



Synthesis and Properties of Transition Metal Complexes Containing Thiazole Derived Schiff base Ligands

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ABSTRACT

Although ligands containing four donor atom are tetradentate ligand of Thiazole moiety which coordinated with transition metal ions. The complex of m-NTA and m-MTA are studies by different spectral technique. Here we are synthesizing the thiazole derivatives Schiff base as a ligands, L1=N,N'E,N,N'E)-N,N'-(1,3-phenylene bis (methanylylidene) bis (5-nitrobenzo [d] thiazole L2-amine (NTA) and L2 = N,N'E,N,N'E)-N,N'-(1,3-phenylene bis (methanylylidene) bis (5-methyl thiazole L2-amine (MTA), and coordinated with transition metals (Co, Ni, Cu, Zn, and Cd) using lone-pair coordination method. These synthesized complexes were identified by FT-IR spectra, UV-Visible spectra, mass spectra and cyclic voltammetry and having characteristic absorption and potential high-performance CV which show a different type of stable transition metal complex. The electrochemical study was also carried out for these complexes which show the clear redox behaviour of complexes. The significant change in CV properties is exhibited by CV graphs where we can see a prominent reduction peaks M(II) to M is showing at -0.4 V. We found that in the case of L2 there is less prominent reduction peaks observed in comparison to L1.

Keywords: Schiff Base, Electrochemical Study, Coordination Complexes, Transition Metals Complexes.

INTRODUCTION

Cyclic voltammetry study of transition metal complexes is showing a significant role in pesticide sensing and kinetic study of complexes.¹ These Schiff base-metal complexes having different types of metal ions behave as an electrolyte and changes their behaviour with electrical conductance and characteristic nature with different solvents.^{2,3} They show specific deviation in cyclic voltammograms,

which is useful in the material sense.⁴ Organic compounds metal ion complexes are having characteristic nature towards conjugating material and are used for the examination of water, soil, food, and drug sampling.⁵ Cyclic voltammetry is one of the most affordable techniques for the study of physiological and biological samples.⁶ Synthesis of the metal complex for the quality of research required proper complexation of the different types of metals. Great considerations have been given to the



synthesized polynuclear or mononuclear transition metal complexes because of their different types of topologies and potential values in fluorescence,⁷⁻⁹ catalytic reactions,¹⁰ adsorptions,¹¹ magnetic material,¹² biomedical mimicking,¹³ and sensors.¹⁴ The industrial effluent is treated with the help of some physiochemical techniques used like precipitation method, filtration process, floatation technique, adsorption method, oxidation processes, bleaching, zonation, Fenton oxidation method, ion exchange processes, reverse osmosis, and some biological methods in aerobic and anaerobic condition consequently.¹⁵⁻¹⁷ Since recent years, Schiff base ligands drew great attention due to simplicity in their synthesis and multicity in topological structure.¹⁸ These synthesized Schiff base ligands form coordination complexes with transition metal ions in their various oxidation states.¹⁹ These types of ligands play a significant role in controlling the modification of organic reactions which are catalysed by their transition metal complexes.²⁰ The metal complexes in Schiff base play an important role in catalysis.²¹ magnetism, medicinal and material sciences.²² Due to their great coordination capacity, Schiff base ligands have been widely used to synthesize polynuclear metal complexes.²³ It is a long-range phenomenon termed Photo-induced electron transfer (PET)²⁴. Metallo-receptors have attracted huge interest from researchers due to their selective interaction with cations and anions²⁵. The need for the designing of new macrocyclic ligands becomes inevitable. The selective chelation for certain specific metal ions by the macrocyclic ligands raises their importance manifold²⁶. Co(III) Schiff base complexes that show activation on photo stimuli have evolved as reliable candidate's strategies of pro-drugs²⁷. The advancement of computational photochemistry has significantly improved and elaborated the applications by qualitative estimation of the emission processes to quantitative interpretation of emission spectroscopy as well as photo reactivity^{28,29}. Coordination complexes of Schiff base with Zn(II) are promising candidates for type II vapochromic materials. These complexes are Lewis acid species. Sensors are chemical entities acting as molecular devices in transforming chemical input into analytically relevant signals³⁰. Metal ions are generally regarded as harmful to the ecological system when released as industrial pollutants. They alter the nature of soil and water and become extremely harmful³¹. Cadmium metal

