

## Potentiometric, Thermodynamics and DFT Calculations of Some Metal(II)-Schiff Base Complexes Formed in Solution.

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Formation constants of the complexes formed in solution from reaction between a ligand named [(3E,3'E)-3,3'-(ethane-1,2-diylbis(azanylylidene))bis(N-(pyridin-2-yl)butanamide)] (EDAP) and chloride salts of Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> were estimated in 50 % DMSO-water solution at different temperatures. The stability order for the complexes greatly agree with Irving-Williams stability order that is Zn<sup>2+</sup> < Cu<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup>. The concentration distributions of the various complex species in solution were estimated as a function of pH using speciation computer program. The temperature effect as well as the thermodynamic parameters were also reported for the free EDAP ligand and M(II) Schiff base complexes. DFT method has been utilized to obtain geometrically optimized structures for the studied complexes. The theoretical calculations were in agreement with the calculated values of stability constants.

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**Keywords:** Schiff base; Protonation; DFT; Copper(II) complexes, Potentiometry.

### 1. INTRODUCTION

Protonation constant is crucial physical and chemical parameter in the chemistry of drug, enzymes and spectrophotometric applications. In the field of drug design, there is a strong relationship between protonation constants and the properties of drug as solubility, lipophilicity, acidity, alkalinity, permeability and transport behavior. In the chemistry of enzymes, it gives good data about the stereochemistry of active site in the enzyme. Moreover, in spectrophotometry, it is a suitable tool to determine the concentration of each species and the suitable pH for the reaction [1-9]. Potentiometry is considered as a crucial method utilized in determination of protonation constants because of its wide applicability and reliability [10-12].

The formation of chelate molecule is important from theoretical, analytical and synthetic point of view. The chelate formation requires certain favorable structural features. Schiff bases and their complexes intensively investigated due to their versatile medical applications including remarkably antituberculosis [13], antibacterial [14,15], antitumor [16,17], antifungal [15,18], antimalarial [19] and anti-inflammatory [20,21]. The coordination properties of Schiff base ligands and the possible various biological activities of their metal complexes recently paid great attention from researchers however, limited research has been done for protonation and complex formation equilibria of Schiff bases and their metal complexes.

However, to understand the activities of the Schiff bases and their complexes, it is important to have a complete picture about the thermodynamics and solution equilibria involved in the reactions. The stability constant gives an idea about the extent of bonding between the bonding atoms in a ligand and metal ion. Also, the concentration of a complex in solution can be predicted on the basis of the stability constants. Thus, keeping the above facts in mind and in continuation of our research program [22-32] directed to study ligands of biological significance and their complexes, we have synthesized a Schiff base; (3*E*,3'*E*)-3,3'-(ethane-1,2-diylbis(azanylylidene))bis(N-(pyridin-2-yl)butanamide), EDAP (Scheme 1) and carried out a systematic study on its interactions with some bivalent transition metals at ionic strength 0.1 M NaNO<sub>3</sub> at temperatures 20, 25, 30 and 35 °C in DMSO-water media using potentiometric technique. In the present work, the protonation constants of (EDAP) Schiff base ligand, the temperature effects, thermodynamics, the formation constants and the computational studies of metal complexes were reported.

