		5.82 (1br)	
						5.85 (1s)	2.51 (3s)		3.64 (1br)	
			8a + **8b**			5.81 (1s)	2.38 (6s)		CH_2 obscured	
		43.6	5.9	17.3			2.36 (3s)			
		(43.8)	(5.7)	(17.0)			2.34 (3s)			
8b	1,2-$OC_6H_{10}OH$ (Mo)				1672	5.91 (1s)	2.50 (3s)		6.95 (1br)	
						5.87 (1s)	2.43 (3s)		3.84 (1br)	
						5.71 (1s)	2.39 (3s)		CH_2 obscured	
							2.37 (9s)			

[a] Calculated values in parentheses. [b] Recorded from KBr discs. [c] Recorded at 400 or 270 MHz from solutions in $CDCl_3$; s = singlet, m = multiplet. [d] Assignment of signals to particular pyrazolyl rings (arbitrarily identified as A,B, *etc.*) based on COSY and NOE investigations. [e] Assigned to specific ring protons according to Fig. 3 on the basis of COSY and NOE investigations. [f] Chemical shifts for the methylene protons of the cyclohexane bridge have only been quoted to the nearest 0.05 ppm because they were obtained from cross-peak signals.

and third blue fractions indicated that they were bimetallic species, **1a** and **1b**, whilst the IR spectrum of the second green fraction indicated that it was $[\{MoL(NO)Cl\}_2(\mu\text{-}O)]$ which has been reported previously.[7] The total yield of bimetallic species was 56% with the ratio of the two bimetallic fractions being 2.7:1. This can be compared with the ratio of *cis* to *trans* isomers present in the starting ligand which was 3:1, implying that the first fraction contains the *cis* isomer and the second the *trans* isomer of the diolate ligand. Attempts were made to crystallise both fractions but any crystals formed became opaque and non-crystalline when removed from the mother-liquor. Mounting the crystals in solvent vapour did not stabilise the crystals and attempts to obtain X-ray data were abandoned. The reaction between $[WL(NO)Cl_2]$ and cyclopentane-1,3-diol was carried out similarly to give two bimetallic fractions, **2a** and **2b**. Cyclopentanol reacted with $[ML(NO)Cl_2]$ (M = Mo or W) in the presence of triethylamine to produce good yields of $[M(L)(NO)Cl(OC_5H_9)]$ (M = Mo **3** or W **4**).

The reaction between $[MoL(NO)Cl_2]$ and the cyclohexane-1,4-diol yielded two fractions containing bimetallic species, **5a** and **5b**, which could be separated by chromatography. Proton NMR studies indicated that both fractions contained mixtures of isomers. Although monometallic species could be detected in the reaction mixture, these appeared to convert into bimetallic species during purification so that attempts to isolate pure samples of the monometallic species failed. The reaction between $[MoL(NO)Cl_2]$ and cyclohexane-1,3-diol again gave low yields of bimetallic complexes and column chromatography afforded only one pure bimetallic fraction, **6**. The bimetallic complex **7** could be obtained, also in low yield, from the reaction between $[MoL(NO)Cl_2]$ and *trans*-cyclohexane-1,2-diol. A more efficient route to **7** is to synthesize the monometallic species, **8a** and **8b**, by using a large excess of diol then treat this mixture with further $[MoL(NO)Cl_2]$. Although yields of the bimetallic complex were still very low, evidence could be found for the production of only one isomer, possibly because one species is so thermodynamically unstable that it isomerises quickly into the more stable form which is isolated.

Spectroscopic studies

The IR spectra of the new compounds each contained a band attributable to ν_{max}(BH) at *ca.* 2550 cm^{-1} together with others consistent with the presence of the L ligand. In addition all contained a band attributable to ν_{max}(NO) (Table 1). These appeared in the region 1665–1675 cm^{-1} for the molybdenum complexes and 1633–1635 cm^{-1} for their tungsten counterparts, consistent with their formulation as monoalkoxide derivatives.[4] Positive-ion FAB mass spectra of the complexes contained molecular ions in addition to fragment ions consistent with their formulation.

Proton NMR spectra afforded the most detailed structural information about the new complexes and contain three main groups of signals. First the pyrazolyl H^4 signals appear as a group of singlets in the region δ 8.5–9.0 with total relative areas of 6 for the bimetallic and 3 for the monometallic complexes. Secondly the pyrazolyl 3- and 5-methyl signals appear as a group of singlets the in the region δ 2.3–2.6 with total relative areas of 36 for the bimetallic and 18 for the monometallic complexes. Thirdly there is a group of signals attributable to the diolate ligand. These will include a resonance at low field due to the proton in the {CHOMo} group along with higher-field resonances attributable to the $\{CH_2\}$ groups although, in some cases, these are obscured by the pyrazolyl-methyl signals.

