FORMATION OF TRIMETALLIC COMPOUNDS CONTAINING REDOX-ACTIVE NITROSYL MOLYBDENUM TRIS(3,5-DIMETHYLPYRAZOLYL)-BORATO GROUPS. SCHIFF BASE COMPLEXES CONTAINING TWO MOLYBDENUM CENTRES LINKED BY *META* HYDROXY COPPER SCHIFF BASE LIGANDS

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ABSTRACT. The reaction of [Mo(NO)Tp*Cl₂] [Tp* = tris(3,5-dimethyl-pyrazolyl)borate] with copper(II) Schiff base complexes derived by condensation of two mole equivalents of 2,4-dihydroxybenzaldehyde with a diamine [1,2-C₆H₄(NH₂)₂, NH₂(CH₂)ₙNH₂, n = 2-5] affords trimetallic species containing three potential redox centres. The IR, UV-vis and EPR spectroscopic properties of these compounds are described and it is shown that, with increasing polymethylene bridges of the Schiff base ligands, the complexes distort from planarity probably towards tetrahedral structures. From cyclic and differential pulse voltammetry it is shown that the trimetallic species primarily undergo two sequential one electron reduction associated with the reduction of [Mo(NO)Tp*Cl]⁺ centres. By determination of conproportionation constants for the mono-reduced species, it is established that there is very weak interaction between the two [Mo(NO)Tp*Cl]⁺centres in the trimetallic complexes. It is also demonstrated that the *meta*-substituted [Mo(NO)Tp*Cl]⁺ centres reduce at potentials more anodic than their *para*-substituted analogues. Reduction potentials of these complexes are also shown to be solvent dependent.

INTRODUCTION

Following our earlier report that the reaction of a series of Schiff base copper complexes of type **1** (M = Cu, M' = H) with two mole equivalents of [Mo(NO)Tp*Cl₂], produce trimetallic complexes, in which [Mo(NO)Tp*Cl]⁺ occupy *para* position in the benzene ring in Compound **1**, this reaction has been used to produce further examples of trimetallic complexes in which the peripheral [Mo(NO)Tp*Cl]⁺ groups are *meta* with respect to the two oxygen atoms in compounds of type **2** [1]. In our earlier investigations we demonstrated that the trimetallic species [**1**, M = Cu, M' = Mo(NO)Tp*Cl] exhibited electrochemical behaviour in which the two peripheral [Mo(NO)Tp*Cl]⁺ centres interact weakly via the linking copper Schiff base framework [1]. Such electrochemical properties are much less significant than those encountered in similar ferrocenyl species of type **3** [Fe{η⁵-C₅H₄SMo(NO)Tp*Cl}₂] in which the two [MoNOTp*Cl]⁺ redox centres transmit their inductive effect very efficiently through the organic and organometallic framework [2].

Of even greater significance are bimetallic species such as {Mo(NO)Tp*Cl}₂Z (Z = -C₆H₄O⁻ or -NHC₆H₄NH) in which the two [Mo(NO)Tp*Cl]⁺ interact strongly [3] when compared to similar analogues of the type {Mo(NO)Tp*Cl}₂OC₆H₄ZC₆H₄O (Z = CH₂CH₂, O, CO, SO₂) in which there are very weak or no interactions at all [4].
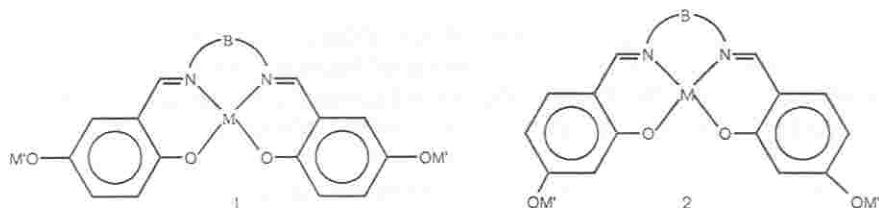
B = C_6H_4 or $(CH_2)_n$,   n = 2-5   M' = $[Mo(NO)Tp^*Cl]^+$ or H M = H_2 or Cu

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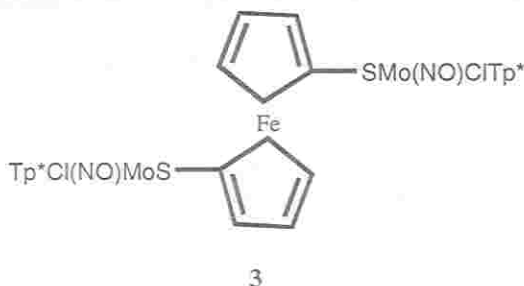
To investigate further the possibility of fine tuning the interaction between two $[Mo(NO)Tp^*Cl]^+$ redox centres via a Schiff base copper framework, species of type **2** in which the two $[Mo(NO)Tp^*Cl]^+$, redox centres are attached via the *meta*-hydroxy positions of each benzene ring giving for example [**2**, M = Cu, M' = $Mo(NO)Tp^*Cl$] are synthesized. This paper reports the syuthesis of a series of trimetallic complexes containing molybdenum nitrosyl groups linked by copper(II) Schiff base metal complexes. The spectroscopic and electrochemical properties of the new complexes are discussed.

