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Bimetallic mixed oxidation state complexes derived by coupling nitrosyl- and oxo-molybdenum cores[1]

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Abstract

The mixed-valence complexes $[Mo(NO)Tp^{Me,Me}Cl\{O(C_6H_4)_nO\}MoOTp^{Me,Me}Cl]$ $\{Tp^{Me,Me}$ = tris(3,5-dimethylpyrazolyl)borate; $n = 1$ or 2) are paramagnetic (one unpaired electron), are valence-trapped and undergo two one-electron reductions and one one-electron oxidation which were detected by cyclic and square wave voltammetry. The complex $[MoOTp^{Me,Me}Cl(OC_6H_4py)Mo(NO)Tp^{Me,Me}Cl]$ contains two unpaired electrons whose spins are coupled (shown by EPR spectroscopy), and the complex undergoes two one-electron reductions and two one-electron oxidations. The spectroscopic data reveal that the nitrosyl molybdenum and oxomolybdenum metal centres are weakly interacting. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemistry; EPR spectra; Mixed oxidation state; Molybdenum; Nitrosyl; Oxomolybdenum(V)

1. Introduction

Molecular magnets are materials which may be derived either from organic radicals or from oligonuclear metal complexes containing at least one paramagnetic transition metal centre [1]. While the construction of stable multi-centre high-spin magnetically-active organic molecules remains a difficult challenge [2], the assembly of two or more transition metal components of differing spin within chain-like structures incorporating relatively short rigid organic bridges has been more successful, leading, for example, to solids exhibiting bulk ferromagnetic behaviour [3].

The identification of suitable paramagnetic transition metal components which can be linked within a rigid carbon-based architectural framework, and which may couple ferromagnetically, is an important objective in the design and assembly of 'molecular magnets'. At the heart of any successful design and synthesis strategy must be the control of the sign and magnitude of the magnetic exchange interaction *J* which depends critically on the nature of the pathway linking the interacting spins.

In pursuing our goal of constructing molecules with controllable and potentially switchable magnetic properties, we have exploited the simple one-electron rela-

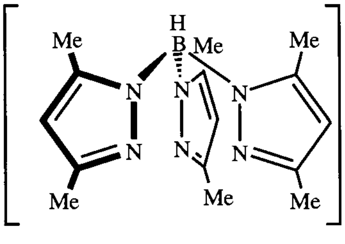

Fig. 1. $[Tp^{Me,Me}]^-$.

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[1] We dedicate this paper to the celebration of the 60th birthday of Professor Brian Johnson, an old friend and (nitrosyl) chemistry enthusiast.

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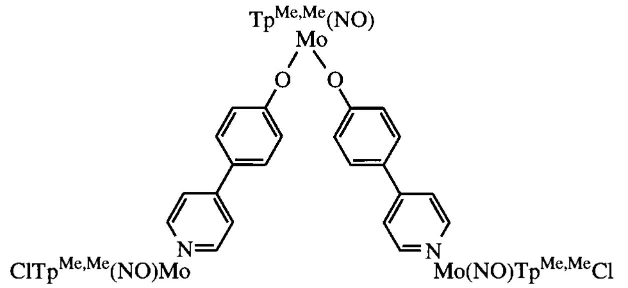

Fig. 2. Idealised structure of [{Mo(NO)Tp^{Me,Me}{(4-OC$_6$H$_4$py)Mo(NO)Tp^{Me,Me}Cl}$_2$].

tionship between the nitrosyl molybdenum couple {Mo(NO)}$^{3+}$/{Mo(NO)}$^{2+}$, which interconverts between a formal 16 and 17 valence-electron (ve) configuration, and similar behaviour in oxomolybdenum species containing the {MoO}$^{n+}$cores with $n = 4$, 3 and 2 which have d^0, d^1 and d^2 (S = 0) configurations.

We have made a number of key observations:in paramagnetic isovalent dinuclear nitrosyl complexes such as [{Mo(NO)Tp^{Me,Me}Cl}$_2$(4,4′-bipy)] (Tp^{Me,Me} = tris(3,5-dimethylpyrazolyl)borate, Fig. 1; metal configuration 17 ve), the sign of J (the magnetic spin exchange constant) can be predicted using a spin-polarisation mechanism, and ferromagnetic behaviour occurs in [{Mo(NO)Tp^{Me,Me}Cl}$_2$(3,4′-bpe)] (bpe = bipyridylethene; $J = +2.4$ cm^{-1}) [4];antiferromagnetic coupling in such dinuclear species can occur over surprisingly long distances, e.g. in the isovalent [{Mo(NO)Tp^{Me,Me}Cl}$_2${py(CH=CH)$_4$py}] (py = C$_5$H$_4$N, ca. 20 Å; $J = -6.6$ cm^{-1}) [5,6];spin correlation, a manifestation of magnetic coupling detected by epr spectroscopy in solution, occurs in the tri-nuclear species [1,3,5-{Mo(NO)Tp^{Me,Me}Cl(pyCH=CH)}$_3$C$_6$H$_3$] and [1,3,5-{Mo(NO)Tp^{Me,Me}Cl(pyC≡C)}$_3$C$_6$H$_3$] (metal hyperfine coupling $A_{Mo} = 1.7$ mT) although the relative signs of J have not yet been determined [7]; ferromagnetic interactions are detected in [{MoOTp^{Me,Me}Cl}$_2$(1,3-OC$_6$H$_4$O)] ($J = +9.8$ cm^{-1}) and [{MoOTp^{Me,Me}Cl}$_3$(1,3,5-O$_3$C$_6$H$_3$])] ($J = +14.4$ cm^{-1}), and the epr spectra of these species in solution exhibit half-field ($\Delta m_s = 2$) and one-third-field ($\Delta m_s = 3$) transitions respectively, indicating that spin correlation occurs [8]; the trinuclear chain [Mo(NO)Tp^{Me,Me}{OC$_6$H$_4$pyMo(NO)Tp^{Me,Me}-Cl}$_2$], Fig. 2, which contains a 17:16:17 mixed-valence system in which the peripheral spins correlate in solution ($A_{Mo} = 2.4$ mT), can be reversibly reduced to the 17:17:17 isovalent anion, in which all three metal centres engage in spin correlation ($A_{Mo} = 1.7$ mT) [9].