The interpretation of the NMR spectra is complicated by the large number of isomeric possibilities in these compounds and, before considering the spectra in more detail, it is necessary to consider the possible isomers which might be obtained. The diol ligands each contain two chiral centres and, in the bimetallic complexes, the addition of two {MoL(NO)Cl} groups introduces two further chiral centres. In principle this could lead to a total of 16 isomers but the number of chemically distinguishable isomers is reduced by the presence of enantiomers and the *meso* forms of some diols. In the case of cyclohexane-1,2-diol only the *trans* isomer was used, further reducing the number of isomers available in this case. The isomeric possibilities for the diols used are summarised in Fig. 2. In the cases of the *cis* and *trans* mixtures, *viz.* cyclopentane-1,3-diol and cyclohexane-1,4- and -1,3-diol, six chemically distinct species can be formed, while for *trans*-cyclohexane-1,2-diol only three such species may be formed.

To assist in the interpretation of their NMR spectra, ^{1}H–^{1}H COSY-45 data were obtained for complexes **1a** and **1b** (at 400 MHz) and COSY-90 data for **2a** and **2b** (at 270 MHz). The results show that the spectrum of **1a** contains two sets of signals assignable to L. Assuming that, on the NMR timescale, the

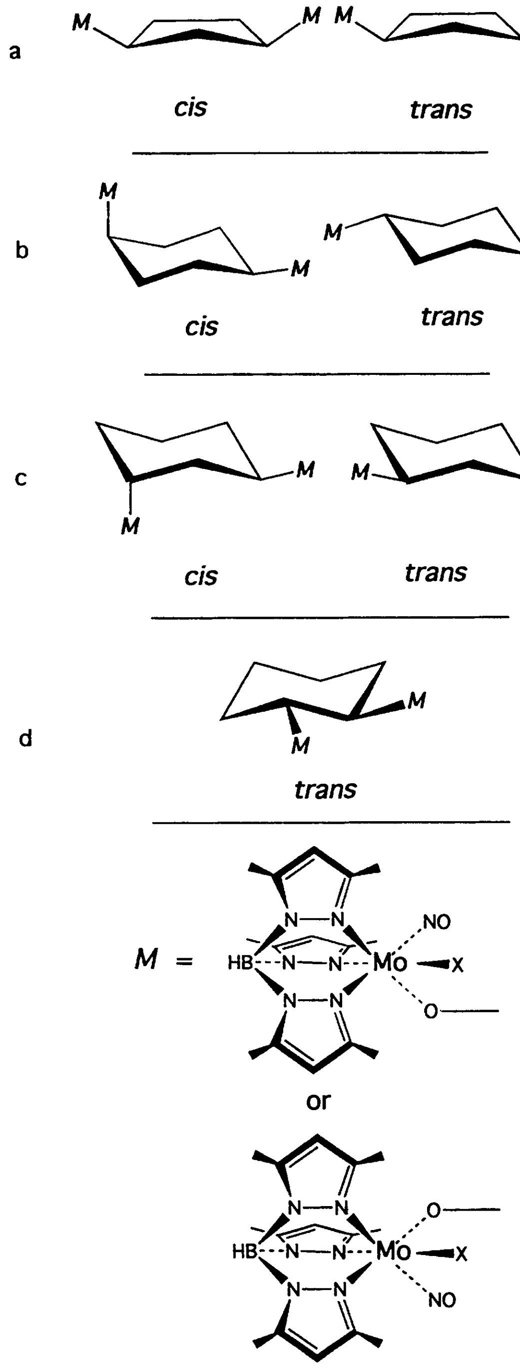

Fig. 1 Possible isomeric structures for the bridging diolate ligands and the {MoL(NO)Cl(O–)} moiety

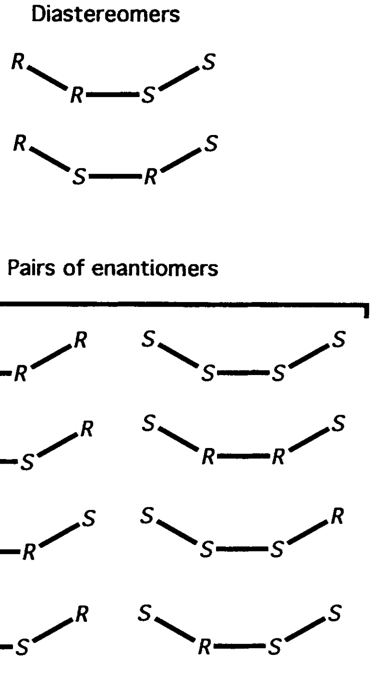

Fig. 2 Possible arrangements for chiral centres in diolate-bridged bimetallic complexes: *R* and *S* are used only to distinguish differences in chirality; no absolute configurations have been determined and these assignments are not intended to apply to the structures shown in Fig. 1

