VARIABLE DENTICITY OF A MULTIDENTATE TERTHIOPHENE DERIVATIVE TOWARDS Ni(II) AND Zn(II) - STRUCTURAL STUDIES

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ABSTRACT. A multidentate ligand, 3,4-bis(2-iminomethylphenol)-2,2':5,2''-terthiophene (L), has been synthesized by the condensation of 3,4-diamino-2,2':5,2''-terthiophene and salicylaldehyde. The ligand and Ni(II) and Zn(II) complexes were synthesized and characterized by IR, NMR, UV-Vis, AAS, MS, molar conductivity and magnetic susceptibility measurements. The ligand behaves as neutral ONS-ONS bis-chelant towards Ni(II) in $[Ni_2LCl_4(H_2O)_2]\cdot4H_2O$ and as dibasic ONNO donor towards Zn(II) in $[ZnL(NH_3)_2]$. The dinuclear Ni(II) complex exhibits subnormal magnetic moment at room temperature due to metal-metal interaction through extended conjugation. The participation of the ring sulfur in bonding towards Ni(II) and the non-participation of the same towards Zn(II) are notable features. Octahedral geometries are proposed for both complexes. Cyclic voltammetric studies revealed electrochemical polymerization of the free ligand (L) but not of the Ni(II) and Zn(II) complexes.

KEY WORDS: Variable denticity, 3,4-bis(2-Iminomethylphenol)-2,2':5,2''-terthiophene, Octahedral, Ni(II) complex, Zn(II) complex, Voltammetric studies

INTRODUCTION

One of the reasons for widespread use of heterocyclic compounds is that their structures can be subtly manipulated to achieve the required functional modification [1-6]. Such variations may include differences in acidity or basicity, susceptibility to attack by electrophiles or nucleophiles and polarity, which are the direct consequences of variation in electronic distribution across the molecular frame [3]. Heterocyclics containing oxygen or sulfur as heteroatoms have been relatively less investigated in metal complex formation in comparison with the nitrogen heterocyclics.

A number of applications have been proposed for conducting polythiophenes, including field effect transistors, electroluminescent devices, solar cells, photochemical resistors, nonlinear optical devices, batteries, and diodes [7, 8]. A number of diverse thiophene compounds have been reported in the literature to have germicidal properties and some of them have insecticidal properties [9-11].

Terthiophene precursors, which are presently attracting significant investigation for chemical and electrochemical polymerization to generate optically potential materials [2], have not been systematically studied for the synthesis of metal complexes. The presence of metal ions as chelated systems may positively contribute towards modifying the optical properties and also produce desirable magnetic properties for a wider range of applications [12-14]. In order to obtain polythiophene-metal chelates of the said desirable properties, the synthesis of precursor monomeric thiophene complexes, followed by chemical or electrochemical polymerization, appears to be a reasonable route. This investigation focuses attention on designing a new multidentate S-heterocyclic system and synthesizing its metal complexes with a view to generate metal chelate precursors suitable for chemical or electrochemical manipulations leading to

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optical and magnetic applications. This communication, however limits the contents to the synthesis, characterization and voltammetric studies of Ni(II) and Zn(II) complexes.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. The solvents used were purified by distillation prior to use.

Instrumentation

Melting points were determined on Electrothermal IA 92000, digital melting point apparatus. IR spectra were recorded on Perkin-Elmer BTX FT-IR spectrometer in the range of 4000-400 cm^{-1} using KBr pellets. The metal contents in the complexes were estimated by Buck Model Scientific 210 VGB flame atomic absorption spectrophotometer. The electronic (UV-Vis) absorption spectra were measured on Spectronic Genesy's 2PC UV-Vis spectrophotometer in the 200-800 nm range. NMR data were collected using Bruker Avance 400 spectrometer at 400.13 MHz (^{1}H NMR) and 100.6 MHz (^{13}C NMR). The magnetic susceptibility of the Ni(II) complex was measured by using MSB-AUTO, Sherwood Magnetic Balance. Molar conductivities of complexes in nitrobenzene were recorded at room temperature using EC 214 conductivity meter (Hanna Instrument). Mass spectrum of the ligand was recorded on Thermo Finnegan high temperature insertion probe. The sample was ramped from RT up to 300 ^{o}C.