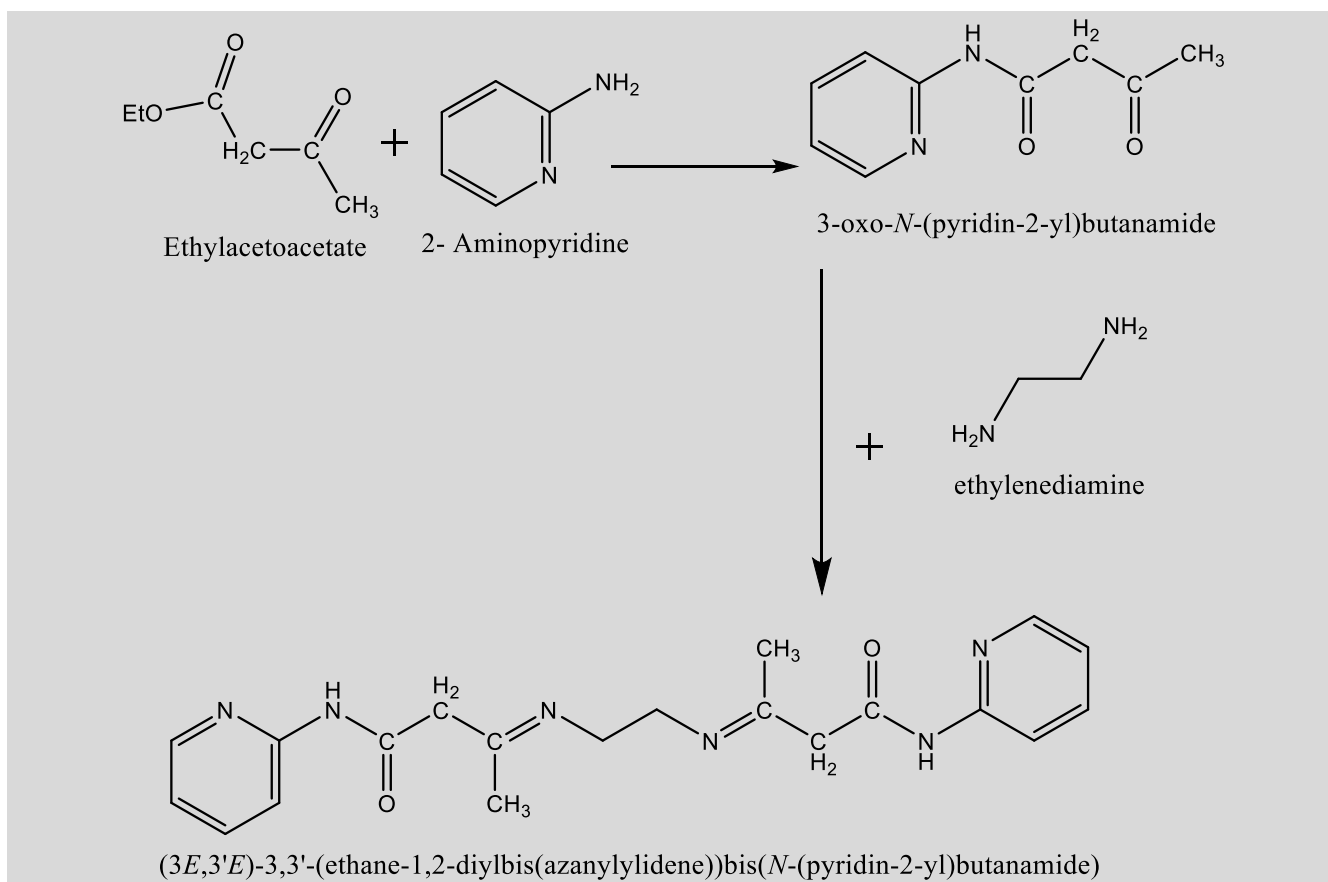
## 2. EXPERIMENTAL

### 2.1. Chemicals and reagents

The chemical reagents such as HNO<sub>3</sub>, NaOH and NaNO<sub>3</sub> were purchased from BDH and used without ultra-purification. Hydrated CuCl<sub>2</sub> (≥ 99.99 %), CoCl<sub>2</sub> (98 %) and NiCl<sub>2</sub> (99.9 %) as well as anhydrous ZnCl<sub>2</sub> (≥ 99 %) salts were purchased from Sigma-Aldrich Chemicals Company. Ethylenediamine (98%), 2-aminopyridine (98%), ethylacetoacetate, xylene and DMSO were provided by Aldrich Chemicals Company.

### 2.2. Synthesis of (EDAP) ligand

The (EDAP) ligand [(3*E*,3'*E*)-3,3'-(ethane-1,2-diylbis(azanylylidene))bis(N-(pyridin-2-yl)butanamide)] was prepared as described previously [33] (Scheme 1).



**Scheme 1.** Synthesis of EDAP Schiff base ligand

### 2.3. Instrumentation

A Metrohm 848 Titrino supplied with a Dosimat unit (Switzerland-Herisau) have been utilized for potentiometric titrations. The Metrohm device consists of different connected units as thermostatted glass-cell, a magnetic stirring, a glass electrode, a thermometric probe, a microburet delivery tube as well as a salt bridge connected with the reference cell and filled with 0.1 M KCl solution in which saturated calomel electrode was dipped. A thermostated water bath unit is used to maintain cell temperature during titration. Due to the low solubility of the synthesized Schiff base compound and its possible hydrolysis in aqueous solution all samples were prepared in 50 % water-DMSO mixture.

### 2.4. Potentiometric titrations

The protonation constants of the ligand and the formation constant of complex were estimated by potentiometric technique using the method that described previously in literature [25]. The standard buffer solutions have been utilized to calibrate accurately the glass electrode according to NBS specifications. Buffer solutions are potassium hydrogen phthalate (pH = 4.008) and a mixture of [KH<sub>2</sub>PO<sub>4</sub> + Na<sub>2</sub>HPO<sub>4</sub> (pH = 6.865)] at 25.0 °C [11]. All samples were titrated in presence of nitrogen atmosphere using a standard solution of 0.05 M NaOH free from CO<sub>2</sub>. NaOH solution was accurately standardized by standard potassium hydrogen phthalate solution. Stock solutions of metal salts were

prepared and standardized by EDTA solution [34]. The sample solution prepared by mixing equal volumes of DMSO and water to avoid hydrolysis of ligand during titration. Moreover, the ionic strength was kept constant during titration using  $\text{NaNO}_3$  as supporting electrolyte.