cyclopentane symmetry is maintained, only two out of the six chemically distinct isomers of [{ML(NO)Cl}$_2$(1,3-O$_2$C$_5$H$_8$)] would give two sets of L signals. (Fig. 2 shows that three chemically distinct bimetallic species are possible for both the *cis* and the *trans* isomers of cyclopentane-1,3-diol and within each group of three only one species has two metal environments.) Bearing in mind the 3:1 *cis*:*trans* isomer ratio in the cyclopentane-1,3-diol used and assuming that the more abundant bimetallic fraction **1a** is that produced from the *cis* isomer of the diol, its identity can be assigned as the *RSRR*/*SRSS* isomer (using *R* and *S* arbitrarily to denote the different chiralities at the terminal molybdenum and internal carbon centres). The ^{1}H NMR spectrum of **1a** is in accord with its formulation as a single *cis* isomer in that the resonance at δ 2.9 assigned to proton 2b in Fig. 3 has a large coupling (14.3 Hz) which, in a five-membered ring, can only arise from geminal coupling to 2a. Hence, 2a and 2b are not equivalent. This can result from the presence of a *cis* configuration or from a longer-range ring or steric interaction. However, in this latter case irradiation of the overlapping signals due to 1b and 3b should give roughly equal nuclear Overhauser effects (NOEs) to both 2a and 2b. In fact this NOE experiment gives a substantial NOE to 2b, but has little effect on 2a. The NOE magnitudes also identify the resonance at δ 1.9 as due to 4a (or 5a).

The signals in the spectrum of complex **1b** appear to result from a mixture of two symmetrical isomers, in a roughly 2:1 proportion. The key piece of evidence in support of this model is a resonance at δ 3.0 which does not show any large couplings. It does, however, have two smaller equal couplings from 1b and 3a. It therefore follows that this resonance must be an A$_2$ pair of protons in a fully symmetric isomer. The other assignments follow from the correlation spectroscopy (COSY) and from NOE experiments. It seems therefore that the isomers present in **1b** are *RRRR*/*SSSS* and *SRRS*/*RSSR*. It is not possible to say which isomer is which, but the spectrum of the major component exhibits anomalous chemical shifts for 2a/2b and 4b/5a.

The one-dimensional ^{1}H NMR spectra of complexes **2a** and **2b** appear to show that both fractions are pure, unsymmetrical single isomers. Only one unsymmetrical isomer is possible for the *cis* ligand and one for the *trans*. The 270 MHz COSY-90 spectra have also been obtained for these compounds and a comparison of the COSY pattern for **2a** with that of **1b** shows them to be similar, once chemical shift differences have been taken into account. On this basis it follows that **2a** has a *cis*-diolate bridge and is the *RSRR*/*SRSS* isomer. Assuming that the unsymmetrical nature of the species under discussion is caused by the metal environments and not by an unsymmetrical ligand distortion, then it follows that **2b** has a *trans*-diolate bridge and that the isomer is *RSSS*/*SRRR*. The signals appearing at δ 2.73 and 2.21 in the COSY spectrum are visible in the one-dimensional spectrum and both integrate to one proton. However, both these signals show equal small coupling to two protons. The COSY spectrum shows both these protons to be coupled to the 1a/3b signals. It would seem then that the