It is therefore possible to design significant magnetic coupling into short molecular chains based on molybdenum nitrosyl or oxo centres coupled to oligonucleating poly-phenolato and/or -pyridyl ligands. In dinuclear species where the nitrosyl molybdenum fragments are bridged by asymmetric ligands such as OC$_6$H$_4$py, e.g. [{Mo(NO)Tp^{Me,Me}Cl}$_2$(OC$_6$H$_4$py)], we showed that the unpaired spin on the pyridyl molybdenum nitrosyl fragment is valence-trapped ($A_{Mo} \approx 5.0$ mT) but on reduction to the monoanion, which generates the isovalent 17:17 valence electron system, the spins are correlated ($J \gg A_{Mo}$; $A_{Mo} \approx 2.5$ mT) [10]. However, what we do not know is whether spin-correlation in solution, and detectable magnetic coupling in the solid state, will occur in complexes containing both paramagnetic molybdenum nitrosyl and oxomolybdenum cores. The issue is whether and how the differences in formal metal oxidation state and therefore electronic structure, and in π-acidity or -basicity in the different metal cores, will significantly influence the properties of the dinuclear species.

Extensive spectroscopic studies of both the nitrosyl and oxo molybdenum species, by us [8,11–14] and others [15], have shown that there are strong electronic similarities between the two systems. Dealing first with the nitrosyls, we define the Mo–N–O bond system as the z axis, so that the remaining donor atoms lie on the x and y axes, and the metal d$_{z^2}$ and d$_{x^2-y^2}$ orbitals are engaged in σ bonding. It also follows that the d$_{xz}$ and d$_{yz}$ orbitals are stabilised by strong interaction with the π*(NO) orbitals, thereby leaving the d$_{xy}$ orbital as the lowest unoccupied d orbital in species containing the Mo(NO)$^{3+}$core. In formal oxidation state terminology and assuming the nitrosyl group to be bound as NO$^+$, reduction of a 16 to a 17 ve species means conversion of Mo(II) (d^4) to Mo(I) (d^5), the d$_{xy}$ orbital accommodating the added electron. Similar arguments can be applied to the oxomolybdenum species, in which the z-axis is defined by the Mo=O bond, the d$_{xz}$ and d$_{yx}$ orbitals are involved in π-bonding with the O^{2-} (π-) donor, and the only orbital which can accommodate the unique electron in the oxomolybdenum(V) system is d$_{xy}$ [11,15].Our first objective in elaborating magnetic chains of molybdenum centres with redox-mediated switching capability was therefore to make dinuclear mixed nitrosyl/oxo molybdenum species. Our second goal was to generate paramagnetic species in which unpaired electrons were located on two different types of molybdenum centre, and to discover whether the unpaired spins could interact in a significant way.

2. Results and discussion

2.1. Syntheses

Two synthetic strategies were employed: reaction either (a) of preformed [Mo(NO)Tp^{Me,Me}Cl{O(C$_6$H$_4$)$_n$-OH}] {$n = 1$ (**1**) or 2 (**2**)} with [MoOTp^{Me,Me}Cl$_2$], or (b) of preformed [MoOTp^{Me,Me}Cl(OC$_6$H$_4$py)], **3**, with

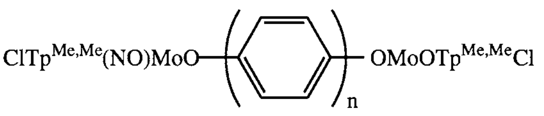

Fig. 3. Idealised structure of $[Mo(NO)Tp^{Me,Me}Cl\{O(C_6H_4)_nO\}MoOTp^{Me,Me}Cl]$, **4** ($n = 1$) and **5** ($n = 2$).

$[Mo(NO)Tp^{Me,Me}Cl_2]$. Route (a) would require the use of the known mononuclear diphenolato species [11,12], and should lead to $[Mo(NO)Tp^{Me,Me}Cl\{O(C_6H_4)_nO\}\text{-}MoOTp^{Me,Me}Cl]$ $\{n = 1$ (**4**) or 2 (**5**); Fig. 3$\}$ having one unpaired electron located on the oxomolybenum(V) centre. Route (b) should afford $[MoOTp^{Me,Me}Cl\text{-}(OC_6H_4py)Mo(NO)Tp^{Me,Me}Cl]$ **6** (Fig. 4), in which both metal centres are paramagnetic.

In the event, both strategies were successful although the yields of the desired products were relatively low and we could detect several other byproducts of the reactions. In particular, we recognised the ever-present and common feature of all substitution processes involving $\{Mo(NO)Tp^{Me,Me}\}$ species, namely the hydroxo and oxo species $[Mo(NO)Tp^{Me,Me}(OH)_2]$ (pink) and $[\{Mo(NO)Tp^{Me,Me}Cl\}_2O]$ (green) [16]. We were also aware of decomposition products arising from oxomolybdenum species, but in none of the reactions did we attempt to identify what these were since there were many of them in very low yields. The new species **3**, **4**, **5** and **6** were separated from the impurities and unreacted starting materials by column and plate chromatography, normally using silica gel. Although we have reported **1** and **2** earlier, they were mainly detected as by-products of reactions designed to maximise the production of dinuclear species, and so a description of their deliberate synthesis is included in this paper. In both syntheses, significant amounts of $[\{Mo(NO)Tp^{Me,Me}Cl\}_2\{O(C_6H_4)_nO\}]$ could not be avoided but were separated chromatographically.

Elemental analytical data for all compounds are given in Table 1. Some of the species afforded useful EI mass spectral data, but all compounds were amenable to FAB positive ion mass spectrometry, and parent ions were detected in all cases (Table 1).