Cyclic Voltammetry

Prior to electropolymerization, the glassy carbon electrode was polished with alumina-water slurry on polishing cloth pads to a mirror-like finish and rinsed with deionized water. After polishing, the electrode was pretreated in 0.5 M H_2SO_4 by cycling the potential between -0.5 to +1.4 V at 100 mV/s until a reproducible background was obtained.

The cyclic voltammogram of a 0.1 M of blank solution (TEATFB/CH$_3$CN solution) was recorded between 0.0 and +1.6 V (*vs* Ag/AgCl) at a scan rate of 100 mV/s. Electrodeposition of L, and its Ni(II) and Zn(II) complexes were attempted by repeated potential cycling (ten times) of a 5 mM solution of the monomers in the potential range between 0.0-1.6 V (*vs* Ag/AgCl) at a scan rate of 100 mV/s. After each run, the film was rinsed with the electrolyte to remove excess monomers from the electrode surface.

2,5-Dibromo-3,4-dinitrothiophene (2) [15] (Scheme 1)

Concentrated H_2SO_4 (74.3 mL), fuming H_2SO_4 (114 mL) and fuming HNO_3 (63 mL) were combined in a 1 L round bottomed flask and cooled in an ice bath. 2,5-Dibromothiophene **1** (22.94 g, 95 mmol) was added dropwise maintaining the temperature at 20-30 ^{o}C. The mixture was allowed to react for a total of 8 h and then poured over 515 g of ice. The solid residue was recovered by suction filtration, washed with distilled water and recrystallized from hot isopropyl alcohol to obtain **2** (28.95 g, 92%). Mp: 135.3-136 ^{o}C [15]. IR (cm^{-1}): ν_a and ν_s of N=O at 1545 and 1345, respectively, ν_{C-N} (C-N str. of nitro compound at 1082), ν_{C-S-C} (C-S-C ring str. at 899), $\nu_{-C=C}$ (-C=C in plane ring vibration at 1500, 1454, 1390, and 1317), ν_{C-Br} (C-Br str. at 669); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 113.4 (C-2, C-5), 140.7 (C-3, C-4).
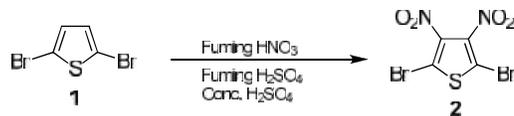
Scheme 1. Synthesis of 2,5-dibromo-3,4-dinitrothiophene (**2**).

*3',4'-Dinitro-2,2':5,2''-terthiophene (**3**) [16] (Scheme 2)*

A solution of 2,5-dibromo-3,4-dinitrothiophene (20 g, 60 mmol), tributyl(thiophene-2-yl)stannane (38.2 mL) and PdCl$_2$(PPh$_3$)$_2$ (0.844 g, 1.2 mmol) in toluene (200 mL), was refluxed for 12 h under nitrogen atmosphere. The mixture was cooled and the solvent was removed over a rotary evaporator. The residue was separated by suction filtration to offer compound **3** (17.48 g, 86%), which was recrystallized from toluene-methanol. Mp: 143-143.6 $^{\circ}$C [16]. IR (cm^{-1}): ν_a and ν_s of N=O at 1545 and 1352, respectively, ν_{C-N} (C-N str. of nitro compound at 1077 and 1067), ν_{C-S-C} (C-S-C ring str. at 856), $\nu_{C=C}$ (-C=C in plane ring vibration at 1500, 1417, 1385, and 1304), $\nu_{C=C-H}$ (C=C-H out of plane bending at 705), ν_{C-H} (C-H str. of thiophene at 3075); ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.63 (*d, J* = 5.2 Hz, 2H,) 7.56 (*d, J* = 3.8 Hz, 2H) 7.2 (*dd, J* = 5.2, 3.6 Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 135.88, 133.94, 131.33, 131.25, 128.46, 128.04; DEPT-135 (100.16 MHz, CDCl$_3$): δ 131.33, 131.25, and 128.46.
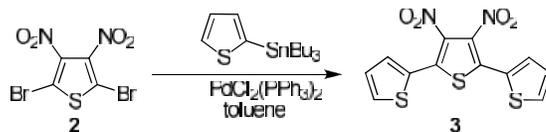
Scheme 2. Synthesis of 3',4'-dinitro-2,2':5,2''-terthiophene (**3**).

