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Original Article

Synthesis, Characterization, Thermodynamics Studies and Antibacterial Activity of Same Mononuclear Complexes with Ligand Derived from 4-Aminoantipyrine with Threonine Amino Acid

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ABSTRACT

The heterocyclic ligand potassium 2-(((Z)-1,5-dimethyl-4-((E-1-(4-nitrophenyl) ethylidene) amino)-2-phenyl-1,2-dihydro-3H-pyrazol-3-ylidene) amino)-3-hydroxybutanoate (K_4-AP-NO_2A-Thr) has been synthesized under the thermal condition from the combination of 4-aminoantipyrine, 4-nitroacetophenone, and Threonine. A new series of transition metal complexes of Mn(II), Co (II), Ni(II),Cu(II) and Zn (II) has been produced from the Schiff base(K_4-AP-NO_2A-Thr). The geometry structures of the ligand and the complexes were determined through FT-IR, UV-Vis, ^{1}H-NMR spectroscopy, (C.H.N) analysis, as well as molar conductance and magnetic susceptibility. These studies revealed that tetrahedral structure was suggested for Co (II) and Cu (II) complexes. Yet, the octahedral structure was suggested for Mn(II), Ni (II) and Zn (II) complexes. In-vitro antibacterial activity of the synthesized ligand and its complexes against (*S. aureus*, *K. aureus*) was evaluated through the disc diffusion method. Thermodynamic values were studied by conductivity methods. The conductivity of solution complexes prepared at different temperatures in aqueous water was measured using the Lee-Wheaton equation to obtain the values of ionic molar conductivity (Λ), the association constant (K_A), distance parameter (R), and (Λ_o).

Keywords: Schiff base, 4-amino antipyrine, Threonine, conductivity, lee-Wheaton equation.

Introduction

Heterocyclic compounds are the most important organic compounds due to their chemical ,technical and biological significance [1]. They contain nitrogen atoms that are important structural units for drug development [2]. Among the various heterocyclic compounds, pyrazoles are considered essential bioactive systems that are wide represented in biologically active groups compounds [3]. Antipyrine is the first compound derived from pyrazolone synthesized by Knorr [4, 5]. Antipyrine molecular chemistry has received a great deal of attention in medicinal and synthetic chemistry, and also in materials science, because of its varied applications [6]. Therefore, it is used as antipyretic, analgesic [7] non-steroidal anti-inflammatory drug [8]. 4-amino antipyrine is one of the antipyrine derivatives that has revealed a wide range of biological activities, e.g. antimicrobial activity, painkiller and antiviral activity, due to the present free

amino group which is used to prepare an azo methine compound by condensation with carbonyl compounds (aldehyde or ketone). Furthermore, it can form stable complexes with metal ions [9-11]. These resulting metal complexes have some applications in the analytical and pharmacological fields [12]. In the investigations conducted on Schiff complexes of base metals derived from-4 aminoantipyrine, a Schiff base derived from 4-AAP was prepared with the cysteine amino acid and furan-2-carbaldehyde, then reacted with some transition metals which formed complexes measured by different spectral methods and the bacterial efficacy was evaluated on K .pneumoniae ,E .coli and Bacillussubtilis aureus [13]. A new ligand was prepared from Schiff base 4-aminoantipyrine with benzil and glycine amino acid, then it was used to prepare several dual complexes that have octahedral shapes and evaluated the biological activity on species of bacteria: Escherichia coli, Pseudomonas Aeruginosa, Staphylococcus Aureus, Klebsiella pneumonia [14]. Another study was conducted on a voltammetric technique for electrochemical sensing and quantification of agranulocytosis risk inducing metabolite of 4-Aminoantipyrine at a gold electrode. The gold electrode exhibited excellent selectivity in the presence of a large excess of interferents, this method is employed for recovery study of 4-AAP in spiked urine and serum samples [15].

The 4-aminoantipyrine (4-AAP) method was employed to determine total phenolic compounds in wastewater, with a specific focus on evaluating the efficiency of ultrasound wave enhancement. Experimental data were acquired and analyzed using a smartphone to identify optimal conditions. In the procedure, a sample or standard phenol solution was injected into a carrier stream, reacted with 4-aminoantipyrine reagent, and subsequently treated with ultrasound at 46 kHz. Results indicated that ultrasonic irradiation significantly reduced the analytical peak height, which is attributed to decreased measurement sensitivity. This reduction likely stems from ultrasound-induced disruption of the bonding interaction between phenolic compounds and the 4-AAP reagent [16].

Electrochemistry studies chemical transformations resulting from electrical current passing through matter, bridging thermodynamics with other areas of chemistry. This field enables investigation of ionic interactions, especially at electrode surfaces as well as the properties of electrolytic solutions, ion behavior, and interfacial phenomena at submerged electrodes [17]. Conductivity measurement is a highly accurate physical method with broad utility in characterizing electrolytic solutions and determining concentrations. It is applicable across diverse solvents, a wide range of temperatures and pressures, and remains effective even in dilute solutions [18]. Research into conductivity methods has advanced considerably over the past fifty years, yielding important theoretical developments. Kholorauch was the first to derive a key equation in this area, building upon the Debye Hückel theory of ionic atmospheres and the Onsager equation to establish a foundational relationship [19].

$$\Lambda = \Lambda_o - b\sqrt{C}$$

To determine the equivalent conductivity at infinite dilution for weak electrolytes, the Kohlrausch Law of Independent Migration of Ions is applied. This law states that at infinite dilution, all electrolytes are completely dissociated, and each ion contributes independently to the total conductivity [17]. One application of this law involves measuring the electrical conductivity of solutions containing 1-butyl-3-alkylimidazolium salts with inorganic anions (Br^-, BF_4^-, PF_6^-) in acetone or acetonitrile. From these measurements, the limiting molar conductivity ($\Lambda°$) and the dissociation constant (Ka) at infinite dilution were calculated within a temperature range of 298-323 K [20]. In another application, the effect of solvents on the ionic behavior of glutamic acid was studied. Conductivity measurements were performed on dilute solutions of glutamic acid in ethanol, methanol, and water at 37 °C, and the data were analyzed using the Lee–Wheaton equation. Theoretical calculations using PM3, HF, and DFT methods, combined with CPCM and COSMO solvation models, were also employed to examine the properties of glutamic acid [21]. In this study, a novel Schiff base ligand (K4-AP-NO2A-Thr) derived from 4-aminoantipyrine was synthesized and characterized, along with its Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes. An electrochemical investigation of these new complexes, as well as free threonine amino acid, was carried out using aqueous dilute solutions at various temperatures.

