

SYNTHESIS AND CHARACTERIZATION OF REDOX-ACTIVE COMPLEXES OF MOLYBDENUM(II) NITROSYL LINKED TO *P*-FUNCTIONALIZED IRON(III)-SCHIFF BASES

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Abstract

Characterization of heterobinuclear complexes containing molybdenum(II) nitrosyl metal fragment, $\text{Mo}(\text{NO})\text{T}_p^*\text{Cl}$; T_p^* = tris(3,5-dimethylpyrazolyl) borate linked to *p*-functionalized $\text{Fe}(\text{Salen})\text{Cl}$; by IR, UV, MS and elemental analysis is herein described. The electrochemical behavior, investigated by both cyclic and differential pulse voltammetry, indicates that the monometallic $\text{Fe}(\text{Salen})\text{Cl}$ complexes exhibit one reduction peak which may be associated with the reduction of iron center while the heterobinuclear molybdenum-iron complexes exhibit two reduction peaks which may be associated with the reduction of both molybdenum and iron centers. The reduction potential of iron is more cathodic in $\text{Fe}(\text{Salen})\text{Cl}$ than in the binuclear complex showing that the electron deficient molybdenum nitrosyl center modestly influences its reduction potential.

Keywords

$\text{Fe}(\text{Salen})\text{Cl}$ complexes, *para*, molybdenum(II) nitrosyl, voltammetry, reduction potential

INTRODUCTION

The research on complexation reactions has always been of great interest because of the numerous applications of the polynuclear complexes, which have certain properties different from those of their mononuclear components¹. Metal complexes find numerous applications in the area of analytical, environmental, electrochemical chemistry and biological sciences²⁻⁶. However, poor stability and solubility limit their extensive and diversified applications. In the last two decades, synthesis and studies on macro-ligands, functionalized ligands and mixed ligands complexed with a variety of metal ions have been reported⁷⁻⁸. Model

compounds suitable for investigating the phenomena associated with the interaction of two or more metal centers have been constructed. However, more efforts have been put on homobimetallic complexes with less attention being paid to the class of heterobimetallic derivatives⁹. In order to understand the electronic communication within heterobimetallic complexes, we conducted synthesis and studies on the electrochemical properties of complexes of type **1** where the $[\text{Mo}(\text{NO})\text{T}_p^*\text{Cl}]^+$ metal fragment is linked to a guest cation through a variety of Schiff base ligands (with a saturated linkage at B)¹⁰.

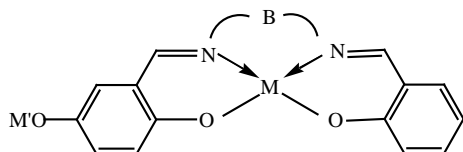


Fig 1: B = C_6H_4 , $(\text{CH}_2)_n$; $n = 2-4$, M = H_2 , or Mn, M' = H or $\text{Mo}(\text{NO})\text{T}_p^*\text{Cl}$

We showed that the voltammograms of manganese(II) Schiff base precursors had one similar reduction peak which may be

associated with the reduction of the manganese(II) center and that the reduction potentials are insensitive to the changes in the length and degree of saturation of the polymethylene backbone. The voltammograms of the corresponding bimetallic complexes exhibited two reduction peaks which may be associated with the reduction of both manganese(II) and molybdenum centers. Neither reduction potential of each metal center was affected by the presence of the other. Earlier work on similar type of bimetallic complexes with zinc(II) and copper(II) ions as guest cations however gave results showing that the molybdenum center reduces at a more anodic potential compared to the manganese (II) center¹¹⁻¹². This shows that the central metal coordinated in the Schiff base cavity may influence the redox behavior of the peripheral molybdenum nitrosyl group. In order to investigate the effect of the other 3d series metals on the reduction potential of Mo(NO)³⁺, we synthesized similar bimetallic complexes of type **1** with iron(III) incorporated as the guest ion in the Schiff base cavity. In this paper, we report their synthesis, characterization and electrochemical properties.