2.2. IR and electronic spectral characterisation

The IR spectra show ν_{BH} and other absorptions characteristic of the $Tp^{Me,Me}$ ligand. As expected, ν_{NO} is useful diagnostically, occurring at ca. 1680 cm^{-1} in **1** and **2**, and at 1674 and 1679 cm^{-1} in **4** and **5**. This very slight shift to lower frequencies is hardly significant, implying that the oxomolybdenum fragment in **4** and **5** is barely influencing the electron density around the molybdenum nitrosyl group. In **6**, however, the molybdenum nitrosyl centre is reduced with respect to that in **4** and **5** and, again, the shift in position of ν_{NO} (1615 cm^{-1}) relative to that in other similar mixed valence species such as $[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$ $\{\nu_{NO} = 1687$ (phenolato), 1611 (pyridyl) $cm^{-1}\}$ is insignificant [5,10]. Similarly, $\nu_{Mo=O}$, at ca. 950 cm^{-1}, is relatively insensitive to the proximity of a molybdenum nitrosyl fragment.

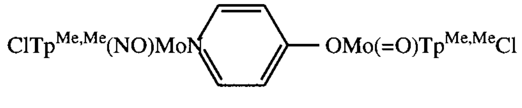

Fig. 4. Idealised structure of $[MoOTp^{Me,Me}Cl(OC_6H_4py)Mo(NO)Tp^{Me,Me}Cl]$, **6**.

The electronic absorptions in the region 500–600 nm in the VIS/UV spectra of **4** and **5** are probably due to phenolate → Mo^V charge transfer, the value in **5** being higher than that in **4** because of the extended bridging ligand in the former. This absorption probably obscures the weaker phenolate $\rightarrow \{Mo(NO)\}^{3+}$ charge transfer which normally occurs in the range 460–560 nm [10]. The weak absorption detected in **4** at 735 nm is probably a $Mo^V(d_{xy}) \rightarrow Mo{=}O(\pi^*)$ transition [14].

2.3. Electrochemical characterisation

The cyclic (CV) and square wave voltammograms (SWV) of the new complexes **4**, **5** and **6** showed that all three species underwent two sequential reductions and at least one oxidation (Table 2). The CVs and SWVs were recorded in dichloromethane (the SWV of **6** is shown in Fig. 5), and although no coulometric experiments were attempted, we have assigned each of the reductive electrode processes, the first oxidations in **4** and **5**, and both oxidations in **6** as one-electron transfers. This is reasonable in the light of the behaviour of comparable compounds and of the chemistry of these new complexes. The electrode reactions are quasi-reversible at best, and that associated with the first oxidation in **5** is either irreversible or, possibly, a two electron transfer: we incline to the former, but the second oxidation process is clearly irreversible, only an anodic wave being detectable.

To determine the origin of these redox processes, it is necessary to refer to earlier CV data obtained from the nitrosyl phenolato complexes $[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4O)]$ and $[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4C_6H_4O)]$ [12] (Table 2). In both of these there are two one-electron reductions, E_f(red1) being -0.72 V (vs F_c/F_c^+ couple) in the former and -0.75 V in the latter; reduction of mononuclear $[Mo(NO)Tp^{Me,Me}Cl(OPh)]$ occurs at -0.79 V. So it seems reasonable to associate E_f(red1) in **4** (-0.95 V) and in **5** (-0.89 V) with reduction of the molybdenum nitrosyl phenolato portion of the molecule, there being only a small interaction between the redox orbital on

Table 1
Analytical, mass spectrometric, selected IR and electronic spectral data

	Elemental analysis[a]			FABMS	$\nu_{\rm NO}/\nu^{\rm b}_{\rm MoO}$	Electronic spectra[c]
	C	H	N			
4	43.2(42.7)	4.89(4.88)	17.3(18.0)	1013(1011)	1764(NO) 948(MoO)	735 (7.06sh), 589(11.2), 375(8.76sh), 268(17.5sh)
5	47.1(46.4)	5.20(5.34)	16.3(16.8)	1089(1087)	1679(NO) 948(MoO)	573(23.6), 385(22.2sh), 273(58.4)
6	46.5(45.8)	4.99(4.84)	18.1(18.3)	1075(1073)	1615(NO) 953(MoO)	508(4.56), 399(11.0sh), 329(18.8), 281(17.4)

[a] Calculated values in parentheses.
[b] In KBr discs, $\rm cm^{-1}$.
[c] In $\rm CH_2Cl_2$ at room temperature, $\lambda_{\rm max}$ in nm (ε in $\rm dm^3\ mol^{-1}\ cm^1$).

each metal fragment as determined by the size of $\Delta E_{\rm f}$. The CV of $[\{\rm MoOTp^{Me,Me}Cl\}_2(OC_6H_4O)]$ has again two reduction waves in which $E_{\rm f}(\rm red1) = -1.19$ V while $[\{\rm MoOTp^{Me,Me}Cl\}_2(OC_6H_4C_6H_4O)]$ undergoes a two-electron reduction (-1.13 V) [14]; reduction of $[\rm MoOTp^{Me,Me}Cl(OPh)]$ occurs at -1.21 V. These processes are largely metal-based (mainly d_{xy}) and are significantly more cathodic than those in the symmetrical nitrosyl species, which are both metal and ligand based [12], and so we associate $E_{\rm f}(\rm red2)$ in **4** (-1.45 V) and **5** (-1.22 V) mainly with the oxomolybdenum fragment of the molecules.

