Spectroscopic and electrochemical investigation of mixed – ligand transition metal complexes with 2N-salicylidine-5-(p-nitrophenyl)-1, 3, 4-thiadiazole and 5, 5’-Me$_2$bipy in aqueous medium

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Abstract

Herein we reported the spectroscopic and electrochemical investigation of four transition metal complexes viz. VO(II), Co(II), Ni(II) and Cu(II) of 2N-salicylidine-5-(p-nitrophenyl)-1, 3, 4-thiadiazole Schiff base ligand (L) and 5,5’-dimethyl-2,2’-bipyridine (Me$_2$bipy) in the aqueous (1: 1: 1 molar ratio) medium. Transition metal complexes were characterized by microanalysis, FT-IR, electronic absorption and mass spectroscopy.

Electrochemistry of transition metal complexes was studied in aqueous medium by using cyclic voltammetry (CV) at glassy carbon working electrode (GCE) versus Ag/AgCl. The reduction potential of the VO (II) and Cu (II) becomes more negative with increasing scan rate while Co (II) and Ni (II) positive show easier reduction.

Keyword: Bipyridine, transition metals, cyclic voltammetry, UV-Vis., mixed-ligand.

Introduction

The bidentate (2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole) Schiff base ligands were investigated from the condensation reaction of 4-nitrobenzoic acid, thiosemicarbazide and phosphorus oxychloride respectively. Their mixed-ligand complexes with transition metal ions viz. VO (II), Co (II), Ni (II) and Cu (II) played a vital role in the development of inorganic chemistry[1] as widely investigated coordination compounds are significantly important in biochemical, analytical, antimicrobial[2]. They have been also used as antibacterial, antifungal, anticancer[3], antitubarcular, hypertensive and hypothermic reagents[4].

Attractive coordination chemistry of especially azo compounds derived from nitrobenzoic acid, thiosemicarbazide and phosphorus oxychloride is not well explored[5]. Azo Schiff base ligands are very important compounds and have attracted more attention in academic research and applied research[6].

1,3,4-thiadiazole derivatives possess interesting biological activity probably conferred to them by the strong aromaticity of this ring system which leads to great *in vivo* stability and generally, a lack of toxicity for higher vertebrates including humans. When diverse functional groups that interact with biological receptors, are attached to this ring, compounds possessing outstanding properties are obtained. Except for some antibacterial sulfonamides (albucid and globucid), possessing historical importance, the most interesting examples are constituted by 5-amino-l, 3, 4-thiadiazole-derivatives[7]. In addition, the chemistry and the applications of these new Schiff base thiadiazole derivatives could be extensively studied by coordinating to various metal ion moieties[8, 9].

The present investigation deals with the spectroscopic and electrochemistry of the transition metal complexes of 2N-salicylidine-5-(p-nitrophenyl)-1, 3, 4-thiadiazole (L) Schiff Base ligand[9] and 5, 5’-dimethyl-2, 2’-bipyridine (Me$_2$bipy) in the aqueous medium (1: 1: 1 molar ratio). Spectral (FT-IR, UV-Vis. and Mass spectroscopy) and electrochemical behavior of transition metal complexes viz; VO(II), Co(II), Ni(II) and Cu(II) were examined by using cyclic voltammetric (CV) at GCE working electrode versus Ag/AgCl, reference electrode, containing 0.2 M NaClO$_4$ as supporting electrolyte in aqueous medium.

Material and Methods

All reagents including solvents were procured commercially and used without any further purification. Microanalysis (C, H, N and S) was carried out on a Fison EA 1108 analyzer. The infrared (FTIR) spectra were recorded by using FTIR.8300 Shimadzu spectrophotometer by using KBr disc in the frequency range of 4000–200 cm^{-1}. The ultraviolet–visible (UV– Vis) spectra were recorded by using a Lambda-35 model. Mass spectra were recorded on a Micromass UK Platform II LC-MS spectrometer.

Preparation of ligands and complexes solutions: 50% ethanol solution of the metal ions [VOSO$_4$.3H$_2$O, CoCl$_2$.6H$_2$O, NiCl$_2$ .H$_2$O and CuCl$_2$.H$_2$O] was added to 50% ethanol solution of 2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole[10,11] (L) in 1:1 (metal: ligand) molar ratio. Then, the mixture of transition metal complexes of Schiff Base ligand is mixed with the 50% ethanol solution of 5,5’-dimethyl-2,2’-bipyridine (1:1:1 molar ratios) to get transparent and clear solution. The stock solutions (1 x 10^{-}

^{2}M) of 2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole (L) Me_2bipy and transition metal complexes were prepared in the aqueous medium (1: 1: 1 molar ratio). More dilute (1 x 10^{-3} M) solution were prepared by accurate dilution.