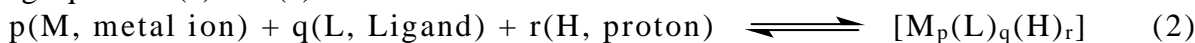
As known, the calculated formation constants using potentiometric method have been carried out using concentration of hydrogen ion expressed in molarity. However, the concentration in pH-meter have been expressed in activity coefficient  $-\log a_{\text{H}^+}$  (pH). Therefore, Van Uitert and Hass equation (Eq. 1). This equation was used to convert the pH-meter readings (B) to  $[\text{H}^+]$  [35, 36].

$$-\log_{10} [\text{H}^+] = B + \log_{10} U_H \quad (1)$$

Where  $\log_{10} U_H$  is the correction factor for the solvent composition and ionic strength for which B is read.  $\text{pK}_w$  Values for titrated samples were estimated as described previously [37]. All precautions and procedures follow the literature conditions [38- 40].

The protonation constants of the (EDAP) ligand were estimated potentiometrically by titrating ( $40 \text{ cm}^3$ ) of ( $1.25 \times 10^{-3} \text{ M}$ ) ligand solution with standard sodium hydroxide solution. The formation constants of the metal (II) complexes were estimated by titration ( $40 \text{ cm}^3$ ) of  $[\text{MCl}_2 \cdot n\text{H}_2\text{O}]$  ( $1.25 \times 10^{-3} \text{ M}$ ) + (EDAP) ( $1.25 \times 10^{-3} \text{ M} / 2.5 \times 10^{-3} \text{ M}$ ).

The equilibrium constants which were calculated from the titration data according to the following equations (2) and (3).



$$\beta_{pqr} = \frac{[\text{M}_p(\text{L})_q(\text{H})_r]}{[\text{M}]^p [\text{L}]^q [\text{H}]^r} \quad (3)$$

## 2.5. Data Processing

The MINQUAD-75 computer program has been used to calculate ca. 100 reading for each titration [41]. The SPECIES program [42] has been utilized to give the species distribution diagrams for the studied samples.

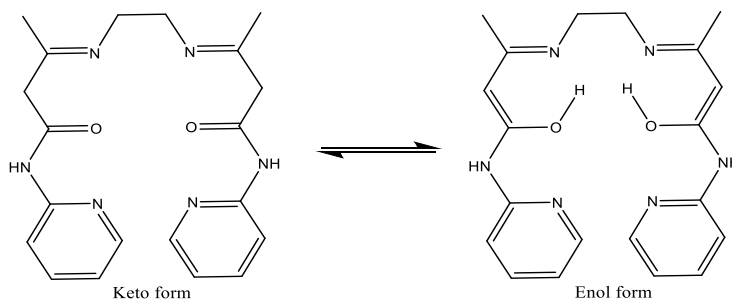
## 2.6. Computational studies

DFT calculations were performed using DMOL<sup>3</sup> program [43-45] in Materials Studio package [46]. DFT semi-core pseudopotentials calculations (dspp) were done with the double numerical basis sets as well as polarization functional (DNP) [47]. The RPBE functional is based on the generalized gradient approximation (GGA) as best correlation functional [48, 49].

# 3. RESULTS AND DISCUSSION

## 3.1. Protonation constants of EDAP Schiff base ligand

The proton dissociation constants ( $\log K^{\text{H}}$ ) of the ligand have been used for the calculation the formation constant of the Schiff base complexes. Moreover, the Schiff base ligand shows high flexibility to coordinate to the metal ion in the two tautomer keto-enol forms (Scheme 2).



**Scheme 2.** Keto-enol tautomerism of EDAP ligand

The proton dissociation of enolic OH group occurs in so far strongly basic conditions, that is outside of the practical pH range of the methodology and so it couldn't be practically attained.

**Table 1.** Protonation constants of EDAP-Schiff base in DMSO-H<sub>2</sub>O (v/v) at different temperatures and I = 0.1 M.

System	T(°C)	q	r <sup>a</sup>	log <sub>10</sub> β <sup>b</sup>	S <sup>c</sup>	log K <sub>N-Py</sub>	log K <sub>N-imino</sub>
EDAP	20	1	1	7.03±0.04	3.1 E-7	7.03	4.51
		1	2	11.54±0.07			
	25	1	1	6.92±0.05	1.2 E-6	6.92	4.45
		1	2	11.37±0.08			
	30	1	1	6.83±0.04	2.5E-7	6.83	4.39
		1	2	11.22±0.06			
35	1	1	6.73±0.05	2.9E-7	6.73	4.33	
	1	2	11.06±0.07				