widely used in various industries become a harmful pollutant when treatment of industrial waste is not performed properly. The sensing of such metallic industrial pollutants in nature is performed with the help of sensors³². Chlorambucil reported by Neamati is found to be effective in targeting mitochondria selectively due to which it has prominent anticancer activity³³. This area has drawn huge attention and research is at its highest rate for developing such compounds. The design and development of such a molecular complex that possesses both intense luminescence and high-efficiency co-sensitizing DSSCs (Dye-Sensitized Solar Cells) are of primary importance. The combination of both these is the thrust for the development of new sensors. All the design and development protocols aimed to achieve excellence in both luminescence and DSSCs³⁴. In this work, we design and synthesized transition metal complexes with Schiff base³⁵. These Schiff base of 5-nitrobenzo [d] thiazol-2-amine (NTA) and 1,3-phenylene bis (methanylylidene)) bis (5-methyl thiazol-2-amine (MTA) were prepared in same manner following our previous work (36). Here we continue their structural and electrochemical study with coordination complexes formation with Co(II), Ni (II), Cu (II), Zn (II) and Cd (II).

In the previous work, we have been synthesized the ligands of 1,3-phenylene bis (methanylylidene) bis (5-nitrobenzo [d] thiazol-2-amine (**NTA**) and 1,3-phenylene bis (methanylylidene)) bis(5-methyl thiazol-2-amine (**MTA**) via Schiff base synthesis and coordinated with the metals of Neodymium(Nd), Cerium(Ce) and Promethium(Pr) and studied for fluorescence as well as tested for biological activity such as anti-bacterial and inflammatory³⁶. But here we have replaced the metal centres with other metals such as Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The synthesized complexes were 1,3-phenylene bis(methanylylidene) bis(5 nitrobenzo[d]thiazol-2-amine), Metal (II) and 1,3-phenylenebis(methanylylidene)) bis (5-methylthiazol-2-amine), Metal (II) which were labelled as M(II)-NTA and M(II)-MTA respectively.

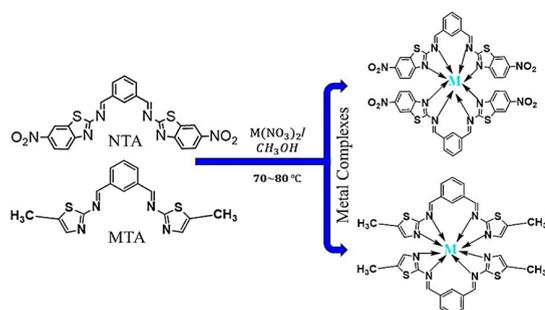
EXPERIMENTAL MATERIAL AND METHOD

All required chemicals and metal salts were purchased through commercial sources. Solvents were purchased analytical grade from S.D. chemicals

and all the used metal salts for complexation were purchased from LOBA Chemie India. Melting points all reported are uncorrected, recorded using an electro-thermal melting point apparatus. Thin-layer chromatography (TLC) was performed by using E-Merck pre-coated 60 G254 plates observing in UV light. FT-IR Spectra recorded utilizing shimadzu FT-IR Spectrophotometer. Electrochemical studies were recorded in software NOVA version 1.10.1.9 and mass study characterized by XEVO G2S QPOF instrument.

Synthesis procedure

In the typical synthesis method, we have taken the ligand and metal salts (metal nitrates hexahydrate) in 2:1 ratio respectively in the methanol solvent and stirred for two hours at the temperature of 70-80°C. Here we take 2 mmol (2 equivalent) ligand in 10 mL methanol in a beaker and make it completely soluble, then in a separate beaker take 1 mmol (1 equivalent) nitrates of metal salt in similarly methanol. Ligand solution in round bottom flask and let it stirrer for 10 min then add metal salt solution via dropper drop wise. Observed this reaction by the TLC method and recorded the progress of the reaction. In many complexes, the formation process found instant colour and the precipitate formation whereas in other cases it required some time. Run these reactions for 2–3 hours. The synthesised product in the washing with ethanol solution and then again removed in the excess part of the solvent at room temperature. Further obtained pure form of the compounds and take the weight and evaluate yield and measure melting point and characterization.