EXPERIMENTAL

Materials

Commercial reagents obtained from Aldrich Chemical Company (UK) were used as supplied. All solvents were distilled prior to use. Molybdenum(II) nitrosyl compound [Mo(NO)T_p*Cl₂; T_p* = tris(3,5-dimethylpyrazolyl) borate] was prepared according to the literature method¹³. Iron(III) chloride was dried in a desiccator over phosphorous(V) oxide for 24 hours. Chromatographic purification of the

bimetallic complexes was accomplished on silica gel columns using dichloromethane and *n*-hexane as eluants.

Physical Measurements

IR spectral data were obtained from Shimadzu FTIR-8400 spectrometer while electronic spectra were recorded from Unicam U2000. Mass spectra were obtained using ESI as the source of ionization while elemental analyses were carried out on C,H,N elemental analyzer model vario EL3 (Elementar). Cyclic and differential pulse voltammetric data were obtained from Autolab potentiostat/galvanostat PGSTAT 12 electrochemical analyzer with 0.1 M [Bu₄N]PF₆ as the support electrolyte and MeCN, CH₂Cl₂ and DMSO as the solvents. The working electrode was made of glassy carbon; the reference electrode was Ag/AgCl while platinum wire was used as the counter electrode. Although ferrocene was used as an internal standard, the formal redox potentials in volts were recorded vs Ag/AgCl reference electrode and they were taken as the average of anodic and cathodic peak potentials.

Syntheses of Schiff Base Ligands

Procedure for Synthesis of Schiff Bases

A solution of *o*-phenylenediamine (1.17 g, 10.86 mmoles) in 20 ml absolute ethanol was added dropwise to a solution of 2,5-dihydroxybenzaldehyde (1.50 g, 10.86 mmoles) and salicylaldehyde (1.15 ml, 10.86 mmoles) in 100 ml absolute ethanol. The solution mixture was thoroughly shaken, refluxed for 2hr and then filtered while hot. The solvent was evaporated *in vacuo* yielding a red oily liquid which was then triturated with diethylether. A red solid obtained was thoroughly washed with

diethylether and dried in air for 2 days (yield; 3.30 g, 91.7 %). The remaining Schiff base ligands [(1), B = (CH₂)_n; n = 2-4, M = H₂, M' = H] were prepared in a similar manner replacing the *o*-phenylenediamine with the appropriate diamine. The solids obtained were then used in the preparation of the subsequent iron(III) Schiff base precursors.

Syntheses of Fe(Salen)Cl Complexes

Procedure for Synthesis of Fe(Salen)Cl [(1), B = C₆H₄, M = Fe, M' = H]

A solution of iron(III) chloride (0.42 g, 2.60 mmoles) in 30 ml absolute ethanol was added dropwise to a solution of Schiff base [(1), B = C₆H₄, M = H₂, M' = H] (0.86 g, 2.60 mmoles) in 30 ml absolute ethanol. The reaction mixture formed a brown solution after shaking and turned dark red on refluxing for 2 days. It was then cooled, filtered and the black residue obtained was thoroughly washed with ethanol (3 x 50 ml) followed by Diethyl ether (3 x 50 ml) and then dried (yield; 0.34 g, 34.0 %). The remaining iron(III) Schiff base precursors were prepared in a similar manner by reacting the appropriate Schiff base ligand [(1), B = (CH₂)_n; n = 2-4, M = H₂, M' = H]

and iron(III) chloride and they gave comparable yields.