EXPERIMENTAL

The precursor compound $[Mo(NO)Tp^*Cl_2]$ was prepared according to the literature method [5, 6]. Other standard reagent materials were obtained from commercial sources and were used without further purification. All synthetic reactions except those involving preparation of free Schiff base ligands and their copper derivatives, were carried out under nitrogen. Silica gel 60 (70-230 mesh) was used for column chromatography and dichloromethane, hexane and tetrahydrofuran as eluants.

IR and UV-visible spectra were measured using PE 1600 FTIR series, Shimadzu UV-240 and PE-Lambda 2 spectrophotometers, respectively. EPR measurements were made using a Bruker Esp 300E in an X-band field, the data being calibrated with reference to external DPPH (g = 2.0037). Elemental analyses were performed by microanalytical laboratory of School of Chemistry of Bristol. Mass spectra were recorded on a Kratos MS 80 instrument by positive ion FAB using either a glycerol or NOBA matrix. ^{1}H NMR spectra of free Schiff base ligands were obtained using JEOL GX 270 spectrometers.

Cyclic and differential pulse voltammetry were carried out using EG & G PAR 273A galvanostat and potentiostat. Solutions in acetonitrile, dichloromethane and DMSO were *ca* 1 x 10^{-3} M in the complex with *ca* 0.1 M [n-Bu$_4$N][PF$_6$] as the base electrolyte. The working and counter electrodes were a platinum bead and platinum wire, respectively, while saturated

calomel electrode (SCE) was used as the reference electrode. All the formal potentials were taken as the average of anodic and cathodic peak potentials. Differential pulse voltammetry was carried out using a pulse amplitude of 10 mV and I vs E relationship recorded. To obtain ΔE_f values, the separation between the two reduction potentials from differential pulse voltammetric waves, the relationship developed by Richardson and Taube was used [7]. A graph of $W_{\frac{1}{2}}$ (differential pulse voltammogram peak-width at half-height) versus ΔE_f was constructed.

Synthesis of Schiff base ligands (2, M = H$_2$, M' = H, B = diamine). In general all the free Schiff base ligands were synthesized in ways similar to those used in the synthesis of *para*-hydroxyl analogues of type 1 (M = H$_2$, M' = H; B = diamine) [1] except that 2,4-dihydroxybenzaldehyde was used as the carbonyl compound in these reactions. Specific syntheses are given below.

Synthesis of the copper Schiff base precursor (2, M = Cu, M' = H, B = C$_6$H$_4$). A solution of copper acetate (0.172 g, 0.86 mmol) in absolute ethanol (30 cm^3) was treated dropwise with an ethanolic solution of Schiff base (2, M = H$_2$, M' = H, B = C$_6$H$_4$) (0.29 g, 0.86 mmol). The solution turned reddish brown. The mixture was refluxed for 5 h and then cooled. A brown solid settled out. The solid was filtered off and washed thoroughly with diethyl ether and dried in vacuo (yield 0.3 g, 78.9%).

Synthesis of the copper Schiff base precursor [2, M = Cu, M' = H, B = (CH$_2$)$_2$]. This compound was prepared in a similar manner to that above, using copper acetate (0.23 g, 1.02 mmol) and (2, M = H$_2$, B = CH$_2$CH$_2$, M' = H) (0.305 g, 1.02 mmol). The purple precipitate was filtered off and washed thoroughly with ethanol and diethyl ether and dried in vacuo (yield 0.35 g, 85%). The other copper Schiff base precursors {(2, M = Cu, M' = H, B = (CH$_2$)$_3$, M = Cu, M' = H, B = (CH$_2$)$_4$, M = Cu, M' = H, B = (CH$_2$)$_5$)} were all prepared in the same way, and in comparable yields.

Synthesis of trimetallic complexes [2, M = Cu, M' = Mo(NO)Tp*Cl, B = diamine]. In general these complexes were prepared by treatment of one mole equivalent of the copper Schiff base complexes (2, M = Cu, B = diamine, M' = H) suspended in toluene with two molar equivalents of Mo(NO)Tp*Cl$_2$ in presence of small amounts of triethylamine. The reaction mixture was refluxed for a period of between one day and six days. The cooled solutions were filtered, the solvent partially reduced in vacuo and the remaining solution chromatographed on a silica gel column 60 (70-230 mesh). The major red fractions were eluted by a mixture of dichloromethane/hexane/THF in 6:3:1 ratio, respectively, and the solvent was evaporated in vacuo. The red solution obtained in this step was then triturated with n-hexane affording the desired compounds as red solids. Chromatography showed the presence of varying amounts of green species. The preparations of individual trimetallic complexes are as follows.