Cyclic voltammetry: The software driven BAS electrochemical system, model Epsilon (Bioanalytical Systems, Inc; U.S.A.) was employed for all the electrochemical studies. 1×10^{-2} M stock solutions of these complexes were prepared in the desired solvent. More dilute (1×10^{-3} M) solutions were prepared by accurate dilution. The working electrode was glassy carbon disc electrode (GCE), the counter electrode was a platinum wire and reference electrode Ag/AgCl in saturated KCl (E°= +199mV vs NHE). Purging and blanketing of nitrogen (99.999% pure) were done for analyte solution placed in the electrochemical cell of 15 ml capacity for 20 min. Great care was taken in the electrode pretreatment. Mechanical polishing of the working electrode (GCE) was done over a velvet microcloth with an alumina suspension. The electrode was rinsed with doubly distilled water after each polishing and ultrasonicated in ethanol and water for 5 min.

The bare GCE was subjected to electrochemical deposition. Controlled potential electrolysis (CPE) was carried out for calculating the number of electrons involved in the reduction process. Electrolysis was done in 1×10^{-3} M aqueous solution of a complex containing 0.2M $NaClO_4$ in a BASi Bulk electrolysis cell, consisting of reticulated carbon working electrode, coiled platinum auxiliary electrode dipped in a separate cell containing 0.2M $NaClO_4$ in aqueous solution only and Ag/AgCl as a reference electrode. Nitrogen gas was initially purged for 30 min with constant stirring of solution and then N_2 was blanketed over the constantly stirred cell solution during the electrolysis. All the electrochemical experiments were performed at a constant temperature 25±0.5°C.

Results and Discussion

The transition metal complexes of 2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole and 5, 5'-dimethyl-2, 2'-bipyridine were obtained in (1:1:1 molar ratio) 50% aqueous medium. The mixture of transition metal complexes has been characterized by micro-analysis, FT-IR, UV-Visible and mass spectroscopy. The micro-analysis for C, H, N and S as well as molecular weight of the mixed-ligand complexes obtained is in agreement with the predicted formula for solution mixture of these transition metal complexes viz: $[VO(L)(bipy)]SO_4$, 1; $[Co(L)(bipy)(H_2O)Cl]Cl$, 2; $[Ni(L)(bipy)](ClO_4)_2$, 3 and $[Cu(L)(bipy)(H_2O)](ClO_4)_2$, 4. The proposed structure of transition metal complexes 1 and 3 are given in figure 1(a) and (b).

The FT-IR spectral data of the transition metal complexes of (2N-salicylidene-5-(p-nitro phenyl)- 1,3,4-thiadiazole) Schiff Base lignad and 5,5;-dimethyl-2,2'-bipyridine were recorded at pH 5.5 and given in the table 2. The FT-IR of all these transition metal complexes and free ligands were recorded in the range 4000 – 500 cm^{-1} by Thermo- Scientific Nexus 470 spectrophotometer equipped with a smart endurance attenuated total reflectance accessory and a deuterated tryglycine sulfate detector with a universal Zn-Se KBr accessory operating at 25°C.

The FT-IR spectral data of ligands showed some characteristic stretching bands at 1635 cm^{-1} and 1115 cm^{-1} assigned to the ν (C = N) and ν (C – O), respectively[12-19] which could be found in the transition metal complexes 1-4 at 1627 cm^{-1}, 1605 cm^{-1}, 1608 cm^{-1} , 1607 cm^{-1} and 1118 cm^{-1} to 1123 cm^{-1} (Table 1) respectively. The band at 1623 cm^{-1} in these transition metal complexes 1-4 is assigned to pyridine ring stretching[12-19].

It should be noted that the coordination of Me_2bipy to transition metal ions is through the N atom in the chealation[20].The bands at 508 cm^{-1} to 504 cm^{-1} and 475 cm^{-1} to 485 cm^{-1}(Table 1) indicate that the presence of M-O and M-N in the lower wave number region signifies the complexation through N and O atoms from the lignads[20].

The electronic absorption spectral data of the ligands and their transition metal complexes 1-4 were examined in the aqueous solution (Table 2). The ligands showed three absorption bands at 209 nm, 254 nm and 346 nm respectively. The electronic band at 209 nm is assigned to the inter-ligand $\pi \rightarrow \pi^*$ transitions[21] while the others bands at 254 nm and 346 nm are assigned to the second and third inter-ligand $n \rightarrow \pi$ and $n \rightarrow \pi^*$ transitions[21] respectively.

Table 1
IR spectral data for (L) ligand and their mixed-ligand complexes 1-4

Compound	ν (C=N)	ν (C - O)	ν (M - O)	ν (M - N)	ν (C - H) Pyridine ring stretching
(L)	1635	1115	-	-	-
1	1627	1123	508	485	1023
2	1605	1120	504	478	1023
3	1608	1118	506	475	1023
4	1607	1120	504	477	1023

