

β - Tolyal Alanine Derived Schiff Base Complexes – Synthesis Characterization and Antimicrobial Assessment

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Abstract

A series of Schiff base complexes of Cu, Ni, Co, Zn and Cd derived from 3(amino)-3-p-tolylpropanoic acid) and 2-hydroxybenzaldehyde have been synthesized and characterized by elemental analyses, molar conductance, thermal analysis, FT-IR, UV-Vis spectra, ¹H NMR and LCMS-MS techniques. The spectral characterization confirms the formation of ligands and complexes. The evidences from the above results suggest the ligand to be a tridentate ion. The electrochemistry of these complexes has been extensively studied by cyclic voltammetry technique. The evidences from the infrared frequency predictions showed excellent agreement with the prepared complexes and displayed the proper coordination sites of the Schiff base towards the metal ions. The coordination of the ligand to the metal ions is in a tridentate manner through phenolic-oxygen, azomethine-N and carboxylic oxygen. The corrosion inhibitor efficiency of mild steel in the presence and absence of the Schiff base ligand was studied using potentiodynamic polarisation. The antibacterial activity of the ligand and the complexes were screened against five bacterias viz., Escherichia coli, Proteus vulgaris, Pseudomonas aeruginosa, Staphylococcus aureus and Bacillus Subtilis. The minimum inhibitory concentration (MIC) data revealed that most of the complexes are more potent than the ligand against the bacterial species. The antioxidant activities of all the complexes against DPPH (1, 1- diphenyl -2-picrylhydrazyl radical) were linear with increase in concentration of the complex. When compared to the ligand the complexes exhibited high antioxidant property.

Keywords: Antimicrobial activity, Antioxidant activity, Corrosion inhibition, CV studies, Schiff base, Transition metal complexes.

INTRODUCTION

Amino acids play central roles both as building blocks of proteins and as intermediates in metabolism. They are classified as essential and non-essential amino acids. β - alanine is a naturally occurring non-essential amino acid and is the building block of carnosine, a molecule that helps to buffer acid in muscles, increasing physical performance. In addition to the above key factor, β -alanine also exhibits neurotransmitter activity, by activating glycine and GABA (gamma- aminobutyric acid) receptors [1], and promotes anti-glycation effects because it increases carnosine levels in the body. Due to biological stress there was an increased level of β -alanine, which regulates excitotoxic responses and prevents neuronal cell death. β - alanine plays a protective role involving in preservation of enzyme structure and function. It suppresses heat-induced LDH inactivation, prevented LDH (Lactate dehydrogenase) aggregation, and reactivated thermally denatured LDH. β - alanine has chaperone like activity and may play a cellular role in the preservation of enzyme function. It can also act like an osmolyte, and may be able to help with proper protein folding.

Carnosine appears to be an anti-oxidant and anti-aging compound. Schiff base metal complexes of essential amino acids have been an interesting topic of research because of their use as antibacterial [2-5], antifungal [6, 7], anti-inflammatory [8], and antiradical agents [9]. Recently amino acid Schiff base complexes are largely studied for DNA cleavage property as they can be used for cancer therapy [10-12]. The Schiff base transition metal complexes are attractive oxidation catalysts because they are cheap, easy to synthesis and because of their chemical

and thermal stability [13 - 15]. Complexes of glycine and alanine find application as chiral synthons [16]. Salicylaldehyde-amino acid Schiff base complexes are used as non-enzymatic models for the metal - pyridoxal system. They act as key intermediates in metabolic reactions like transamination, decarboxylation, elimination, racemization which require pyridoxal as a cofactor [17, 18]. There have been many reports on the synthesis and properties of α -amino acids but only fewer reports are presented for β - amino acids more specifically β –alanine. Also, Carnosine a dipeptide of β –alanine and histidine has antioxidant property. This has created a lot of interest in the synthesis and studies of substituted β –alanine based Schiff base complexes. We have already reported the biological activity of Ln (III) alanine amino acid Schiff base complexes [2, 3]. In this continuation we here report the synthesis, characterization and antimicrobial assessment of tolyl β -alanine derived Schiff base complexes.

MATERIALS AND METHODS

Chemicals used for the preparation of the ligands and complexes were purchased from Aldrich and used as such. The amino acid **AA** and ligand **SL** were characterized by ¹H NMR and LC-MS. The IR spectra of the ligands and complexes in KBr (4000–400 cm⁻¹) were recorded on a Jasco FT/IR-6300 Spectrometer. A background spectrum was run before recording the spectra for each sample. ¹H NMR spectra were recorded in DMSO-d₆, CDCl₃ with TMS as an internal standard on a Bruker 400MHz spectrometer. Electronic absorption spectra of the ligand and complexes in DMF were recorded on a Perkin-Elmer Lambda 45 UV-Visible spectrophotometer. Molar

conductivity of 10^{-3} mol L⁻¹ solutions of the complexes in DMF was measured on Digital DCM conductivity meter. Elemental analysis was performed using Perkin-Elmer CHN 2400 analyzer. The metal content of the complexes was determined by titration with EDTA using xylenol orange as indicator [19].

Synthesis of 3-amino-3-(p-tolyl) propanoic acid AA

5g of 4-methyl benzaldehyde (4mol, eq) dissolved in methanol was mixed to 4.3g of malonic acid (1mol, eq) dissolved in methanol. To the above solution 6.4g of ammonium acetate (2mol, eq) was added and stirred in an oil bath preheated at 80°C for 26 hours. The precipitate obtained was filtered, washed with ethanol and dried at 80°C overnight. The dried product was recrystallized from ethanol to get pure 3-amino-3-(p-tolyl) propanoic acid.