Synthesis of [2, M = Cu, M' = Mo(NO)Tp*Cl, B = C$_6$H$_4$]. This compound was obtained by reacting an appropriate copper precursor {2, M = Cu, M' = H, B = C$_6$H$_4$}(0.265 g, 0.626 mmol) suspended in toluene, with Mo(NO)Tp*Cl$_2$ (0.62 g, 1.25 mmol). A few drops of triethylamine were added to the mixture which was refluxed under nitrogen for 2 days. The solution mixture was evaporated in vacuo and the red residue dissolved in a minimum volume of dichloromethane and chromatographed using hexane/dichloromethane mixture. The first wine-red fraction was eluted using 50% hexane in dichloromethane. The solid obtained from

this fraction was not sufficient for characterization. Minor green species was also eluted and discarded. The third red brown species was eluted using 80% dichloromethane in hexane and precipitated with n-hexane. The solid was then dried in vacuo (yield 0.3 g, 36.2%).

Synthesis of [2, $M = Cu$, $M' = Mo(NO)Tp^*Cl$, $B = (CH_2)_2$]. This complex was obtained from the appropriate copper precursor (2, $M = Cu$, $M' = H$, $B = (CH_2)_2$) (0.206 g, 0.57 mmol) and [Mo(NO)Tp*Cl$_2$] (0.56, 1.13 mmol). The reaction was carried out in toluene in the presence of a few drops of triethylamine. The mixture was refluxed for 5 days under nitrogen. Within this time the solution mixture had turned dark red. The mixture was cooled and the volume reduced. The concentrated solution was then chromatographed on silica gel 60 (70-230 mesh) and the major red fraction was eluted with 2% THF in CH$_2$Cl$_2$. Precipitation was effected by addition of n-hexane. The red solid was dried in vacuo (yield 0.23 g, 31.8%).

Synthesis of [2, $M = Cu$, $M' = Mo(NO)Tp^*Cl$, $B = (CH_2)_3$]. This complex was obtained in an identical manner to {2, $M = Cu$, $M' = Mo(NO)Tp*Cl]^+$}, chromatographed and the major red compound eluted and precipitated on addition of n-hexane (yield 0.25 g, 36.2%).

Synthesis of [2, $M = Cu$, $M' = Mo(NO)T_p.Cl$, $B = (CH_2)_4$]. This complex was obtained from the appropriate copper precursor {$M = Cu$, $M' = H$, $B = (CH_2)_4$} (0.2 g, 0.513 mmol) and Mo(NO)Tp*Cl$_2$ (0.507 g, 1.03 mmol) and the mixture was refluxed for 3 days and then cooled. Chromatographed as before afforded major wine red and dark red fractions, besides green and yellow species. Only the major dark red and wine-red eluates were retained. These were concentrated separately and solids precipitated with n-hexane. Only the dark red solid proved to be trimetallic whereas there was no copper in the wine red solid. (Yield 0.3 g, 38.3%).

Synthesis of [2, $M = Cu$, $M' = Mo(NO)Tp^*Cl$, $B = (CH_2)_5$]. This complex was obtained in a similar way to the above trimetallic complexes by using the appropriate copper precursor Schiff base complex {2. $M = Cu$, $M' = H$, $B = (CH_2)_5$}. (0.17 g, 0.42 mmol) and [Mo(NO)Tp*Cl$_2$](0.41 g, 0.84 mmol). The mixture was refluxed for 6 days under nitrogen; chromatographed as before revealed both wine-red and red-brown fractions. Only the red-brown fraction proved to be trimetallic whereas there was no copper in the wine red solid. complex. (Yield 0.28 g, 36.8%).

RESULTS AND DISCUSSION

Synthetic studies. The general procedure for obtaining *meta*-functionalized Schiff base ligands [2, $M = H_2$, $M' = H$, $B =(CH_2)_n$, n = 2-5] was as previously reported [1]. These ligands were obtained as yellow precipitates except [2, $M = H_2$, $M' = H$, $B = C_6H_4$] which was recovered as a red-orange solid. The ligands were obtained in relatively high yields.

The precursor copper Schiff base complexes [2, $M = Cu$, $M' = H$, $B = (CH_2)_n$, n = 2-5] were generally obtained by reacting preformed Schiff base ligands with copper acetate in a 1:1 molar ratio in ethanol. These complexes were isolated as hydrated neutral compounds. Elemental analyses of these species are in good agreement with their formulations.

The trimetallic species [2, $M = Cu$, $M' = [Mo(NO)Tp^*Cl]^+$, $B = C_6H_4$, (CH$_2$)$_n$, n = 2-5] were obtained by reaction of the preformed copper Schiff base complexes [2, $M = Cu$, $M' = H$, $B = C_6H_4$, (CH$_2$)$_n$, n = 2-5] with [Mo(NO)Tp*Cl$_2$] in a 1:2 molar ratio in the presence of a

small amount of triethylamine in dry toluene under dinitrogen. The use of triethylamine was to facilitate deprotonation of the phenolic hydroxyl groups of the Schiff base copper precursor complexes and probably to trap HCl liberated in the reaction as triethyl ammonium salt [Et₃NH]⁺Cl⁻. The reaction mixture was refluxed for 1-5 days to ensure completion of the reaction. The crude trimetallic complexes were isolated by filtering the solution while hot, cooling and evaporating the filtrate to dryness. Purification of the desired compounds was effected by column chromatography followed by recrystallization and reprecipitation in dichloromethane and n-hexane, respectively.