Dinuclear diphenolato molybdenum nitrosyls do not appear to oxidise in the voltage range $0 \rightarrow +1.50$ V. However, their oxomolybdenum analogues do [14], the process being due formally to oxidation of $\rm Mo^V$ to $\rm Mo^{VI}$ although there is probably some admixture with bridging ligand oxidation (hydroquinone → semiquinone → quinone). The CVs of both dinuclear species have two oxidation waves, $E_{\rm f}(\rm ox1)$ being at $+0.26$ V in $[\{\rm MoOTp^{Me,Me}Cl\}_2(OC_6H_4O)]$ and $[\{\rm MoOTp^{Me,Me}Cl\}_2(OC_6H_4C_6H_4O)]$ in $+0.44$ V although oxidation of $[\rm MoOTp^{Me,Me}Cl(OPh)]$ occurs at $+0.68$ V. On the basis of these data we think it reasonable to assign the anodic electrode processes observed in the CVs of **4** ($+0.47$ V) and **5** ($+0.43$ V) to oxidation of the oxomolybdenum phenolate fragments of the molecules.Molybdenum nitrosyl pyridine complexes exhibit reduction processes significantly more cathodic than those in comparable phenolato analogues, and all show oxidation behaviour. For example, $[\rm Mo(NO)Tp^{Me,Me}Cl(py)]$ reduces at -2.01 V and oxidises at $+0.04$ V in one-electron steps [5]. However, the electrochemistry of **6** should be compared with that of $[\{\rm Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$ [10] and $[\{\rm Mo(NO)Tp^{Me,Me}Cl\}_2(4,4'\text{-bipy})]$ [5]. From the data obtained from the two nitrosyl species referred to above, we conclude that the more cathodic reduction, $E_{\rm f}(\rm red2)$ (-2.13 V), in **6** (see Fig. 5) is mainly associated with the $\{\rm Mo(NO)Tp^{Me,Me}Cl(py)\}$ fragment and is significantly ligand-based. This may be compared with $E_{\rm f}(\rm red2)$ in $[\{\rm Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$ (2.00 V) which is associated with the same fragment [10]. Following the same line of argument, $E_{\rm f}(\rm red1)$ (-1.08 V) should be due to the $\{\rm MoOTp^{Me,Me}Cl(OC_6H_4\text{-})\}$ group and is therefore mainly $\rm Mo(V) \rightarrow Mo(IV)$. On the oxidation side, and again in comparison with $[\{\rm Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$ ($E_{\rm f}(\rm ox) = +0.12$ V), $\rm E_f(ox1)$ at $+0.02$ in **6** may be associated with the nitrosyl pyridyl fragment while that at $+0.82$ V ($E_{\rm f}(\rm ox2)$) should presumably be due to the oxomolybdenum fragment—a substantial shift from the oxidative processes detected in **4** and **5**.

After comparison of the values of $\Delta E_{\rm f}$ obtained from the dinuclear species reported in Table 2 we can summarise the data as follows.

1. In symmetrical dinuclear complexes, the interaction between the redox centres on reduction is at least an order of magnitude larger in the nitrosyl complexes than in the oxo species. Since $\Delta E_{\rm f}$ is really a reflection of coulombic repulsion on the second reduction following addition of the first electron, it is apparent that the effect is more efficiently transmitted in nitrosyl complexes than either symmetric dinuclear oxo species or in the asymmetric complexes **4** and **5**. This may be a function of better overlap between the d_{xy} orbital and the bridging ligand π-orbitals in the nitrosyl species, in which the metal is in a low formal oxidation state, than in the oxomolybdenum(V) where the d_{xy} orbital is contracted because of the high oxidation state.
2. In the asymmetric species **4** and **5** there is a reduction in $\Delta E_{\rm f}$ as the bridging ligand lengthens, paralleling the behaviour in all other comparable compounds [11,12,14], and is due to the separation of charges implicit in the more extended structures of compounds having two or more aromatic rings in the bridge.

Table 2
Electrochemical data obtained from the new mixed metal complexes and related symmmetrical binuclear species

Complex	Reduction processes[a]			Oxidation processes[a]		
	E_f(red2) $-1 \to -2$	E_f(red1) $0 \to -1$	ΔE_f^b	E_f(ox1) $0 \to +1$	E_f(ox2) $+1 \to +2$	ΔE_f^b
$[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4O)]$	-1.18^c	-0.72^c	460	—	—	
$[Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4C_6H_4O)]$	-0.85^c	-0.75^c	110			
$[Mo(NO)Tp^{Me,Me}Cl(OPh)]$		-0.79^c		—		
$[Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$	-2.00	-0.65^d	1350	$+0.12^{d,e}$		
$[Mo(NO)Tp^{Me,Me}Cl\}_2(4,4'\text{-bipy})]$	-2.17^f	-1.41^f	765	$+0.01^f$		
$[Mo(NO)Tp^{Me,Me}Cl(py)]$		-2.01^f		$+0.04^f$		
$[\{MoOTp^{Me,Me}Cl\}_2(OC_6H_4O)]$	-1.44^g	-1.19^g	25			
$[\{MoOTp^{Me,Me}Cl\}_2(OC_6H_4C_6H_4O)]$	$-1.13^{g,h}$	0	$+0.44^g$	$+0.92^g$	480	
$[MoOTp^{Me,Me}Cl(OPh)]$		-1.21^g		$+0.68^g$		
$[MoOTp^{Me,Me}Cl(OC_6H_4O)Mo(NO)$ $\text{-}Tp^{Me,Me}Cl]$, **4**	$-1.45(149)$	$-0.95(123)$	501	$+0.47(114)$	—	
$[MoOTp^{Me,Me}Cl(OC_6H_4C_6H_4O)Mo(NO)$ $\text{-}Tp^{Me,Me}Cl]$, **5**	$-1.22(180)$	$-0.89(159)$	330	$+0.43(234)$	$+0.92^i$	$(\sim 500)^j$
$[MoOTp^{Me,Me}Cl(OC_6H_4py)Mo(NO)$ $\text{-}Tp^{Me,Me}Cl]$, **6**	$-2.13(133)$	$-1.08(110)$	1056	$+0.01(108)$	$+0.82(120)$	805

[a] In V, vs. ferrocene/ferrocenium couple, ($E_p^c - E_p^a = 100$ mV).
[b] $\Delta E_f = E_f(\text{red1}) - E_f(\text{red2})$ or $E_f(\text{ox1}) - E_f(\text{ox2})$, in mV.
[c] Data from [12].
[d] Data from [10].
[e] Two electron oxidation.
[f] Data from [5].
[g] Data from [14].
[h] Two-electron reduction.
[i] Irreversible process, anodic peak only observed.
[j] Estimated.