Syntheses of Bimetallic Complexes

*Procedure for synthesis of Mo – Fe(III) bimetallic complex [(1), B = C₆H₄, M = Fe, M' = Mo(NO)T_p*Cl]*

A solution of Mo(NO)T_p*Cl₂ (0.30 g, 0.60 mmoles) in 50 ml dry toluene was added to a suspension of Fe(Salen)Cl [(1), M = Fe, M' = H, B = C₆H₄] (0.23 g, 0.60 mmoles) in 50 ml dry toluene, followed by a few drops of Et₃N. The mixture was refluxed for 6 days under nitrogen, forming a purple solution. It was then filtered while hot, cooled and the filtrate evaporated *in vacuo*, forming a purple solid. The solid was dissolved in a minimum amount of CH₂Cl₂ and then chromatographed on a silica gel column. The major purple fraction was eluted using 5 % *n*-C₆H₆ in CH₂Cl₂ (v/v). The eluate was dry evaporated, forming purple crystals which were washed with *n*-C₆H₆ and then dried for 1 day (yield; 0.18 g, 35.3 %). The remaining bimetallic complexes were prepared in a similar manner using the appropriate iron(III) Schiff base precursors [(1), B = (CH₂)_n; n = 2-4, M = Fe, M' = H] and Mo(NO)T_p*Cl₂ and they gave comparable yields.

RESULTS AND DISCUSSION

Synthetic studies

The Schiff base ligands were obtained as yellow precipitates except [(1), B = C₆H₄, M = H₂, M' = H] which was recovered as a red-orange solid. Fe(Salen)Cl complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] were generally obtained by reacting the preformed Schiff base ligands with iron(III) chloride in a 1:1 molar ratio in

ethanol. The bimetallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] were obtained by reacting Fe(Salen)Cl complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] with Mo(NO)T_p*Cl₂ in a 1:1 molar ratio in the presence of small amounts of triethyl amine in dry toluene under nitrogen. Triethyl amine was added to facilitate deprotonation of the phenolic hydroxyl

group of the Fe(Salen)Cl complexes and probably to trap HCl liberated in the reaction as triethyl ammonium salt $[\text{Et}_3\text{NH}]^+\text{Cl}^-$.

The reaction mixtures were refluxed for 6-7 days to ensure completion of reaction. The crude bimetallic 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 re-crystallization in *n*-hexane. The bimetallic complexes were generally obtained as red microcrystalline powder except [(1), B = C₆H₄, M = Fe, M' = Mo(NO)T_p*Cl] which was purple. The percentage yields for the bimetallic complexes were generally low; 30–35 %. This could be attributed to the competing side reactions which produced, *inter alia*, significant amounts of the green *oxo*-bridged bimetallic molybdenum nitrosyl complex, $\{\text{Mo}(\text{NO})\text{T}_p^*\text{Cl}\}_2\text{O}^{15}$. Other products were

also formed although in very minute quantities.

Mass spectral data obtained for Fe(Salen)Cl showed *m/z* peaks which were 35.5 mass units less than the molecular weight of the parent compound; a decrease which may be attributed to the loss of the axial chlorine atom attached to iron. Molar conductivity values obtained at 25^oC in DMF, DMSO and MeCN solvents were less than the quoted values for 1:1 type of electrolytes, suggesting that they are non-electrolytic¹⁶. Elemental analyses for all the complexes were consistent with their formulations. They however, showed that the binuclear complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] were solvated with 0.5 moles of C₆H₄ used as solvent during re-crystallization. The micro-analytical and mass spectral data together with a few selected physical properties of Fe(Salen)Cl and their corresponding molybdenated *para*-complexes are summarized in table 1.