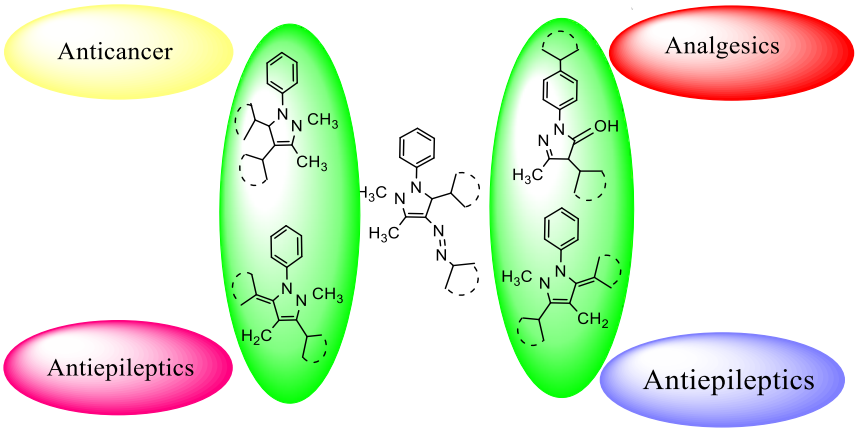


Figure 1: Some of medical applications for the antipyrine nucleus

Materials & Methods

Chemicals and Solvents

All chemicals were purchased from Fluorochem, Molekula, and Merck and were used without further purification. The metal salts Mn(II) chloride, Co(II) chloride, Ni(II) chloride, Cu(II) chloride, and Zn(II) chloride, as well as 4-aminoantipyrine and the amino acid threonine, were used as received. Organic solvents, including ethanol, methanol, diethyl ether, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), were of spectroscopic grade and obtained from Scharlau and Cristalco.

Synthesis of the Schiff Base Ligand

Step 1

A solution of 4-aminoantipyrine (2.03 g, 0.01 mol) in 15 mL of ethanol was added to a solution of 4-nitroacetophenone (1.65 g, 0.01 mol) in 15 mL of ethanol, and the mixture was refluxed for 3 h. After cooling to room temperature, the resulting orange crystals were filtered [22,23] and recrystallized from methanol to afford compound (3), namely (E)-1,5-dimethyl-4-((1-(4-nitrophenyl)ethylidene)amino)-2-phenyl-1,2-dihydro-3H-pyrazol-3-one.
Orange crystals; yield: 77%, m.p.: 148 °C. The reaction pathway is illustrated in Scheme 1.

Step 2

Threonine amino acid (1.19 g, 0.01 mol) was dissolved in 20 mL of ethanol in a round-bottom flask. Subsequently, 20 mL of hot ethanolic KOH solution (0.22 g) was added with stirring. The second compound (3) was then added in the same molar ratio as in the previous step, and the reaction mixture was refluxed for 3 h [22,23]. An orange crystalline precipitate formed, which was filtered, recrystallized from methanol, and dried to yield the Schiff base ligand (L). The synthesis route is shown in Scheme 1.

Synthesis of the Metal Complexes

The Schiff base ligand (0.489 g, 0.001 mol) was dissolved in ethanol. Ethanolic solutions of the metal salts—Co(II) (0.2379 g), Ni(II) (0.2377 g), Cu(II) (0.1704 g), and Zn(II) (0.2444 g)—were added to the ligand solution in a 1:1 (L:M) molar ratio. The reaction mixture was refluxed with stirring at 85 °C for 4 h. The resulting products were filtered and repeatedly washed with an ethanol–water mixture [24], then dried. The synthetic pathway is illustrated in Scheme 1.

Electrical Conductance

Instrument: Professional benchtop conductivity meter (BC3020).

Preparation of Solutions

A threonine solution was prepared at a concentration of 1×10^{-4} M by dissolving 0.000119 g in 10 mL of conductivity-grade water. Similarly, solutions of the Mn(II) and Ni(II) complexes were prepared at the same concentration by dissolving 0.00068 g and 0.00072 g, respectively.