Scheme 1. Schematic diagram of synthesis process of the complexes M-NTA and M-MTA Metal Complexes formation

RESULT AND DISCUSSION

Co(II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal

salt (cobalt nitrate) 0.182 g in methanol. Solid honey gold powder; yield- 70% (0.355 g), MP-287°C; FT-IR (cm⁻¹): 3860.86, 2361.42, 1649.37, 1291.58, 747.50; **(SI-1)**, UV-Vis. Absorption at 367 nm (λ_{max}); ESI-MS(e/z): 547.43 (calculated) ; Elemental estimation: C 48.27; H 2.21; Co 10.77; N 15.35; O 11.69; S 11.71 (approx.), C 48.22; H 2.15; Co 10.82; N 15.45; O 11.63; S 11.75 (observed).

Ni(II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (nickel nitrate) 0.182 g in methanol; solid wine red powder; yield- 78% (0.396 g), MP-256°C; FT-IR(cm⁻¹): 3843.92, 3743.73, 3648.55, 2361.84, 1692.72, 1330.68; **(SI-2)**, UV-Vis absorption at 363 nm(λ_{max}); ESI-MS (e/z): 545.19 (calculated), 545.97 (observed) SI-11; Elemental estimation: C 48.29; H 2.21; N 15.36; Ni 10.73; O 11.70; S 11.72 (approx.), C 48.31; H 2.24; N 15.30; Ni 10.68; O 11.71; S 11.65 (observed).

Cu(II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (copper nitrate) 0.187 g in methanol; solid golden brown powder; yield- 63% (0.323 g), MP-254°C; FT-IR (cm⁻¹): 3843.70, 3678.18, 2361.88, 1692.91, 1293.63, 748.54; **(SI-3)**, UV-Vis absorption at 365nm (λ_{max}); ESI-MS (e/z): 550.97 (calculated), 550.92(observed) SI-12; Elemental estimation: C 47.86; H 2.19; Cu 11.51; N 15.22; O 11.59; S 11.62 (approx.), C 47.81; H 2.29; Cu 11.47; N 15.14; O 11.62; S 11.53 (observed).

Zn(II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1mmol metal salt (zinc nitrate) 0.189 g in methanol; solid lemon yellow powder; yield- 75% (0.387 g), MP-271°C; FT-IR (cm⁻¹): 3860.85, 3744.05, 3678.18, 2361.56, 1741.83, 1693.02, 1291.95, 747.36; **(SI-4)**, UV-Vis absorbance at 372nm (λ_{max}); ESI-MS (e/z): 553.88 (calculated); Elemental estimation: C 47.71; H 2.18; N 15.17; O 11.55; S 11.58; Zn 11.80 (approx.), C 47.74; H 2.23; N 15.20; O 11.50; S 11.53; Zn 11.87 (observed).

Cd(II)-L1: It synthesized by using 2 mmol ligand (NTA) 0.448 g in methanol and 1 mmol metal salt (cadmium nitrate) 0.236 g in methanol; solid orange powder; yield- 71% (0.470 g), MP-289°C; FT-IR (cm⁻¹): 3843.90, 3743.79, 3648.38, 2361.82, 1741.81, 1692.65, 1292.07, 1120.19,

745.78; **(SI-5)**, UV-Vis absorbance at 382 nm (λ_{max}); ESI-MS (*e/z*): 601.94 (calculated); Elemental estimation: C 43.97; H 2.01; Cd 18.71; N 13.99; O 10.65; S 10.67 (approx.); C 44.03; H 2.11; Cd 18.63; N 14.09; O 10.55; S 10.71 (observed).

Co (II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol (cobalt nitrate) 0.182 g in methanol; solid yellow powder; yield-64% (0.403 g), MP-234°C; FT-IR (cm^{-1}): 3860.90, 3743.64, 3678.16, 3648.52, 3619.40, 2361.73, 1741.68, 1693.20, 1646.38, 1515.72, 1464.35, 1425.79; **(SI-6)**, UV-Vis absorption at 371 nm (λ_{max}); ESI-MS (*e/z*): 385.37(calculated); Elemental estimation: C 49.84; H 3.69; Co 15.25; N 14.58; S 16.60 (approx.); C 49.87; H 3.66; Co 15.29; N 14.54; S 16.64 (observed).

Ni(II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (nickel nitrate) 0.182 g in methanol; solid duty green powder; yield- 77% (0.485 g), MP-252°C; FT-IR (cm^{-1}): 3843.77, 3743.74, 3678.15, 3648.65, 3619.41, 2361.63, 1741.67, 1693.12, 1646.38, 1516.03, 1463.92, 1396.44, 827.82; (SI-7), UV-Vis absorbance at 363nm (λ_{max}); ESI-MS (*e/z*): 385.13(calculated); Elemental estimation: C 49.90; H 3.66; N 14.55; Ni 15.24; S 16.65 (approx.); C 49.95; H 3.61; N 14.50; Ni 15.19; S 16.67 (observed).