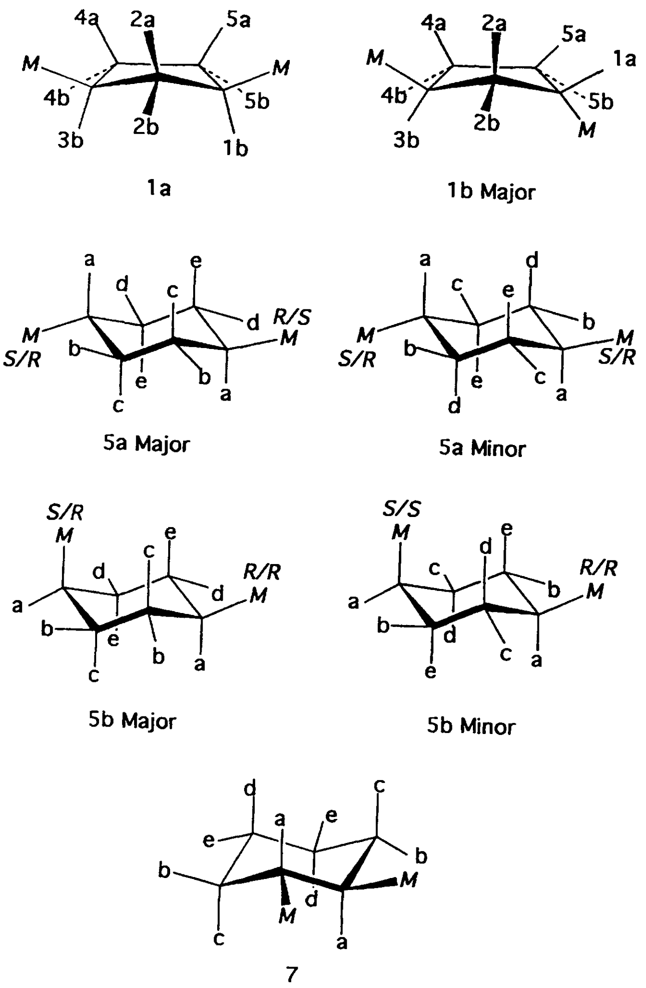

Fig. 3 Proposed isomeric structures for complexes **1a**, **1b**, **5a**, **5b** and **7**; M is as defined in Fig. 1

signals at δ 2.73 and 2.21 are the 2a/2b signals (Fig. 3). However, neither the one-dimensional nor the COSY spectrum shows coupling between these two signals. The only other explanation is that the second fraction is a mixture of two symmetric isomers in a 1 : 1 mixture. Since four fractions were separated by chromatography then the second explanation seems unlikely, but no explanation can be offered for the apparent lack of coupling between these two signals. The rest of the signals can be assigned from the COSY spectrum which provides further evidence for the initial structural assignment.

A ^{1}H homonuclear COSY-45 study was carried out at 400 MHz on complexes **5a** and **5b**. In this way it was possible to assign all the signals in individual isomers. Correlation spectroscopy is sensitive to small coupling (*ca.* 0.2 Hz) which often cannot be resolved in one-dimensional spectra so that ^5J coupling can often be observed. In all cases coupling was observed between the pyrazole methyls and the pyrazole aromatic proton and, using this coupling, signals for each pyrazole ring in the complexes could be correlated. In the case of both **5a** and **5b** major and minor components were found to be present in the approximate proportions 2 : 1. The spectra of **5a** indicate that both components are symmetric. The signals for the minor component can be assigned more easily than those for the major component. It is apparent from the large couplings that this isomer has axial protons attached to the 1,4 carbons. In addition, the existence of coupling between the protons labelled d and e (again large) confirms that the cyclohexanediolate ligand is in the *trans* form and that the assignment given is correct. It follows from the symmetry of the protons on the cyclohexane bridge that the chirality of the metals must be the same, hence this isomer is *SS*/*RR*. The assignment for the major component is less certain. Again there is a large coupling for the protons attached to the 1,4 carbons, but the methylene signals are only separated into two pairs. Within each of these pairs it is apparent that there are two signals, but the assignment cannot be regarded as certain. It follows that if the assignment is correct then the chirality of each metal must be different, hence the isomer is *RS*.

The second fraction **5b** contained three species. The least-abundant corresponded to the minor component in **5a**. The other two components are different isomers from those present in **5a** although their COSY patterns are similar. It follows then that the signals are from the *cis*-cyclohexane ring with either rapid axial–equatorial flipping, or a more complicated conformation. In this case it appears that the major component is *RR*/*SS*, whereas the minor component is *RS*. It should be noted that in the *RS* isomer although the individual signals could be resolved for two of the protons, the signals still fall into two pairs. However, there is no coupling apparent between the pairs which suggests that each pair is confined to one side of the ring. This was not the case in the *RS* isomer in **5a**.

From the COSY studies the structure of two of the fractions has been assigned with some confidence. However, it should be noted that even in these cases the methylene signals have only been assigned relative to one another and not relative to the absolute chirality of the metal centres. The spectra have also shown that column chromatography appears to separate the fractions into *cis*- and *trans*-cyclohexane isomers although it is always possible that isomerisation occurred after the separation process. One aspect of the NMR spectrum of the 1,2-diol bimetallic deserves comment. The signals assignable to the pyrazole rings are spread over a larger chemical shift range than for the other bimetallic species studied. This spreading effect has also been noticed in the spectrum of $[\{MoL(NO)Cl\}_2(\mu\text{-}O)]$ and appears to be a consequence of bringing the metal centres close together. The signals were assigned by decoupling experiments which, although they did not completely confirm the proposed *trans*-ring conformation, did confirm that the product was a single symmetric isomer and hence meant that the species must be *SSSS*/*RRRR* or *SRRS*/*RSSR*.