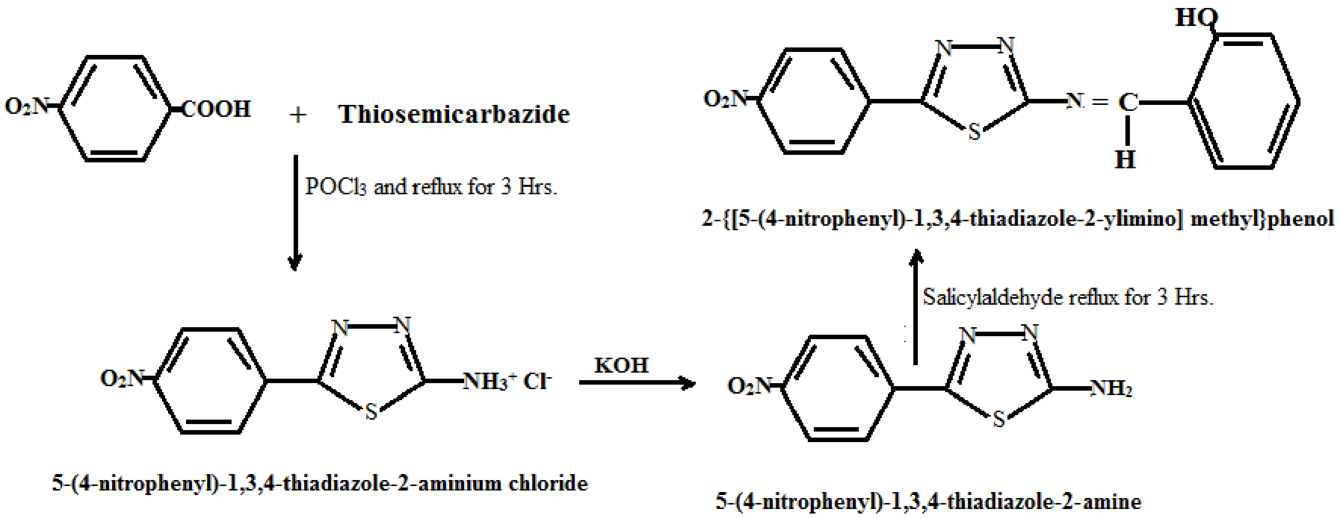


Figure 1(a): Preparation of Schiff Base (2-{[5-(4-nitrophenyl)-1, 3, 4-thiadiazole-2-ylimino] methyl} phenol Ligand

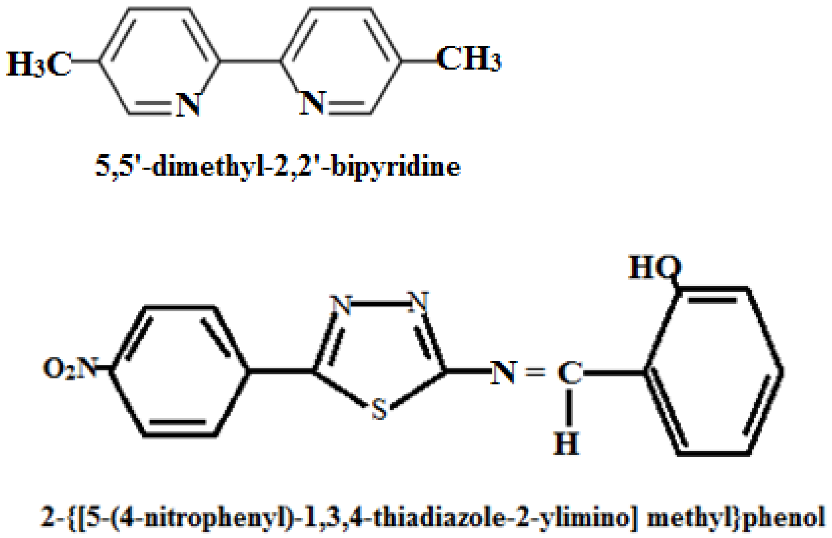


Figure 1(b): Ligands used for the synthesis of mixed-ligand complexes with transition metal complexes

Table 2
Electronic absorption spectral data for Schiff base ligand and their mixed-ligand complexes 1-4

Compound	Color	Absorption band(nm)	Assignment
1	Greenish	421	LMCT
2	Brown	214, 267, 456, 638	π- π^*, d – d, LMCT
3	Greenish blue	603, 456	d – d, LMCT
4	Pale green	638, 456	d – d, LMCT
(L)	Color less	209, 254, 346	π- π^*, n – π, n – π^*

The band at 421 nm in VO: L: Me$_2$bipy is assigned to d – d transition from the nitrogen atoms (2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole and aromatic diimine) to VO (II) metal center[21]. The bands appeared at 214 nm, 267 nm, 456 nm and 638 nm respectively for complex Co: L: Me$_2$bipy attributed to $^4A_2 \rightarrow {}^4T_2^{(F)}$, $^4A_2 \rightarrow {}^4T_1^{(F)}$, LMCT (Ligand to metal charge transfer) and $^4A_2 \rightarrow {}^4T_2^{(F)}$ and $^4A_2 \rightarrow {}^4T_1^{(P)}$ transitions[21] respectively. The bands at 603 nm, 638 nm and 456 nm in the complex 3 are assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) [21] and LMCT in the complexes Ni: L: Me$_2$bipy and Cu: L: Me$_2$bipy.