¹H NMR: (DMSO-d₆, 25°C): δ 12.53 [s, 2H, NH₂], 8.71 [s, 1H, OH], 8.40 and 4.74 ppm [t, 2H, CH₂], 2.60 ppm [q, 1H, C-HA], 2.8 ppm [q, 1H, C-HB], 2.48 [s, 3H, Ar-CH₃]. FT-IR (ν, cm⁻¹): 3896–3305 (br, -OH); 3369–3176 (br, -NH₂); 1691 (s, -C=O), 1502 (m, asym COO⁻); 1390 (m, asym COO⁻).

LCMS-ESI-MS spectrum: [m/e 180.06, C₁₀H₁₂NO₂⁺], MS/MS C₁₀H₁₂NO₂⁺ [m/e 163.05, C₁₀H₁₁O₂⁺].

Synthesis of 3-((2-hydroxybenzylidene)amino)-3-(p-tolyl)propanoic acid SL

1.22g of 2-hydroxy benzaldehyde in ethanol (1mol, eq) was added dropwise to 1.79g of 3-amino-3-(p-tolyl) propanoic acid (1mol, eq) dissolved in water with continuous stirring. The mixture was refluxed for 6 hrs, was reduced to a minimum volume. The yellow coloured precipitate obtained was filtered washed with ethanol and dried in a vacuum desiccator.

Synthesis of Schiff base metal complexes

Five metal complexes were synthesized by the addition of 1mmol of the corresponding metal salts (CuSO₄.5H₂O, CoSO₄.6H₂O, NiSO₄.6H₂O, ZnSO₄.7 H₂O and CdSO₄) to 1mmol of SL in Ethanol. The mixture was refluxed for 24 h at 50°C. After stirring, the complexes were filtered and washed with ethanol and dried in vacuum. The complexes were characterized by elemental analysis (C, H, N %), FT-IR, UV and TGA/DTA techniques.

Potentiodynamic polarization (Tafel plot)

The inhibition of mild steel corrosion by using the Schiff base ligand has been studied by polarization measurements [20]. Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 760C. A three-electrode cell assembly was used. The metal is used as working electrode of the three electrodes. A Silver-silver chloride electrode was used as the reference electrode with platinum as the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), corrosion rate and Tafel slopes (anodic = β_a and cathodic = β_c) were calculated and tabulated in Table 4.

DPPH free radical scavenging activity

Free radical scavenging activity of the ligand SL as well as its transition metal complexes was determined using the reported procedure [19] by measuring the change in the absorbance of DPPH[•] (1, 1-diphenyl-2-picrylhydrazyl radical) at 517 nm spectrophotometrically. Stock solutions

of 500 μM of all the samples and DPPH[•] were prepared in DMF. Different concentrations of the samples (500, 1000, 1500, 2000 and 2500 μL) were prepared. DMF solvent was used as control. The reaction mixtures were thoroughly mixed by shaking the test tubes vigorously and incubated at 25°C for 60 min in a water bath in the dark. Absorbance at 517 nm was measured and the solvent interference was corrected throughout. The scavenging effect was calculated using the following equation.

$$\text{Scavenging activity (\%)} = (A_0 - A_s) / A_0 * 100$$

Where A_s is the absorbance of the DPPH[•] in the presence of the tested compound and A₀ is the absorbance of the DPPH[•] in the absence of the tested compound (control). The data for antioxidation is presented by means of ± Standard Deviation of three determinations.

Antimicrobial Studies

The Schiff base ligand and the complexes were screened for biological activity against three gram negative and two gram positive bacteria viz., Escherichia coli, Proteus vulgaris, Pseudomonas aeruginosa and Staphylococcus aureus and Bacillus Subtilis by following the reported procedure [21]. Ciprofloxacin was used as the standard. The stock solution (1 mg / mL) of the ligand and the complexes (test chemicals) were prepared in DMF solution. The stock solution was further diluted with sterilized distilled water to 25, 50 and 100 μg / mL dilutions. The test chemicals of different dilutions were added to sterile blank antimicrobial susceptibility disks. The bacteria were subcultured in agar medium and the disks were kept onto the same. The Petridishes were incubated for one day at room temperature. Antibacterial activity of the ligand and metal complexes were determined by measuring the zones of growth inhibition surrounding the disks. The standard was also screened under similar conditions for comparison. The solvent DMF alone was added to a separate disk and used as control, and it showed no activity against microbial strains.

RESULTS AND DISCUSSION

The ligand 3-((2-hydroxybenzylidene) amino)-3-(p-tolyl) propanoic acid SL was synthesized from 3-amino-3-(p-tolyl) propanoic acid and 2-hydroxy benzaldehyde. Five metal complexes of SL were synthesized using the respective metal salts. UV-Vis, IR, TGA / DTA spectroscopic techniques were used to characterize the complexes. The complex compounds were coloured and are non-hygroscopic powders. They are of fairly good stability as seen from their decomposition temperature. The melting point is sharp indicating the purity of the prepared Schiff base. They are soluble in common organic solvents like DMF, DMSO, acetonitrile and partially soluble in ethanol. The molar conductance of the ligand and the complexes in DMF showed values between 90 – 120 indicating their electrolytic nature [22]. The results of elemental analyses (C, H, N) molar conductance, colour and molecular formula are tabulated in Table 1. The results obtained are in good agreement with those calculated for the suggested formula. The synthesis and structure of the Schiff base under study is shown in Scheme 1.