*3',4'-Diamino-2, 2':5,2''-terthiophene (**4**) [16] (Scheme 3)*

Compound **3** (3 g, 8.9 mmol) was suspended in ethanol (31.26 mL) and conc. HCl (62.49 mL). To the mixture, a solution of anhydrous SnCl$_2$ (163 mmol, 31 g) in ethanol (62.49 mL) was added. The mixture was stirred at 30 $^{\circ}$C for 24 h and poured in to a cold 25% NaOH (250 mL). Toluene (200 mL) was added to the above mixture, and then the reaction mixture was shaken vigorously and filtered though celite. The phases were separated and the aqueous layer was extracted with toluene. The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure to offer compound **4** (2.24 g, 91%) as yellowish brown solid. Mp: 98.4-99.7 $^{\circ}$C [16]. IR (cm^{-1}): ν_{NH2} (N-H str. of primary amine at 3439, 3373, 3303, and 3296), ν_{N-H} (N-H bending of primary amine at 1624), ν_{C-N} (C-N str. of primary amine at 1353 and1213), ν_{C-S-C} (C-S-C ring str. at 842), $\nu_{C=C}$ (-C=C in plane ring vibration at 1510, 1532, 1489, and 1444), $\nu_{C=C-H}$ (C=C-H out of plane bending at 688), ν_{C-H} (C-H str. of thiophene at 3094). ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.12 (*d, J* = 2.4 Hz, 2H), 7.29 (*d, J* = 5 Hz, 2H), 3.6 (*brs*, 4H of NH), 7.13 (*dd, J* = 13.6, 10.4 Hz, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ 135.96, 133.6, 127.8, 124.0, 123.9, 110.1; DEPT-135 (100.6 MHz, CDCl$_3$): δ 127.8, 124.0, 123.9.
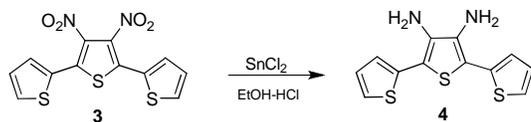
Scheme 3. Synthesis of 3´,4'-diamino-2,2':5,2''-terthiophene (**4**).

*3,4-bis(2-Iminomethylphenol)-2,2':5,2''-terthiophene (**L**)*

Compound **4** (3 g, 11 mmol) and salicylaldehyde (2.633 g, 23.9 mmol) were dissolved in acetic acid (155 mL) and heated at 60 ^{o}C for 8 h. The mixture was then cooled to room temperature and the precipitate was collected by filtration, washed with water and methanol and dried to yield a brownish yellow solid, which was further purified by silica gel column chomatography using petroleum ether:ethyl acetate (9:1) as eluent to obtain the pure ligand **L** (3.3 g, 62%). Mp: 198-199 ^{o}C.
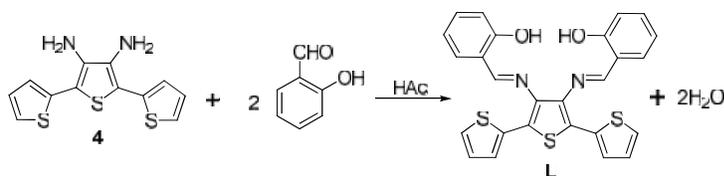
Scheme 4. Synthesis of 3,4-bis(2-iminomethylphenol)-2,2':5,2''-terthiophene (**L**).