Electrochemical investigation of 2N-salicylidene-5-(p-nitro phenyl)- 1,3,4-thiadiazole and their mixed-ligand complexes 1-4 in aqueous medium: The cyclic voltammogram scan of Schiff Base ligand in the potential range 0.0 mV to 1400 mV produced only one irreversible reduction peak at Epc = -1330 mV to -1377 mV at 25 mVs^{-1} to 100 mVs^{-1} (Figure 3). It should be noted that it does not exhibit any anodic peak potential (Epa) corresponding to the cathodic peak potential which means that the system is totally irreversible.

The electrochemical data of transition metal complexes 1-4 and aromatic diimine were tabulated in the table 3 and figure 3 and 4. The VO^{2+} complex 1 exhibits quasi-reversible cathodic and anodic peaks (redox couple) $VO^{2+/+}$at Epc = -825 mV, Epa = -687 mV, $E^{0'}$= -756 mV, Δ Ep = 138 mV. The cathodic and anodic peak current ratio is greater than 1.0 in the potential range +1000 mV to -1500 mV at 100 mVs^{-1} scan rate versus Ag/AgCl reference electrode in the aqueous (1:1: 1 molar ratio) medium. The cathodic peak potential of complex 1 becomes more negative increases with increasing scan rate. The current ratio Ipa/Ipc is also greater than one (>1.0) which means weak adsorption of electrogenerated[22,23] complex species on the surface of the glassy carbon working electrode (GCE).

