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Synthesis, physical and electrochemical characterization of mono- and heterobinuclear *m*-functionalized iron(III) Schiff base complexes

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Abstract Mo(NO)$T_p^*Cl_2$ (T_p^* = 3,5-dimethyl pyrazole) when reacted with *m*-functionalized Fe(III) Schiff base complexes; the Schiff base ligands being derived from condensation of 2,4-dihydroxybenzaldehyde or salicylaldehyde with a variety of α,ω-diamines [1,2-$C_6H_4(NH_2)_2$, $NH_2(CH_2)_nNH_2$; $n = 2$–4] affords bimetallic complexes containing two potential reduction centers. The compounds were characterized by physicochemical and spectroscopic methods. It is shown that as the polymethylene carbon chain of the Schiff base backbone increases, the physicochemical and spectroscopic properties also change gradually. Electrochemical data show that the *m*-functionalized complexes reduce at potentials less cathodic than their *p*-substituted analogues. It is also shown that the redox potentials are solvent dependent.

Introduction

In recent years, there has been considerable interest in the coordination chemistry of Schiff bases with various metal ions. This is partly due to their capability to act as multidentate N–N and N–O donors which results in the formation of mono- or polynuclear complexes [1]. Their wide application in areas such as catalysis [2], various biological systems [3, 4], polymers [5] and dyes industry [6] has been reviewed by Kumar and coworkers [7]. Schiff base metal complexes have been extensively studied due to their synthetic flexibility, selectivity and sensitivity toward the central metal atom. The ability to bridge metal centers allows for the synthesis of discrete, heterocycle-bridged polynuclear complexes which have been shown to possess interesting and unusual electrochemical or magnetic properties [8, 9] because the bridge can mediate exchange between the metal centers. Previous studies on the synthesis, characterization and electrochemical behavior of poly-functionalized Schiff base metal complexes of types **L1** and **L2** where various 3*d* metal atoms are linked to Mo(NO)T_p^*Cl metal fragment centers through Schiff base ligands have shown that there are weak electronic interactions between the molybdenum centers and the metal atoms through the bridging ligands [10–13] (Figs. 1, 2).

As a part of our continuing work on the coordination properties of heterobinuclear complexes linked by asymmetric tetradentate Schiff base ligands, we herein report the synthesis, characterization and electrochemistry of complexes of type **L3** in which the peripheral redox active molybdenum nitrosyl functionality is attached to the Schiff base ligands at the *m*-position (Fig. 3).

Experimental

Reagents

All the reagents with an exception of Mo(NO)$T_p^*Cl_2$ were obtained from Sigma Aldrich Chemical Company Limited (UK) and used without further purification. The compound Mo(NO)$T_p^*Cl_2$ was prepared according to the literature

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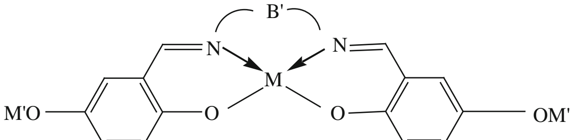
method, although with slight modifications [14]. All the solvents used were of analar grade. Whenever required, the solvents were dried according to the standard literature procedures [15]. Iron(III) chloride was dried in a desiccator over phosphorous(V) oxide for 24 h before use. All the synthetic reactions except those involving the preparation of Schiff base ligands and their iron(III) mononuclear derivatives were carried out under nitrogen. All the bimetallic complexes were purified through column chromatography using silica gel 60 (70–230 mesh). The purity of the synthesized compounds was checked by melting point and TLC techniques.