Cu(II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (copper nitrate) 0.187 g in methanol; solid dandelion powder; yield- 73% (0.492 g), MP-241°C; FT-IR (cm^{-1}): 3843.89, 3743.75, 3619.30, 2361.91, 1693.21, 1646.28, 1516.35, 1461.99, 1329.98, 1297.32, 1127.26, 822.56, 750.38; (SI-8), UV-Vis absorbance at 273-328nm (λ_{max}); ESI-MS (*e/z*): 389 (calculated); Elemental estimation: C 49.28; H 3.62; Cu 16.29; N 14.37; S 16.44 (approx.); C 49.23; H 3.59; Cu 16.32; N 14.34; S 16.47 (observed).

Zn(II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (zinc nitrate) 0.189 g in methanol; solid yellow powder; yield- 75% (0.507 g), MP-238°C; FT-IR (cm^{-1}): 3844.06, 3743.66, 3678.39, 3648.44, 3619.38, 2361.85, 1741.68, 1693.33, 1646.35, 1515.73, 1425.97 cm^{-1} ; **(SI-9)**, UV-Vis absorbance at 368nm (λ_{max}); ESI-MS (*e/z*): 391.00 (observed) **SI-13**; Elemental estimation: C 49.05; H 3.60; N

14.30; S 16.37; Zn 16.69 (approx.); C 49.12; H 3.64; N 14.10; S 16.34; Zn, 16.73 (observed).

Cd(II)-L2: It synthesized by using 2 mmol ligand (MTA) 0.326 g in methanol and 1 mmol metal salt (cadmium nitrate) 0.236 g in methanol; solid tiger yellow powder; Yield 67% (0.485 g), MP-247°C; FT-IR (cm^{-1}): 3860.8 3743.68, 3678.16, 3648.49, 3619.44, 2361.97, 1741.78, 1693.11, 1646.58, 1515.69, 1425.85, 1330.44; (SI-10), UV-Vis absorbance at 360nm (λ_{max}); ESI-MS (*e/z*): 440.91 (observed) **SI-14**; Elemental estimation: C 43.79; H 3.22; Cd 25.61; N 12.77; S 14.61 (approx.); C 43.76; H 3.20; Cd 25.66; N 12.79; S 14.59 (observed).

Table1: Physical properties of complexes

Sr. No	Complexes	Yield (%)	m.p.(°C)	Max. wavelength (nm)
1	Co(II)-L1	70% (0.355g)	287	352 nm
2	Ni(II)-L1	78% (0.396g)	246	364 nm
3	Cu(II)-L1	63% (0.323g)	254	362 nm
4	Zn(II)-L1	75% (0.387g)	271	368 nm
5	Cd(II)-L1	71% (0.470g)	289	340 nm
6	Co(II)-L2	64% (0.403g)	234	369 nm
7	Ni(II)-L2	77% (0.485g)	252	369 nm
8	Cu(II)-L2	73% (0.492g)	241	401 nm
9	Zn(II)-L2	75% (0.507g)	238	362 nm
10	Cd(II)-L2	67% (0.485g)	247	367 nm

FT-IR Spectroscopy

The complexation of ligands with the different metal ions was supported with the help of IR spectra. A shift in -C=N bands was observed after a thorough examination of IR spectra of ligands and different metal complexes.³⁷ The FT-IR transmittance spectrum of the two ligands shows the -C=N- stretching frequency bands at $\sim 1686.11 \text{ cm}^{-1}$ and $\sim 1687.56 \text{ cm}^{-1}$ (respectively for ligand L1 and L2 where L1= benzothiazole and L2= thiazole) further these bands shifted to lower frequencies in the FT-IR spectra of all transition complexes of these ligands ($1515\text{--}1530 \text{ cm}^{-1}$)^{38,39}. This shift is attributed to the presence of -C=N- imine bond nitrogen in coordination via lone pair donation to the vacant orbital in different metal ions. Consequently, the IR spectra suggest that the different metal ions in the different complexes are bonded with four nitrogen lone pair (-C=N- imine bond) atoms of the Schiff base. These ligand acts as a tetradentate ligands in coordination complexes Figure 1 that means (SI-1 to SI-10).