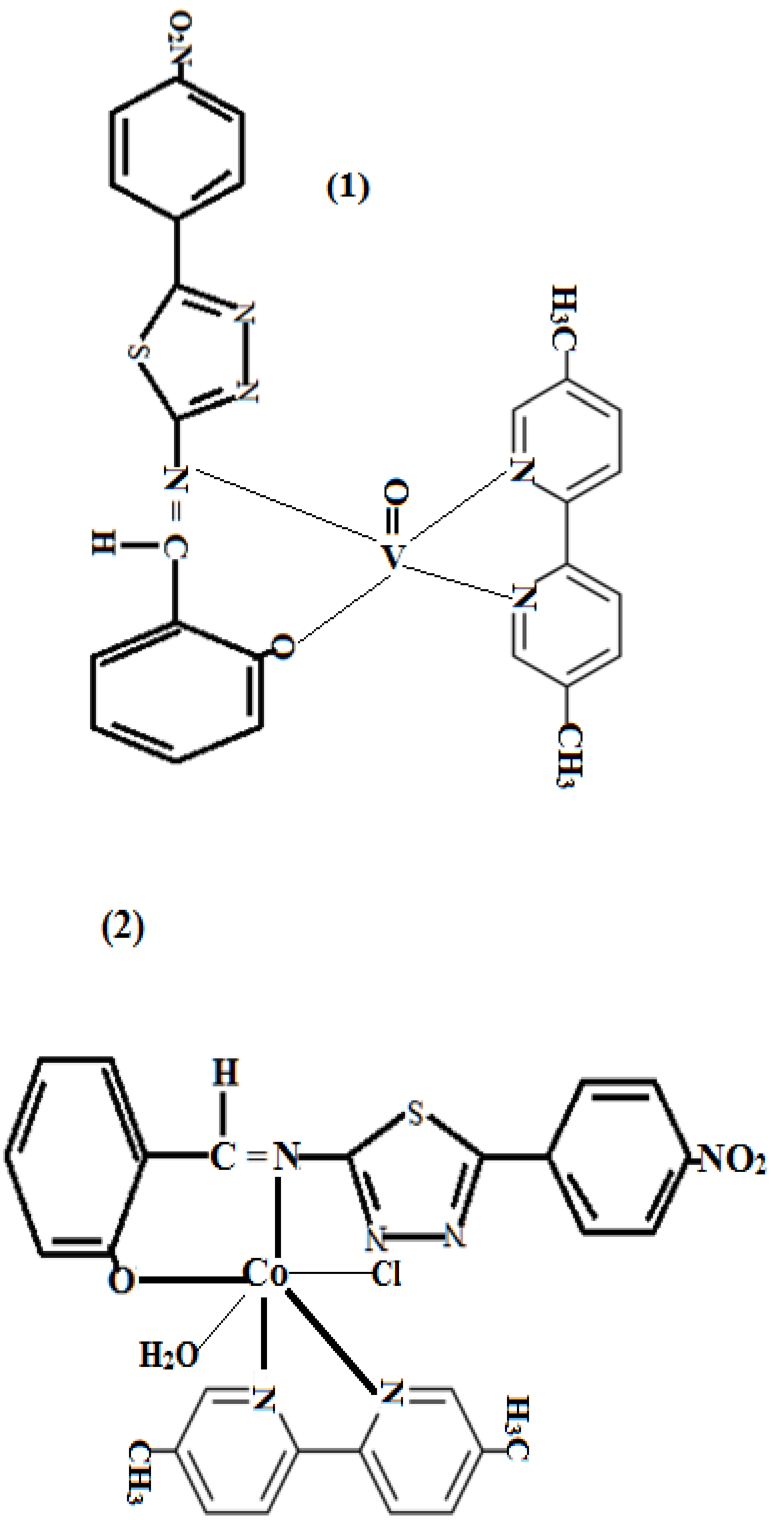


Figure 2: Proposed structure of mixed ligand complexes 1 and 3

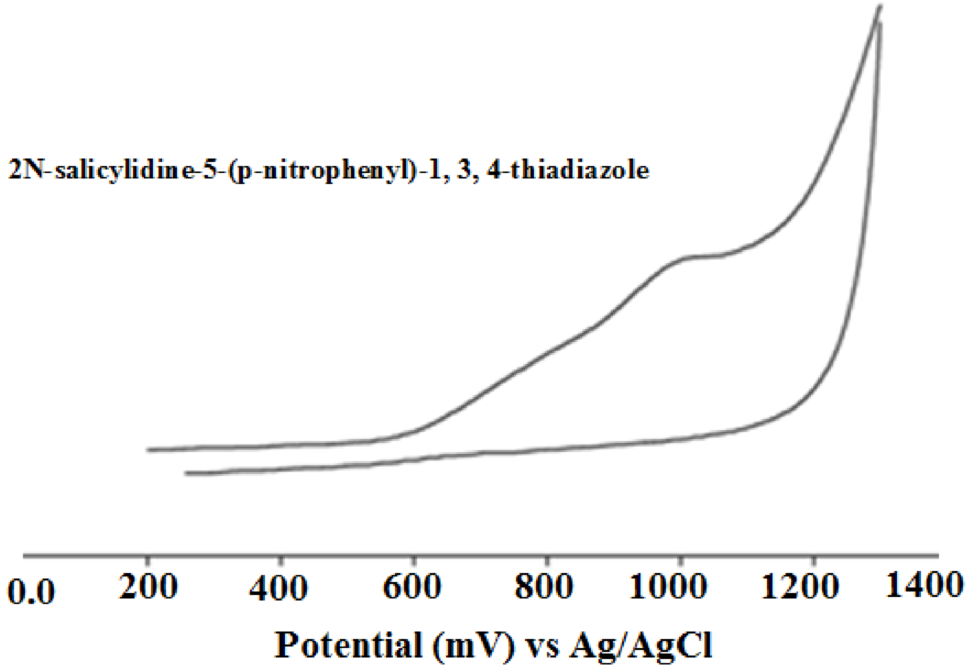


Figure 3: Cyclic voltammogram of 2N-salicylidene-5-(p-nitro phenyl)-1,3,4 thiadiazole ligand in aqueous medium containing 0.2 M $NaClO_4$ as supporting electrolyte at GCE

Table 3
Cyclic voltammetric data for mixed-ligand complexes 1-4

Complex 1	**Epc(mV)**	**Epa(mV)**	**E0'(mV)**	**ΔEp(mV)**	**Ipc/Ipa**
Scan rate					
25	-802	-696	-694.0	106	1.8
50	-816	-689	-752.5	127	2.2
100	-825	-687	-756.0	138	2.7
200	-830	-685	-757.5	145	3.2
300	-830	-675	-752.5	155	3.8

Complex 2	**Epa1 (mV)**	**Epc1 (mV)**	**Epa2 (mV)**	**Epc2 (mV)**	**$E^{0'}1$ (mV)**	**$E^{0'}2$ (mV)**	**ΔEp1 (mV)**	**ΔEp2 (mV)**	**Ipa1/Ipc1**	**Ipa2/Ipc2**
Scan rate										
25	530	460	-80	-185	495.0	-132.5	70	105	1.0	0.5
50	530	460	-88	-188	495.0	-138.5	70	100	1.0	0.5
100	530	460	-88	-188	495.0	-138.5	70	100	1.0	0.6
200	530	460	-96	-190	495.0	-143.0	70	94	1.0	0.8
300	530	460	-100	-192	495.0	-146.0	70	92	1.0	0.8

Complex 3	**Epa(mV)**	**Epc(mV)**	**Epc'(mV)**	**ΔEp(mV)**	**E0'(mV)**	**Ipa/Ipc**
Scan rate						
25	1090	985	-1190	105	1037.5	0.7
50	1095	987	-1192	108	1041.0	0.7
100	1100	990	-1198	110	1045.0	0.8
200	1110	995	-1198	125	2105.0	0.8

Complex 4	**Epc(mV)**	**Epa(mV)**	**ΔEp(mV)**	**$E^{0'}$(mV)**	**Ipa/Ipc**
Scan rate					
25	-208	-110	98	-159.0	1.0
50	-215	-112	103	-163.5	1.2
100	-222	-114	108	-168.0	1.3
200	-224	-114	110	-169.0	1.4