Ni(II)-L complex

Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) (0.2 g, 0.84 mmol) was dissolved in methanol (20 mL). To the mixture, a solution of the ligand (0.2 g, 0.412 mmol) in dichloromethane (20 mL) was added. The mixture was refluxed for 2 h. Aqueous ammonia diluted with methanol (1:19 v/v) was added to the mixture until the pH was 6 and then the mixture was refluxed for 14 h. The precipitate was filtered off, washed with methanol and finally with dichloromethane and dried in vacuum to afford the Ni(II)-L complex (0.23 g, 68%) as a deep brown solid. Mp: stable up to 350 ^{o}C.

Zn(II)-L complex

Anhydrous zinc chloride (ZnCl$_2$) (0.112 g, 0.82 mmol) was dissolved in methanol (10 mL). To the mixture, a solution of the ligand (0.2 g, 0.412 mmol) in dichloromethane (20 mL) was added. The mixture was refluxed for 2 h. Aqueous ammonia diluted with methanol (1:19 v/v) was added to the mixture until the pH was 7-7.5 and then the mixture was refluxed for 6 h. The precipitate was filtered off, washed with methanol and dichloromethane and finally dried in vacuum to afford the Zn(II)-L complex (0.18 g, 70%) as a light yellow solid. Mp: decomposes at 254 ^{o}C.

RESULTS AND DISCUSSION

The Ni(II)-L and Zn(II)-L complexes were obtained as powders with high melting points and low solubility in organic solvents. These complexes are colored compounds. Some of the important physical characteristics of the ligand, and the complexes are listed in Table 1.

Estimation of Ni(II) and Zn(II) by AAS

The molar ratios of the metal to ligand of both the complexes were obtained from the determination of metals using atomic absorption spectroscopy (Table 2).

Based on elemental analysis and AAS data, the metal complexes are formulated as $Ni_2LCl_4 \cdot 6H_2O$ and $ZnL(NH_3)_2$.

Table 1. Some physical properties of the ligand, Ni(II) and Zn(II) complexes.

Compound	Color	Mp/decomposition temperature (^{o}C)	Yield (%)	Solubility
Ligand (**L**)	Greenish yellow	198-199 ^{o}C (Mp)	62	Soluble in ethyl acetate, dichloromethane, chloroform, toluene
Ni(II)-L complex	Deep brown	Stable up to 350 ^{o}C	68	Soluble in hot acetonitrile and nitrobenzene
Zn(II)-L complex	Light yellow	254 ^{o}C (dec.)	70	Soluble in hot DMSO and nitrobenzene

Table 2. Metal determination data.

Metal complex	Percentage of metal (mass)		Metal to ligand ratio
	Found (%)	Calculated (%)	
Ni-L	12.89	13.76	2:1
Zn-L	10.64	11.21	1:1

The ^{1}H-NMR of the ligand (**L**) shows nine proton resonances. The two-proton singlet at δ 8.5 is attributed to the olefinic hydrogens on the imine carbon atoms (C7'''). The thiophene ring protons appeared at 7.16 (*d*, H3',3"), 7.27 (*d*, H5',5") and 7.33 (*dd*, H4',4"). The two-proton doublet of doublets centered at δ 6.85 and 7.02 are attributed to H-5''' and H-4''', respectively. The remaining two-proton doublets at δ 6.98 and 7.23, are attributable to H6''' and H3''', respectively (Table 3). The two-proton broad singlet at δ 12.5 is due to the phenolic OH protons. The ^{13}C NMR spectrum of the ligand (**L**) indicates 13 carbon resonances, of which five are due to quaternary carbon atoms and the remaining eight are due to methine carbons (Table 3).

Table 3. The ^{1}H and ^{13}C NMR spectral data of the ligand (**L**).