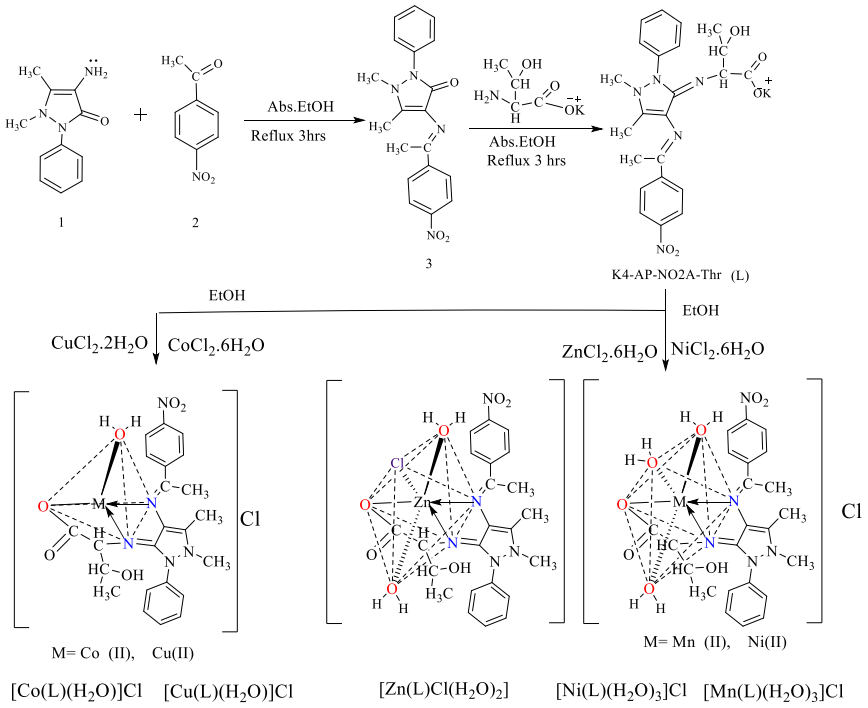
Conductivity Measurements

Conductivity measurements were performed by placing 20 mL of conductivity-grade water in the measurement cell and adjusting the temperature to the desired value. The conductivity of the pure solvent was first recorded. Subsequently, a fixed volume of the prepared solution (1×10^{-4} M) was added, and the mixture was stirred for 30 s, allowed to settle for 60 s, and then measured. This procedure was repeated 14 times, with 0.1 mL added each time. The same procedure was applied to the metal complexes. Conductivity measurements were carried out at 20, 25, 30, 35, and 40 °C [17].

Characterization

Melting points were determined using the open capillary method on a Stuart SMP10 apparatus and were uncorrected. Spectral analyses were conducted at the Department of Chemistry, Gaziosmanpaşa University, Tokat, Turkey. Elemental microanalysis was performed using an Elementar Vario Micro Cube analyzer.

^{1}H NMR spectra were recorded on a Bruker BioSpin GmbH (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal reference, and chemical shifts are reported in δ (ppm). FT-IR spectra were recorded using an ATR Alpha Platinum Bruker spectrophotometer over the range 400–4000 cm^{-1}. Electrical conductivity measurements of the complexes were performed at 25 °C using a Jenway 4510 conductivity meter. Magnetic susceptibility measurements were carried out using a Magnetic Susceptibility Balance (MSB_MKI). Electronic spectra were recorded in DMF using a UV–Vis spectrophotometer (Analytik Jena), and metal contents were determined by ICP-AES.



Scheme 1. Preparation of the ligand and corresponding metal complexes.

Results & Discussion

Structure configuration of the ligand: The newly synthesized ligand was characterized using elemental analysis, FT-IR spectroscopy, and ^{1}H NMR spectroscopy. In the IR spectrum of the ligand, the characteristic absorption bands of the –NH$_2$ group and the carboxylic group of the amino acid disappeared, while new bands attributed to the imine (–C=N–) group appeared at approximately 1655 cm^{-1}. The ^{1}H NMR spectrum of the ligand recorded in DMSO-d$_6$ is summarized in Table 1 and illustrated in Figure 2.