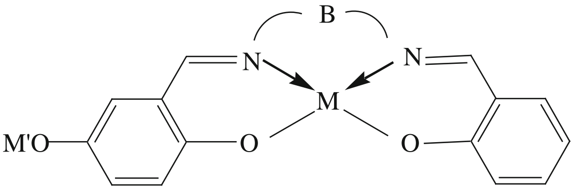
Instrumentation

Carbon, hydrogen and nitrogen contents were determined microanalytically on an elemental analyzer model vario EL3 (Elementar Analysensysteme GmbH). Mass spectra were obtained using a Micromass/Waters LCT Mass Spectrometer while electronic spectra of the compounds were recorded in ethanol or DMSO solution (10^{-3} M) on a Hitachi U2000 UV/Vis spectrophotometer with 190–1,100 nm wavelength range. IR spectra were recorded as KBr disks in a Shimadzu FTIR-8400 spectrometer with a range of 4,000–250 cm^{-1}. ^{1}H NMR spectra were recorded on Varian Mercury 200 MHz NMR spectrometer in DMSO-d_6 solvent, using TMS as an internal standard. Electrochemical data were obtained with a Metrohm/Eco Chemie Autolab PGSTAT12 Potentiostat/Galvanostat with glassy carbon as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode. Solutions in MeCN, DMSO and CH_2Cl_2 were ca. 1×10^{-3} mol dm^{-3} in the complex with 0.1 mol dm^{-3} [n-Bu_4N][PF_6] as the base electrolyte. Cyclic and differential pulse voltammetric measurements were taken at scan rates of 200 and 20 mV/s, respectively. All formal reduction potentials were taken as an average of the anodic and cathodic potentials.



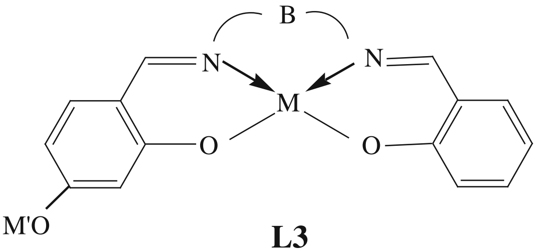
L1

Fig. 1 $B' = C_6H_4$, $(CH_2)_n$; $n = 2, 3, 4, 5$; M = Cu, Ni or Pd; $M' = \mathrm{Mo(NO)}T_p^*\mathrm{Cl}$



L2

Fig. 2 $B = C_6H_4$ or $(CH_2)_n$; $n = 2$–4, $M = H_2$ or Fe; $M' = H$ or $\mathrm{Mo(NO)}T_p^*\mathrm{Cl}$



L3

Fig. 3 $B = C_6H_4$ or $(CH_2)_n$; $n = 2$–4, $M = H_2$ or Fe; $M' = H$ or $\mathrm{Mo(NO)}T_p^*\mathrm{Cl}$

Syntheses

*Schiff base ligand [**L3**, $B = C_6H_4$, $M = H_2$, $M' = H$]*

A solution of *o*-phenylenediamine (1.2 g, 10.9 mmol) in ethanol (10 ml) was added dropwise to a mixed solution of 2,4-dihydroxybenzaldehyde (1.5 g, 10.9 mmol) and salicylaldehyde (1.2 ml, 10.9 mmol) in ethanol (30 ml). The mixture was refluxed for 2 h, filtered while hot, and the solvent evaporated in vacuo. A red oily product obtained was first triturated with diethyl ether, thoroughly washed with diethyl ether and then dried yielding a red solid (yield, 3.0 g, 84 %). The remaining Schiff base ligands [***L3***, $B = (CH_2)_n$; $n = 2$–4, $M = H_2$, $M' = H$] were prepared in a similar manner, replacing the *o*-phenylenediamine with the appropriate diamine. The solids obtained were then used in the subsequent preparation of the iron(III) Schiff base precursors.

*Iron(III) Schiff base precursor [**L3**, $B = C_6H_4$, $M = Fe$, $M' = H$]*

A solution of iron(III) chloride (0.4 g, 2.6 mmol) in ethanol (30 ml) was added dropwise to a solution of Schiff base [***L3***, $B = C_6H_4$, $M = H_2$, $M' = H$] (0.9 g, 2.6 mmol) in ethanol (30 ml). The red solution formed on shaking was refluxed for 48 h to drive the reaction to completion. The solvent was evaporated in vacuo, the solid formed on concentration washed with ethanol (3 × 50 ml), and diethyl ether (3 × 50 ml) then dry-evaporated to provide a brown solid (yield; 0.3 g, 32 %). The remaining iron(III) Schiff base precursors were prepared in a similar manner by reacting the appropriate Schiff base ligand and iron(III) chloride, and they gave comparable yields.