Table 1: Elemental, Physical and Mass Spectral Data [(1), B = C₆H₄ or (CH₂)_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 ₆ H ₄	Fe	34.0	0	56.8 (56.9)	3.7 (3.3)	6.9 (6.6)	386	19.97	24.60	33.45
H	(CH ₂) ₂	Fe	44.4	0	51.2 (51.4)	3.9 (3.7)	7.6 (7.5)	338	21.53	24.62	20.28
H	(CH ₂) ₃	Fe	44.8	0	52.7 (52.6)	4.3 (4.1)	7.5 (7.2)	352	7.44	2.33	9.15
H	(CH ₂) ₄	Fe	45.2	0	53.9 (53.7)	4.8 (4.5)	7.3 (7.0)	366	28.07	29.45	29.36
Mo(NO)T _p *Cl	C ₆ H ₄	Fe	35.3	0.5 C ₆ H ₁₄	49.8 (49.4)	5.3 (5.1)	13.9 (13.7)		39.30	13.51	40.23
Mo(NO)T _p *Cl	(CH ₂) ₂	Fe	35.5	0.5 C ₆ H ₁₄	46.7 (46.5)	5.4 (5.2)	14.5 (14.4)		40.20	12.37	41.52
Mo(NO)T _p *Cl	(CH ₂) ₃	Fe	30.6	0.5 C ₆ H ₁₄	47.2 (47.1)	5.6 (5.4)	14.4 (14.1)		20.35	13.52	20.30
Mo(NO)T _p *Cl	(CH ₂) ₄	Fe	30.6	0.5 C ₆ H ₁₄	47.9 (47.7)	5.7 (5.5)	14.2 (13.9)		40.15	10.35	30.51

^a molecules of solvent of crystallization

Spectroscopic studies

A summary of the IR data obtained for all the complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = H₂ or Fe, M' = H or Mo(NO)T_p*Cl] is given in table 2. Although Schiff bases may exist in two tautomeric forms; the *keto* enamine which is characterized by ν_{NH} at 3057–3070 cm⁻¹ and $\nu_{\text{phenolic C=O}}$ at 1651 cm⁻¹; and the phenol imine which is characterized by $\nu_{\text{C=N}}$ at 1629–1634 cm⁻¹ and $\nu_{\text{phenolic C-O}}$ at 1271–1278 cm⁻¹, upon complexing with metal ions, they may exist only in the phenol imine form¹⁷. The $\nu_{\text{C=N}}$ and $\nu_{\text{phenolic C-O}}$ however, shifted to lower stretching frequencies in the Fe(Salen)Cl (**Table 2**), an observation which has been made previously in zinc(II) and copper(II) complexes of similar Schiff base ligands¹⁸. The bathochromic shift in the $\nu_{\text{phenolic C-O}}$ in the Fe(Salen)Cl confirms the participation of oxygen in the C-O-Fe bond¹⁹. Other notable bands not observed in the Schiff bases but found in these complexes were in the 405–427 cm⁻¹ and 492–513 cm⁻¹ regions. These may be attributed to $\nu_{\text{phenolic C-O-Fe}}$ and $\nu_{\text{Fe}\leftarrow\text{N}}$ respectively¹⁹, confirming that the iron(III) ions are bonded to the Schiff bases

via the phenolic oxygen and imino nitrogen as illustrated in figure 1.

All the bimetallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] exhibited sharp peaks at 2522 cm⁻¹ and 1258–1274 cm⁻¹, attributable to ν_{BH} and $\nu_{\text{phenolic C-O}}$ respectively while $\nu_{\text{C=N}}$ and ν_{NO} peaks appeared at 1607–1608 cm⁻¹ and 1654–1659 cm⁻¹ respectively. As KBr pellets, peaks due to $\nu_{\text{C=N}}$ and ν_{NO} overlapped to give a broad unsymmetrical band in the 1640-1660 cm⁻¹ region, thereby showing solid state effect. The value of ν_{NO} in the bimetallic complexes was lower than the value obtained in the molybdenum precursor molecule, Mo(NO)T_p*Cl₂; $\nu_{\text{NO}} = 1702$ cm⁻¹ and this may be due to substantial $d_{\pi}\text{-}p_{\pi}$ back-donation into nitrosyl (NO) antibonding orbitals which in effect reduces the NO bond order and hence its stretching frequency. In addition to these bands, four characteristic absorption bands of the pyrazolyl groups occurred in the 1457-1558 cm⁻¹ region. The stretching frequencies obtained for all these complexes were however, only slightly sensitive to the changes in the polymethylene carbon chain length of the Schiff base backbone.