The trimetallic compounds were generally obtained as red brown microcrystalline solids in moderate yields. Besides these complexes, side products - the green oxo species $[\{Mo(NO)Tp^*Cl\}_2O]$ and other products were also produced as observed before [8]. Elemental analyses of the trimetallic complexes and copper Schiff base complexes are depicted in Table 1. All the complexes gave satisfactory analysis for C, H, N. However, the copper Schiff base precursors retain between 0.5 and 1.5 moles of water in their crystal lattice while the trimetallic complexes [2, M = Cu, M' = $Mo(NO)Tp^*Cl$, B = $(CH_2)_3$ and $(CH_2)_4$] retain 0.5 mol of hexane used as solvent [1].

The major peaks observed in FAB mass spectra are listed in Table1 and confirm the basic structures of compounds 2. No attempt is made to discuss the cracking pattern of these complexes. However, it was generally observed that FAB spectra often have other peaks at m/z values, corresponding to the loss of $[Mo(NO)Tp^*Cl]^+$ group from the complexes.

Table 1.   Elemental, physical and mass spectra data obtained from type (2) complexes.
[M = Cu, M' = H or $Mo(NO)Tp^*Cl$ B = diamine].

Compound				Elemental analysis[a]			MS data
M	B	M'	Solvent[b]	%C	%H	%N	[{M}⁺][c]
Cu	C₆H₄	H	1.5H₂O	55.1(55.0)	3.9(3.9)	6.2(6.4)	410(410)
Cu	(CH₂)₂	H	0.5H₂O	52.0(51.8)	4.1(4.1)	7.6(7.6)	362(362)
Cu	(CH₂)₃	H	0.5H₂O	53.7(53.1)	4.5(4.4)	7.3(7.3)	376(376)
Cu	(CH₂)₄	H	0.5H₂O	54.1(54.2)	5.5(4.8)	6.7(7.0)	390(390)
Cu	(CH₂)₅	H	1.0H₂O	54.1(54.1)	5.3(5.2)	6.6(6.6)	404(404)
Cu	C₆H₄	Mo(NO)Tp*Cl	0	43.7(44.1)	5.1(4.4)	17.3(16.5)	1326(1325)
Cu	(CH₂)₂	Mo(NO)Tp*Cl	0	43.7(43.2)	4.3(4.2)	16.9(17.5)	1278(1277)
Cu	(CH₂)₃	Mo(NO)Tp*Cl	0.5C₆H₁₄	45.1(45.0)	5.0(4.9)	16.7(16.8)	1290(1291)
Cu	(CH₂)₄	Mo(NO)Tp*Cl	0.5C₆H₁₄	45.3(45.4)	4.7(5.0)	16.8(16.6)	1307(1305)
Cu	(CH₂)₅	Mo(NO)Tp*Cl	0	44.6(44.6)	4.6(4.7)	16.6(17.0)	1319(1319)

[a]Found (calc). [b]molecule of solvent of crystallisation. [c]heaviest ion detected by FAB mass spectrometry; found (calc for parent ion).

Spectroscopic studies. The principal IR bands of free Schiff base ligands, their copper complexes, and trimetallic complexes are listed in Table 2. IR spectral data for free Schiff bases (2, M = H₂, M' = H and B = diamine) show strong absorption bands between 1610 and 1634 cm⁻¹ due to azomethine C=N stretch. The νC=N is slightly sensitive to the changes in polymethylene carbon chain length of the Schiff base backbone (Table 2). The azomethine C=N stretch exhibited bathochromic shift on coordination to copper, an observation which may be attributed to the decrease in bond order of C=N on its involvement in the coordination

to the metal ion. Such shifts were previously observed for cobalt(II) complexes of Schiff base ligands [9]. In the trimetallic species [2,M = Cu,M'= Mo(NO)Tp*Cl,B = C_6H_4,$(CH_2)_n$ n = 2-5], the azomethine C=N stretching frequencies appear as intense bands in the region between 1605 and 1644 cm^{-1}

Table 2.   IR and electronic spectral data obtained from type (2) complexes.
             [2, M = Cu, M' = H, or Mo(NO)Tp*Cl, B = diamine].