Electrochemical studies

Cyclic voltammetry and differential-pulse voltammetry have been used to investigate the extent of metal–metal interaction in the bimetallic complexes and the results are presented in Table 2. All of the complexes, mono- and bi-metallic, exhibited reduction waves in the region expected for monoalkoxide derivatives.[8] In accord with precedent[9] the tungsten complexes exhibited reduction potentials some 500 mV more negative than those of their molybdenum-containing counterparts. Although the NMR data indicate that two isomers are present in **1b**, **5a** and **5b**, their cyclic voltammograms appeared to represent the behaviour of a single compound. Either the electrochemical properties of the two isomers are identical or they are sufficiently similar that the presence of the minor component is not detectable. In all cases the scan-rate dependence of the reduction processes was measured in order to test the reversibility of the redox processes under investigation, and the peak anodic current was plotted against the square root of the scan rate. In the case of the bimetallic systems the scan-rate dependence was only performed on the first, or less negative, wave. All the waves studied are non-Nernstian. Multiple scans showed that, at room temperature, the cathodic and anodic currents are not constant but decay slowly with time, and the scan-rate plots all showed some curvature. The origin of this 'quasi-reversible' behaviour could be the dissociation of Cl^- following reduction as a similar but more rapid process occurs with related iodoalkoxides.[8,10] However, slow electron transfer may also be involved.

In order to obtain further information on the nature of the

Table 2 Electrochemical data for mono- and bi-metallic complexes from cyclic and differential-pulse voltammetry in CH_2Cl_2[a]

Complex	$E_f(1)$[b]/V	$\Delta E_p(1)$[b]/mV	$E_f(2)$[c]/V	$\Delta E_p(2)$[c]/mV	ΔE_f[d]/mV	K_c[e]
1a	−0.655	85	−0.873	100	220	5 360
1b	−0.645	85	−0.775	75	230	7 910
2a	−1.175	110	−1.359	110	184	1 310
2b	−1.175	135	−1.364	120	189	1 600
3	−0.718	210	—	—	—	—
4	−1.225	150	—	—	—	—
5a	−0.666	98	−0.828	105	162	557
5b	−0.699	95	−0.833	120	160	515
6	−0.706	102	−0.892	120	193	1 870
7	−0.706	105	−1.008	80	302	131 400
8a	−0.650	145	—	—	—	—
8b	−0.622	150	—	—	—	—

[a] Under these conditions, for ferrocene–ferrocenium $E_f = 0.555 \pm 0.005$ V *vs.* SCE with $\Delta E_p = 80 \pm 10$ mV. [b] Values of E_f (V *vs.* SCE from differential-pulse voltammetry) and ΔE_p (separation in mV between the anodic and cathodic wave peak potentials from cyclic voltammetry) for the first reduction wave. [c] Values of E_f and ΔE_p for the second reduction wave where present. [d] Difference between first and second reduction potentials taken from differential-pulse voltammetry. [e] Comproportionation constant calculated from $\log_{10} K_c = \Delta E_f/59$.

Table 3 The UV/VIS and spectroelectrochemical data for $[\{MoL(NO)Cl\}_2(\mu\text{-}1,3\text{-}O_2C_5H_8)]$ **1a**

Species	T/K	$\tilde{\nu}_{max}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})
1a	273	17 120 (400), 31 570 (22 330)
	263	17 120 (230), 31 530 (23 120)
1a$^-$	263	17 650 (330), 33 200 (13 790)
1a^{2-}	263	17 700 (160), 19 300 (450), 26 970 (2 250), 36 000 (sh) (9 260), 38 700 (17 080)

reduced species a spectroelectrochemical study was carried out on complex **1a** in an OTTLE cell at −10 °C in dichloromethane. Electrolysis was carried out at −0.75 V relative to a Ag–AgCl reference electrode and the UV/VIS/NIR spectrum monitored. The resulting OTTLE plot shows two isosbestic points which indicate a clean conversion of one species into another. Reoxidation at −0.20 V produced an identical OTTLE plot also with two isosbestic points which indicates that the electrolysis is reversible. A second OTTLE plot was obtained by monitoring the conversion of the singly reduced species into the doubly reduced one. Electrolysis was carried out at −1.2 V. One isosbestic point was observed in this case and reoxidation again produced an identical plot indicating a reversible conversion. One of the main purposes in carrying out the study was to monitor the NIR region in order to look for any evidence of intervalence charge-transfer i.v.c.t. bands. However, no indication of any such bands was found so it must be concluded that, unless the i.v.c.t. band has an absorption coefficient below *ca.* 100 dm^3 mol^{-1} cm^{-1} and/or an energy below 6000 cm^{-1}, no such band is present. The data obtained are shown in Table 3. The major change on reduction is the loss of the band at 31 570 cm^{-1}. It could be argued that this band has merely lost intensity and shifted due to the electric field exerted by the reduced metal centre to become the band at 31 530 cm^{-1} of the singly reduced species. The doubly reduced species possesses charge-transfer bands at higher energy. In addition, all three spectra display some weak bands between 17 000 and 19 000 cm^{-1}; these are almost certainly d–d transitions. The nature of the charge-transfer bands remains a matter for speculation.[11]