Table 2: IR and Electronic Spectral Data [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = H₂ or Fe, M' = H or Mo(NO)T_p*Cl]

Compound			IR spectral data (cm ⁻¹)						U.V-Vis spectral data	
M'	B	M	$\nu(\text{C=N})$	$\nu(\text{ph.CO})$	$\nu(\text{MO})$	$\nu(\text{MN})$	$\nu(\text{NO})$	$\nu(\text{BH})$	λ_{max} (nm), (ϵ) dm ³ mol ⁻¹ cm ⁻¹	
H	C ₆ H ₄	H ₂	1629	1271					283(7680), 316(4390), 330(2039)	
H	(CH ₂) ₂	H ₂	1634	1276					256(6826), 340(5650)	
H	(CH ₂) ₃	H ₂	1632	1278					256(7336), 320(5281)	
H	(CH ₂) ₄	H ₂	1632	1276					256(6761), 345(4647)	
H	C ₆ H ₄	Fe	1620	1272	405	503			294(7350), 320(6097), 358(3910), 495(457)	
H	(CH ₂) ₂	Fe	1625	1283	427	498			262(6427), 318(5629), 386(4085), 483(398)	
H	(CH ₂) ₃	Fe	1630	1284	417	513			302(6816), 376(4676), 512(436)	
H	(CH ₂) ₄	Fe	1631	1285	416	492			256(6011), 320(5857), 510(481)	
Mo(NO)T _p *Cl	C ₆ H ₄	Fe	1608	1274	418	523	1654	2522	230(7860), 320(6509), 425(232), 512(273)	
Mo(NO)T _p *Cl	(CH ₂) ₂	Fe	1608	1267	419	...b	1659	2522	232(7183), 311(5238), 432(302), 504(197)	
Mo(NO)T _p *Cl	(CH ₂) ₃	Fe	1608	1258	422	523	1659	2522	232(8361), 315(6410), 430(351), 523(245)	
Mo(NO)T _p *Cl	(CH ₂) ₄	Fe	1607	1259	420	525	1658	2522	232(8361), 318(5410), 434(365), 524(204)	

....b = broad band. IR data was obtained as KBr pellets. U.v-vis spectral data for Schiff base was obtained in EtOH while those of the monometallic and bimetallic complexes were obtained in DMSO and CH₂Cl₂ solvents respectively.

The electronic spectral data for all the complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = H₂ or Fe, M' = H or Mo(NO)T_p*Cl] is given in table 2. The Schiff base ligands exhibited intense intra-ligand absorption bands in the 256-345 nm region. Bands at 256-283 nm and 316-345 nm may be attributed to benzene $\pi-\pi^*$ and imine $\pi-\pi^*$ transitions respectively²⁰. Fe(Salen)Cl monometallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] had similar spectral features as the Schiff base ligands [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = H₂, M' = H] although they shifted to higher wavelengths (262-386 nm). They also exhibited additional very broad but weak peaks in the 483-512 nm region. These peaks may be attributed to the charge transfer (CT) bands which appear in the near UV region and usually obscure almost completely the very weak spin-forbidden *d-d* transition bands²¹. As the polymethylene carbon chain of the Schiff base backbone increased in length, there occurred a small bathochromic shift of the absorption peaks to longer wavelength. This may be attributed to the distortion of their square pyramidal configuration towards trigonal bipyramidal configuration. This kind of distortion has been observed in complexes of cobalt(II)-*N*-methyl salicylaldehyde²².

In the bimetallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl], other than peaks observed in the Fe(Salen)Cl complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H], there were additional weak peaks in the 425-434 nm region. These peaks could be attributed to the presence of [Mo(NO)T_p*ClO-Ar] chromophore and may be associated with

the metal-ligand charge transfer (MLCT) between the molybdenum center and the phenoxide (OAr) moiety of the coordinated Schiff base. The noticeable decrease in the intensity of these bands may be due to loss of energy to other transitions¹⁸.