| Compound | | | IR spectral data[a] | | | UV-vis spectral data |
M	B	M'	vC=N	vNO	vBH	λ_{max} $(\in)^b$
Cu	C_6H_4	H	1608			550(broad, vw)^c, 393(20410), 324(4989), 267(13588)
Cu	$(CH_2)_2$	H	1623			572(139, 348(22,200), 294(37,000), 260(42666)
Cu	$(CH_2)_3$	H	1606			613(131), 350(12,589) 294(24,815), 260(23667)
Cu	$(CH_2)_4$	H	1605			658(276), 358(21,877), 294(30,853), 258(29130)
Cu	$(CH_2)_5$	H	1619			667(112), 349(21,646) 289(45,823)
Cu	C_6H_4	Mo(NO)Tp*Cl	1605	1677	2554	700(broad), 480(10,162) 305(17,642)
Cu	$(CH_2)_2$	Mo(NO)Tp*Cl	1623	1690	2554	700(broad), 450(16,029) 340(31,519), 295(36,335)
Cu	$(CH_2)_3$	Mo(NO)Tp*Cl	1603	1690	2554	700(broad), 480(11,966) 310(18,595)
Cu	$(CH_2)_4$	Mo(NO)Tp*Cl	1644	1693	2554	700(broad), 480(12,366)
Cu	$(CH_2)_5$	Mo(NO)Tp*Cl	1622	1689	2554	700(broad), 480(16,790) 305(28,818)

[a]cm^{-1} in CH_2Cl_2 (for trimetallic complexes) and in DMSO for copper Schiff base complexes, [b]in nm, ε in dm^3 mol^{-1}cm^{-1} [c]vw, very weak.

The IR spectra of the trimetallic complexes in solution (CH_2Cl_2) were also characterized by v(BH) and v(NO) at 2554 cm^{-1} and in the range 1677-1693 cm^{-1}, respectively. Generally the v(NO) stretch for the trimetallic complexes are higher than those (1668-1680 cm^{-1}) in trimetallic complexes prepared previously [1] [1, M = Cu, M' = Mo(NO)Tp*Cl, B = diamine] but are similar to v(NO) for bimetallic complexes containing phenolato bridging ligands, which fall in the range 1678-1685 cm^{-1} [10].

The electronic spectra of the precursor copper Schiff base complexes [2, M = Cu, M' = H, B = C_6H_4, $(CH_2)_n$, n = 2-5] and their trimetallic derivatives [2, M = Cu, M' = Mo(NO))Tp*Cl, B = C_6H_4, $(CH_2)_n$, n = 2-5] in DMSO and dichloromethane, respectively, are summarized in Table 2. The data show that as in the *para* analogues [1, M = Cu, M' = H, B = C_6H_4, $(CH_2)_n$, n = 2-5], the copper chelates exhibit absorption peaks falling in the range 667-550 nm, consistent with the presence of planar Cu(II) species with a $N_2O_2^{2-}$ donor atom set [11]. However there is a remarkable, though small bathochromic shift of absorption bands as the polymethylene carbon chain of the Schiff base ligands lengthens, an indication of a slight change in structure of the complexes perhaps from planar to tetrahedral [12]. Such distortions have been observed in related copper Schiff base complexes [13]. Intraligand transitions in these complexes appear as intense bands in the region 398-260 nm and are believed to be of

$\pi \rightarrow \pi$ * or $n \rightarrow \pi$* character. In the visible spectra the trimetallic complexes [2, M = Cu, M' = Mo(NO)Tp*Cl, B = C_6H_4, $(CH_2)_n$, n = 2-5] show very broad bands at ca 700 nm which appear as tails of the more intense bands at 480 nm. The failure to obtain well resolved d-d bands in these complexes may be due to their masking by the intense charge transfer bands in the UV region which is a common phenomenon [14, 15]. Transitions due to the conjugated imine chromophore in trimetallic complexes appear in the range 310-305 nm.

As for their *para*-analogues, magnetic moments for these compounds fall in the range 1.87-2.19 BM and although these values are higher than the spin only values for copper ions, it is clear that these species exists as mononuclear species of copper.

EPR.spectral studies. The EPR spectral data of the copper chelates and their trimetallic derivatives at room temperature and of frozen glasses are summarized in Table3. The spectra were recorded at X-band frequencies and like their *para*-analogues exhibit four lines due to hyperfine interaction with ^{63}Cu (69.1%, I = 3/2) and ^{65}Cu(30.9%). The general features of the spectra are similar to those discussed earlier [1] except that these species [2, M = Cu, M' = H, B = C_6H_4, $(CH_2)_n$, n = 2-5] exhibit isotropic g-values between 2.009-2.118 in DMF. Corresponding isotropic A values for the precursor copper Schiff base complexes fall in the range 54.0-86.7 G in DMF. The isotropic g-values for the trimetallic complexes [2,M = Cu, M' = Mo(NO)Tp*Cl] fall in the range 2.001-2.110 and their isotropic A value lie in the range 78.7-88.4 G. It was also observed that for the compounds, which exhibit proton hyperfine splittings, the ^{14}N coupling constants are ca 14 G and proton superhyperfine coupling constants ca 7.0 G. Apart from the general observation that the spectra of both copper precursor complexes and their trimetallic derivatives, broaden as the polymethylene carbon chain lengthens, superhyperfine splitting due to the coupling of the unpaired electron on copper with two equivalent nitrogen nuclei of the Schiff base ligands were also observed for [2, M = Cu, M' = H, Mo(NO)Tp*Cl, B = C_6H_4, CH_2CH_2]. This observation was explained in our previous work [1] and fits very well with a similar explanation by Maki and McGarvery for the splitting pattern of copper Schiff base complexes [15]. In other species like: [2, M = Cu, M' = H, Mo(NO)Tp*Cl, B = $(CH_2)_n$] no ligand hyperfine splitting could be resolved at room temperature.