UV-Vis spectroscopy

The optical properties were characterized by UV-Vis spectroscopic analysis and their several

function characteristic properties. The UV-Vis characterization of the Schiff base (ligand L-1 & L-2) and five different types of derivative complex formation and collect with UV spectrum. Fig. 2(a) and (b) UV spectrum of the ligand is found at low absorption spectrum observe. Comprised with ligand and complex molecules the complex molecule is

a high absorption value obtained respectively.⁴⁰ The UV-Vis spectrum found that two different types of absorption peak due to the presence of different fictional moiety like the first one arises C=C (247nm) due to π - π^* transition and the second one is the presence of C=N (354nm) attributed to $n \rightarrow \pi^*$ transition band.⁴¹

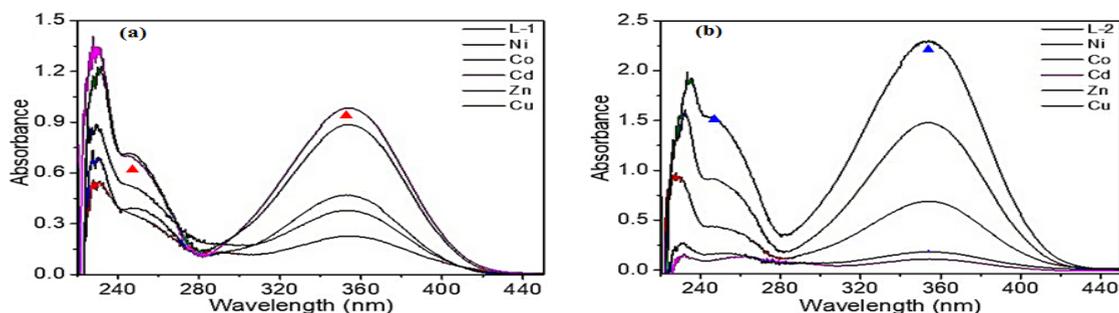


Fig. 2. Characterization of the UV-Vis spectrum with Schiff base (ligand L-1 & L-2) and different type complexes (a) and (b)

Fluorescence studies

The optical characteristics properties were characterized by fluorescence spectroscopy analysis. The as-synthesis ligand and various types of derivatized transition metal complex show the different characteristic properties due to the few transition because of the ligand to metal transition.⁴²⁻⁴⁴ the solution was prepared in an aqueous solution of the ethanol. The ligand and complex with

dispersible in the ethanol solution and further used as fluorescence at the normal room temperature. The solution was taken as a 3 mL fixed volume of ligand and complex mixture in an aqueous phase. The collection of the fluorescence spectrum of the ligand and complexes. Shows the Fig. 3 (a) and (b) was the back excitation spectra showing. Then the figure (c) and (d) correspond to fluorescence emission spectrum data was collected by (a) and (b).