3. Taking into account ΔE_f (reduction) for $[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$ (1350 mV) and for $[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4C_6H_4O)]$ (≤ 36 mV) it is evident that there is an interaction between the two redox centres in **6**, but it is reduced relative to that of $[\{Mo(NO)Tp^{Me,Me}Cl\}_2(OC_6H_4py)]$.
4. Oxidation of the dinuclear species usually occurs in two steps, and ΔE_f (ox) is substantial, in contrast to dinuclear nitrosyls where the oxidation processes appear to be mainly metal-based and there is virtually no interaction between the two redox centres.
5. Our inability to detect oxidation processes in species containing the $\{Mo(NO)Tp^{Me,Me}Cl(\text{phenolate})\}$ fragment indicates that this occurs above the oxidative breakdown of the medium ($> +1.50$ V). So it is difficult to make realistic comparison of ΔE_f (ox) in comparable symmetric nitrosyl and oxo species with the data obtained from the asymmetric compounds. However, such data as we have obtained indicates that there is very little difference in ΔE_f (ox) between $[\{Mo(NO)Tp^{Me,Me}Cl\}_2\{O(C_6H_4)_nO)]$ and $[Mo(NO)\text{-}Tp^{Me,Me}Cl\{O(C_6H_4)_nO\}MoOTp^{Me,Me}Cl]$.
6. Replacement of $\{Mo(NO)\}$ in $[Mo(NO)Tp^{Me,Me}Cl\}_2\text{-}(OC_6H_4py)]$ by an oxomolybdenum group, forming **6**, causes an apparent decrease in ΔE_f (red), but the presence of the nitrosyl molybdenum group has only a slight effect on the oxidation of the oxomolybdenum fragment (E_f(ox2), $+0.82$ V).

These observations suggest that there is only a small electrochemical interaction between the nitrosyl and oxo-molybdenum redox centres.

2.4. EPR spectral characterisation

Both **4** and **5** contain one unpaired electron. The EPR spectra of both species at room temperature in dichloromethane solution appear as 'singlet + sextet' multiplets $\{^{95}$Mo (15.9%) and ^{97}Mo (9.6%) have $I = 5/2\}$ with $g = 1.940$ and $A_{Mo} = 50.16$ G. Since many related complexes containing the oxomolybdenum(V) group have g-values at 1.939 and $A_{Mo} \approx 50$G, we conclude that the unpaired electron in **4** and **5** is localised on the $MoOTp^{Me,Me}$ group.

The situation in **6** is different since both metal centres have one unpaired electron. Here, the EPR spectrum

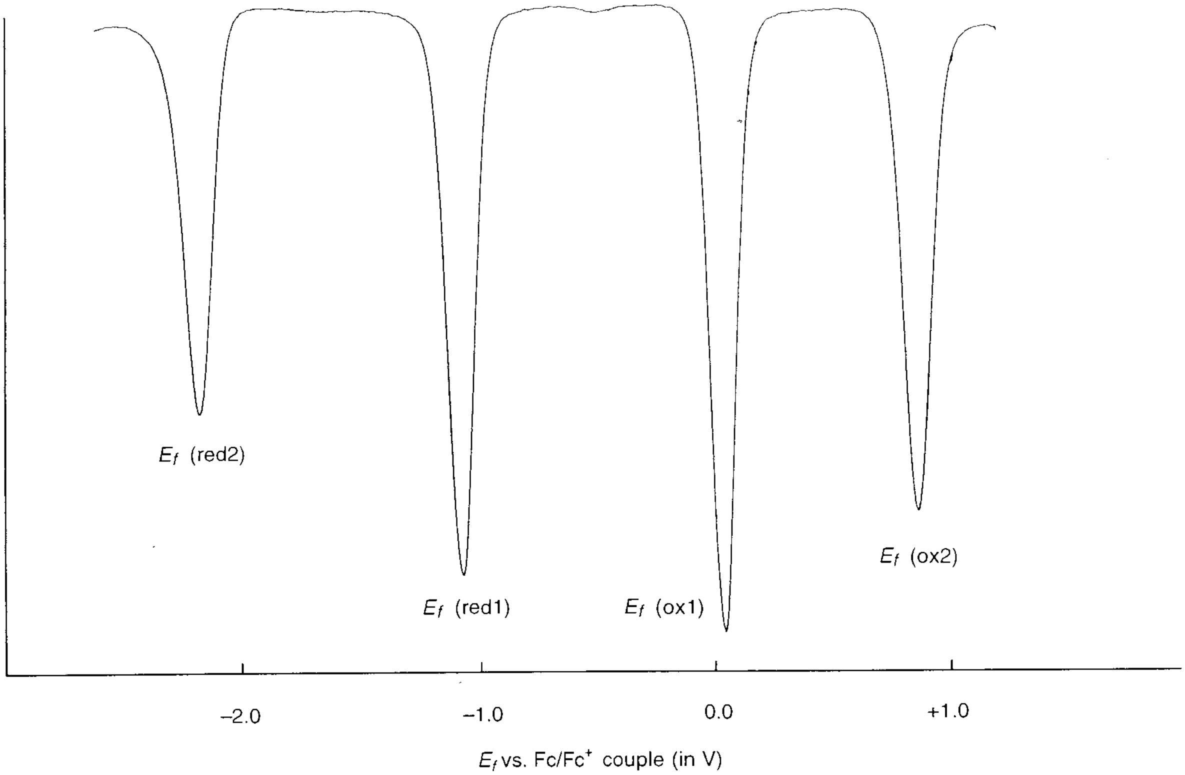

Fig. 5. Square-wave voltammogram of [MoOTp^{Me,Me}Cl(OC$_6$H$_4$py)Mo(NO)Tp^{Me,Me}Cl], **6**, in CH$_2$Cl$_2$, showing E_f(red2), E_f(red1), E_f(ox1) and E_f(ox2).