(L)
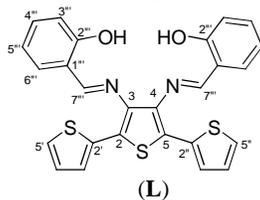
H	^{1}H data δ (ppm)	C	^{13}C data (δ ppm)
OH	12.5 (2H, *bs)*	C7'''	169.12 (C-H)
H7'''	8.5 (2H, *s*)	C2'''	160.92 (*q*)
H4',4"	7.3 (2H, *dd*)	C3,4	137.44 (*q*)
H5',5"	7.27 (2H, *d*)	C2,5	134.18 (*q*)
H3'''	7.23 (2H, *d*)	C5',5"	133.9 (C-H)
H3',3"	7.16 (2H, *d*)	C3'''	132.9 (C-H)
H4'''	7.02 (2H, *dd*)	C4',4"	127.45 (C-H)
H6'''	6.98 (2H, *d*)	C3'3"	126.51 (C-H)
H5'''	6.85 (2H, *dd*)	C4'''	125.57 (C-H)
		C2',2"	122.75 (*q*)
		C6'''	119.4 (C-H)
		C1'''	118.75 (*q*)
		C5'''	117.34 (C-H)

In ^{1}H-NMR spectrum of the Zn-L complex, the phenolic OH proton signal was absent, confirming deprotonation and its subsequent involvement in coordination. One additional broad singlet signal at δ 3.25 is due to the NH signal of the coordinated ammonia.

Mass spectrum

The mass spectrum of the ligand (**L**) displayed a molecular ion peak at *m/z* 486 corresponding to a molecular formula of $C_{26}H_{18}S_3N_2O_2$. Fragment ions appeared at *m/z* 485, 469, 393, 380, 366, 226, 227, 127, 120, 86, 84, 51 and 49. The base peak at *m/z* 84 is presumably due to the thiopene radical cation.

Conductivity measurements

The molar conductance values of the Ni(II) and Zn(II) complexes were recorded in nitrobenzene. The molar conductance values of both the complexes are less than 20 S cm^2 mol^{-1} indicating their non-electrolyte nature. In view of this, the following conclusions are made: (i) all the chlorides in the Ni(II) complex are in the coordination sphere and the ligand is present in the neutral state and (ii) As there are no chlorides in the Zn(II) complex (identified through the absence of precipitation upon decomposition of the complex in nitric acid and subsequent treatment with silver nitrate) [17], the ligand is likely to be in deprotonated and L^{2-} state. This is justified by the fact that the Zn(II) complex separated from the reaction mixture at a higher pH (7.0-7.5), while the Ni(II) complex was formed at pH = 6.

Infrared spectra

Comparison of the IR spectrum of the free ligand with the spectra of the metal complexes (Table 4) reveals that the ligand exhibits different modes of chelation towards Ni(II) and Zn(II). The results show that it behaves as a neutral bis-ONS donor towards Ni(II) and as a dibasic ONNO donor towards Zn(II).

The free ligand spectrum shows bands at 3448, 1612, 1572, 1178 and 845 cm^{-1}, which are assignable to νOH (phenolic, hydrogen bonded), νC=C (aromatic), ν(C=N), ν(C-O) and ν(C-S-C), respectively. In plane thiophene ring vibrations have been observed 1300, 1384, 1457, and 1482 cm^{-1}.

The salient features of the spectra of the metal complexes are summarized below.

Ni(II) complex

A broad band centered as 3400 cm^{-1} is assignable to νOH (phenolic and H$_2$O). The bands observed at 3062, 1528, 1223, and 852 cm^{-1} are assignable to νCH (azomethine), ν(C=N), ν(C-O) and ν(C-S-C), respectively. Persistence of νOH suggests that the phenolic functions are not deprotonated, but positive shift in ν(C-O) from 1198 in the free ligand to 1223 cm^{-1} in the complex supports the involvement of the phenolic oxygen in coordination. Further, the negative shift in ν(C=N) from 1752 to 1528 cm^{-1} reveals that the azomethine nitrogen is bonded to the metal. A positive change is noted with respect to ν(C-S-C), which suggests coordination though the ring sulfur. These observations establish that the ligand is offering two sets of ONS sequences in Ni(II) binding. This is adequately matching with the proposed formula of the complex. Medium intensity bands at 950 and 645 cm^{-1}, due to rocking and wagging modes, confirm the presence of coordinated water. Other non-ligand bands are assignable to Ni-O and Ni-N stretching. The νNi-S and Ni-Cl are not in the frequency range of the spectrum.