A major point of interest in the electrochemical results is the effect of the bridging ligand structure on the electrochemical properties of the complexes. Some variations in the first reduction potentials with the nature of the alkoxide ligand may be seen in the data from Table 2. Among the molybdenum complexes a comparison of the members of pairs of separated isomers, either mono- or bi-metallic, reveals only small differences of 10–30 mV among the first reduction potentials. However, these are greater than the experimental error of *ca.* ± 5 mV expected when comparing a potential difference of this sort and appear to be significant in the cases of **5a** and **5b** and of **8a** and **8b**. It is known that steric effects can affect redox potentials in these systems[12] if they affect p_π–d_π interactions between the donor atom and the metal centre.[13] It is possible that similar factors are operating here and that different isomers experience differing degrees of structural distortion arising from steric interactions between the bulky L and the alkoxide ligands. Compared to their cyclopentanolate-containing counterparts (**3** and **4**), the first reduction waves of the molybdenum and tungsten pentane-1,3-diolate complexes (**1a**, **1b**, **2a** and **2b**) show shifts to more positive potentials of 50–70 mV. However, this may merely reflect the introduction of the nearby electronegative oxygen substituent in the diolate complexes. A difference of similar magnitude, but reversed direction, is found between the mono- and bi-metallic cyclohexane-1,2-diolate complexes **8a** or **8b** and **7**. Here the second oxygen atom is present in both systems but the isomeric relationship between the mono- and bi-metallic complexes is uncertain and may play some part in the potential difference observed.

The primary objective of this work was to examine the effect of the bridging-ligand structure on the metal–metal interaction. The potential difference between the first and second reduction processes (ΔE_f) may be used to calculate the comproportionation constant, K_c for formation of the mixed-oxidation-state complex from its isovalent oxidised and reduced partners using the relationship $\log_{10} K_c = \Delta E_f/59$ when ΔE_f is in mV.[3] The interaction between two metal centres has two components, an electrostatic through-space interaction and a through-bond interaction. The through-bond interaction will comprise through-σ-bond inductive effects and through-π-bond mesomeric effects. The contribution from mesomeric effects can be clearly seen by comparing systems containing aryl bridges with their counterparts containing saturated bridges. Thus a ΔE_f value of 460 mV has been obtained[5a] for $[\{MoL(NO)Cl\}_2(1,4\text{-}O_2C_6H_4)]$ compared to respective values of 162 and 160 mV for **5a** and **5b** a decrease of some 300 mV on removing the mesomeric contact between the two redox centres. In contrast the difference in ΔE_f values between $[\{MoL(NO)Cl\}_2(1,3\text{-}O_2C_6H_4)]$, where there is no mesomeric link,[5b] and **6** amounts to only 67 mV.

Separating the contributions to ΔE_f from through-space and through-bond effects in complexes with saturated bridges is less simple. The ΔE_f values for the molybdenum complexes **1a**, **1b**, **5a**, **5b**, **6** and **7** correlate well with the number of bonds separating the metal centres (Fig. 4). However, the metal–metal distance and the number of bonds separating the metal centres are not independant variables. It is notable that the differences in ΔE_f between members of the isomeric pairs **1a**/**1b**, **2a**/**2b**, **5a**/**5b**, where the number of bonds remains constant but the distance changes, are only *ca.* 10 mV or less. Furthermore the

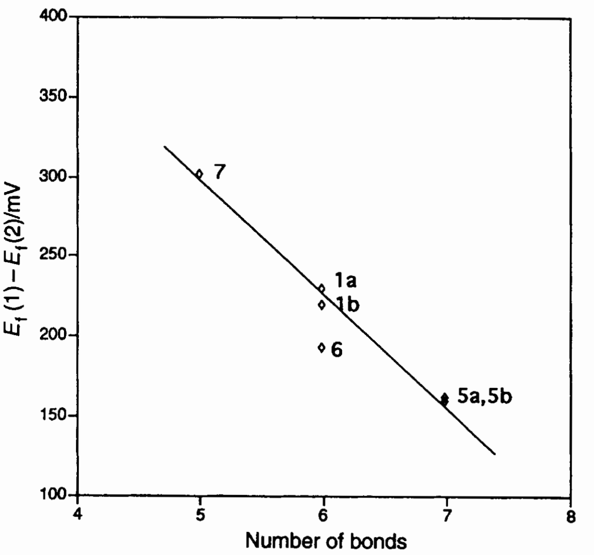

Fig. 4 Plot of ΔE_f against the number of bonds separating the metal centres in complexes **1a**, **1b**, **5a**, **5b**, **6** and **7**

values of ΔE_f are less by some 40 mV for the tungsten complexes **2a** and **2b** than for the molybdenum complexes **1a** and **1b**, although little structural difference would be expected between the two types of complex.[14] These observations would suggest that electronic through-bond interactions between the metal centres contribute to the observed ΔE_f values for these saturated bridge systems. However, the absence of an identifiable i.v.c.t. band in the spectroelectrochemical study means that direct evidence of a through-bond electronic interaction between the metal centres in these complexes is lacking. Consequently no definitive comment can be made regarding the origin of the potential difference ΔE_f.