Table 1 Elemental, physical and mass spectral data [***L3***, $B = C_6H_4$ or $(CH_2)_n$; $n = 2$–4, M = Fe, M' = H or $Mo(NO)T_p^*Cl$]

Compound			Yield (%)	Solvent[a]	Found (Calculated) %			MS data	Conductance Ω^{-1} cm^2 mol^{-1}		
M'	*B*	*M*			C	H	N	$[M]^+$–Cl	DMF	DMSO	MeCN
H	C_6H_4	Fe	31.90	0	57.1 (56.9)	3.9 (3.3)	6.7 (6.6)	386	11.78	17.97	3.91
H	$(CH_2)_2$	Fe	39.80	0	51.6 (51.4)	3.8 (3.7)	7.4 (7.5)	337	19.07	25.53	15.29
H	$(CH_2)_3$	Fe	44.80	0	52.7 (52.6)	4.3 (4.1)	7.3 (7.2)	352	17.42	38.45	12.42
H	$(CH_2)_4$	Fe	49.70	0	53.8 (53.7)	4.6 (4.5)	7.1 (7.0)	366	14.86	13.79	4.28
$Mo(NO)T_p^*Cl$	C_6H_4	Fe	23.50	0.5 C_6H_{14}	49.6 (49.4)	5.9 (5.1)	13.8 (13.7)		20.22	12.21	10.21
$Mo(NO)T_p^*Cl$	$(CH_2)_2$	Fe	43.80	0.5 C_6H_{14}	46.8 (46.5)	5.4 (5.2)	14.3 (14.4)		42.07	13.34	30.59
$Mo(NO)T_p^*Cl$	$(CH_2)_3$	Fe	40.80	0.5 C_6H_{14}	47.0 (47.1)	5.5 (5.4)	14.2 (14.1)		30.22	19.22	33.41
$Mo(NO)T_p^*Cl$	$(CH_2)_4$	Fe	44.80	0.5 C_6H_{14}	47.7 (47.7)	5.6 (5.5)	14.0 (13.9)		32.61	12.81	15.33

[a] Molecules of solvent of crystallization

*Molybdated iron(III) Schiff base complex [**L3**, $B = C_6H_4$, M = Fe, $M' = Mo(NO)T_p^*Cl$]*

A mixture of $Mo(NO)T_p^*Cl_2$ (0.3 g, 0.6 mmol) and iron(III) Schiff base precursor [***L3***, $B = C_6H_4$, M = Fe, M' = H] in dry toluene (100 ml) in the presence of a small amount of Et_3N was refluxed for 6 days under nitrogen. The red-brown solution obtained was filtered while hot and the solvent evaporated in vacuo to afford a brown solid which was dissolved in a minimum amount of CH_2Cl_2 and then chromatographed on a silica gel column. The predominant orange fraction was eluted with a mixture of 10 % *n*-C_6H_{14} in CH_2Cl_2 (v/v) and the solvent evaporated in vacuo. The solid obtained was washed with *n*-C_6H_{14} and then dried to provide red crystals (yield; 0.12 g, 24 %). Minor quantities of brown, purple and green species were detected by chromatography but could not be isolated in sufficient amount for characterization. The remaining molybdated binuclear complexes prepared in a similar manner using the appropriate iron(III) Schiff base precursors and $Mo(NO)T_p^*Cl_2$ gave comparable yields.

Results and discussion

Synthetic studies

The Schiff base ligands were obtained as yellow precipitates except [***L3***, $B = C_6H_4$, $M = H_2$, M' = H] which was red. The mononuclear iron(III) Schiff base precursors were obtained as black solids in moderate yields except [***L3***, $B = C_6H_4$, M = Fe, M' = H] which was brown. They were generally obtained by reacting the preformed Schiff base ligands with iron(III) chloride in a 1:1 molar ratio in ethanol. Air- and moisture-stable binuclear complexes were obtained by reacting the mononuclear iron(III) Schiff base precursors with $Mo(NO)T_p^*Cl_2$ in a 1:1 molar ratio in dry toluene in the presence of small amounts of triethylamine. The triethylamine was used to deprotonate the phenolic hydroxyl group of the Schiff base iron(III) precursors and trap HCl liberated in the reaction as $Et_3NH^+Cl^-$. The binuclear complexes were obtained as red microcrystalline solids in low yields, 23–45 %, and this may be attributed to the competing side reactions which produced the green *oxo*-bridged $\{(Mo(NO)T_p^*Cl)_2O$ and other products [16]. The elemental analytical results for all the adducts were in good agreement with the proposed formulae as shown in Table 1. They, however, showed that the binuclear complexes retain 0.5 mol of C_6H_{14} in their crystal lattice. ESI mass spectral data (Table 1) for the iron(III) Schiff base complexes were also consistent with their formulations. Molar conductivities of 1×10^{-3} mol dm^{-3} solutions of the complexes at 25 °C in DMSO, DMF and MeCN lay in the range associated with non-electrolytes [17, 18].