Electrochemical studies

The electrochemical properties of the monometallic and bimetallic complexes were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in DMSO, CH₂Cl₂ and MeCN solvents. The monometallic complexes exhibited relatively low solubility in CH₂Cl₂ and MeCN and their electrochemical properties were therefore investigated in DMSO only. The bimetallic complexes were investigated in both CH₂Cl₂ and MeCN to establish the solvent dependence of their redox potentials. Redox potentials were measured at temperatures of 22 ± 1°C at 200mV/s scan rate for CV and 20mV/s scan rate for DPV, with typical reading error in the range of ±10mV. Sample solutions contained 1 x 10⁻³ mol dm⁻³ of the complex.

When Fe(Salen)Cl complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] were scanned in DMSO from 0.0 to -1.0 V and back, similar reversible reduction waves were observed for all the complexes, the formal reduction potential falling in the range of -0.639 to -0.680 V (**Table 3**). The cathodic peaks may be associated with Fe³⁺ + e⁻ → Fe²⁺ process while the corresponding anodic peaks may be associated with Fe²⁺ → Fe³⁺ + e⁻ process. Peak potential separations between cathodic and anodic waves were within the range of 78-81 mV and these values are not far from

the expected theoretical value of $\Delta E = 59$ mV for a reversible one electron transfer process. The deviations from 59 mV may be due to uncompensated solution internal resistance and non-ideality of the cell geometry. When ferrocene was added to the analyte solution under investigation, $\Delta E_{\text{ferrocene}}$ values ranged between 63–70 mV. On scanning from 0.0 to 1.0 V and reversing the scan direction, similar anodic waves which may be attributed to $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+} + e^-$ process were observed between 0.625 and 0.710 V (**Table 3**) for all the Fe(Salen)Cl complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H]. No corresponding cathodic peaks were observed; both at high and low scan rates, and this may be attributed to the instability and transient nature of the Fe⁴⁺ ions in solution. As the polymethylene carbon chain of the Schiff base backbone lengthens, the formal reduction potentials shifted cathodically by about 20 mV while the anodic peak potential for the oxidation process shifted anodically by an average of 45 mV, probably suggesting that the redox orbitals are ligand-based.

When the bimetallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] were scanned in MeCN from 0.0 to -1.5 V and scan polarity reversed, two broad reversible reduction

waves were observed for all the complexes, the formal reduction potential falling in the range of -0.758 to -0.787 V and -0.514 to -0.549 V (**Table 3**). In comparison to the voltammograms of Fe(Salen)Cl monometallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H], the potentials at -0.758 to -0.787 V in the bimetallic complexes may be assigned to $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ reduction process although it is more cathodic by about 110 mV than in the corresponding monometallic complexes. This implies that the presence of molybdenum center modestly modifies the electron distribution of the central iron(III) ion in the tetradentate Schiff base cavity. The potential at -0.514 to -0.549 V may be assigned to $\text{Mo}(\text{NO})^{3+} + e^- \rightarrow \text{Mo}(\text{NO})^{2+}$ reduction process. When compared to other related complexes of similar molybdenum centers, this was found to be more cathodic by about 80 mV, showing that the presence of iron also affects the reduction potential of molybdenum¹⁸. On scanning from 0.0 to 1.5 V and reversing the scan polarity, one well-defined irreversible oxidation wave attributable to iron(III) and/or ligand oxidation processes was observed, the electrode potential falling in the range of 1.201 to 1.226 V for all the complexes (**Table 3**).