appears as a slightly broadened 'singlet + sextet' with evidence of further spin multiplicity at the outer edges of the signal, and $g = 1.959$ and $A_{Mo} = 27.80$ G. For strong spin correlation ($J \gg A_{Mo}$) we would expect a 'singlet + sextet + undecet' multiplet, the singlet arising from the $I = 0$, $I = 0$ nuclear spin combination, the 1:1:1:1:1:1 sextet from the $I = 5/2$, $I = 0$ combination, and the 1:2:3:4:5:4:3:2:1 undecet from the $I = 5/2$, $I = 5/2$ combination. Our inability to observe fully the outer hyperfine splitting components may be due to anisotropic effects and line broadening. However, the spectra show unambiguously that the spins are correlated. The g-values for [{Mo(NO)Tp^{Me,Me}Cl}$_2$(bipy)] and related species averages 1.978 [5], for [{MoOTp^{Me,Me}Cl}$_2$(OC$_6$H$_4$O)], [{MoOTp^{Me,Me}Cl}$_2$(OC$_6$H$_4$C$_6$H$_4$O)] and related phenolato complexes it averages 1.940 [14], but in **6** it is 1.959, exactly half way between the two extremes represented by the nitrosyl(pyridyl)molybdenum and oxomolybdenum cores. This is a very rare phenomenon, one which we have encountered only once previously in the epr spectrum of [{Mo(NO)Tp^{Me,Me}Cl}$_2$(OC$_6$H$_4$py)]$^-$ where $g = 1.973$, exactly midway between that of [Mo(NO)Tp^{Me,Me}Cl(OC$_6$H$_4$py)]$^-$ (1.969) and that of [Mo(NO)Tp^{Me,Me}Cl(pyC$_6$H$_4$OMe)] (1.978) [10]. This means that we are able to predict g-values with some accuracy in oligometallic molybdenum nitrosyl and oxo species containing different donor atom environments. Furthermore, at 77 K, we have observed a half-field ($\Delta M_s = 2$) transition at $g = 4.071$, with an intensity of 10% that of the $\Delta M_s = 1$ transition. We have not previously observed half-field transitions in symmetrical dinuclear nitrosyl complexes, but this is a common occurrence in symmetrical dinuclear oxomolybdenum compounds [14]. The reason for this is unclear at the moment.

3. Conclusions

The two dinuclear phenolato complexes **4** and **5** exhibit very similar spectroscopic properties. Their electrochemical properties are consistent with the reduction processes $\{Mo(NO)\}^{3+}$(16ve) → $\{Mo(NO)\}^{2+}$(17ve) and then $\{MoO\}^{3+}$(Mo^V) → $\{MoO\}^{2+}$(Mo^{IV}). The difference between the two reduction potentials, ΔE_f $\{E_f(red1) - E_f(red2)\}$ is larger in **4** than in **5**, indicating that there is some coulombic interaction through the bridging group, as has been detected elsewhere [5,10–13]. Oxidation of these complexes is largely due to the process $\{MoO\}^{3+}$(Mo^V) → $\{MoO\}^{4+}$(Mo^{VI}). However, the EPR data show unambiguously that the complexes are valence-trapped, identical to [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$(OC$_6$H$_4$py)] and [{Mo(NO)[HB(dmpz)$_3$]Cl}$_2$(1,4-OC$_6$H$_4$O)]$^-$ [10,12].

Complex **6** has two unpaired electrons, and its EPR spectrum shows that the two spins are correlated. This behaviour is analogous to that in $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(OC_6H_4py)]^-$ and $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(4,4'\text{-bipy})]$ [5,10]. The complex undergoes two sequential reductions corresponding first to the process $\{MoO\}^{3+}(Mo^V) \rightarrow \{MoO\}^{2+}(Mo^{IV})$ and then to $\{Mo(NO)\}^{2+}(17ve) \rightarrow \{Mo(NO)\}^+(18ve)$. The large value of ΔE_f detected in the CV of **6** is partly due to the very considerable electronic difference between the two redox centres and also to the ability of the bridging ligand to exist in quinonoidal forms which strongly increase negative charge at the pyridyl terminus and reduce it at the phenolate terminus. The complex also undergoes two oxidations corresponding to the processes $\{Mo(NO)\}^{2+}(17ve) \rightarrow \{Mo(NO)\}^{3+}(16ve)$ and then $\{MoO\}^{3+}(Mo^V) \rightarrow \{MoO\}^{4+}(Mo^{VI})$. Again, a large ΔE_f was detected, but generally the electrochemical data are consistent with weak interaction between the nitrosyl and oxo-molybdenum centres.

Westcott and Enemark have shown that while the SOMO in the oxomolybdenum(V) and the LUMO in the nitrosylmolybdenum cores have very similar symmetry, being based on molybdenum d_{xy}, they have significantly different energies [15]. From our perspective, this means that there is little chance of delocalisation of the unpaired spin in dinuclear complexes having one unpaired electron. It also follows that the general properties of **4** and **5** are very similar to those of $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(OC_6H_4py)]$ and that of **6** to $[\{Mo(NO)[HB(dmpz)_3]Cl\}_2(4,4'\text{-bipy})]$.

These results pose two interesting questions: (i) does reduction of **4** and **5** in a one-electron step afford a monoanion having spectroscopic properties similar to **6** (i.e. strong spin correlation) and (ii) are the unpaired electrons in **6** coupled ferromagnetically? The bridging ligand in **6** has an odd number of atoms and, following our earlier successes in the prediction of the sign of J in a series of paramagnetic dinuclear complexes having diphenolato and dipyridyl bridging ligands, we would expect the unpaired electrons to be coupled ferromagnetically. The answers to these questions must await more detailed spectroelectrochemical, EPR and magnetic susceptibility studies of **4**, **5**, and **6**, and their symmetrical analogues, $[\{MoO[HB(dmpz)_3]Cl\}_2\{O(C_6H_4)_nO\}]$.