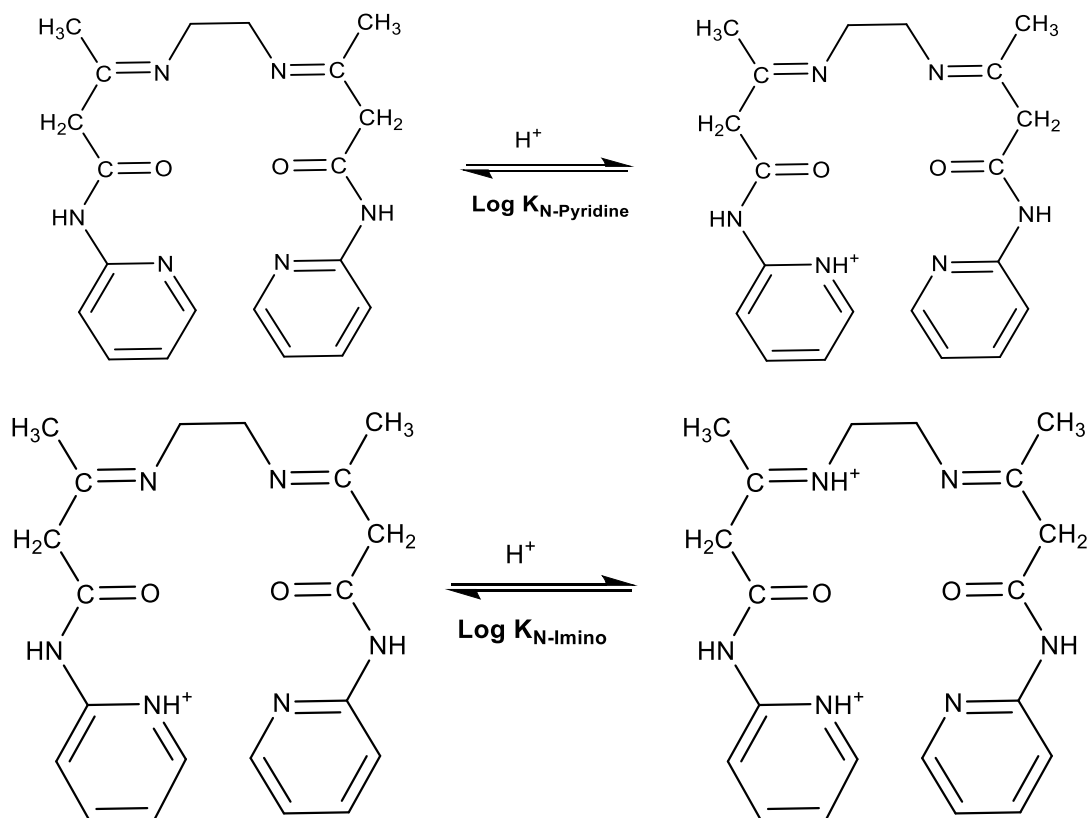
<sup>a</sup> q and r are stoichiometric coefficients corresponding to EDAP ligand and H<sup>+</sup> respectively

<sup>b</sup> Standard deviations are given in parentheses, <sup>c</sup> Sum of squares of residuals

pK<sub>i</sub> values for EDAP ligand are listed in (Table 1). This Schiff base acts as diprotic acid as shown in (Scheme 3) and the two protonation constants for EDAP Schiff base ligand are calculated according to Eqs. 4 and 5.