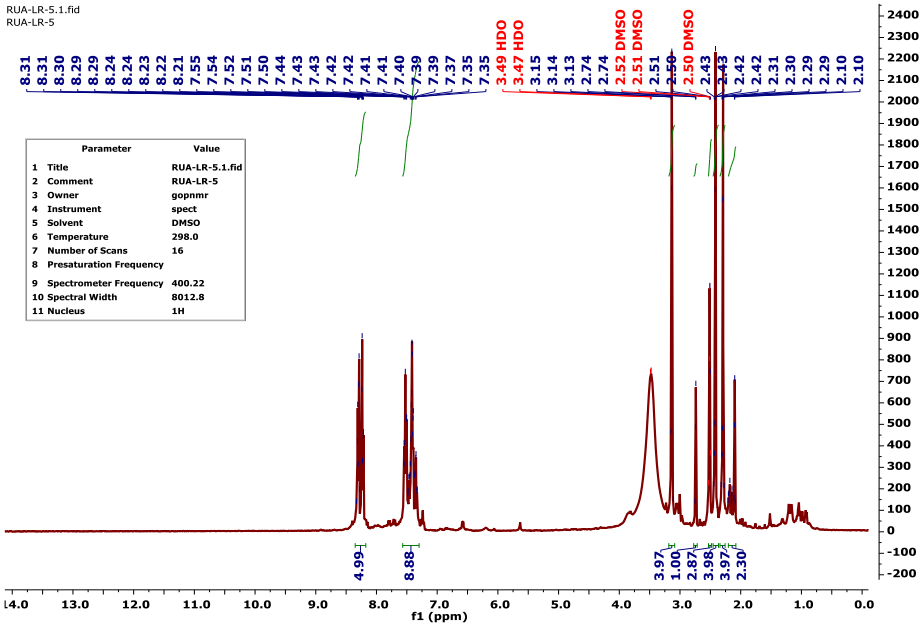


Figure 2. 1H-NMR, spectrum of the free ligan

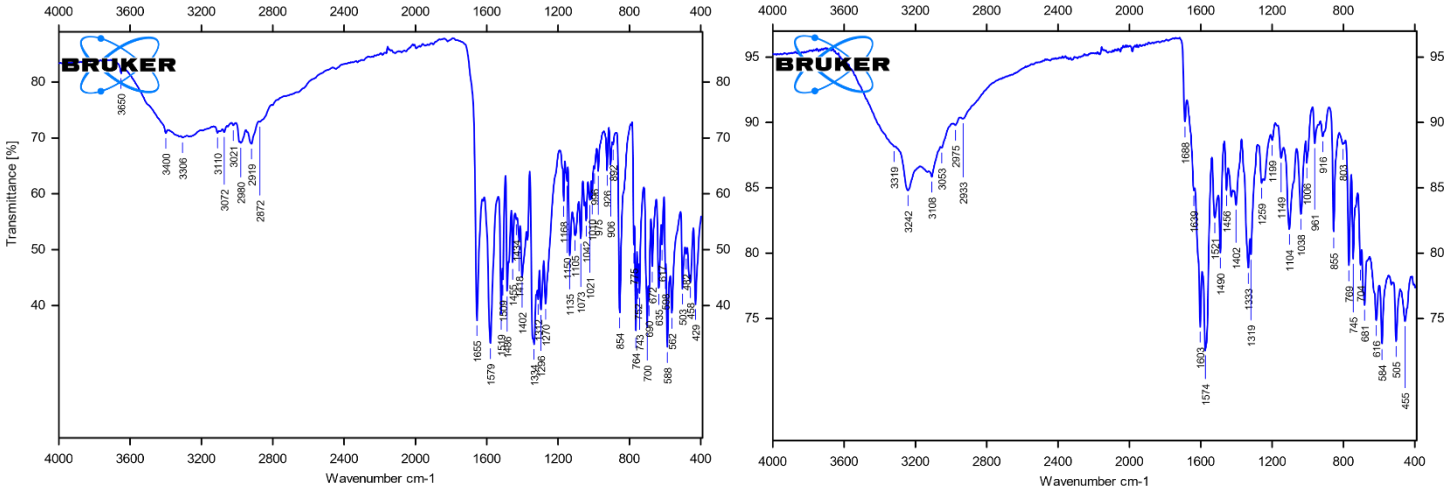


Figure 3. IR spectrum of the free ligand L and Ni (II) complex.

Table1: ^{1}H-NMR data of ligand

δ ppm	Assignment
2.10	CH_3-CH(d,3H) Threonine
2.29	CH_3-C=N(S,3H)
2.30	CH-COO (S, H) Threonine
2.74	CH_3-C (S,3H) antipyrine
3.14	CH_3-N(S,3H) antipyrine
3.47	CH_3-CH-OH (S, H) Threonine
6.75	OH-CH (d, H) Threonine
7.39-8.30	Aromatic(M,9H)

Structural characterization of the metal-ligand complexes

The complexes are soluble in DMF and DMSO at room temperature is almost complete, but insoluble in water. Table 1 presents the analytical data, physicochemical properties, and characterization techniques of the ligand and its metal complexes. Molar conductance measurements were carried out on freshly prepared DMF solutions of the complexes at a concentration of 1.0×10^{-3} M. The synthesized

complexes exhibited high molar conductivity values, indicating electrolytic behavior, with the exception of the Zn (II) complex, as summarized in Table 1.

Table 2. Physical properties UV-Vis, conductivity, magnetic, and FT-IR results

compound		$C_{23}H_{24}KN_5O_5$ (L)	[Mn (L)$(H_2O)_3$]Cl	[Co(L)(H_2O)]Cl	[Ni(L)$(H_2O)_3$]Cl	[Cu (L)(H_2O)]Cl	[Zn(L)Cl$(H_2O)_2$]
Color		Orange	Orange	Brownish	Grey	Black	Brown
M.p		133ºC	126 ºC	**123**ºC	**166**ºC	**112**ºC	**140**ºC
Yield		81%	89%	79%	90%	71%	92%
C.H.N, Found (calc.) %	**C**	56.43 (56.11)	----	49.08 (48.27)	46.14 (45.82)	48.68 (48.27)	47.03 (46.85)
	H	4.94 (5.05)	----	4.66 (4.44)	5.05 (4.74)	4.62 (4.29)	4.81 (4.53)
	N	14.31 (14.19)	----	12.44 (12.07)	11.70 (11.24)	12.34 (11.95)	11.13 (10.89)
µeff (B.M)		--		4.03	3.03	1.84	diamagnetic
Conductivity	**Ω- 1cm2mol-1**		76.1	57.7	87.9	92.4	31.5
IR spectra	**υ (OHbroad)**	---	3324	3211	3319	3291	3323
	ν (COO-asymmetric)	1486	1581	1592	1574	1593	1562
	υ (-C=N)	1655	1636	1627	1639	1644	1612
	(COO-symmetric)	1455	1418	1403	1402	1385	1424
	υ (M-O)	--	530	584	585	561	563
	υ (M-N)	---	440	455	455	432	440
	υ (C-O)	1150	1135	1104	1129	1106	1137
UV-vis. Nm	**Amax**	**266 314**	**326 312 262**	**623**	862 734 416	**866**	**359 310 235**
Stoichiometry	**M: L**	--		1:1	1:1	1:1	1:1

Antibacterial activity: The antibacterial activity of the ligand and its metal complexes was evaluated against selected Gram-positive (G^+) bacteria, Staphylococcus aureus, and Gram-negative (G^-) bacteria, Klebsiella pneumoniae. The results obtained are summarized in Table 3 and illustrated in Figure 4 and were compared with the standard drug Ciprodar. Among the synthesized complexes, the Cu (II) complex exhibited the most promising antibacterial activity against both types of bacteria and showed the highest activity overall.