Conclusion

Although the characterisation of complexes derived from the $\{MoL(NO)Cl\}^+$ moiety and cyclopentane-1,3-diol, cyclohexane-1,3- and -1,4-diol is complicated by the number of isomeric forms which may be present, it has been possible to separate and identify fractions corresponding with the *cis* and *trans* forms of the diol ligand. Differences in the isomeric form of the diols can have a measureable, but small, effect on the electrochemical properties of the complex formed. A comparison of ΔE_f values for $[\{MoL(NO)Cl\}_2\{1,4\text{-}O_2C_6H_4\}]$ and $[\{MoL(NO)Cl\}_2\{1,4\text{-}O_2C_6H_{10}\}]$ indicates that mesomeric effects contribute *ca.* 300 mV to the value of ΔE_f for the aryl-bridged complex. In contrast the difference in ΔE_f between $[\{MoL(NO)Cl\}_2\{1,3\text{-}O_2C_6H_4\}]$ and $[\{MoL(NO)Cl\}_2\{1,3\text{-}O_2C_6H_{10}\}]$, where mesomeric effects are absent, is less than one quarter of the value for the complexes with the 1,4-substituted bridges. Spectroelectrochemical studies of $[\{MoL(NO)Cl\}_2\{1,3\text{-}O_2C_6H_{10}\}]$ provided no direct evidence to support the proposal that electronic through-bond metal–metal interactions are present in the compounds with saturated bridges.

Experimental

All commercial reagents were used as supplied; $[ML(NO)Cl_2]$ (M = Mo or W) were prepared according to previously described methods.[15] 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 in 60 × 4 or 20 × 2 cm columns. Elemental analyses were carried out by the Microanalytical Laboratory, The University of Birmingham.

The IR spectra were recorded using using KBr pellets and a PE 297 spectrometer; UV/VIS spectra using a Shimadzu UV-240 spectrometer using a matched cell containing solvent in order to correct for background effects, 270 MHz ^1H NMR spectra from solutions in $CDCl_3$ using a JEOL GX270 spectrometer at the University of Birmingham and mass spectra using a Kratos MS80RF spectrometer. Cyclic and differential-pulse 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_2Cl_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. A scan rate of 200 mV s^{-1} was used and the effect of scan rate on diffusion current was assessed over the range 10–500 mV s^{-1}. Spectroelectrochemical measurements were made in the Chemistry Department of the University of Edinburgh using a Perkin-Elmer Lambda 9 spectrometer; samples were electrolysed in an OTTLE cell using a Metrohm potentiostat.

Reactions

$[MoL(NO)Cl_2]$ and cyclopentane-1,3-diol: complexes 1a and 1b. The complex $[MoL(NO)Cl_2]$ (0.502 g, 1.01 mmol) was added to toluene (100 cm^3) and cyclopentane-1,3-diol (*ca.* 0.054 g, 0.53 mmol) added using a glass rod. Triethylamine (1 cm^3) was added and the mixture heated under reflux overnight. Additional $[MoL(NO)Cl_2]$ (0.205 g, 0.42 mmol) was added and heating continued for 2 h. The mixture was then cooled, filtered and evaporated to dryness. Purification by column chromatography using CH_2Cl_2–hexane (4:1 v/v) as the eluent afforded three fractions. The first and third blue fractions contained the products **1a** and **1b** respectively (297 mg, 41%; 110 mg, 16%).

$[WL(NO)Cl_2$ with cyclopentane-1,3-diol: complexes 2a and 2b. The complex $[WL(NO)Cl_2]$ (0.500 g, 0.86 mmol) was added to toluene (100 cm^3) and excess of cyclopentane-1,3-diol (five drops) added. Triethylamine (1 cm^3) was then added and the mixture was brought to reflux. After 1 h the purple mixture was cooled, filtered and evaporated to dryness. Column chromatography using CH_2Cl_2 as the eluent afforded four purple fractions of which the third and fourth contained insufficient material for further study so that only only the first two were fully characterised (**2a**; 26.2 mg, 5%; **2b**; 62.7 mg, 12%).