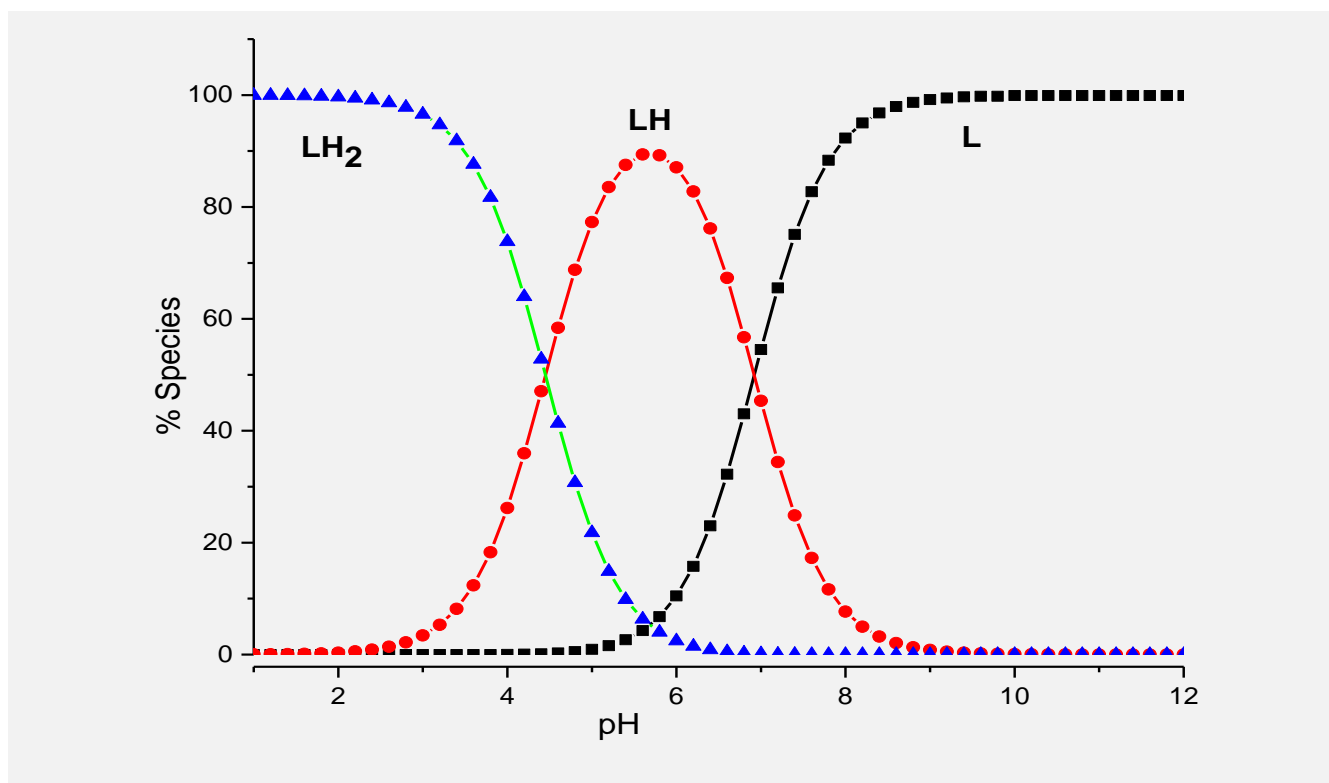


The log<sub>10</sub>K<sub>1</sub> value is associated to the protonation of the (N-Pyridine) site and log<sub>10</sub>K<sub>2</sub> value corresponds to the protonation of the (N-imino) site in EDAP ligand.



**Scheme 3.** Protonation equilibria of EDAP ligand

The study of protonation equilibria for the Schiff base ligand under study cannot be performed in aqueous solution because it is insoluble in water. DMSO solvent has been widely used for potentiometric studies of both protonation and formation equilibria. The mixture DMSO-water 50 %:50 % was best chosen solvent to give soluble and stable Schiff base solution. The use of these mixed solvents has some advantages over pure DMSO that are:- (i) pure DMSO is very hygroscopic and controlling its water content is difficult [50] which in turn would extensively affect reproducibility of our experiment. (ii) However, a mixture of 50%:50% DMSO-water has only small hygroscopic nature. (iii) A further advantage of this type of mixed solvents is its compatibility with the standard glass electrode, so that the pH measurements may be performed in a similar way to that employed in a purely aqueous solution. In contrast, the use of pure DMSO is not favourable to potentiometry. (iv) Another advantage of the DMSO-water mixture is its large acidity range ( $pK_w = 15.52 \pm 0.1$ ) [38,51] which allows studying the deprotonation equilibria of weak acids which could be hardly studied in pure water [50, 52].



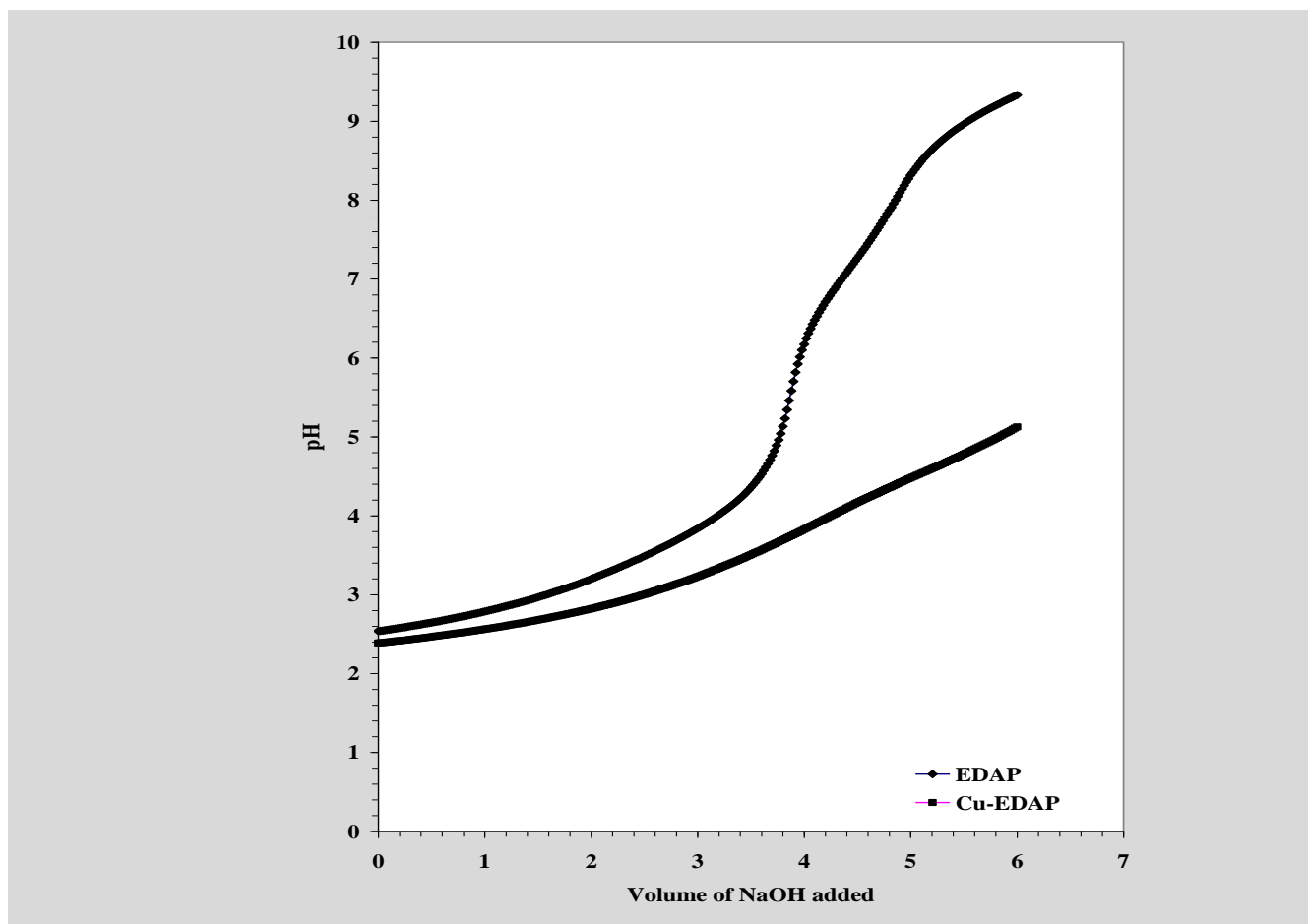
**Figure 1.** Concentration distribution diagram of various species as a function of pH in the EDAP system (EDAP = 1.25 M, T = 25 °C, I = 0.1 M).