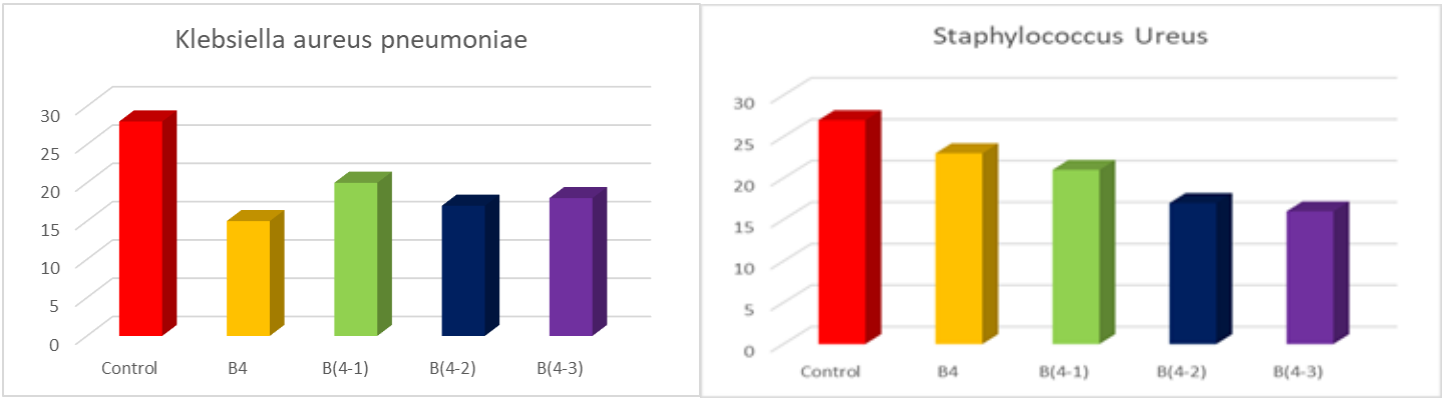


Figure 4. Antibacterial activity of compounds agents (a) Staphylococcus aureus (b) Bacillus subtilis

Table 3. Antimicrobial action of the ligands and their complexes

Symbol	Compound	Staphylococcus aurous inhibition zone (mm)	Klebsiella aureus inhibition zone (mm)
B4 (L)	$C_{23}H_{24}KN_5O_5$	23	15
B(4-2)	[Co(L)(H_2O)]Cl	17	17

B(4-3)	$[Ni(L)(H_2O)_3]Cl$	16	18
B(4-1)	$[Cu(L)(H_2O)]Cl$	21	20
Control		27	28

Conductivity Measurements and Analysis

The aqueous solutions of threonine and its Mn (II) and Ni (II) complexes were studied using conductivity measurements. Initially, the specific conductivity was measured at different temperatures in the range of 298–313 K. The equation describing the conductivity behavior of these solutions can be expressed as follows.

$$M^{+}_{aq.} + X^{-}_{aq.} \xleftrightarrow{Ka} (M^{+n}_{aq.}\ X^{-}_{aq.})$$

Ka: association constant

From this equation, it can be inferred that the chemical compounds dissociate into two ions, indicating that the solutions behave as symmetrical electrolytes of the (1:1) type, where the positive ion is denoted as M^+ and the negative ion as X^-. The equivalent conductivity of the solutions was calculated using a specialized computational program, and the Kohlrausch equation was applied to determine the type of electrolyte. After entering the conductivity data, physical parameters, temperature, and additive weights, a plot of equivalent conductivity versus √concentration was constructed. The resulting relationship indicated that the solutions behave as weak electrolytes [21].

Table 4. Equivalent conductance of Threonine in water at different temperatures

Conc. (mole/L) *10^{-6}	**$\sqrt{C}$ (mole/L) *10^{-4}**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 293 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 298 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 303 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 308 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 313 K**
5.09	7.1355	314.2407	328.9578	326.127	390.1571	**314.3524**
1.05	10.2450	166.7301	174.7823	169.4312	207.4399	**172.3110**
1.50	12.2505	123.2702	128.2703	123.2749	150.0149	**129.3708**
1.97	14.0296	99.0696	106.0132	103.7650	122.4230	**103.5794**
2.47	15.7158	83.0004	89.3230	86.1558	102.0304	**87.2631**
2.90	17.0354	74.0854	78.1429	78.3971	90.2425	**77.0455**
3.36	18.3421	66.8775	70.2250	70.4761	80.0906	**68.5370**
3.87	19.6780	60.6880	63.7907	65.7400	75.1546	**63.3496**
4.30	20.7406	58.1159	58.7654	62.7353	69.7712	**59.8511**
5.58	23.6262	47.4741	55.9251	58.4156	65.9713	**57.3238**
6.02	24.5445	45.6479	53.1848	55.3718	61.5188	**53.7645**
6.55	25.5996	43.4887	51.0559	53.9918	58.7459	**51.4660**
7.00	26.4497	42.1676	49.3873	51.4366	56.1107	**49.5223**
7.40	27.2090	41.8729	47.7073	50.1685	55.4514	**48.4161**

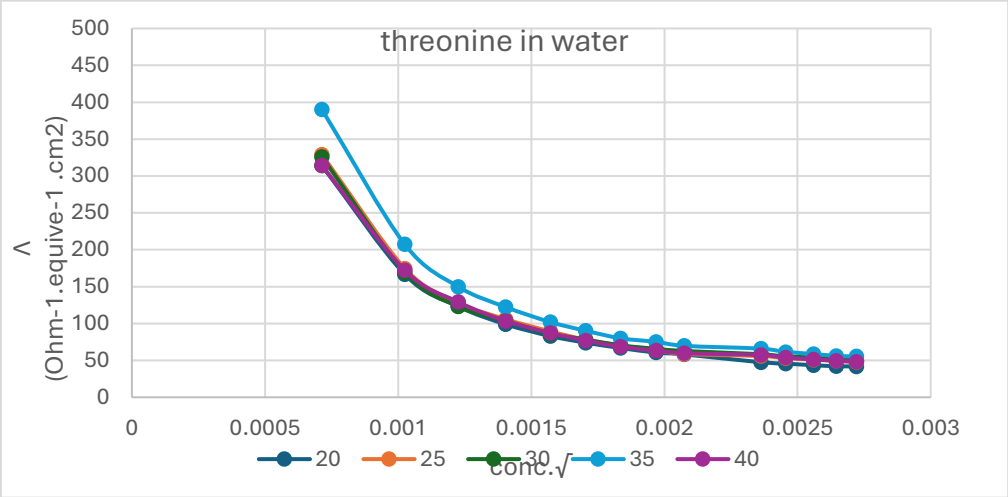


Figure 5. Equivalent conductance of Threonine in water between (298-313) °K

Table 5. Equivalent conductance of Threonine with Ni in water at different temperatures.