The observation that g_{iso} values increase/decrease in antiparallel fashion with the lengthening of the bridging Schiff base backbone (Table 3) coupled with the fact that these compounds show poor resolutions of ^{14}N-hyperfine splittings as the bridging chain increases, suggest some changes in molecular geometry of the compounds.

The frozen EPR spectra of the copper precursors and their trimetallic derivatives at liquid nitrogen temperature (77 K) (Table 3) show three clear bands in the $g_{//}$ region with the fourth band partially hidden under the more complicated $g_\perp$ band. Since the $g_\perp$ regions of the EPR spectra are not well resolved, and are further complicated by the presence of hyperfine and superhyperfine couplings, $g_\perp$ and copper hyperfine splitting constant $A_\perp$ were calculated using the relationship $g_{iso} = 1/3(2g_\perp + g_{//})$ and $A_{iso} = 1/3 (2A_\perp + A_{//})$, respectively.

For the copper precursors (2, M = Cu, M' = H, B = diamine) the $g_{//}$ and $g_\perp$ components occur in the range $2.21 < g_{//} < 2.280$ and $2.033 < g_\perp < 2.050$, respectively. $A_{//}$ and $A_\perp$ fall in the range $135.6 < A_{//} < 203.8$ G and $13.1 < A_\perp < 28.6$ G, respectively. For the trimetallic complexes $g_{//}$ and $g_\perp$ lie in the range $187.6 < A_{//} < 203.2$ G and $23.3 < A_\perp < 33.7$. The data in Table 3 show that as the polymethylene carbon chain of the bridging ligand increases, the $g_{//}$ of the copper chelate complexes increases regularly while that of the $A_{//}$ decreases. Trimetallic complexes show similar trends in both $g_{//}$ and $A_{//}$. These observations plus the fact that $g_{//} > g_\perp > 2.0$ for all the complexes is consistent with distortion of the complexes from

planar to tetrahedral geometries and indicates that the unpaired electrons reside in the d_{x2-y2} ground state orbital.

Table 3.　　Magnetic moments and EPR data obtained from type (2) complexes [2, M = Cu, M' = H or Mo(NO)T$_p$*Cl, B = diamines]. $g_{//}$

Compound			Magnetic moment		EPR spectral data						
M	B	M'	μ_{eff}^a	g_{iso}^b	$g_{//}^c$	$G_\perp^c$	$A_{iso}^{b,d}$	$A_{//}^{c,d}$	$A_\perp^{c,d}$	$\{A_N^{1}H\}^{b,e}$
Cu	C$_6$H$_4$	H^h	2.19	2.092	2.210	2.033	85.2	203.8	25.9	14.1 (7.0)
Cu	(CH$_2$)$_3$	H^h	1.89	2.111	2.244	2.045	78.3	187.2	23.9	14.3 (7.3)
Cu	(CH$_2$)$_2$	H^h	1.87	2.094	2.209	2.037	86.7	203.0	28.6	14.2(7.3)
Cu	(CH$_2$)$_4$	H^h	2.04	2.118	2.255	2.050	66.4	161.1	19.1	12.8
Cu	(CH$_2$)$_5$	H^h	2.19	2.110	2.280	2.025	54.0	135.6	13.1	
Cu	C$_6$H$_4$	Mo(NO)T$_p$*Cl^i		2.001	2.209	1.897	84.4	203.2	25.0	14.2(7.3)
Cu	(CH$_2$)$_2$	Mo(NO)T$_p$*Cl^i		2.097	2.210	2.041	88.1	202.2	31.1	14.0
Cu	(CH$_2$)$_3$	Mo(NO)T$_p$,Cl^i		2.105	2.245	2.035	85.0	187.6	33.7	13.5
Cu	(CH$_2$)$_4$	Mo(NO)T$_p$*Cl^{i,f}		2.107	2.243	2.039	78.7	189.5	23.3	13.5
Cu	(CH$_2$)$_5$	Mo(NO)T$_p$*Cl^{i,g}		2.110	-	-	-	-	-	-

^{a}in B.M., ^{b}obtained in solution, ^{c}obtained from frozen glasses of solution, ^{d}in Gauss, ^{e14}N and ^{1}H hyperfine couplings in Gauss, ^{f}estimated g_{iso} and A_{iso} value (copper lines were too broad), ^{g}estimated g_{iso} value (only room témperature value could be found, other epr parameters could not be calculated for copper lines were too broad), ^{h}in DMF solution, ^{i}in CH$_2$Cl$_2$ solution.

Electrochemical studies. The electrochemical studies of the new complexes [2, M = Cu, M' = Mo(NO)Tp*Cl] were investigated by cyclic voltammetry in dichloromethane and acetonitrile at a platinum bead working electrode. Solutions contained *ca* 1 x 10^{-3} mol dm^{-3} of the complexes while 1 x 10^{-1} mol dm^{-3} of [n-Bu$_4$N][PF$_6$] was used as the base electrolyte.