Herein, two protonation constants were calculated for EDAP ligand and the SPECIES program was utilized to give the distribution of EDAP ligand species as a function of pH (Fig.1). The species distribution graph is a good tool for obtaining complete picture about the concentration of each species present as a function of pH. It enables us to obtain the best conditions for preparation a solid complex as pH, concentration and ligand:metal ratio. At low pH, (EDAP) exists initially in a fully protonated form with maximum percent of 100% as  $H_2L$  below  $pH < 2$ . On addition of base, pH value increases so the ( $H_2L^{2+}$ ) species loses its first proton from an imino group to form ( $HL^+$ ), which is the predominant species at  $pH = 5.6$ . As conditions become more alkaline, the second proton released from protonated pyridine ring begins deprotonation to the free ligand (L) reaching a maximum percent of 99.8 % at  $pH = 9.6$ . The  $\log K_{N-imino}$  values ranges from (4.45-4.51) is similar to that found in literature for the imino group (4.40) [53-55]. In addition, the  $\log K_{N-pyridine}$  values ranges from (6.72-7.03) is similar to that found in literature for the pyridine moiety (6.37-7.10) [56-59].

### 3.2. Stability constants of the Schiff base complexes

The formation constants of M(II)-Schiff base complexes in DMSO-water mixture were computed using the Miniquad-75 program. It was found that the pH titration curves of all complexes were situated at lower than that of the free Schiff base ligand curve as they required more alkali to have the same pH as the free Schiff base. The protons of the protonated complexes can be easily replaced by

metal ion and this enhances formation of complex. The potentiometric titration curve of Cu<sup>(II)</sup>-Schiff base complex as a representative example was given in (Fig. 2).



**Figure 2.** Potentiometric titration curve of the Cu-EDAP system (Cu-EDAP = 1.25 M, T = 25 °C, I = 0.1 M).

The stoichiometric stability constants of M(II)-complexes of the investigated Schiff base ligand at different temperatures are listed in (Table 2). The data recorded in (Table 2) demonstrate the formation of the metal complexes with stoichiometric coefficients 110 and 111.

The  $pK_a$  values of the protonated complex has been computed using Eq. 6 [60,61].

$$pK_a = \log \beta_{111} - \log \beta_{110} \quad (6)$$

The obtained  $pK_a$  value for the Schiff base ligand is in accord with of pyridine ring (6.92). As mentioned above, the lower value (5.61) for the Cu-complex than the free ligand (6.92) owe to acidification upon complexation. For example, the  $pK_a$  value Cu(II) complex diminishes to 5.61 by 1.31 pH difference from 6.92 of free ligand.