$[MoL(NO)Cl_2]$ and cyclopentanol: complex 3. The complex $[MoL(NO)Cl_2]$ (0.560 g, 1.13 mmol) was added to toluene (50 cm^3) and the mixture brought to reflux. An excess of cyclopentanol (2 cm^3) and triethylamine (1 cm^3) were added and the mixture heated for 20 min. The resulting blue solution was cooled, filtered and evaporated to dryness. Purification by column chromatography with CH_2Cl_2 as the eluent afforded a major blue band containing the product which was recrystallised from CH_2Cl_2–hexane (0.512 g, 82%).

$[WL(NO)Cl_2]$ and cyclopentanol: complex 4. The procedure described for complex **3** was followed using $[WL(NO)Cl_2]$ (0.524 g, 0.90 mmol) and a total heating time of 15 min to give, after purification, a purple solid (0.490 g, 86%).

$[MoL(NO)Cl_2]$ with cyclohexane-1,4-diol: complexes 5a and 5b. The complex $[MoL(NO)Cl_2]$ (0.50 g, 1.02 mmol) was stirred together with cyclohexane-1,4-diol (0.0595 g, 0.51 mmol) in toluene (60 cm^3); triethylamine (0.5 cm^3) was added and the mixture heated under reflux for 15 h. The blue precipitate which formed was filtered off and washed with water, to remove amine salts, followed by Et_2O. The dried precipitate was then dissolved in CH_2Cl_2, filtered and purified by column chromatography using CH_2Cl_2 as the eluent. Two blue fractions were separated and recrystallised from CH_2Cl_2–hexane (**5a**, 36 mg, 6%; **5b**, ?? mg, ?%) (Found: C, 43.9; H, 5.7; N, 21.5. Calc. for $C_{36}H_{50}BCl_2Mo_2N_7O_2 \cdot 0.33C_6H_{14}$: C, 43.4; H, 5.3; N, 21.3%).

[MoL(NO)Cl$_2$] with cyclohexane-1,3-diol complex 6. The complex [MoL(NO)Cl$_2$] (0.497 g, 0.96 mmol) was stirred together with cyclohexane-1,3-diol (0.060 g, 0.051 mmol) in toluene (60 cm^3), triethylamine was added (0.5 cm^3) and the mixture heated under reflux for 15 h. The resulting blue solution was cooled, filtered, evaporated to dryness and the solid so obtained redissolved in CH_2Cl_2 and separated into four fractions by column chromatography using CH_2Cl_2–hexane (90:1 v/v) as the eluent. Only the first blue fraction was found to be a pure bimetallic complex, **6** (5 mg, 1%).

[MoL(NO)Cl$_2$] with *trans*-cyclohexane-1,2-diol: complex 7. *trans*-Cyclohexane-1,2-diol (0.5 g, mmol) was added to a solution of [MoL(NO)Cl$_2$] (0.250 g, 0.51 mmol) in hot toluene (50 cm^3). The mixture was brought to reflux, triethylamine (1 cm^3) added after 45 min, then the solution was cooled, filtered and evaporated to dryness. The blue solid was redissolved in CH_2Cl_2 and purified by column chromatography using CH_2Cl_2 as the eluent. The main blue fraction was collected and the product precipitated from a CH_2Cl_2–hexane mixture by slow evaporation. The resulting blue powder was washed with pentane and dried (180 mg, 69%).

This product (0.051 g, 5.0×10^{-2} mmol) was mixed with [MoL(NO)Cl$_2$] (0.021 g, 4.3×10^{-2} mmol), toluene (50 cm^3) added and the mixture heated to reflux. Triethylamine (1 cm^3) was then added. After heating for 24 h the solution was cooled, filtered and evaporated to dryness. The resulting solid was purified by column chromatography in two stages, first using CH_2Cl_2 as the eluent to give a main greenish fraction which was collected and further purified using CH_2Cl_2–hexane (1:1 v/v) as the eluent, the main blue fraction being collected, **7** (2.2 mg, 10%).

[MoL(NO)Cl$_2$] with *trans*-cyclohexane-1,2-diol complexes 8a and 8b. The complex [MoL(NO)Cl$_2$] (0.5014 g, 1.02 mmol) was stirred together with *trans*-cyclohexane-1,2-diol (0.1128 g, 0.970 mmol) in toluene (60 cm^3), triethylamine was added (0.5 cm^3) and the mixture heated under reflux for 15 h. The blue solution was cooled, filtered and evaporated to dryness. The solid obtained was redissolved in CH_2Cl_2 and separated into five blue fractions by column chromatography using CH_2Cl_2–hexane (90:10 v/v) as the eluent. The fourth and fifth fractions contained the respective monometallic complexes (**8a**, 21 mg, 4%; **8b**, 47 mg, 10%).

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