4. Experimental

4.1. General details

The starting materials $[Mo(E)Tp^{Me,Me}Cl_2]$ (E = NO or O) were prepared by standard procedures [17,18], as was HOC_6H_4py [10] and 1,4-dihydroxybenzene and 4,4′-diphenol were used as purchased (Aldrich). All reactions were carried out under N_2 in dry glassware, and were monitored by thin layer chromatography (TLC). The new compounds were usually purified by column or plate chromatography using silica gel 60 (70–230 mesh) with CH_2Cl_2 alone or mixed with either n-hexane or THF as eluant. IR and electronic spectra were recorded using a PE1600 FTIR and PE Lambda-2 spectrophotometers, ^1H NMR spectra were obtained using a JEOL GX270 or λ-300 instruments, EI and FAB (+ve ion) mass spectra using a VG-Autospec instrument, and epr spectra were obtained with a Bruker EPS-300E spectrometer in CH_2Cl_2/THF solutions (1:1 v/v) at room temperature. Electrochemical measurements were made using a PC-controlled EC & G PAR model 273A potentiostat, with platinum-bead working and counter electrodes, a saturated calomel electrode as reference, pre-dried CH_2Cl_2 as solvent and $[Bu^n_4N][PF_6]$ (ca. 0.1 mol dm^{-3}) as base electrolyte. Ferrocene was added as internal standard, and all potentials are quoted relative to the ferrocene/ferrocenium couple.

4.2. Synthesis of mononuclear precursors

*4.2.1. $[Mo(NO)Tp^{Me,Me}Cl(OC_6H_4OH)]$, **1***

$[Mo(NO)Tp^{Me,Me}Cl_2]$ (1.48 g, 0.03 mol) was added slowly to 1,4-$C_6H_4(OH)_2$ (0.5 g, 0.045 mol) in toluene (80 cm^3) and then NEt_3 (ca.0.3 cm^3) was added, the mixture being then refluxed overnight. The resulting mauve mixture was evaporated to dryness in vacuo, the crude product was dissolved in the minimum volume of CH_2Cl_2 and the solution chromatographed on silica gel. Elution using pure dichloromethane afforded the dark blue/purple dinuclear species $[\{Mo(NO)Tp^{Me,Me}Cl\}_2 OC_6H_4O]$, which was removed, and the desired product was obtained by elution using CH_2Cl_2/THF mixtures (7.5% volume of THF). The compound was isolated as a mauve solid (0.76 g, 45%).

*4.2.2. $[Mo(NO)Tp^{Me,Me}Cl(OC_6H_4C_6H_4OH)]$, **2***

This compound was obtained in the same way as $[Mo(NO)Tp^{Me,Me}Cl(OC_6H_4OH)]$ above, using $[Mo(NO)Tp^{Me,Me}Cl_2]$ (2.0 g, 0.04 mol), 4,4′-$HOC_6H_4C_6H_4OH$ (1.1 g, 0.06 mmol), NEt_3 (1 cm^3) in toluene (100 cm^3). The desired compound was isolated as a mauve solid (0.44 g, 17%).

*4.2.3. $[MoOTp^{Me,Me}Cl(OC_6H_4py)]$, **3***

To a solution of 4(4′-HOC_6H_4)py (0.33 g, 0.019 mol) in toluene (80 cm^3) was added $[MoOTp^{Me,Me}Cl_2]$ (1.4 g, 0.029 mol) and NEt_3 (1.0 cm^3). The mixture was refluxed overnight affording a very dark solution which was evaporated to dryness in vacuo, affording a mauve residue. This solid was redisssolved in the minimum volume of dichloromethane and chromatographed over silica gel using CH_2Cl_2/THF mixtures (9:1 v/v). The first two bands, one brown and the other yellow-green (probably unreacted $[\mathrm{MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}_2]$), were discarded but the third mauve band afforded the desired compound after evaporation of the eluting mixture in vacuo, and was obtained as a mauve solid (0.42 g, 36%).

4.3. Synthesis of dinuclear complexes

4.3.1. $[\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl(OC_6H_4OMoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}]$, **4**

To a solution of $[\mathrm{MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}_2]$ (0.56 g, 0.012 mol) and $\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl(OC_6H_4OH)}]$ (0.35 g, 0.062 mol) in toluene (100 cm^3) was added NEt_3 (1 cm^3) and the mixture was refluxed overnight giving a dark blue solution. This was then evaporated to dryness in vacuo and the residue was purified on a silica gel column using $\mathrm{CH_2Cl_2}$/n-hexane (initially 7:3 v/v) as eluant. The first yellow-green band (probably unreacted $[\mathrm{MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}_2]$) was discarded but the second blue band contained the desired dinuclear product. This was eluted from the column and the solvent evaporated in vacuo to dryness giving the compound as a slightly impure dark blue solid (0.2 g, 32%). Further purification was effected by silica gel plate chromatography, again using $\mathrm{CH_2Cl_2}$/n-hexane mixtures (8:2 v/v) which caused the separation of a pink and green band (these may be $[\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{(OH)}_2]$ and $[\{\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl}\}_2\mathrm{O}]$ formed by hydrolytic decomposition of molybdenum nitrosyl species on the column), followed by the expected blue band which contained purer dinuclear product. Further plate chromatography of the blue band provided even purer material, but in ever-decreasing yields.

4.3.2. $[\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl(OC_6H_4C_6H_4O)MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}]$, **5**

This compound was prepared in the same way as $[\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl(OC_6H_4OMoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}]$ above, and was isolated as a purple solid. Chromatographic separation was achieved most effectively using 9:1 $\mathrm{CH_2Cl_2}$/n-hexane (v/v) mixtures and final purification was achieved using alumina plates. The yield of the compound was 0.26 g (34%).

4.3.3. $[\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl(pyC_6H_4O)MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}]$, **6**

Triethylamine (2 cm^3) was added to a solution of $[\mathrm{Mo(NO)Tp}^{\mathrm{Me,Me}}\mathrm{Cl}_2]$ (0.3 g, 0.61 mmol) and $[\mathrm{MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl(OC_6H_4py)}]$ (0.25 g, 0.41 mmol) in toluene (100 cm^3). The mixture was refluxed overnight and the resulting black mixture was then evaporated to dryness in vacuo. The resulting brown residue was chromatographed on silica gel using $\mathrm{CH_2Cl_2}$/THF (98:2 v/v) as eluant, the initial weak yellow/orange (unreacted $[\mathrm{MoOTp}^{\mathrm{Me,Me}}\mathrm{Cl}_2]$, green, pale pink/brown and darker green bands were discarded, but the next dark brown band afforded the desired compound which was collected, the solvent being evaporated in vacuo giving the product was a brown solid (0.11 g, 25%).