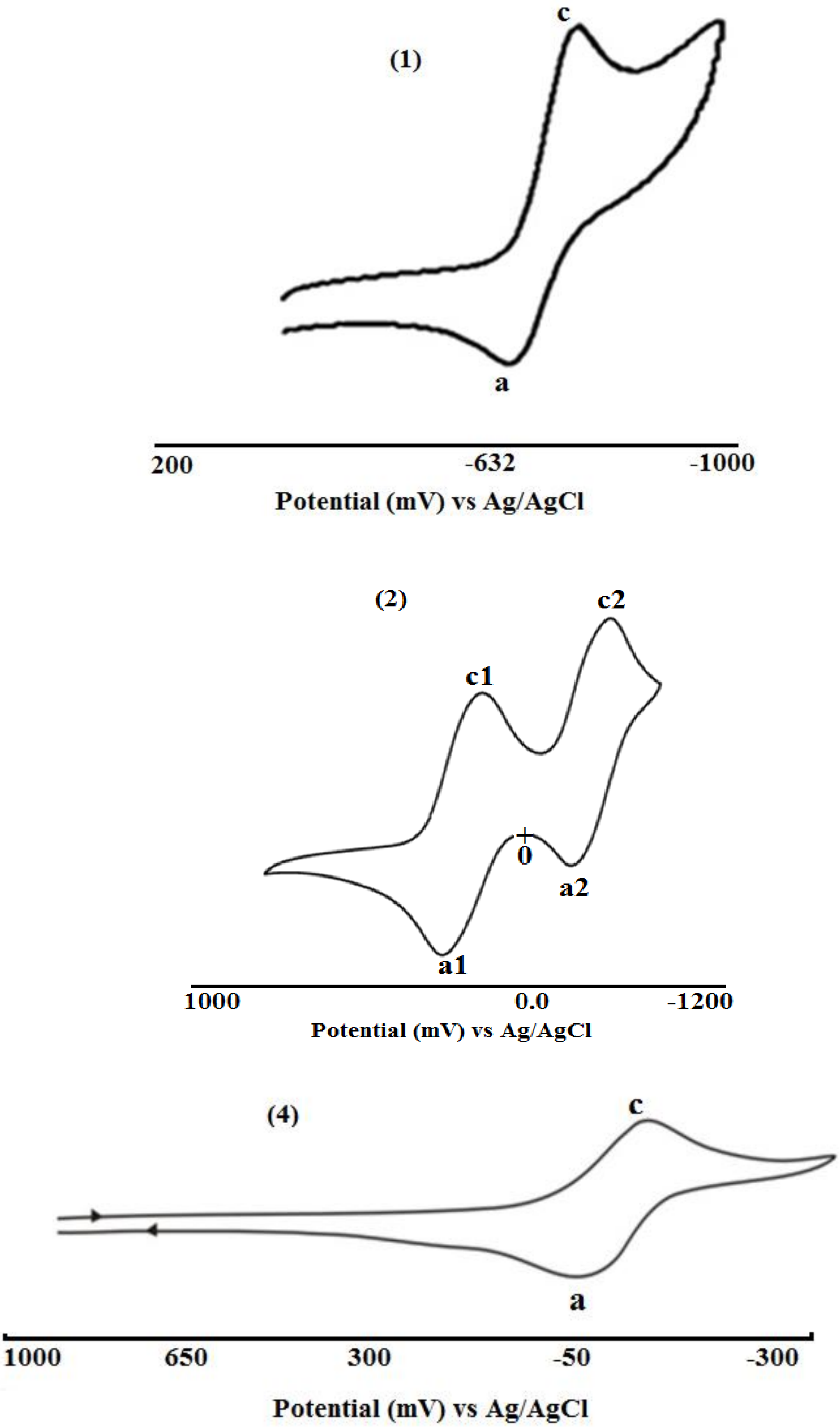


Figure 4: Cyclic voltammograms of mixed-ligand transition metal complexes 1, 2 and 4 in the aqueous medium containing 0.2 M $NaClO_4$ supporting electrolyte at GCE

The cobalt complex 2 shows two redox couples in the potential range 0.0 mV to +1000 mV and then +1000 mV to -1200 mV in aqueous medium containing 0.2M $NaClO_4$ as supporting electrolyte at GCE working electrode versus Ag/AgCl at Epa1= 530 mV, Epc1= 460 mV, $E^{0'}1$= 495.0 mV and ΔEp1= 70 mV assigned to the quasi-reversible one electron redox couple $Co^{3+/2+}$ (Figure 4). Similarly, second cathodic and anodic peak potentials are exhibited at Epc2= -188 mV, Epa2= -88 mV, $E^{0'}2$= -138.0 mV and ΔEp2= 100 mV at 100 mVs^{-1} scan rate for second redox couple assigned to $Co^{+/2+}$ [22]. Both redox couples are assigned to the single electron transfer $Co^{3+/2+}$ and $Co^{+/2+}$ [22] respectively. Overall, it is $2e^-$ (two) electrons transfer redox process[22] (Figure 4).