Spectroscopic studies

The principal IR data are summarized in Table 2. The Schiff base ligands showed characteristic bands associated with the azomethine $\nu_{C=N}$ and $\nu_{\text{phenolic C–O}}$ at ca 1,628–1,635 cm^{-1} and 1,278–1,280 cm^{-1}, respectively. These stretching frequencies showed a bathochromic shift on coordination to iron, an observation which may be attributable to the decrease in their bond order when they coordinate to the metal ion. Other notable bands not observed in the Schiff base ligands but found in the mononuclear adducts were in the 405–417 cm^{-1} and 497–499 cm^{-1} regions. These may be attributed to $\nu_{\text{phenolic C–O–Fe}}$ and $\nu_{Fe \leftarrow N}$, respectively [19]. Compared to their corresponding *p*-analogues [***L2***, $B = C_6H_4$ or $(CH_2)_n$; $n = 2$–4, M = Fe, M' = H], $\nu_{C=N}$, $\nu_{\text{phenolic C–O}}$, $\nu_{\text{phenolic C–O–Fe}}$ and $\nu_{Fe \leftarrow N}$, stretches for the *m*-complexes appeared at lower frequencies. Similar observations have been made in *m*-functionalized manganese(II) complexes of similar Schiff base ligands [20]. The IR of the bimetallic complexes

Table 2 IR and electronic spectral data [***L3***, B = C_6H_4 or $(CH_2)_n$; n = 2–4, M = H_2 or Fe, M' = H or Mo(NO)T^*_pCl]

Compound			IR spectral data (cm^{-1})						UV–Vis spectral data
M'	*B*	*M*	ν(C=N)	ν(ph.CO)	ν(MO)	ν(MN)	ν(NO)	ν(BH)	λ_{max} (nm), (ε) dm^{3}mol^{-1}cm^{-1}
H	C_6H_4	H_2	1,628	1,279					255 (9,964), 281 (5,608), 329 (4,528)
H	$(CH_2)_2$	H_2	1,634	1,280					254 (9,210), 282 (7,753), 308 (4,080), 371 (4,174)
H	$(CH_2)_3$	H_2	1,633	1,279					252 (7,850), 284 (8,903), 310 (6,344), 370 (4,341)
H	$(CH_2)_4$	H_2	1,635	1,278					254 (8,077), 278 (6,304), 306 (4,638), 370 (4,511)
H	C_6H_4	Fe	1,617	1,282	405	497			284 (10,511), 332 (8,007), 487 (2,184)
H	$(CH_2)_2$	Fe	1,628	1,283	413	499			284 (9,223), 321 (6,465), 486 (1,646)
H	$(CH_2)_3$	Fe	1,629	1,280	416	499			283 (9,933), 320 (6,837), 489 (1,890)
H	$(CH_2)_4$	Fe	1,625	1,282	417	499			283 (10,823), 325 (7,566), 487 (1,484)
Mo(NO)T^*_pCl	C_6H_4	Fe	1,608	1,264	411	…b	1,659	2,522	312 (7,547), 434 (1,462), 487 (1,484)
Mo(NO)T^*_pCl	$(CH_2)_2$	Fe	1,608	1,263	416	…b	1,659	2,522	278 (8,562), 316 (7,840), 430 (1,231), 510 (938)
Mo(NO)T^*_pCl	$(CH_2)_3$	Fe	1,607	1,263	413	528	1,659	2,522	272 (9,622), 318 (7,266), 432 (1,506), 496 (640)
Mo(NO)T^*_pCl	$(CH_2)_4$	Fe	1,608	1,264	426	…b	1,659	2,522	320 (8,319), 434 (1,181), 493 (842)

IR and UV–Vis spectral data for Schiff bases were obtained in EtOH, while those of the monometallic and bimetallic complexes were obtained in DMSO and CH_2Cl_2 solvents, respectively

b Broad band

showed strong absorption bands (in CH_2Cl_2) attributable to ν_{BH} and ν_{NO} at 2,522 and 1,659 cm^{-1}, respectively. $\nu_{C=N}$ was observed at 1,607–1,608 cm^{-1}. ν_{NO} was lower than in the precursor molecule Mo(NO)$T^*_pCl_2$; ν_{NO} = 1,702 cm^{-1}, and this may be attributed to the substantial d_{Π}–p_{Π} back donation into NO antibonding orbitals which in effect reduces its bond order. Four characteristic absorption bands associated with the pyrazolyl groups were also observed in the range of 1,457–1,558 cm^{-1}.