The cyclic voltammetric data for the trimetallic complexes are summarized in Table 4. Like their *para*-analogues [1], the new complexes exhibited a broad reversible two electron reduction wave in dichloromethane and acetonitrile solvents. The formal reduction potentials {E$_f$) for the complexes ranged between -0.46 to -0.59 V in CH$_2$Cl$_2$ and between -0.39 to -0.42 V in CH$_3$CN which is consistent with the reduction of Mo(NO)Tp*Cl (O-aryl), centres in the complexes by comparison with related species [4, 16].

The values of ΔE_p [the difference in peak potentials (E$_p^c$- E$_p^a$)] for the complexes generally fall in the range 80-150 mV in acetonitrile and 100-170 mV in dichloromethane whereas for ferrocene under similar conditions they fall in the range 60-100 mV in acetonitrile and 100-120 mV in dichloromethane (Table 4). The values of ΔE_p in both solvents are independent of the voltage scan rates. The expected theoretical values of ΔE_p = 120 mV for a reversible sequential two-one electron transfer, (for a reversible one electron process ΔE_p should be 59 mV), ΔE_p for the trimetallic complexes in both solvents are reasonably close to the theoretical value for two sequential electron transfer, in which the two peripheral Mo(NO)Tp*Cl redox centres interact weakly. This is consistent with the previously observed behaviour of the *para*-copper analogues [1] and palladium and nickel analogues [17]. The data in Table 4, show that the reduction potential of the trimetallic complexes described in this paper are solvent dependent with compounds reducing at more anodic potentials in CH$_3$CN than in CH$_2$Cl$_2$. It is apparent that within the series of the trimetallic complexes [2, M = Cu, M' = Mo(NO)Tp*Cl, B = diamine], the reduction potentials of the molybdenum fragments do not

vary significantly with the length of the polymethylene carbon framework of the bridging ligands in both CH_3CN and CH_2Cl_2 solvents. The small but significant differences in the reduction potentials across the series of the complexes thus do not reflect the expected changes in structure of the complexes.

Table 4. Cyclic voltammetric data obtained from type (2) complexes [2, M = Cu, M' = Mo(NO)T$_p$*Cl, B = diamine].

Compound			In dichhoromethane			In acetonitrile			
M	B	M'	E^a_f	E^b_p	ΔE^c_p	E^a_f	ΔE^b_p	ΔE^c_p	$(i_p/i_p^a)^d$
Cu	C_6H_4	Mo(NO)T$_p$*Cl	-0.59	170	100	-0.42	101	89	1.0
Cu	(CH_2)	Mo(NO)T$_p$*Cl	-0.46	161	118	-0.42	150	69	0.98
Cu	(CH_2)	Mo(NO)T$_p$*Cl	-0.57	169	100	-0.39	114	63	1.0
Cu	(CH_2)	Mo(NO)T$_p$*Cl	-0.58	139	120	-0.39	118	90	1.0
Cu	(CH_2)	Mo(NO)T$_p$*Cl	-0.54	101	120	-0.39	86	100	1.0

^{a}in V, 0.1 mol dm^{-3} in [n-Bu$_4$N][PF$_6$] as base electrolyte, ca 1x10^{-3} mol dm^{-3} in complex, scan rate 200 mVs^{-1}, error ± 10 mV; ^{b}E$_p^c$ -E$_p^a$ in mV for the complexes; ^{c}E$_p^c$ - E$_p^a$ in mV for ferrocene in the same cell under the same conditions; ^{d}ratio of cathodic to anodic peak currents for the complexes (for ferrocene in the same cell and under same condition, i$_p^c$/i$_p^a$ = 1.0).

Comparison of data in Table 4 with that from related trimetallic complexes in which Mo(NO)Tp*Cl fragments are attached to the para-position of the benzene ring (with respect to the two oxygen atoms bonded to copper) of the copper Schiff base complexes [1] reveals that the reduction potential for the Mo(NO)Tp*Cl centres are influenced only slightly when their positions in the benzene ring of the Schiff base framework is changed form meta to para although this influence is small. This difference in reduction potentials for the related trimetallic species is of no significance other than to imply that possibly the LUMO's in the class of compounds discussed here have less electron charge density than LUMO's of their para-analogues.

In view of the suggestion that the complexes discussed here undergo two sequential one-electron reduction exhibited a broad unresolved reduction wave in their cyclic voltammograms, all the complexes were examined by differential pulse voltammetry (DPV) in the range -0.4 to -0.6 V in acetonitrile. Results are depicted in Table 5. Basing our DPV observations on those of Richardson and Taube [7] who derived a relationship between E$_f$ (formal reduction potential) and the width at half height (W$_{1/2}$) of a differential pulse voltammetric peak for systems where the interaction between redox centres in the same molecule is small, the complexes described here indicate that the Mo(NO)Tp*Cl redox centres interact weakly. The ΔE_f for these compounds fall between 50-95 mV (Table 5) whereas the theoretically calculated separation ΔE_f for two non-interacting centres is 35.6 mV [7]. The conproportionation constants (K$_c$) for the equilibrium