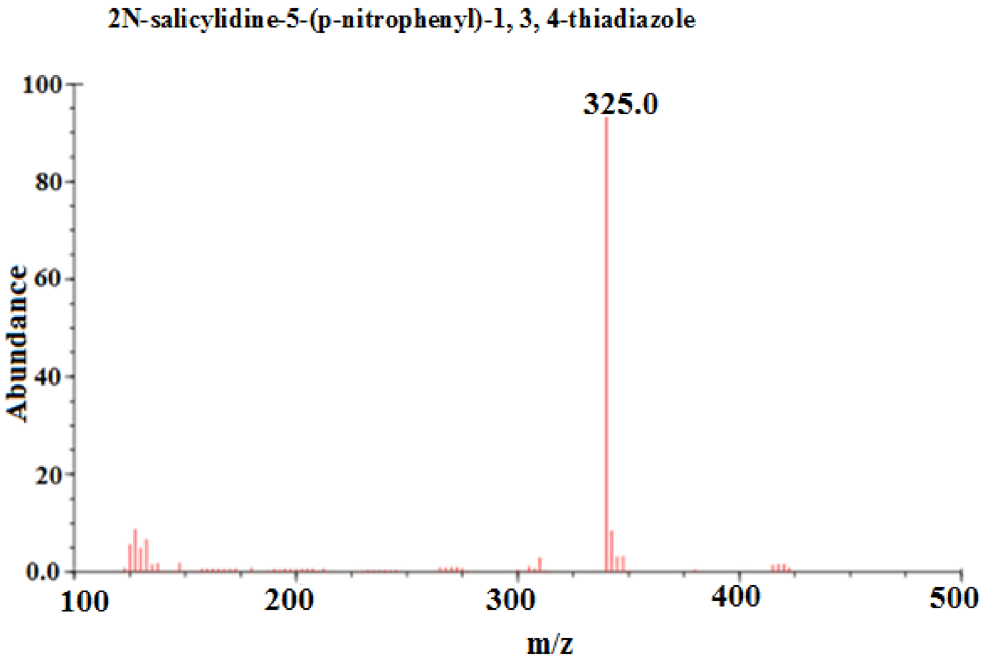
It is interesting to note that the anodic to cathodic current ration Ipa1/Ipc1 is greater than one (>1.0) for the first redox couple $Co^{3+/2+}$ indicating weak adsorption of the electrogenerated Co^{2+} complex species with 2N-salicylidene-5-(p-nitro phenyl)- 1,3,4-thiadiazole and Me_2bipy aromatic diimine on the surface of the GCE electrode, while the current ratio Ipa2/Ipc2 for second redox couple $Co^{+/2+}$ is less than one (<1.0) , indicating that the electron transfer is followed by a chemical reaction (EC mechanism)[24] .The plots of Ipc1 or Ipc2 versus square root of the scan rate ($\nu^{1/2}$) give a straight line passing through origin, showing that both these reduction process are diffusion controlled [24].

The nickel complex 3 has also been studied by cyclic voltammetry in the presence of 0.2 M $NaClO_4$ as supporting electrolyte in aqueous solution at 100 mVs^{-1} scan rate. The complex 3 shows quasi-reversible redox couple in the potential region 0 mV to +1500 mV with Epa= 1100 mV, Epc= 990 mV, ΔEp= 110 mV and $E^{0'}$= 1045.0 mV (Table 3) respectively. The oxidation has been assigned as $Ni^{2+/3+}$ [23-30]. In the cathodic potential region (0.0 mV to -1500 mV), complex 3 shows one irreversible cathodic peak at -1198 mV with respect to the GCE working electrode. The cathodic peak potential is assigned to the conversion of $Ni^{2+/0}$ [23-30].

The complex 4 shows a quasi-reversible redox couple in the potential range +1000 mV to -300 mV with Epc= -222 mV, Epa= -114 mV, ΔEp= 108 mV and $E^{0'}$= 168.0 mV at 100 mVs^{-1} scan rate (Table 3 and figure 4). The redox couple has been assigned to the $Cu^{2+/+}$ one electron transfer electrochemical EC mechanism [23-30].

Mass spectroscopy: The mass spectral data of 2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole ligand and their mixed-ligand complexes with Me_2bipy were recorded and investigated. The mass spectral data for these mixed-ligand complexes 1-4 adequately supported the proposed geometry. The mass spectrum of the 2N-salicylidene-5-(p-nitro phenyl)- 1,3,4-thiadiazole ligand and their complexes is showing that the molecular ion peaks are in good agreement with their suggested empirical formula as indicated to C, H, N (micro-analysis). The mass spectrum fragmentation pattern of 2N-salicylidene-5-(p-nitro phenyl) - 1, 3, 4-thiadiazole ligand shows that the peak of m/z 325 corresponds to its molecular weight related to formula $[C_{15}H_{10}O_3N_4S]$.

The mass spectrum of these complexes showed molecular ion peaks at m/z= 698, 628, 727 and 634, (Figure 5) respectively which correspond to the molecular weight of compounds supporting the structure of these complexes[30-32]. The fragment ion peak at 155 corresponds to the 5, 5'-Me_2bipy in these complexes[31-35].