Table 1 Analytical and Physical data of ligand and complexes

Compound	Color	Mol. Formula	Elemental Analysis Found (Cal)				$\Lambda \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
			C	H	N	M	
SL(C ₁₇ H ₁₇ NO ₃)	Yellow		71.39 (71.36)	5.65 (5.61)	5.40 (5.20)	-	-
[CuSL(H ₂ O)]SO ₄	Green	C ₁₇ H ₁₉ CuNO ₈ S	44.4 (44.3)	4.12 (4.15)	3.05 (3.04)	13.78 (13.79)	120
[Ni SL(H ₂ O)]SO ₄	Green	C ₁₇ H ₁₉ NiNO ₈ S	44.87 (44.77)	4.21 (4.20)	3.06 (3.07)	12.88 (12.87)	62
[CoSL(H ₂ O)]SO ₄	Black	C ₁₇ H ₁₉ CoNO ₈ S	44.76 (44.74)	4.22 (4.20)	3.04 (3.07)	12.93 (12.91)	112
[ZnSL(H ₂ O)]SO ₄	Yellow	C ₁₇ H ₁₉ ZnNO ₈ S	44.13 (44.12)	4.13 (4.14)	3.02 (3.03)	14.11 (14.13)	118
[CdSL(H ₂ O)]SO ₄	Brown	C ₁₇ H ₁₉ CdNO ₈ S	40.03 (40.05)	3.74 (3.76)	2.74 (2.75)	22.03 (22.05)	90

Table 2 IR (cm⁻¹) and UV (nm) spectral data

Compound	$\nu(\text{OH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu_{\text{svm}}(\text{COO}^-)$	$\nu_{\text{asvm}}(\text{COO}^-)$	λ_{max}
SL	-	1695	1623	-	-	-	-	235,252, 281
CuSL	3195	1685	1606	455	518	1388	1544	288, 328
NiSL	3200	1660	1608	425	525	1392	1554	255,287, 326,391
Co SL	3218	1660	1606	433	536	1369	1562	267,325, 378,312
ZnSL	3199	1662	1606	458	590	1392	1558	287, 324
CdSL	3197	1677	1608	428	570	1394	1554	258, 348

¹HNMR

The ¹H NMR spectra of the amino acid 3(amino)-3-p-tolylpropanoic acid) in DMSO-d₆ shows signals of two quartets at δ 2.60 to 2.8ppm. The strong singlet at δ 3.52 ppm is assigned for the methyl proton attached to the benzene ring. The doublet at δ 4.73 to 4.75 ppm is due to methine proton. The doublets in δ 7.04–8.4 ppm region are assigned to the protons of aromatic ring groups. The broad singlet at δ 12.53 ppm is due to the primary amine group. The ¹HNMR data is in accordance with the following LCMS-ESI-MS. From the mass spectrum the following data were observed, m/e value of 180.06 due to C₁₀H₁₂NO₂⁺ and MS/MS of C₁₀H₁₂NO⁺ gave m/e value of 163.05 daltons, due to elimination of NH₂ group to give C₁₀H₁₁O₂⁺.

TGA /DTA

The Thermogravimetric and differential thermal analysis for the synthesized complexes have been obtained in nitrogen atmosphere between 30 – 800 °C. One representative thermogram of Schiff base Cu complex is shown in Fig 1. The TGA results showed that the complex is thermally stable in the temperature range 30°C – 223 °C. Further there is a weight loss of 4.1% corresponding to one water molecule at 100°C. With further increase in temperature above 200 °C the decomposition of the ligand starts, there is a weight loss of 21.4% corresponding to SO₄ moiety. The decomposition of the complex starts at 223 °C and gets completed at 450 °C with one decomposition step. After 450°C the metal gets converted into its corresponding oxide. The thermal behavior of other

complexes is similar to that of the above complex. It shows two major degradation steps. The first step is the elimination of coordinated water molecule and the second step is the elimination of the ligand and the complex is finally converted into MO₂ [23].

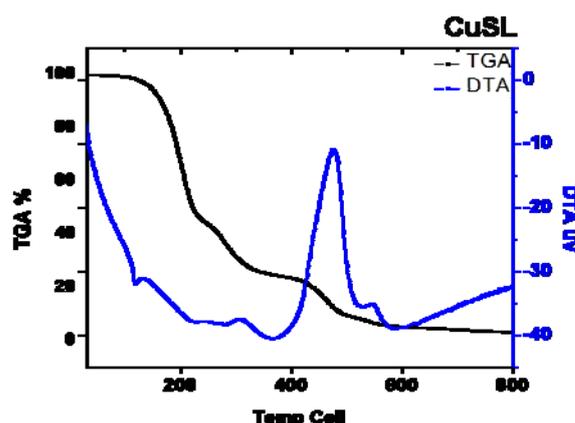


Fig 1 TGA/DTA of CuSL complex

Electronic Spectra

The electronic spectra of the ligand and complexes were recorded using DMF as solvent at room temperature. The electronic spectra for the ligand and its transition metal complex were shown in Fig 2 and its numerical values of the maximum absorption wavelength (λ_{max}) are listed in table 2.