**Table 2.** Stability constants of M(II)-EDAP-Schiff base in DMSO-water at different temperatures and I = 0.1 M.

System	T (°C)	p	q	r	log <sub>10</sub> β	S
Cu-EDAP	20	1	1	0	6.27±0.04	7.2E-7
		1	1	1	11.96±0.06	
	25	1	1	0	6.19±0.05	5.6E-7
		1	1	1	11.79±0.06	
	30	1	1	0	6.10±0.04	1.1E-7
		1	1	1	11.62±0.08	
35	1	1	0	6.01±0.04	6.4E-7	
	1	1	1	11.46±0.08		
Ni-EDAP	20	1	1	0	5.83±0.06	5.5E-7
		1	1	1	11.12±0.09	
	25	1	1	0	5.75±0.05	7.4E-7
		1	1	1	10.97±0.07	
	30	1	1	0	5.67±0.04	1.6E-7
		1	1	1	10.81±0.08	
35	1	1	0	5.59±0.04	6.2E-7	
	1	1	1	10.66±0.08		
Co-EDAP	20	1	1	0	5.66±0.04	3.1E-7
		1	1	1	10.9±0.06	
	25	1	1	0	5.61±0.03	4.9E-7
		1	1	1	10.8±0.07	
	30	1	1	0	5.55±0.05	2.5E-7
		1	1	1	10.69±0.06	
35	1	1	0	5.49±0.05	3.9E-7	
	1	1	1	10.57±0.06		
Zn-EDAP	20	1	1	0	4.7±0.04	5.1E-7
		1	1	1	10.85±0.08	
	25	1	1	0	4.66±0.06	2.9E-7
		1	1	1	10.78±0.09	
	30	1	1	0	4.60±0.05	8.2E-7
		1	1	1	10.65±0.08	
35	1	1	0	4.55±0.05	4.5E-7	
	1	1	1	10.56±0.08		

Definitions of stability constants:

$$K_{110} = K_{ML} = [ML] / [M][L];$$

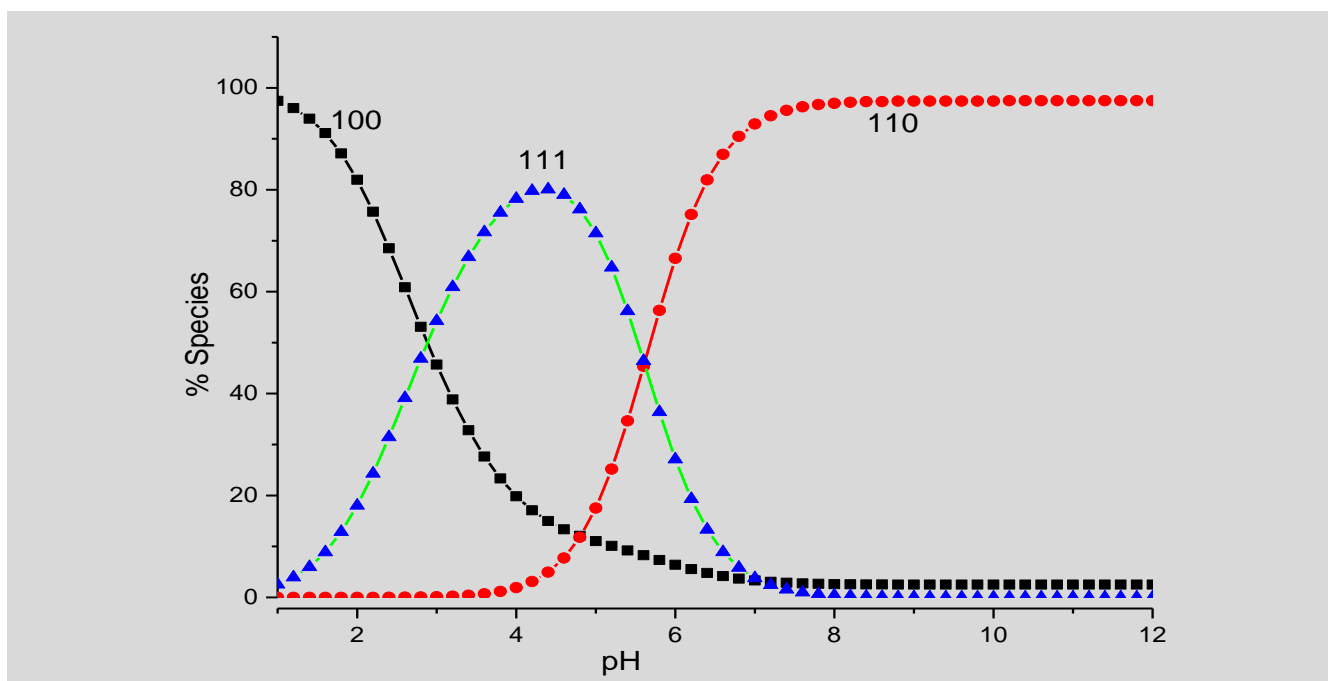
$$K_{111} = K_{MHL} = [MHL] / [ML][H]$$

(L = Schiff base ligand); (Charges are omitted for simplicity).