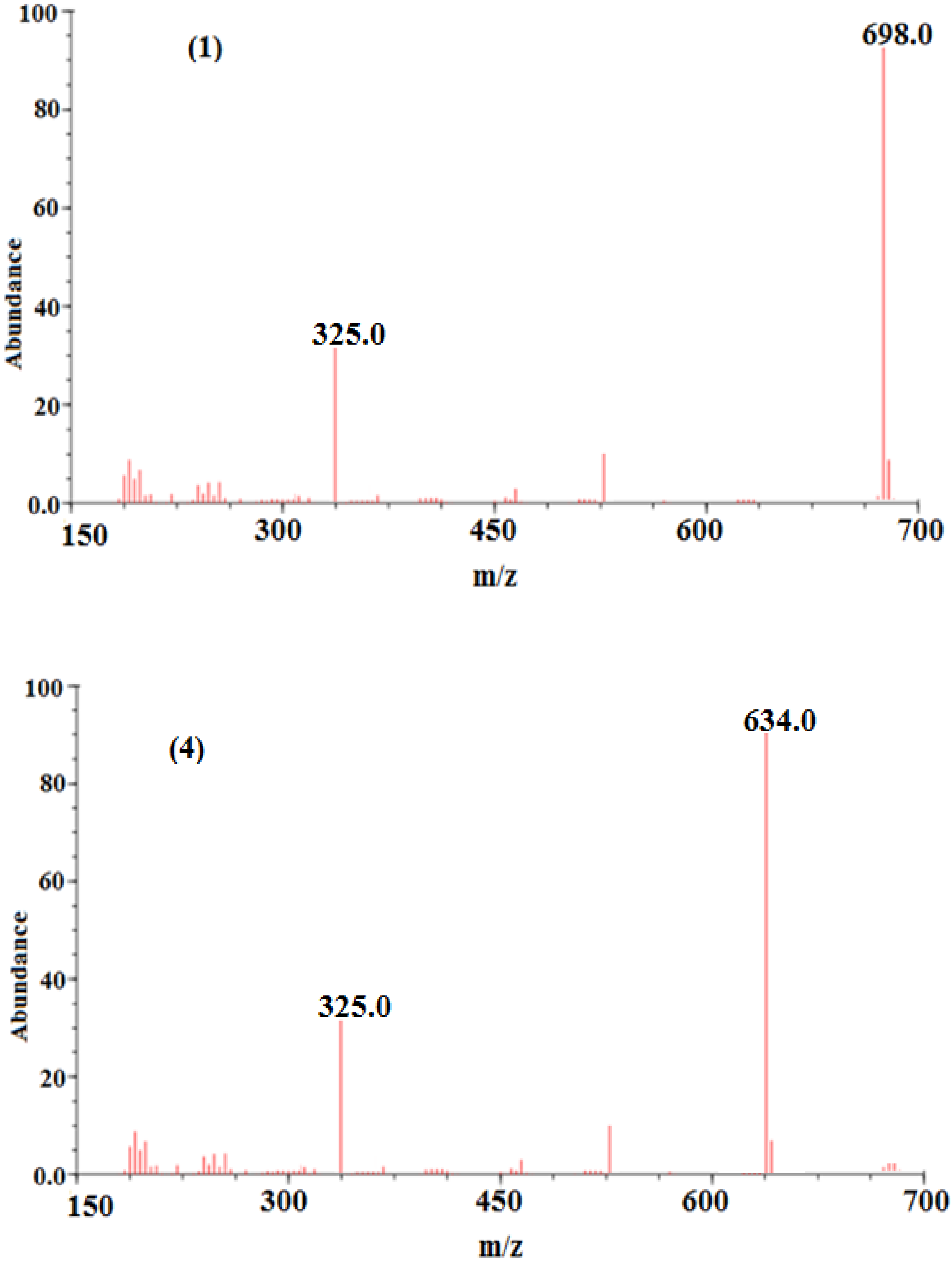


Figure 5: Mass spectra of ligand (L) and their mixed-ligand complexes 1 and 4

Conclusion

The transition metal complexes viz; VO(II), Co(II), Ni(II) and Cu(II) complexes (1-4) of (2N-salicylidene-5-(p-nitro phenyl)- 1,3,4-thiadiazole) Schiff Base ligand and aromatic diimine (5,5'-dimethyl-2,2'-bipyridine) were successfully prepared in the aqueous medium(1: 1: 1 molar ratio). These complexes were characterized by microanalysis, FTIR, UV-Vis and mass spectroscopy respectively. The results are indicating that the 2N-salicylidene-5-(p-nitro phenyl)- 1,3,4-thiadiazole Schiff Base ligand and 5, 5'-Me_2bipy coordinated to metal ions via, N, O atoms and two N atoms respectively. The complexes 1 and 4 are square pyramidal while the remaining complexes 2 and 3 contain octahedral and square planar geometry respectively.

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Electrochemical behavior of these complexes was investigated in the aqueous medium containing 0.2 M $NaClO_4$ as supporting electrolyte at GCE versus Ag/AgCl reference electrode by using cyclic voltammetry (CV). The reduction potential becomes more negative (complexes 1 and 4) with increasing scan rate while 2 and 3 become positive, clearly indicating easier reduction. The order is given as: 1> 4> 2>3.

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