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References

[1] (a) R.J. Rushby, J.-L. Paillaud, in: M.C. Petty, M.R. Bryce, D. Bloor (eds.), An Introduction to Molecular Electronics, Edward Arnold, London, 1995, p. 72; (b) O. Kahn, O. Cador, J. Larionova, C. Mathonière, J.P. Sutter, L. Ouahab, Mol. Cryst. Liq. Cryst., Section A 305 (1997) 1.

[2] (a) H. Tanaka, T. Tokuyama, T. Sato, T. Ota, Chem. Lett. (1990) 1813; (b) P.M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, K. Donovan, G. Grüner, J.D. Thompson, Science 253 (1991) 301; (c) Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, M. Ishikawa, Phys. Rev. B46 (1992) 8906; (d) J. Veciana, C. Rovira, N. Ventosa, M.I. Crespo, F. Palacio, J. Am. Chem. Soc., 115 (1993) 57; (e) A. Lang, H. Naarmann, G. Rosler, B. Gotschy, H. Winter, E. Dormann, Mol. Phys. 79 (1993) 1051; (f) T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, M. Ishikawa, Chem. Lett. (1994) 29; (g) S. Rajca, A. Rajca, J. Am. Chem. Soc. 117 (1995) 9172; (h) M.M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, J. Am. Chem. Soc., 119 (1997) 4369; (I) K. Matsuda, T. Yamagata, T. Seta, H. Iwamura, K. Hori, J. Am. Chem. Soc., 119 (1997) 8058; (j) J. Cirujeda, O. Jurgens, J. Vidal Cancedo, C. Rovira, P. Turek, J. Veciana, Mol. Cryst. Liq. Crystallogr., Section A 305 (1997) 367.

[3] (a) J.K. McCusker, E.A. Schmitt, D.N. Hendrickson, in: D. Gatteschi, O. Kahn, J.S. Miller, F. Palacio (eds.), Magnetic Molecular Materials, NATO ASI E198, Series, Kluwer, Dordrecht, 1991, p. 297; (b) O. Kahn, Molecular Magnetism, VCH, New York, 1993; (c) M.L. Allan, J.H.F. Martens, A.T. Coomber, R.H. Friend, I. Marsden, E.A. Marseglia, A.E. Underhill, A. Charlton, Mol. Cryst. Liq. Crystallogr. 230 (1993) 387; (d) P.J. Vankoningsruggen, J.N. Koga, Y. Ishimaru, H. Iwamura, Angew. Chem. Int. Ed. Engl. 35 (1996) 755; (e) H.L. Nie, S.M.J. Aubin, M.S. Matshuta, R.A. Porter, J.F. Richardson, D.N. Hendrickson, Inorg. Chem. 35 (1996) 3325.

[4] A.M.W. Cargill Thompson, D. Gatteschi, J.A. McCleverty, J.A. Navas, E. Rentschler, M.D. Ward, Inorg.Chem. 35 (1996) 2701.

[5] S.L.W. McWhinnie, J.A. Thomas, T.A. Hamor, C.J. Jones, J.A. McCleverty, D. Collison, F.E. Mabbs, C.J. Harding, L.J. Yellowlees, M.G. Hutchings, Inorg. Chem. 35 (1996) 760.

[6] (a) D. Moryusef, J. Boinvoisin, J.-P. Launay, J.A. McCleverty, M.D. Ward, unpublished work; (b) D. Moryusef, DEA Thesis, Université Paul Sabatier, 1996-7.

[7] A.J. Amoroso, A.M.W. Cargill Thompson, J.P. Maher, J.A. McCleverty, M.D. Ward, Inorg. Chem. 34 (1995) 4828.

[8] V.A. Ung, A.M.W. Cargill Thompson, D.A. Bardwell, D. Gatteschi, J.C. Jeffery, J.A. McCleverty, F. Totti, M.D. Ward, Inorg. Chem. 36 (1997) 3447.

[9] E. Psillakis, J.P. Maher, J.A. McCleverty, M.D. Ward, Chem. Commun. (1998) 835.

[10] A. Das, J.C. Jeffery, J.P. Maher, E. Schatz, M.D. Ward, G. Wollerman, Inorg. Chem. 32 (1993) 2145.

[11] A. Wlodarczyk, J.P. Maher, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Dalton Trans. (1997) 3287.

[12] A. Abdul-Rahman, A.J. Amoroso, T.N. Branston, A. Das, J.P. Maher, J.A. McCleverty, M.D. Ward, A. Wlodarczyk, Polyhedron 16 (1997) 4353.

[13] (a) C.J. Jones, J.A. McCleverty, B.D. Neaves, S.J. Reynolds, H. Adams, N.A. Bailey, G. Denti, J. Chem. Soc. Dalton Trans. (1986) 733; (b) R.C. Cook, J.P. Maher, J.A. McCleverty, M.D. Ward, A. Wlodarczyk, Polyhedron, 20 (1993) 2111.

[14] V.A. Ung, D.A. Bardwell, J.C. Jeffery, J.P. Maher, J.A. McCleverty, M.D. Ward, A. Williamson, Inorg. Chem. 35 (1996) 5290.

[15] B.L. Westcott, J.H. Enemark, Inorg. Chem. 36 (1997) 5404.

[16] A. Wlodarczyk, J.P. Maher, S. Coles, D.E. Hibbs, M.H.B. Hursthouse, K.M.A. Malik, J. Chem. Soc. Dalton Trans. (1997) 2597.

[17] W.E. Cleland Jr., K.M. Barnhart, K. Yamanouchi, D. Collison, F.E. Mabbs, R.B. Ortega, J.H. Enemark, Inorg. Chem. 26 (1988) 1017.

[18] (a) C.J. Jones, J.A. McCleverty, S.J. Reynolds, C.F. Smith, Inorg. Synth. 23 (1985) 4; (b) A.S. Drane, J.A. McCleverty, Polyhedron 2 (1983) 53.