The electronic absorption spectrum of the free ligand showed three bands at 235, 252 and 281 nm corresponding

to $n-\pi^*$ transition state [24,25] and conjugation between the lone pair of electrons of p orbital of N atom in azomethine group and conjugated π bond of the benzene ring. The bands appearing at higher energy are attributed to $\pi-\pi^*$ of the benzene ring and $\pi-\pi^*$ transition of the azomethine group. The absorption band of the Schiff base complexes is slightly shifted to shorter wavelength (blue shift) when compared to those of free ligand. The above modification in the spectra illustrates that the metal is coordinated with the ligand.

IR spectra

The IR spectra of the ligand and the copper complex are presented in Fig.3 and the numerical frequency values of the ligand and complexes were tabulated in the table 2. The IR spectra of the complexes show a sharp band in the range 1623 cm^{-1} corresponding to the existence of $\nu(\text{HC}=\text{N}-)$ group of the azomethine in the free ligand shifted to lower frequency of $\sim 15\text{ cm}^{-1}$ indicating the involvement of this group upon complexation [26,27]. The second coordination site was hydroxyl group of the amino acid. The evidence for the chelation process was obtained from the shifting of the band at 1695 cm^{-1} of $\text{C}=\text{O}$ in the spectrum of free ligand to lower frequency $1660-1685\text{ cm}^{-1}$ [28] in case of the complexes. All complexes exhibit strong band in the region $1544-1562\text{ cm}^{-1}$ and a weaker band in the region $1369-1394\text{ cm}^{-1}$ assigned to asymmetric and symmetric stretching frequencies of COO^- group respectively. An asymmetric and symmetric stretching frequency comes around 212 cm^{-1} , which suggests the monodentate coordination of the carboxyl group of amino acid with the metal ion [29]. The third coordination site was hydroxyl group of the salicylaldehyde group. The formation of new frequency bands observed in the range of $580-595\text{ cm}^{-1}$ which are not present in the free Schiff base are due to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations. The appearance of these vibrations supports the involvement of nitrogen and oxygen atoms of azomethine and hydroxyl groups of the free Schiff base in complexation with the metal ions under investigation. The non-coordination of sulphate ion during complex formation is confirmed by the presence of bands at $1110-1100\text{ cm}^{-1}$ and $605-615\text{ cm}^{-1}$ [30]. The infrared spectra of all the complexes exhibit a broad band in the range of $3100-3250\text{ cm}^{-1}$ due to the presence of water molecules.

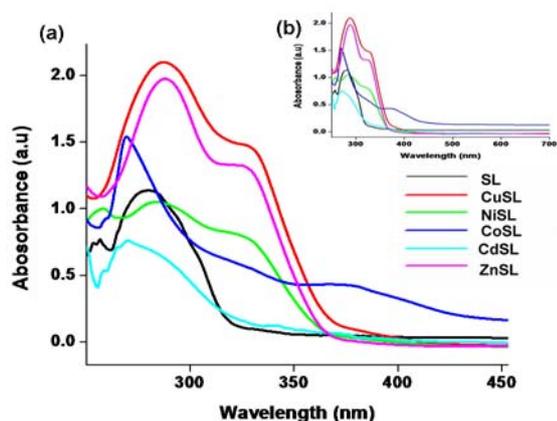


Fig 2 a) UV spectrum of SL and metal complexes b) UV spectrum of SL and metal complexes in the region 450 – 200 nm

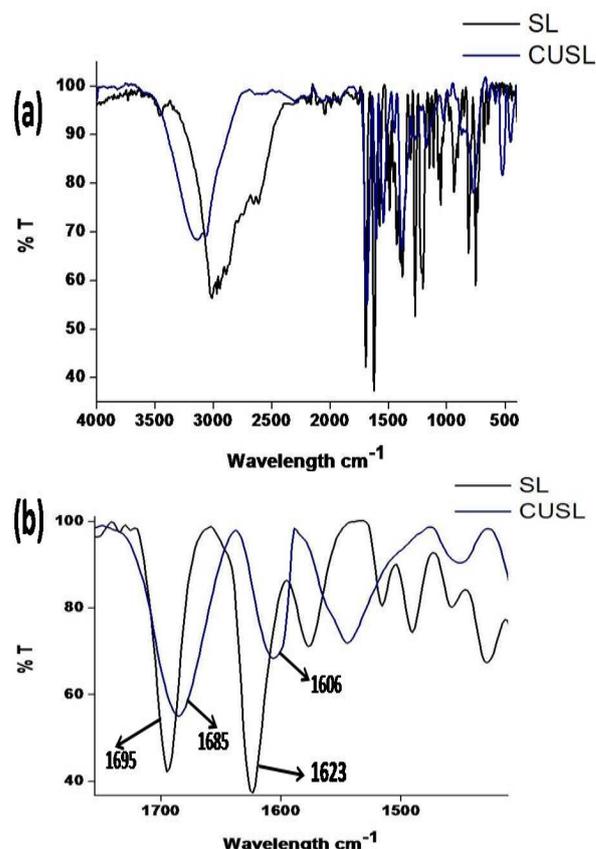


Fig 3 a) IR spectrum of SL and CuSL complex b) IR spectrum of SL and CuSL complex in the region 1500 – 1800 cm^{-1}

CV studies

The cyclic voltammograms of the neat complexes are taken in solution mode, using 0.01 M of the metal complexes in acetonitrile with addition of 0.1 M tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte. A representative cyclic voltammogram of Cu (II) complex is presented in Fig 4. The voltammogram displays a reduction peak at $E_{p,c} = -1.13\text{V}$ with an associated oxidation peak at $E_{p,a} = -0.95\text{V}$ at a scan rate of 100mV/s . The peak separation of this couple (ΔE_p) is 0.18V and increases with scan rate. The ΔE_p is 0.5 and 0.6 at scan rates of 200mV/s and 300mV/s respectively. Thus, the analyses of cyclic voltametric responses at different scan rate gave evidence for quasi-reversible one electron reduction. The most significant feature of the Cu (II) complex is the Cu (II)/Cu (I) couple. The ratio of cathodic to anodic peak height was found to be less than one suggesting a simple one electron transfer, quasi reversible process. However, the peak current increases with increase of square root of the scan rates. This establishes the electrode process as diffusion controlled [31]. All the complexes are electrochemically active and the data is presented in Table 3.