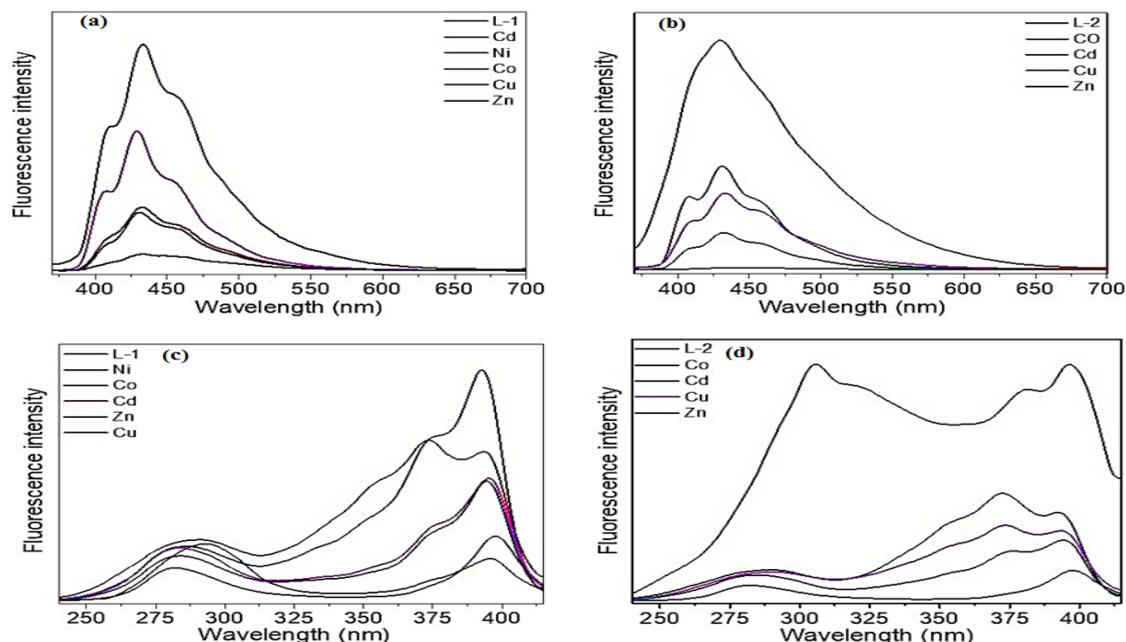


Fig. 3. Characterization of the fluorescence emission spectrum (a) and (b), the back excitation spectrum, fluorescence emission and back excitation spectra is a comparative data analysis ligand and complex (c) and (d)

Mass spectroscopy

The ESI-MS mass spectra of transition metal complexes of previously synthesized ligands were obtained from the molecular peak and other isotopic peaks. Were Cu (II)-L1 showing molecular peak [M⁺] m/z peak at 550.92, [M+1] m/z peak at 551.97, and [M+2] m/z peak at 552.12. Ni(II)-L1 showing molecular

peak m+ m/z peak at 546.96, [M+1] m/z peak at 547.23, and [M-1] m/z peak at 546.87. Zn (II)-L2 showing molecular peak [M⁺] m/z peak at 392.00, [M+1] m/z peak at 393.00. Cd(II)-L2 showing molecular peak [M⁺] m/z peak at 440.91, [M+1] m/z peak at 441.08. These complexes are accurately characterized by mass spectral data shows SI-11 to SI-14.

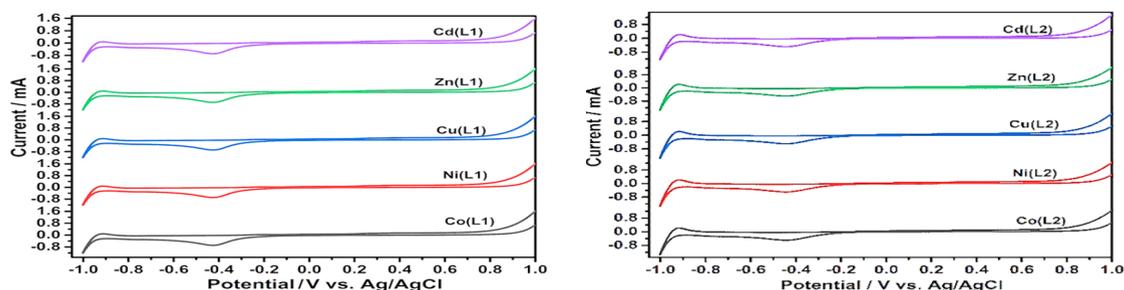


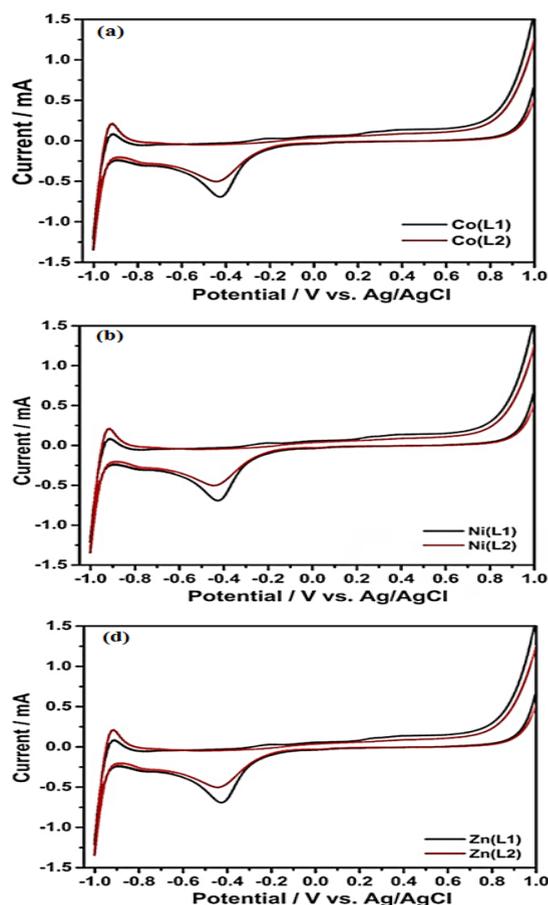
Fig. 4(a) and (b) Cyclic voltammograms of different complexes with MTA ligand recorded at 50 mV s⁻¹ in 0.5 Molar KOH aqueous electrolyte solution. And cyclic voltammograms of different complexes with NTA ligand recorded at 50 mV s⁻¹ in 0.5 Molar KOH aqueous electrolyte solution