Conc. (mole/L) *10^{-6}	**$\sqrt{C}$ (mole/L) *10^{-4}**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 293 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 298 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 303 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 308 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 313 K**
5.11	7.14652	391.5981	324.0117	456.1091	576.5702	**336.7137**
9.55	9.7743	258.1901	230.7386	282.9428	299.8986	**238.8641**
1.46	12.1016	204.8486	201.0318	260.4101	236.589	**208.6638**
1.91	13.8168	181.5905	159.7805	213.466	207.364	**192.5307**
2.40	15.4969	169.3345	152.0739	202.371	183.6718	**176.6976**
2.90	17.0147	155.4395	151.3649	181.8929	171.7154	**168.2898**
3.37	18.3473	149.5237	143.2078	177.1073	162.8853	**156.6299**
3.81	19.5147	147.0485	137.9444	177.4319	156.6439	**151.0139**
4.28	20.6842	141.7986	140.7842	166.9411	152.816	**149.6729**
4.68	21.6331	139.5985	138.1691	158.0941	149.8165	**146.6987**
5.11	22.6016	139.6456	140.2327	158.3005	145.5117	**145.8105**
5.56	23.5734	137.3649	137.2463	153.1013	142.7191	**142.1652**
6.03	24.5624	133.1535	134.9089	151.8403	140.6934	**142.2453**
6.49	25.4772	128.3844	142.0484	153.3153	138.8526	**140.4556**

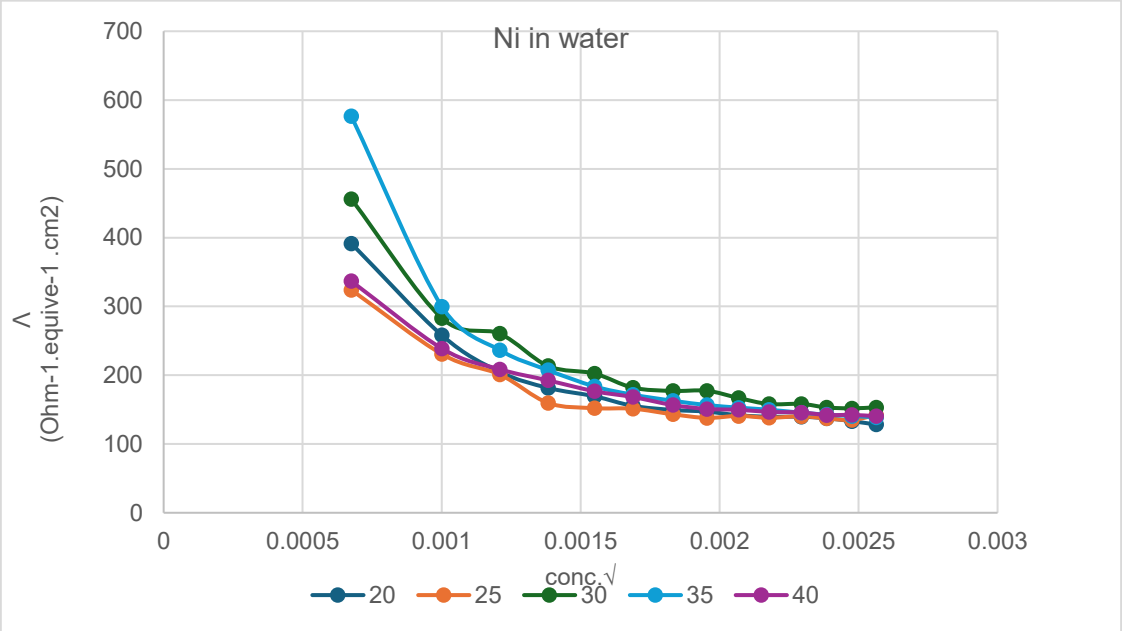


Figure 6. Equivalent conductance of Threonine with Ni in water between (298-313) °K.

Table 6. Equivalent conductance of Threonine with Mn in water at different temperatures

Conc. (mole/L) *10^{-6}	**$\sqrt{C}$ (mole/L) *10^{-4}**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 293 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 298 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 303 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 308 K**	**Λ ($Ohm^{-1}.equive^{-1}.cm^2$) 313 K**
4.56	6.7509	358.3835	334.6505	349.1668	403.8162	**442.5788**
1.00	10.0070	229.6763	194.6511	248.1561	259.3996	**226.4687**
1.46	12.0896	177.8871	168.3822	200.324	211.2954	**198.3719**
1.91	13.8251	155.213	155.8766	172.2474	178.4738	**181.0042**
2.40	15.5011	137.3372	137.2793	158.8793	157.2401	**164.1899**
2.85	16.8750	129.931	128.6068	146.274	149.5459	**151.6017**
3.35	18.3146	126.208	120.3624	142.7731	142.0932	**144.5499**
3.82	19.5358	119.6562	118.8381	136.426	132.6323	**137.4225**
4.28	20.6793	113.8047	114.6869	132.4989	129.4755	**132.9412**
4.74	21.7762	112.4685	111.5094	133.7806	136.8017	**129.9127**
5.26	22.9324	114.0905	111.2898	134.4612	132.918	**125.4838**
5.69	23.8478	110.7755	110.7858	127.354	125.7813	**123.7732**
6.13	24.7561	106.0594	109.5676	131.3934	126.5649	**119.6305**
6.57	25.6305	105.035	108.5494	124.8592	124.0197	**115.7447**