Table 3 Electrochemical data for the metal complexes

Compound	Ep _c (V)	Ep _a (V)
Cu SL	-0.935	-0.411/+0.667
Ni SL	-1.96/-1.18	-0.829/0.836
Co SL	-0.981	-0.831 / 0.765
Zn SL	-1.20	-0.871/+0.850
Cd SL	-1.07	-0.771/+0.950

Table 4 Corrosion parameters of the Schiff base ligand SL immersed in simulated concrete pore solution (Saturated calcium hydroxide solution), obtained by potentiodynamic polarization study

System	bc mV / decade	ba mV/decade	LPR ohm cm ²	I _{corr} A/cm ² x 10 ⁻⁵	Rate gm/hr x 10 ⁻⁵
Blank (mild steel) MS	799	242	789	5.41	5.63
SL (10 ppm) + Mild steel	831	219	964	4.20	4.37

Corrosion inhibition property of the ligand

Corrosion behaviour of mild steel, immersed in simulated concrete pore solution (SCP), (saturated calcium hydroxide solution) in presence of the inhibitor which is the Schiff base ligand SL has been investigated by polarization study. The inhibitor efficiency of the ligand was tested for a series of solution 25, 50, 75, 100, 200, 500 ppm respectively. The ligand showed greater inhibiting property towards corrosion within these ranges of concentration. The minimum inhibitor concentration was found out by decreasing the working concentration below the range of 25 ppm. The minimum inhibitor concentration was found to be 10 ppm respectively. For mildsteel immersed in SCP, the corrosion potential is -646 mv; linear polarization resistance (LPR) is 789 ohm cm² and the corrosion current value (I_{corr}) is 5.41 x 10⁻⁵ A/cm² (Fig. 5). When 10 ppm of SL is added, the LPR value increases to 964 ohm cm² and the corrosion current value increases to 4.20 x 10⁻⁵ A/cm² (Table 4). These observations indicate that the corrosion resistance of mild steel increases in presence of SL [32, 33]. The changes in mildsteel in the presence and absence of the inhibitor are plotted in terms of Tafel plot Fig 5. In the presence of the inhibitors, the Tafel slopes decreased to more negative potentials and increased to more positive potentials relative to the absence of SL. This indicated that the presence of SL is influencing both the cathodic and the anodic processes. Moreover, in the presence of inhibitor, both the cathodic and anodic reactions were obviously suppressed in comparison with those in the absence of SL. The inhibitor molecules adsorbed merely by blocking the reaction sites of iron surfaces leading to the reduction of surface area available for hydrogen evolution. Therefore, it could be concluded that the anodic iron dissolution and cathodic hydrogen evolution reaction were both inhibited by the inhibitor by merely blocking the reaction sites of mild steel surface without affecting the anodic and cathodic reaction mechanism [34]. Also, this suggested the mixed behaviour of the used inhibitors, i.e., mixed type inhibitors [35]. The inhibition mechanism is ascribed to the adsorption of N⁺ on the negative active sites on the metal surface, while the π-electrons of the conjugated systems

adsorbed on the positive active sites of the metal surface [36, 37].

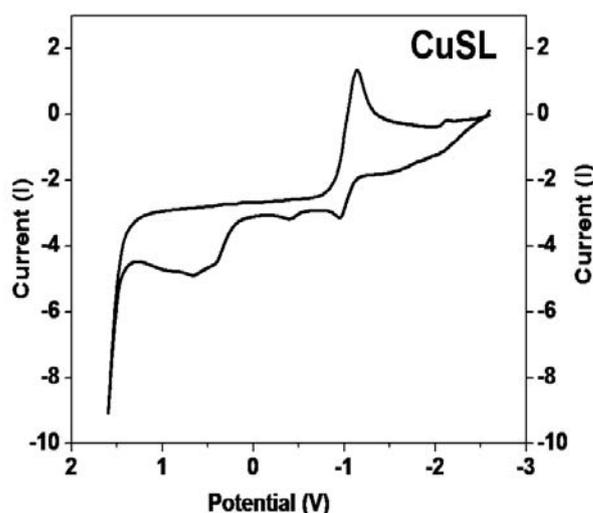


Fig 4 Cyclic voltammogram of CuSL complex

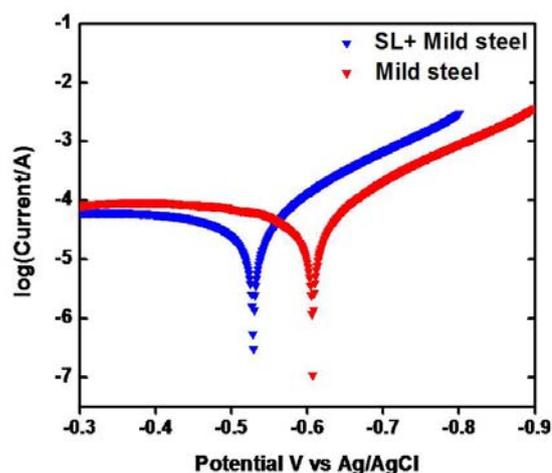


Fig 5 Tafel plot in the presence and absence of inhibitor(SL)