The electronic spectral data of all the adducts synthesized are summarized in Table 2. The Schiff base ligands were dissolved in ethanol, and they showed characteristic UV–Vis spectra in the 254–371-nm region. The absorption band observed at ca 254–284 nm is attributable to π–π^* transitions of the benzene ring, while the absorption band at ca 306–371 nm is attributable to the π–π^* transitions of the C=N group. Absorption bands at ca 370–371 nm may also be attributed to n–π^* transitions of the ligand [21]. The electronic spectra of all the mononuclear adducts (in DMSO) showed additional broad and weak absorption bands at ca 484–489 nm in addition to the intraligand absorption bands. These bands may be attributed to charge transfer bands, which usually almost completely obscure the weak spin forbidden *d*–*d* transitions [22]. In the bimetallic complexes, additional absorption bands consistent with the presence of the Mo(NO)T^*_pCl-OAr chromophore [23] were observed at ca 430–434 nm. Generally as the polymethylene carbon chain (B) of the Schiff base backbone increased, there occurred a small bathochromic shift of about 4 nm to longer wavelengths. Compared to their *p*-analogues, the absorption bands for the *m*-complexes were observed at lower wavelengths.

The ^{1}H NMR spectra for the free Schiff base ligands were run in DMSO-d_6 using TMS as an internal standard. The spectra obtained are generally consistent with their formulations. All the ligands exhibited signals in the 8.74–8.18 ppm and 7.74–6.10 ppm regions attributable to azomethine and aromatic protons, respectively. The signals associated with α-NCH_2 protons appear in the 3.58–3.16 ppm region as triplets as a result of coupling to

Table 3 ^{1}H NMR chemical shifts for Schiff bases [***L3***, B = C_6H_4, or $(CH_2)_n$; n = 2–4, M = H_2, M' = H]

Compound			^{1}H NMR chemical shifts in DMSO-d_6
M'	*B*	*M*	
H	C_6H_4	H_2	13.45{1H, s, O$\underline{H}$}, 9.13{2H, m, OH}, 8.18{2H, s, 2C$\underline{H}$N} 8.16{3H, dd, ArH}, 7.64{4H, s, Ar$\underline{H}$}, 7.56{4H, m, Ar$\underline{H}$}
H	$(CH_2)_2$	H_2	8.54{1H, s, O$\underline{H}$}, 8.33{2H, s, 2C$\underline{H}$N}, 7.30{1H, m, Ar$\underline{H}$}, 7.12{2H, d, Ar$\underline{H}$}, 6.84{1H, t, Ar$\underline{H}$}, 6.20{2H, dd, Ar$\underline{H}$}, 6.12{1H, d, Ar$\underline{H}$}, 3.81{4'H, t, (C$\underline{H}_2$-N)$_2$}
H	$(CH_2)_3$	H_2	8.40{1H,d, OH}, 8.18{2H,d, C$\underline{H}$N}, 7.95{1H, d, Ar$\underline{H}$}, 7.03{6H, m, Ar$\underline{H}$}, 3.41{4H, m, (C$\underline{H}_2$-N)$_2$}, 1.80{2H, quintet, C-(C$\underline{H}_2$)-C}
H	$(CH_2)_4$	H_2	8.51{1H, s, O$\underline{H}$}, 8.28{2H, s, 2C$\underline{H}$N}, 7.30{1H, m, Ar$\underline{H}$}, 7.11{1H, d, Ar$\underline{H}$}, 6.84{1H, t, Ar$\underline{H}$}, 6.19{2H, dd, Ar$\underline{H}$} 6.10(2H, d, Ar$\underline{H}$},1.60{8H, s, (C$\underline{H}_2$C$\underline{H}_2$-N)$_2$}

Table 4 Cyclic voltammetric data [***L3***, $B = C_6H_4$ or $(CH_2)_n$; $n = 2$–4, $M =$ Fe, $M' =$ H or Mo(NO)T^*_pCl] in various solvents