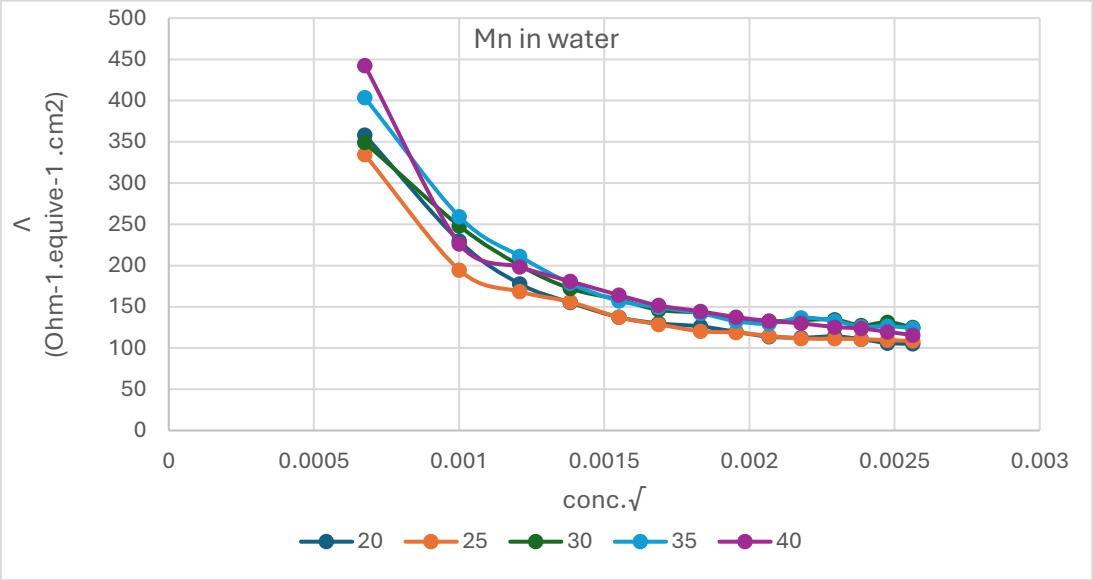


Figure 7. Equivalent conductance of Threonine with Mn in water between (298-313) °K.

The Lee–Wheaton equation was employed for a comprehensive analysis of symmetrical electrolytes at different temperatures [25]. The equivalent conductivity was calculated using a specialized computational program after measuring the electrical conductivity of all studied solutions at a fixed cell constant (1 cm^{-1}). The collected data, including concentration and equivalent conductivity values, were analyzed using dedicated software after inputting the absolute temperature (T), viscosity, density, and dielectric constant of the solutions. Upon completion of the data analysis, the values of the association constant (K_a), equivalent conductance (Λ), the distance parameter (R), and the standard deviation of the best fit, $\sigma_s(\Lambda)$ were obtained. Tables 7-9 present the results of this analysis at different temperatures.

Table 7. the values of Ka, Λ, R(A°) and σΛ of threonine at different temperatures in water

T(K)	Ka	Λ_o	R (Å)	δΛ
293	9827111.5	932.2	1	0.597
298	9872137.3	557.7	1	0.615
303	12522518	1473.7	1	0.572
308	8072009.4	928	1	0.817
313	10912452	941.61	1	0.61

Table 8. the values of Ka, Λ, R(A°) and σΛ of Ni at different temperatures in water

T(K)	Ka	Λ_o	R (Å)	δΛ
293	9312177	932.2	2	0.132
298	3295921	557.7	2	0.117
303	19506026	1473.7	2	0.093
308	6382042	928	2	0.335
313	9539022	941.61	2	0.047

Table 9. The values of Ka, Λ, R(A°) and σΛ of Mn at different temperatures in water

T(K)	Ka	Λ_o	R (Å)	δΛ
293	8972113	812.72	2	0.136
298	9555102	760	2	0.127
303	7934123	838	2	0.106
308	7005858	822.69	2	0.181
313	3219750	610.17	2	0.291

The results for the distance parameter (R) indicate that the complex electrolytes in solution form separated ion pairs. The relatively high values of R suggest that the cations and anions are separated by multiple solvent molecules, and that the degree of association increases with rising temperature. The values of σΛ confirm a good fit of the experimental data [26]. The relationship between ln K_a and 1/T, plotted according to the van't Hoff equation [27], was used to calculate the enthalpy change (ΔH) for the electrolyte dissociation process.

$$\ln Ka = -\frac{\Delta H}{RT} + C$$

The relation gives a straight line for solutions, and ΔG from the equation:

$$\Delta G = -R\,T\ln Ka$$

ΔS values were calculated from the equation:

$$\Delta G = \Delta H - T\,\Delta S$$

Tables 10 show the results.