Zn(II) complex

The spectrum does not show the νOH (phenoloic), indicating the deprotonation of the phenolic function. It presents characteristic strong bands at 3330 and 3220 cm^{-1}, assignable to νNH$_3$. These bands support the presence of ammonia molecules in coordination. The bands observed at 1160 and 645 cm^{-1} due to rocking and wagging modes further confirm ammonia coordination. The spectrum also reveals bands at 3060, 1547, 1243, and 846 cm^{-1} assignable to νCH (azomethine), ν(C=N), ν(C-O) and ν(C-S-C), respectively. The negative shift of νC=N and the positive shift in νCO and no shift in νCSC suggest chelation though azomethine nitrogen and deprotonated phenolic oxygen. Based on these results it is concluded that the ligand behaves as a dibasic ONNO donor [18, 19].

Table 4. Infrared data (cm^{-1}) of the ligand and complexes.

Compound	ν(O-H)	ν (NH$_3$)	ν(C=N)	ν(C-O)	ν(C-S-C)	New bands
The ligand (**L**)	3448 (b)	--	1572 (s)	1198 (m)	845 (w)	--
Ni-L complex	3400 (b)	--	1528 (s)	1223 (s)	852 (m)	950, 668-535 467-450 (m, w)
Zn-L complex	--	3330, 3220 (s)	1547 (s)	1243 (s)	846 (w)	1160 666-500 500-420 (m, w)

Magnetic susceptibility

The magnetic susceptibility of the Ni(II) complex was measured at 22 $^{\circ}$C (295 K). The effective magnetic moment of this complex was found to be 2.04 BM. This subnormal magnetic moment (2.04/2 = 1.02 BM) in comparison with the expected moment corresponding to two unpaired electrons is explained on the basis of the possible antiferromagnetic interaction due to superexchange phenomenon. [20]. Further, the back donation of elections due to electron rich metal ions will facilitate spin pairing via the delocalized π-electron cloud. The skeletal structure presented in Figure 1 is in support of this conclusion.
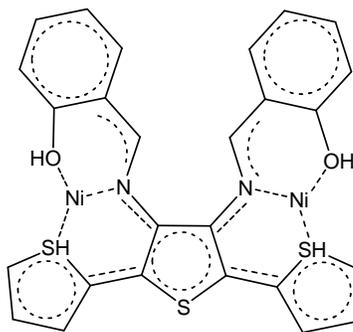
Figure 1. Super-exchange phenomenon favored by extended conjugation.

Binuclearity of Ni(II) complex provides adequate justification for sub-normality of magnetic moments.

Electronic spectra

The electronic spectrum of the ligand shows bands at 42373, 35971, 28818, 25000 cm^{-1}. These are assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, due to aromatic, phenolic and azomethine functions. The spectra of metal complexes show modifications in these band positions as a consequence of metal ligand interaction. Besides three bands observed in the spectrum of Ni(II) complex are assigned to d-d transitions, which are given in Table 5. A moderately intense band tailing into the visible region (28571-23529 cm^{-1}) in the spectrum of the Zn(II) complex is assignable to MLCT. Octahedral geometries are proposed for both complexes (Figure 2).

Table 5. Electronic spectra data of the ligand and complexes.