Compound			In DMSO		In MeCN			In CH_2Cl_2			
M'	B	M	E_f^a	E_a^b	E_f^a	E_f^c	E_a^e	E_c^e	E_f^c	E_a^b	E_a^f
H	C_6H_4	Fe	−0.658	0.631							
H	$(CH_2)_2$	Fe	−0.629	0.607							
H	$(CH_2)_3$	Fe	−0.656	0.666							
H	$(CH_2)_4$	Fe	−0.676	0.743							
Mo(NO)T^*_pCl	C_6H_4	Fe			−0.772	−0.572	1.122	−0.719	−0.506	0.970	1.215
Mo(NO)T^*_pCl	$(CH_2)_2$	Fe			−0.758	−0.537	1.182	−0.718	−0.522	1.008	1.283
Mo(NO)T^*_pCl	$(CH_2)_3$	Fe			−0.782	−0.564	1.182	−0.745	−0.532	1.052	1.321
Mo(NO)T^*_pCl	$(CH_2)_4$	Fe			−0.798	−0.591	1.188	−0.769	−0.548	1.104	1.386

Sample solution 1×10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} [n-Bu_4N][PF_6] base electrolyte, scan rate 200 mV/s, reading error ± 10 mV

[a] Formal reduction potential (V) for the process $Fe^{3+} + e^- \rightarrow Fe^{2+}$

[b] Anodic peak potential (V) for the oxidation of ^-OH to phenoxyl radical

[c] Formal reduction potential (V) for the process $Mo(NO)^{3+} + e^- \rightarrow Mo(NO)^{2+}$

[d] Anodic peak potential (V) for oxidation of metal ion and/or ligand

[e] Cathodic peak potential (V) for the process $Fe^{3+} + e^- \rightarrow Fe^{2+}$

[f] Anodic peak potential (V) for oxidation of ligand

the β-CH_2 protons in the central Schiff base backbone. It was noticeable that all the three phenolic OH protons were not observable, probably due to exchange broadening. This phenomenon has been observed by other authors [13, 24]. The OH signals are, however, observed in compound [***L3***, $B = C_6H_4$, $M = H_2$, $M' =$ H] where the phenolic OH protons show a distinct broad peak at 13.45 ppm which integrates for one proton and as a multiplet centered at 9.13 ppm which integrates for two protons as expected from the structure. Results showing chemical shifts data for the free Schiff base ligands are summarized in Table 3.

Electrochemical studies

The electrochemical properties of the new mononuclear complexes and their binuclear derivatives were investigated by both cyclic and differential pulse voltammetry with 200 and 20 mV/s scan rates, respectively, in DMSO, MeCN and CH_2Cl_2. Solutions contained ca 1×10^{-3} mol dm^{-3} of the complex in 0.1 mol dm^{-3} of [n-Bu_4N][PF_6] base electrolyte. The cyclic voltammetric data are summarized in Table 4. Like their p-analogues [11], all the mononuclear complexes exhibited similar cyclic voltammograms in DMSO, with a reversible reduction wave associated with the $Fe^{3+} \rightarrow Fe^{2+}$ reduction process falling in the potential range of −0.629 to −0.676 V. These formal reduction potentials were, however, less cathodic than the p-analogues by 5–10 mV. As the polymethylene carbon chain (B) of the Schiff base backbone lengthened from $n = 2$ to $n = 4$, a cathodic shift of about 20 mV was observed. Irreversible oxidation waves that may be attributed to the oxidation of ^-OH to a phenoxyl radical were also observed with the anodic peak potential falling in the range of 0.631–0.743 V.

The bimetallic complexes in MeCN also exhibited similar voltammograms with two broad reversible reduction waves associated with the reduction of molybdenum and iron(III) centers falling in the potential ranges of −0.537 to −591 V and −0.758 to −0.798 V, respectively. The reduction potential associated with the reduction of molybdenum, when compared to other related complexes of similar molybdenum centers [25], was found to be more cathodic by about 80 mV. The reduction potential of iron was also more cathodic than the mononuclear adduct by about 130 mV. Multiple scans at varying scan rates yielded nearly superimposable voltammograms, indicating marked stability of the reduction processes of both iron and molybdenum centers. One irreversible oxidization wave that may be associated with the oxidation of $Fe^{3+} \rightarrow Fe^{4+}$ was observed in the potential range of 1.122 to 1.188 V (Table 4). These values were more anodic by about 0.4 to 0.5 V than the corresponding mononuclear adducts. This observation may be attributed to the electron-deficient