BIOLOGICAL ACTIVITY

Antioxidant activity

Antioxidants are the compounds capable of scavenging the free radicals. The ligand and the complexes were evaluated for their in vitro free radical scavenging activity by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. For a comparative study Butylated hydroxyl anisole (BHA) was used as the standard. The percentage inhibition activity was calculated and tabulated Table 5. The free radical scavenging activity % is plotted in fig 6. The antioxidant activities of the complexes are found to increase with increasing sample concentration. The antioxidant effect of the free ligand is between 2.5% to 15% and this may be related with their electron or hydrogen radical releasing ability to DPPH so that it becomes a stable diamagnetic molecule. All the complexes show significantly increased antioxidant activity than the ligand. The Cu (II), Ni (II) and Zn (II) complexes showed higher activity than their corresponding Co (II) and Cd (II) complexes. This may be attributed to the flow of electron density from oxygen atom to H when the ligand coordinates with the metal. This causes the ionization of in DMF more easier which in turn will lead to H abstraction by DPPH.

Antibacterial activity

The minimum inhibitory concentration (MIC) of the ligand SL and its complexes were tested against five bacteria, three gram negative bacteria *Escherichia coli*, *Pseudomonas aeruginosa*, *Proteus vulgaris* and two gram positive bacteria *Staphylococcus aureus*, and *Bacillus subtilis* strains and the results are tabulated in Table 6. A comparative study of the ligands and their complexes (MIC values) indicates that the complexes exhibit slightly higher antibacterial activity than the free ligands (fig 7). This is explained on the basis of Overtone's concept and the Tweedy's Chelation theory [38, 39]. According to Overtone's concept of cell permeability, the lipid membrane surrounding the cell favours the passage of only the lipid-soluble materials and so liposolubility becomes an important factor, which controls the antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. It further increases the delocalization of π -electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity

enhances the penetration of the complexes into lipid membranes and block the metal binding sites in the enzymes of the microorganisms. These complexes also disturb the respiration process of the cell and thus block the synthesis of the proteins that restricts further growth of the organism. Also, the mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group with the active centres of cell constituents, resulting in interference with the normal cell process [40]. Out of the five transition metal complexes the Zn complex has found better antibacterial activity compared to others while the Ni complex has good effect on *proteus vulgaris* bacteria. The antibacterial property is in the following order Zn > Cu > Ni > Cd > Co.

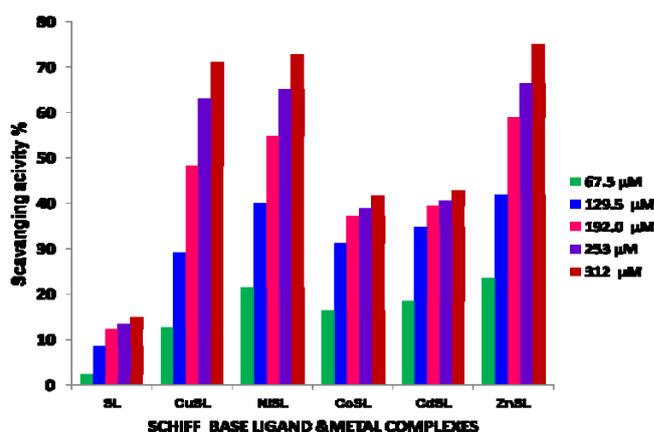


Fig 6 Antioxidant activity % of SL and metal complexes

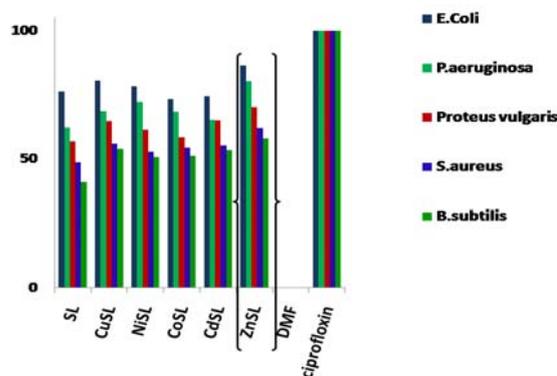
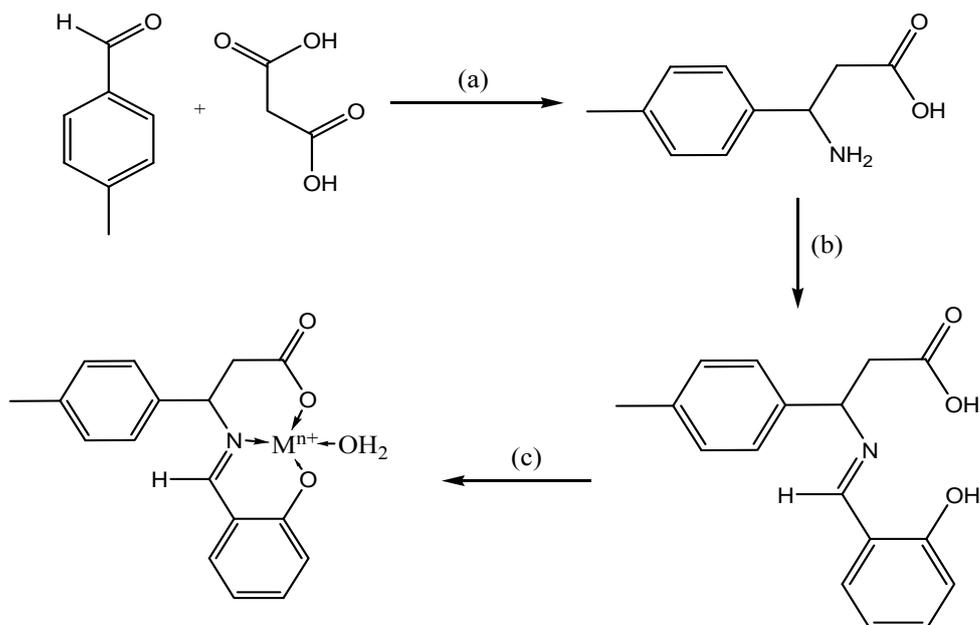