Table 3: Cyclic Voltammetric Data [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H or Mo(NO)T_p*Cl] in various solvents

Compound		In DMSO		In MeCN			In CH ₂ H ₂				
M'	B	M	E _f ¹	E _a ²	E _f ¹	E _f ³	E _a ⁴	E _c ⁵	E _f ³	E _a ²	E _a ⁶
H	C ₆ H ₄	Fe	-0.661	0.645							
H	(CH ₂) ₂	Fe	-0.639	0.625							
H	(CH ₂) ₃	Fe	-0.657	0.652							
H	(CH ₂) ₄	Fe	-0.680	0.710							
Mo(NO)T _p *Cl	C ₆ H ₄	Fe			-0.764	-0.517	1.201	-0.751	0.522	1.022	1.327

Mo(NO)T _p *Cl	(CH ₂) ₂	Fe	-0.758	-0.514	1.225	-0.758	-0.535	1.123	1.335
Mo(NO)T _p *Cl	(CH ₂) ₃	Fe	-0.765	-0.525	1.226	-0.771	-0.547	1.165	1.358
Mo(NO)T _p *Cl	(CH ₂) ₄	Fe	-0.787	-0.549	1.215	-0.778	-0.556	1.197	1.411

Sample solution $1 \times 10^{-3} \text{ mol dm}^{-3}$ in 0.1 mol dm^{-3} $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ base electrolyte, scan rate 200 mV/s, reading error ± 10 mV; ¹ Formal reduction potential (V) for the process $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$, ² Anodic peak potential (V) for the process $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+} + e^-$, ³ Formal reduction potential (V) for the process $\text{Mo}(\text{NO})^{3+} + e^- \rightarrow \text{Mo}(\text{NO})^{2+}$, ⁴ Anodic peak potential (V) for oxidation of metal ion and/or ligand, ⁵ Cathodic peak potential (V) for the process $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$, ⁶ Anodic peak potential (V) for oxidation of ligand

When the bimetallic complexes [(**1**), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] were investigated in CH₂H₂, on scanning from 0 to -1.5 V and back, one similar cathodic wave for all the complexes attributable to the reduction of iron(III) was observed in the potential range of -0.751 to -0.778 V. ΔE between the cathodic and the corresponding anodic waves for all the complexes was greater than 200mV, indicating the near irreversibility of the reduction process of iron(III) in CH₂H₂ solvent. A reversible reduction wave associated with the reduction of the molybdenum center was observed at -0.522 to -0.556 V for all the complexes (**Table 3**). Compared to the E_f values obtained in MeCN, these reduction potentials were found to be less cathodic by about 10 mV. These findings confirm that the redox potentials of the complexes are solvent dependent. It was observed that the reduction potentials for both iron(III) and molybdenum centers became more cathodic as the polymethylene carbon chain lengthens. A possible explanation could be due to probable distortion from the square pyramidal geometry of these complexes towards trigonal bipyramidal geometry as the carbon chain lengthens. The same has been observed in similar copper(II) complexes whose structures change from

square planar towards tetrahedral as the carbon Schiff base backbone lengthens¹⁸.

On scanning from 0.0 to 1.5 V and reversing the scan direction, two irreversible oxidation waves falling in the potential ranges of 1.022 to 1.197 V and 1.327 to 1.411 V for all the complexes were observed (**Table 3**). The waves appearing at 1.022 to 1.197 V may be associated with $\text{Fe}^{3+} \rightarrow \text{Fe}^{4+} + e^-$ oxidation process. The process was found to be more anodic than in the corresponding monometallic Fe(Salen)Cl complexes [(**1**), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] showing that the oxidation of iron in the bimetallic complexes [(**1**), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] is modestly influenced by the proximity of the highly electron deficient Mo(NO)T_p*Cl group. Similar effects have been observed on the oxidation potential of iron in $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{SMo}(\text{NO})\text{T}_p^*\text{Cl}\}_2]$ trimetallic species²³. The other anodic peak wave at 1.327 to 1.411 V may be attributed to a ligand-based oxidation process. While most peaks in the CV were either very broad or ill-formed, in DPV the complexes exhibited very well defined peaks as illustrated in figure 2. The Fe(Salen)Cl monometallic complexes [(**1**), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] were investigated in DMSO and the bimetallic complexes [(**1**), B = C₆H₄ or

(CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] in MeCN and CH₂Cl₂ solvents. They were scanned in the potential

window of -0.3 to -1.0 V at a scan rate of 20 mV/s.