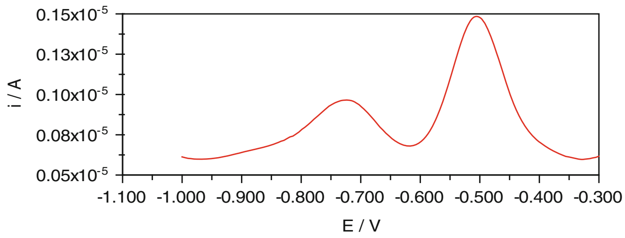


Fig. 4 Differential pulse voltammogram of [**L3**, $B = C_6H_4$, $M =$ Fe, $M' =$ Mo(NO)T^*_pCl] in CH_2Cl_2

Table 5 Differential pulse voltammetric data [***L3***, B = C_6H_4 or $(CH_2)_n$; n = 2–4, M = Fe, M' = H or Mo(NO)T_p^*Cl] in various solvents

Compound			In DMSO	In MeCN		In CH_2Cl_2	
M'	B	M	E^a (V)	E^a (V)	E^b (V)	E^a (V)	E^b (V)^3
H	C_6H_4	Fe	−0.669				
H	$(CH_2)_2$	Fe	−0.656				
H	$(CH_2)_3$	Fe	−0.674				
H	$(CH_2)_4$	Fe	−0.689				
Mo(NO)T_p^*Cl	C_6H_4	Fe		−0.729	−0.529	−0.724	−0.503
Mo(NO)T_p^*Cl	$(CH_2)_2$	Fe		−0.713	−0.507	−0.741	−0.512
Mo(NO)T_p^*Cl	$(CH_2)_3$	Fe		−0.728	−0.527	−0.745	−0.524
Mo(NO)T_p^*Cl	$(CH_2)_4$	Fe		−0.739	−0.544	−0.755	−0.535

Sample solution 1×10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} [n-Bu_4N][PF_6] base electrolyte, scan rate 20 mV/s, reading error ± 10 mV

[a] Peak potential for the process $Fe^{3+} + e^- \rightarrow Fe^{2+}$

[b] Peak potential for the process $Mo(NO)^{3+} + e^- \rightarrow Mo(NO)^{2+}$

molybdenum center which withdraws electrons from the iron center, thus making it more difficult to oxidize. The oxidation peak may also be associated with a ligand oxidation process since these values fall within the typical range of values that have been obtained by others [21].

When the bimetallic complexes were investigated in CH_2Cl_2, a reversible wave associated with the reduction of the molybdenum center was observed in the potential range of −0.506 to −0.548 V, while a quasi-reversible wave associated with the reduction of iron(III) was observed between −0.718 and −0.769 V for all the complexes (Table 4). Two irreversible oxidation waves observed in the potential ranges of 0.944–1.104 V and 1.215–1.386 V may be attributed to the oxidation of iron and the ligand, respectively. These observations show that the redox potentials of this type of electrochemical system are solvent dependent. When the data in Table 4 were compared with those from the corresponding *p*-analogues [11], it was observed that the reduction potentials of the iron and molybdenum centers are influenced by changing H and Mo(NO)T_p^*Cl fragments from *p*- to *m*-position. This difference in the reduction potentials may possibly imply that the *m*-complexes are easier to reduce, probably due to the lowest unoccupied molecular orbitals (LUMO's) of the *m*-analogues having less electron charge density than the LUMO's of their *p*-analogues [21].

The mononuclear iron(III) Schiff base complexes and their binuclear derivatives were also investigated by differential pulse voltammetry. This is because the cyclic voltammograms were either broad or ill-formed. All the mononuclear adducts in DMSO exhibited one well-defined peak in the potential range of −0.656 to −0.689 V. The binuclear adducts in MeCN exhibited two well-defined peaks attributable to the reduction of molybdenum and iron centers at −0.507 to −0.544 V and −0.713 to −0.739 V, respectively. In CH_2Cl_2, the corresponding peak potentials were observed at −0.503 to −0.535 V and −0.724 to −0.755 V, respectively. A typical voltammogram is shown in Fig. 4. These values, similar to what was obtained in cyclic voltammetry, were found to be less cathodic than those of their *p*-analogues. The results are depicted in Table 5.

Conclusion

The redox potentials of the metal centers linked by polydentate Schiff base ligands can be influenced by changing the position of substitution on the benzene ring of the Schiff base framework from *para* to *meta*, and the *m*-complexes reduce at potentials less cathodic than their *para* analogues.

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