Fig 7 Minimum Inhibitory Concentration (MIC) % of SL and metal complexes

Table 5 Antioxidant scavenging activity data of the Schiff base ligand SL and its transition complexes on DPPH^{*} free radical at different concentrations

Antioxidant activity %	*A conc (T conc)				
Compound	60.0 μ M (67.5 μ M)	120 μ M (129.5 μ M)	180 μ M (192.0 μ M)	240 μ M (253 μ M)	300 μ M (312 μ M)
SL	2.5 \pm 0.4	8.6 \pm 0.3	12.3 \pm 0.3	13.5 \pm 0.5	15.0 \pm 0.5
CuSL	12.8 \pm 0.5	29.1 \pm 0.4	48.3 \pm 0.4	63.0 \pm 0.2	71.2 \pm 0.6
NiSL	21.5 \pm 0.3	40.0 \pm 0.5	54.8 \pm 0.5	65.0 \pm 0.3	72.8 \pm 0.7
CoSL	16.5 \pm 0.4	31.2 \pm 0.4	37.3 \pm 0.3	38.9 \pm 0.2	41.8 \pm 0.8
ZnSL	23.5 \pm 0.3	42.0 \pm 0.3	58.9 \pm 0.2	66.4 \pm 0.1	42.9 \pm 0.9

CdSL	18.5±0.4	34.8±0.3	39.6±0.4	40.5±0.3	75.0±0.1
*A conc – actual concentration, T conc – theoretical concentration					
Table 6 Antibacterial activity data of the Schiff base ligand and the complexes against various bacteria.					
Compound	E.coli	P.aeruginosa	P.vulgaris	S. aureus	B. subtilis
SL	76.12	62.23	56.87	48.59	40.89
SLCu	80.43	68.54	64.76	55.98	53.76
SL Ni	78.24	72.11	61.23	52.74	50.58
SL Co	73.19	68.23	58.31	54.34	51.23
SLZn	86.33	60.36	70.19	62.00	58.00
SL Cd	74.32	65.16	64.97	55.11	53.45
DMF	0	0	0	0	0
Ciprofloxin	100	100	100	100	100



where M^{n+} - $CuSO_4 \cdot 5H_2O$, $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$ and $CdSO_4$

Scheme 1 Synthesis of Schiff base AA, SL and metal complexes of SL

- a) Ammonium acetate, methanol with 28 h stirring at $80^\circ C$, b) ethanol, refluxed for 6 h at $80^\circ C$ c) 5ml 0.1M NaOH with $MSO_4 \cdot x H_2O$ in ethanol, refluxed for 6 h at $80^\circ C$

CONCLUSION

In the present studies we have reported the synthesis and spectroscopic characterization of a series of cobalt, nickel, copper, zinc and cadmium complexes with a novel amino acid tridentate schiff base ligand derived from 3(amino)-3-p-tolylpropanoic acid) and 2-hydroxybenzaldehyde. The spectral evidence shows that the complexes are formed through the coordination of phenolic oxygen and the azomethine nitrogen atoms. The redox behaviour of all the complexes follows a diffusion controlled process. The newly synthesized ligand possess good inhibitor action towards mild steel corrosion and the transition metal complexes show better antioxidant and antibacterial activity.

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REFERENCES

- [1] Kuffler, S.W., Edwards, C., *J. Neurophysiol.* 1958, 21, 589 – 610.
- [2] Lekha, L., Kanmaniraja, K., Rajagopal, G., Easwaramoorthy, D., *J. Mol. Struc.* 2014, 1056 307 – 312.
- [3] L.Lekha, L., Kanmaniraja, K., Sivakumar, G., Easwaramoorthy, D., *Int. J. Chem. and Pharm. Sci.* 2013, 4, 48 – 54.
- [4] Nuren Sari, Seza Arslan, Elif Cogoglu, Iffet Sakiyan, *G.U. J. Sci.* 2003, 16, 283 – 288.
- [5] Jian Liu, Sulan Cai, Xin Wang, Lei Liu, Yongmei Wang, *J. Inorg. Biochem.* 2006, 100, 1888 – 1896.
- [6] Zahid. H. Chohan, Arif, Muhammad, M., Akthar, A., Claudiu.T. Supuran, *Bioinorg. Chem. and Appl.* 2006, 2006, 1-13.
- [7] Plesch, G., Friebe, C., Svajlenova, O., Kratsmar – Smogrovic, J., Miynarcik, D., *Inorg. Chim.Acta* 1988, 151, 139 – 143.
- [8] Iqbal, M.S., Khurshid, S.J., Muhammad, B., *Med. Chem. Res.* 2013, 22, 861 – 868.
- [9] Zita Puterova, Jindra Valentova, Zuana Bojokova, Jozef Kozisek, Ferdinand Devinsky, *Dalton Trans.* 2011, 40, 1484 – 1490.
- [10] Laila. H. Abdel-Rahman, Rafat M. El-Khatib, Lobna .A.E.Nassr, Ahmed M. Abu-Dief, *J. Mol. Str.* 2013, 1040, 9 – 18.