Compound	Band position, λ_{max} (cm^{-1})	Assignment of transition
The ligand (**L**)	42373, 35971	$\pi \rightarrow \pi^*$
	28818, 25000	$n \rightarrow \pi^*$
Ni-L complex	43103, 37313, 27933	Intraligand
	16234	$^3A_{2g} \rightarrow {}^3T_{2g}$
	19455	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)
	22936	$^3A_{2g} \rightarrow {}^3T_{2g}$ (F)
Zn-L complex	38911, 33113	Intraligand
	28571-23529	MLCT
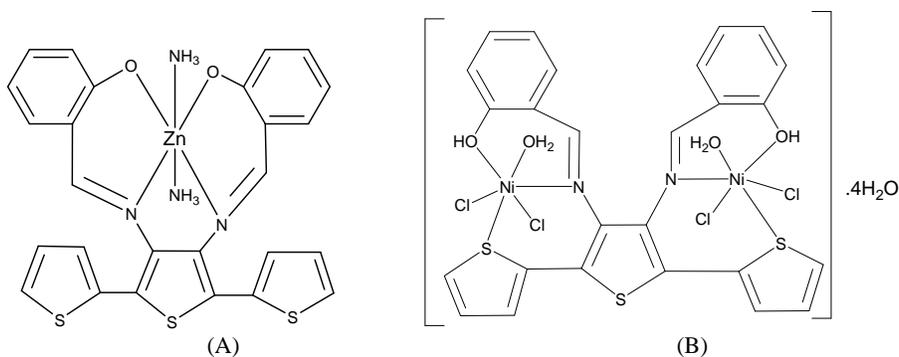
Figure 2. Proposed structures for (A) Zn(II) complex and (B) Ni(II) complex.

Cyclic voltammetry

3,4-bis(2-iminomethylphenol)-2,2':5,2''-terthiopene (L)

Figure 3 shows a series of cyclic voltammograms (CVs) recorded for a 5 mM of the ligand **L** monomer in a 0.1 M Et$_4$NBF$_4$/CH$_3$CN solution, when the potential was cycled between 0.0 and +1.6 V. The CV exhibited three oxidation peaks at +0.63, +1.12 and +1.34 V during the first anodic scan. A reduction peak was observed at +1.18 V in the cathodic scan. The subsequent increase in these peaks indicates the growth of a polymer film on the electrode surface. The CV of the polymer film (poly L) formed on the electrode surface was recorded in a monomer free

supporting electrolyte and is shown in Figure 4. Two oxidation peaks and one reduction peak were observed indicating that the polymer film is electrochemically active.
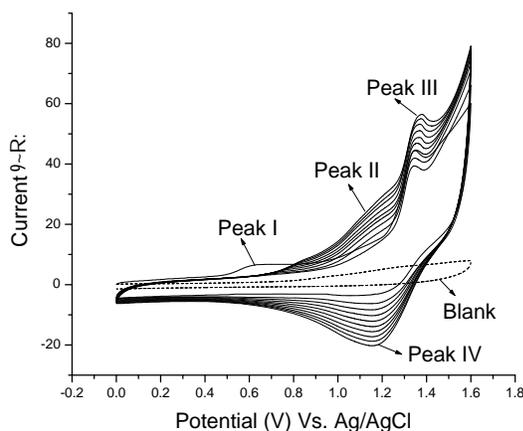
Figure 3. Repeated cyclic voltammograms recorded during the first 10 cycles for the electropolymerization of 5 mM of the ligand **L** in 0.1 M Et$_4$NBF$_4$/CH$_3$CN solutions, scanning anodically from 0.0 to +1.6 V at a scan rate of 100 mV/s.
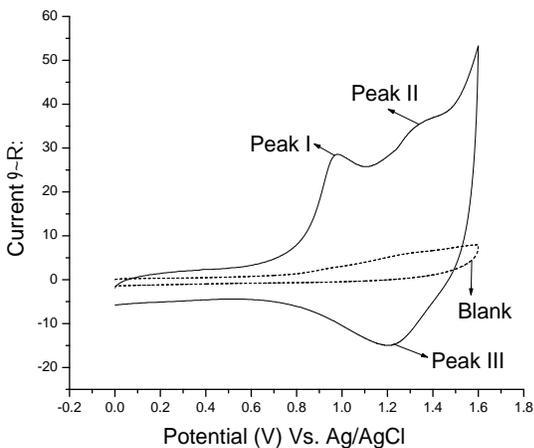
Figure 4. The cyclic voltammogram of polymer film (poly L) in monomer free 0.1 M Et$_4$NBF$_4$/CH$_3$CN solutions at a scan rate of 100 mV/s.