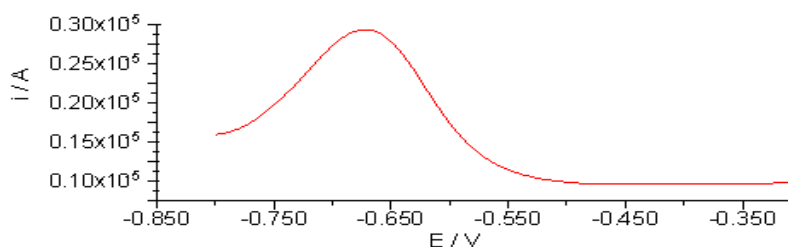


Fig 2: DPV of Fe(Salen)Cl monometallic complex [(1), B = C₆H₄, M = Fe, M' = H] in DMSO

The Fe(Salen)Cl monometallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H] exhibited similar voltammograms with peaks attributable to Fe³⁺ + e⁻ → Fe²⁺ reduction process falling in the potential range of -0.653 to -0.689 V for all the complexes (Table 4). The bimetallic complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = Mo(NO)T_p*Cl] in MeCN exhibited peaks attributable to Fe³⁺ + e⁻ → Fe²⁺ and Mo(NO)³⁺ + e⁻ → Mo(NO)²⁺

reduction processes at -0.738 to -0.741 V and -0.511 to -0.553 V respectively (Table 4). In CH₂Cl₂, they exhibited the corresponding peaks in the potential ranges of -0.745 to -0.759 V and -0.453 to -0.487 V respectively (Table 4). The influence of one metal upon the other, together with the solvent dependence of the redox potentials are quite evident from the DPV data just as it was observed from CV data.

Table 4: Differential Pulse Voltammetric Data [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H or Mo(NO)T_p*Cl] in various solvents

Compound			In DMSO	In MeCN		In CH ₂ H ₂	
M'	B	M	E ¹ (V)	E ¹ (V)	E ² (V)	E ¹ (V)	E ² (V) ³
H	C ₆ H ₄	Fe	-0.671				
H	(CH ₂) ₂	Fe	-0.653				
H	(CH ₂) ₃	Fe	-0.676				
H	(CH ₂) ₄	Fe	-0.689				
Mo(NO)T _p *Cl	C ₆ H ₄	Fe		-0.741	-0.523	-0.745	-0.453
Mo(NO)T _p *Cl	(CH ₂) ₂	Fe		-0.738	-0.511	-0.747	-0.467
Mo(NO)T _p *Cl	(CH ₂) ₃	Fe		-0.743	-0.531	-0.752	-0.475
Mo(NO)T _p *Cl	(CH ₂) ₄	Fe		-0.748	-0.553	-0.759	-0.487

Sample solution 1 x 10⁻³ mol dm⁻³ in 0.1 mol dm⁻³ [n-Bu₄N][PF₆] base electrolyte, scan rate 20 mV/s, reading error ± 10 mV; ¹ Peak potential for the process Fe³⁺ + e⁻ → Fe²⁺, ² Peak potential for the process Mo(NO)³⁺ + e⁻ → Mo(NO)²⁺

CONCLUSION

We have shown that the iron complexes [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Fe, M' = H or Mo(NO)T_p*Cl] in some ways behave differently from their corresponding manganese analogues [(1), B = C₆H₄ or (CH₂)_n; n = 2-4, M = Mn, M' = H or Mo(NO)T_p*Cl]. As the polymethylene carbon chain of the Schiff base backbone lengthens, the reduction potential of iron in both the monometallic and bimetallic complexes becomes more cathodic while the corresponding manganese analogues do not show any significant change in the reduction potential of manganese. Iron also has a greater influence on the reduction potential on the peripheral molybdenum nitrosyl metal fragment than does the manganese. In the iron complexes, the reduction potential of the molybdenum center becomes more cathodic as the carbon chain of the Schiff base backbone lengthens while in the manganese analogues, the reduction potential of the molybdenum center does not change

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