Electrochemical study

The electrochemical study was performed in a three-electrode system in a Pyrex glass cell where the platinum wire, Ag/AgCl (saturated KCl), and metal complexes were used for both purpose as a counter reference, and working electrodes in cyclic voltammetry.⁴⁵ 0.5 M KOH was used as an electrolytic solution. Electrodes were prepared by contact with a copper wire. There are ten electrodes of different metal complexes with ligands MTA and NTA that were prepared and employed in the electrochemical study.⁴⁶ Fig. 4(a). and (b) compares the cyclic voltammetry (CV) study of metal complexes of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and Cd²⁺ with the ligands MTA and NTA respectively.⁴⁷ We observed that the change of ligand environment doesn't make much difference in CV properties which is exhibited by CV graphs where we can see a prominent reduction peaks M²⁺ to M are showing at -0.4 V vs. Ag/AgCl equivalent oxidation peaks are also observed with different oxidative species probably due to M to M⁺ and M to M²⁺.

Figure 5 compares the CV properties of the same metal with different ligands MTA and NTA, we found that in the case of NTA there are less prominent reduction peaks observed in comparison to MTA, these are probably due to the less electron density towards metal when

coordinating with ligand L2.



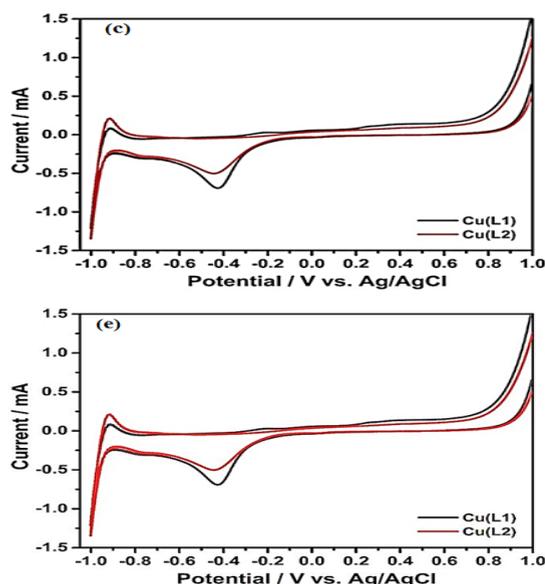


Fig. 5. Comparison of cyclic voltammograms properties of the (a) Co^{2+} , (b) Ni^{2+} , (c) Cu^{2+} , (d) Zn^{2+} , and (e) Cd^{2+} metals with different types of ligands MTA and NTA, recorded at 50 mV s^{-1} in 0.5 Molar KOH aqueous electrolyte solution

CONCLUSION

Summary, here synthesis transition metal complexes with previously synthesized ligands of thiazole derivatives have been characterized based on elemental analysis, FT-IR spectroscopy, ^1H NMR spectroscopy, mass spectroscopy, and UV/Vis spectroscopy. These synthesized metal

complexes are showing excellent photo physical and electrochemical activity. The comparison of base material and formation of few complexes then we have check complex behavior of electrochemical study was performed as a two different type of ligands MTA and NTA and comprised with a different type of metal complexes likewise Co, Ni, Cu, Zn, and Cd metal complex respectively. The CV performance we observed that the change of ligand environment in ligand MTA and NTA with compared with formation of complex and study of CV in the performance of ligand NTA formed complex was highly effective for comparisons of potential current than ligand MTA metal complexes. The above complex much difference in CV properties which is exhibited by CV graphs where we can see a prominent reduction peaks M^{2+} to M are showing at -0.4 V vs. we found that in the case of NTA there are less prominent reduction peaks observed in comparison to MTA.

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