Ni(II)-L complex

Figure 5 shows series of cyclic voltammograms recorded for a 5 mM Ni(II)-L monomer in a 0.1 M Et$_4$NBF$_4$/CH$_3$CN solution, when the potential was cycled between 0.0 and +1.6 V versus Ag/AgCl. The CV exhibited no oxidation peaks indicating that the monomer is difficult to electropolymerize and deposit at the electrode surface. This could possibly be due to the delocalization of the electrons responsible for the radical formation as shown in Figure 1.

Zn(II)-L complex

Figure 6 shows a series of cyclic voltammograms (CVs) recorded for a 5 mM Zn(II)-L monomer in a 0.1 M Et$_4$NBF$_4$/CH$_3$CN solution, when the potential was cycled between 0.0 and +1.6 V versus Ag/AgCl. The CV does not exhibit any increase in oxidation peaks indicating the difficulty of electrodepositing a polymer film on the electrode surface. The reason might be due to the Zn(II) present in the blocked extended conjugation lacks any donor groups on the *para* position relative to phenoxy group to facilitate the polymerization.
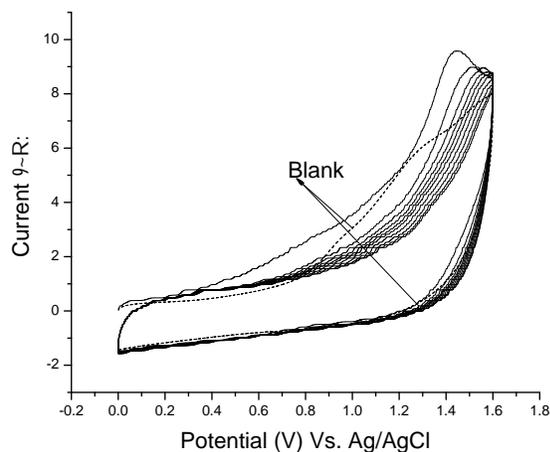
Figure 5. Repeated cyclic voltammograms recorded during the first 10 cycles of 5 mM of Ni(II)-
         L monomer in 0.1 M Et$_4$NBF$_4$/CH$_3$CN solutions scanning anodically from 0.0 to +1.6
         V at a scan rate of 100 mV/s.
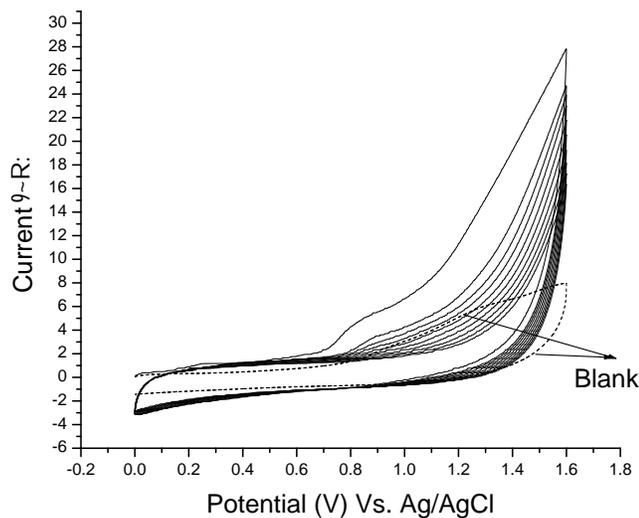
Figure 6. Repeated cyclic voltammograms recorded during the first 10 cycles of 5 mM of Zn(II)-
         L monomer in 0.1 M Et$_4$NBF$_4$/CH$_3$CN solutions, scanning anodically from 0.0 to +1.6
         V at a scan rate of 100 mV/s.

CONCLUSIONS

Synthesis and characterization of a multidentate terthiophene based ligand (**L**) with distinct variability of denticity towards Ni(II) and Zn(II) ions revealed dinuclear ONS-ONS bis-chelation and mononuclear ONNO chelation, respectively. Subnormal magnetic moment of Ni(II) complex conform potential basis for further investigation and applications. Feasibility of electrochemical polymerization of the free ligand and non-feasibility of polymerization of the metal complexes are notable features, which suggest the influence of metal chelation in the reorganization of ligand based electron denticity.

ACKNOWLEDGEMENTS

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