- [11] Neelakantan, M.A., Rusalraj, F., Dharmaraja, J., Johnsonraja, J., Jeyakumar, T., Sankaranarayana Pillai, M., *Spectrochim. Acta Part A* 2008, 71, 1599 – 1609.
- [12] Sangeetha Gowda, K.R., Bhojya Naik, H.S., Vinay Kumar, B., Sudhamani, C, N., Sudeep, H.V., Ravikumar Naik, T.R., Krishnamurthy, G., *Spectrochim. Acta Part A* 2013, 105, 861 – 868.
- [13] Meizhu Rong, Chong Liu, Jinyu Han, Wenbo Sheng, Yufei Shang, Hua Wang, *Catal. Lett.* 2008, 125, 52 – 56.
- [14] Rong-Min Wang, Cheng-Jun Hao, Yun-Pu Wang, Shu- Ben Li, *J. Mol. Catal. A Chem.* 199, 147, 173 – 178.
- [15] Debraj Saha, Tanmoy Maity, Rajesh Bera, Subratanath Konar, *Polyhedron* 2013, 56, 230 – 236.
- [16] Alexander Popkov, Antony Gee, Milan Nadvornik, Antonin Lyeka, *Transition Met. Chem.* 2002, 27, 884 – 8887.
- [17] Metzler, D.E., Snell, E.E., *J. Am. Chem. Soc.* 1952, 74, 979 – 983.
- [18] Casella, L., Gullotti, M., *Inorg. Chem.* 1986, 25, 1293 – 1303.
- [19] Ziyad A. Tahaa, Abdulaziz. Ajlounia, M., Waleed Al Momanib, Abeer A. Al-Ghazawia, *Spectrochimica Acta Part A* 2011, 81, 570–577.
- [20] Negm, N.A., Ghuiba, F.M., Tawfik, S.M., *Corrosion Science* 2011, 53, 3566–357.
- [21] Anil K. Sadana , Yasmin Mirza, Kamal R. Aneja , Om Prakash, *European Journal of Medicinal Chemistry* 2003, 38 533-536.
- [22] W.J. Geary, W.J., *Coord. Chem. Rev.* 1971, 7, 81–122.
- [23] Abdel-Nasser M.A. Alaghaz , Hoda A. Bayoumi, Yousry A. Ammara, Sarah A. Aldhlmani, *J. of Mol. Struct.* 2013, 1035, 383–399.
- [24] Freeman E.S., and Carroll, B.J., *J. Phy. Chem.* 1958, 62, 394-397.
- [25] Mishra A.P., and Khare, M., *J. Ind. Chem. Soc.*, 2000, 77, 367- 370.
- [26] Guo, L., Wu, S., Zeng, F., Zhao, J., *Eur. Polym. J.*, 2006, 42, 1670 - 1675.
- [27] Felico, R.C., Canalleiro, E.T.G., Dockal, E. R., *Polyhedron*, 2001, 20, 261-268.
- [28] Maurya, M.R., Khurana, S., Schulzke, C., and Rehder, D., *Eur. J. Inorg. Chem.* 2001, 2001, 779–788.
- [29] Viswanathamurthi, P., Dharmaraj, N., Anuratha, S., and Natarajan, K., *Transition Met. Chem.* 1998, 23, 337- 341.
- [30] Shakir, M., Shahid, N., Sami, N., Azam, M., Khan, A.U., *Spectrochim. Acta. A: Biomol. Spectrosc.* 2011, 82, 31–36.
- [31] Mithilesh Kumar and Singh, A.K., *Asian Journal of Chemistry* 1998, 10, 233-237.
- [32] A.J. Bard, A.J., Izatt, L.R., (Eds), *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., (Wiley, New York, 2001).
- [33] Noreen Anthony, Benita Sherine, H., and Rajendran, S., *The Arabian Journal for Science and Engineering*, 2010, 35, 41-52.
- [34] Noreen Antony, Benita Sherine, H., and Rajendran, S., *International Journal of Engineering Science and Technology* 2 (2010) 2774-2782.
- [35] Negm, N.A., Aiad, I.A., Tawfik, S.M., *J. Surf. Deterg.* 2010, 13, 503–511.
- [36] Bentiss, F., Lebrini, M., Vezin, H., Chai, F., Traisnel, M., Lagrené, M., *Corros. Sci.* 2009, 51, 2165–2173.
- [37] Ali, S.A., Al-Muallem, H.A., Saeed, M.T., Rahman, S.U., *Corros. Sci.* 2008, 50, 664– 671.
- [38] Anjaneyulu, Y., and Rao, R.P., *Synth. React. Inorg. Met-Org. Chem.* 1986, 16, 257-272.
- [39] Ahmed A. Al-Amiery, Abdul Amir H. Kadhum, and Abu Bakar Mohamad, *Bioinorganic Chemistry and Applications*, 2012, 2012, 1-6.
- [40] Dharmaraj, N., Viswanathamurthi, P., and Natarajan, K., *Transition Met. Chem.* 2001, 26, 105-109.