$$[\{2, M = Cu, M' = Mo(NO)Tp*Cl\}] + [\{2, M = Cu, M' = Mo(NO)Tp*Cl\}]^{2-} \leftrightarrow$$
$$2[\{2, M = Cu, M' = Mo(NO)Tp*Cl\}]^-$$
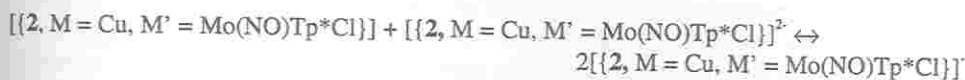
determined using the relationship ΔE_f = 59.16log$_{10}$K$_c$ show that the monoreduced species have small but noticable stabilities (Table 5). This general electrochemical behaviour is consistent

with weak interaction between the two peripheral molybdenum nitrosyl centres. The K_c data for the complexes discussed here are basically similar to those of related *para* copper analogues [1] and apparently indicate that reduced species containing $Mo(NO)Tp^*Cl$ fragments in *meta* positions in benzene ring of central Schiff base complexes are less stable than their *para*-analogues.

Table 5.   Differential pulse voltammetric and con proportionation constants obtained from type (2) complexes [2, M = Cu, M' = $Mo(NO)T_n^*Cl$, B = diamine] in acetonitrile.

M	B	M'	$W_{v_2}^a$	ΔE_f^b	E_o^c	E_f^{fd}	$E_f^{2,d}$	K_c^e
Cu	C_6H_4	$Mo(NO)T_p^*Cl$	159	78.0	-0.385	-0.341	-0.419	20.4
Cu	$(CH_2)_2$	$Mo(NO)T_n^*Cl$	180	95.0	-0.394	-0.342	-0.437	40.4
Cu	$(CH_2)_3$	$Mo(NO)T_n^*Cl$	123	60.0	-0.375	-0.340	-0.400	10.3
Cu	$(CH_2)_4$	$Mo(NO)T_p^*Cl$	145	70.0	-0.394	-0.354	-0.424	15.3
Cu	$(CH_2)_5$	$Mo(NO)T_n^*Cl$	111	50.0	-0.380	-0.350	-0.400	7.0

^{a}Peak width at half height of the DPV curve, ^{b}separation between E_f^1 and E_f^2 determined by graphical methods (ref 7), ^{c}obtained from DPV curve maximum, ^{d}obtained from $E_f = E_c + \frac{1}{2}(\Delta E_f + E_{pulse})$, $E_{pulse} = 10$ mV, ^{e}conproportionation constant $K_c = 10^{\Delta E}/0.0591$.

Also of interest in the electrochemical behaviour of trimetallic complexes investigated here is the estimation of the reduction potential of the copper centres in the complexes. To investigate this behaviour, two experiments were done and data obtained compared. In one experiment electrochemical properties of species containing molybdenum centres [2, M = Cu, M' = Mo(NO))Tp*Cl, B = diamine] were investigated and in the second experiment species of the type (2, M = Cu, M' = H, B = diamine) in which the molybdenum centres are absent were also investigated. The electrochemical properties of the latter compounds (2, M = Cu, M' = H, B = diamine) were investigated by cyclic voltammetry in DMSO because of their low solubility in CH_2Cl_2 and CH_3CN. Electrochemical data of these precursor copper Schiff base complexes [2, M = Cu, M' = H, B = $(CH_2)_n$, n = 2-5] show that except for (2, M = Cu, M' = H, B = C_6H_4) which exhibited a quasirreversible reduction wave centred at -1.21 V, all other complexes exhibited only cathodic peak potential waves without accompanying reverse anodic waves. This phenomenon indicates that the reduction process of these species are totally irreversible. The complexes reduce at potentials between -0.83 to -1.34 V. These irreversible and quasirreversible peaks are associated with the reduction process $Cu^{2+} + e \rightarrow Cu^+$.

The reduction behaviour of trimetallic complexes in which copper centre has been implanted in the central Schiff base cavity is as expected. Two reduction waves were observed in the potential range 0 to -2 V in both CH_2Cl_2 and CH_3CN. The first reduction wave occurs at the potentials varying between -0.39 to -0.42 V in CH_3CN and -0.46 to -0.59 V in CH_2Cl_2 for all the complexes [2, M = Cu, M' =$Mo(NO)Tp^*Cl$, B = C_6H_4, or $(CH_2)_n$ n = 2-5] and is reversible, and the second reduction wave occurring between -0.63 to -1.03 V in acetonitrile is irreversible. From the comparison of the voltammogram of the precursor copper(II) Schiff base complexes, it can be concluded that the first reduction waves in the complexes are associated with the reduction of $Mo(NO)Tp^*Cl$ centres while the second irreversible reduction waves are associated with the reduction of the copper(II) centres on the trimetallic complexes.

CONCLUSION

It can be concluded that as their *para* analogues, the trimetallic complexes described here, demonstrate that the two peripheral molybdenum redox centeres interact weakly via the copper Schiff base framework.

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