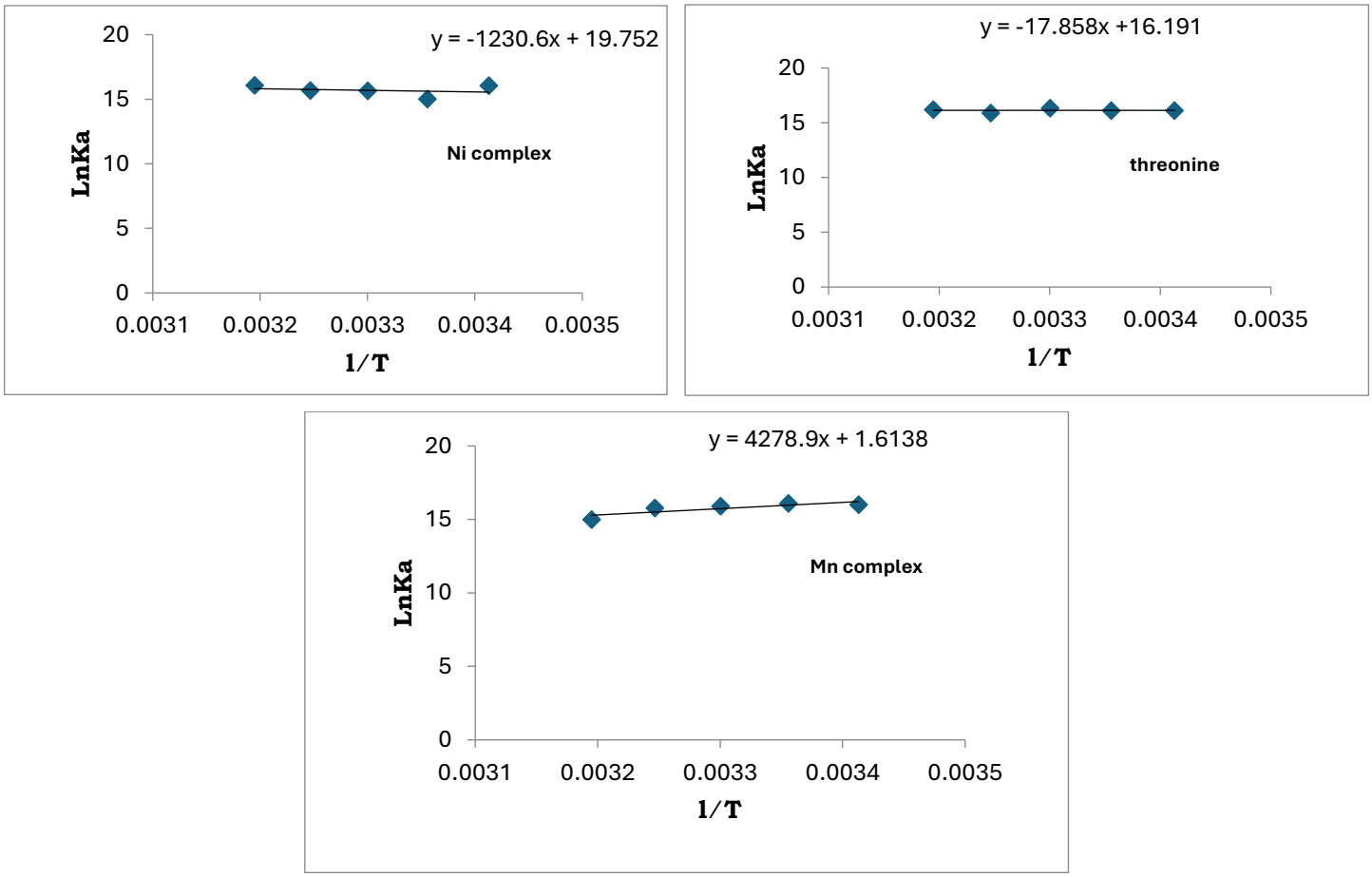


Figure 8. The relation between the Ln ka &1/T of threonine, Ni & Mn complex in water

Table 10. The values of ΔS, ΔG, ΔH, and(1/T) of threonine, Ni & Mn complex at different temperatures in water

		threonine				Ni				Mn			
T (K)	(1/T) (K^{-1})	ΔS J.mol^{-1} K^{-1}	ΔG KJ.mol^{-1}	ΔH KJ.mol^{-1}	LnKa	ΔS J.mol^{-1} K^{-1}	ΔG KJ.mol^{-1}	ΔH KJ.mol^{-1}	LnKa	ΔS J.mol^{-1} K^{-1}	ΔG KJ.mol^{-1}	ΔH KJ.mol^{-1}	LnKa
293	0.003413	134.4	-39.22	149.652	16.1	170.3	-39.09	10.806	16.05	121.6	-39.00	355.76	16.01
298	0.003356	134.4	-39.90		16.11	161	-37.18		15.01	119.5	-39.82		16.07

303	0.0033	136.4	-41.17	16.34	175.2	-42.28	16.79	117.5	-40.02	15.89
308	0.003247	132.7	-40.72	15.9	165.4	-40.12	15.67	115.6	-40.36	15.76
313	0.003195	135.2	-42.17	16.21	168.1	-41.82	16.07	113.8	-38.99	14.98

ΔG (Gibbs free energy) had negative values which means that the reaction was spontaneous towards the association. The ΔH value is positive, indicating that the dissociation of ions was endothermic and the values of ΔS were positive (increased the random with accept some temperature) [28].

Conclusion

A new Schiff base ligand was synthesized via the condensation of 4-aminoantipyrine with 4-nitroacetophenone and the amino acid threonine. Subsequently, metal complexes were prepared with Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) ions. The ligand and its complexes were characterized using various techniques, including C.H.N. elemental analysis, FT-IR, UV-Vis, and ^{1}H NMR spectroscopy. The structural analysis revealed that the complexes adopt two types of geometries: tetrahedral and octahedral. The ligand exhibited tridentate behavior, coordinating to the metal ions through the N atom of antipyrine and the N and O atoms of threonine.

The biological activity of the ligand and its complexes was evaluated against S. aureus and K. pneumoniae, with the Cu (II) complex showing the most promising antibacterial activity against both bacterial strains. A thermodynamic study of some of the complexes indicated that ΔG is negative, confirming that the reactions are spontaneous, ΔH is positive, indicating endothermic ion dissociation, and ΔS is positive, suggesting an increase in randomness with rising temperature.

Conflict of Interest

The authors declare no conflict of interest.

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