<sup>a</sup> p, q and r are stoichiometric coefficients corresponding to metal(II), EDAP ligand and H<sup>+</sup> respectively

<sup>b</sup> Standard deviations are given in parentheses

<sup>c</sup> Sum of squares of residuals

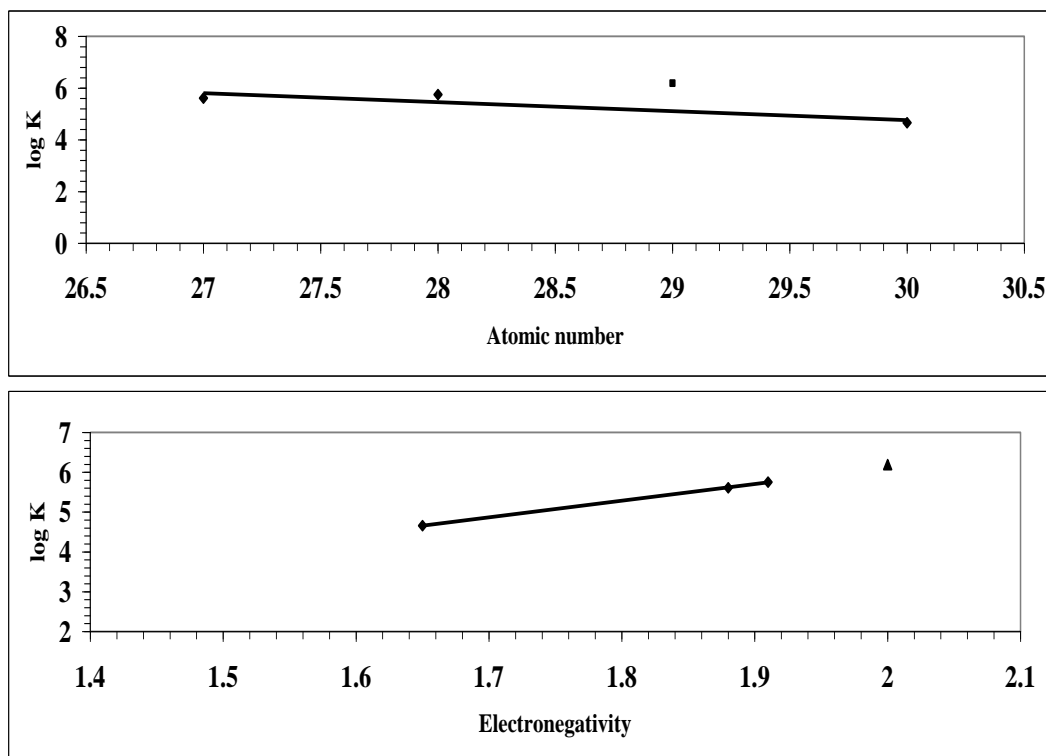


**Figure 3.** Concentration distribution diagram of various species as a function of pH in the Cu-EDAP system (EDAP = 1.25 M, T = 25 °C, I = 0.1 M).

According to the species distribution diagram for Cu-EDAP system (Fig. 3), Copper(II) ions coordinate easily with EDAP molecules forming two different pH species, the deprotonated (Cu-EDAP) and protonated (Cu-HEDAP) species. The later species is formed with 80% at pH = 4.4 while as the former deprotonated species reach to 97% at pH = 7.8.

### 3.3. The relationship between the properties of central metal ion and stability of complexes

Preferential binding of a ligand to one metal instead of another metal is somewhat depends on the relationship between the stability constants of metal complexes and the properties of the metal ions, such as the atomic number, ionic radius, ionization potential as well as electronegativity [62]. In this study, the stability constants of the Schiff base complexes agree with Irving-Williams' order [51,63] where,  $Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$ . Moreover, there was nearly linear relation between the reciprocal of ionic radii ( $1/r$ ) as well as electronegativity of the studied metals and  $\log_{10}K_{ML}$  (Fig. 4). The increase in the electronegativity of metal ions will reduce the electronegativity difference between the bonding atoms in a complex and this enhances the covalent character and consequently the stability of complexes increases.



**Figure 4.** Effect of metal ion properties on the stability constants of metal complexes

Therefore, the formation constant of the  $\text{Cu}^{2+}$  complex becomes larger as compared to the other ones where,  $\log K_{[\text{Cu}(\text{EDAP})]} = 6.19 > \log K_{[\text{Ni}(\text{EDAP})]} = 5.75 > \log K_{[\text{Co}(\text{EDAP})]} = 5.66 > \log K_{[\text{Zn}(\text{EDAP})]} = 4.7$ . Furthermore, the ligand field had given  $\text{Cu}^{2+}$  additional stability due to tetragonal distortion of the octahedral symmetry by the well-known Jahn-Teller effect [64-68]. Additionally, decreasing the charge density on the central metal ion would decrease the electrostatic attraction between coordinating atoms leading to a subsequent decrease in the stability of complexes.

### 3.4. Thermodynamics of solution equilibria

The degree of protonation of a ligand and its complexes is temperature dependent therefore, thermodynamic parameters have been calculated using Eq. 7 and the data given in Table 3 and represented in Figs (5-9).

From Tables 3 and 4, the following remarks have been noticed (I) the negative sign of  $\Delta G$  indicates the exothermic behavior of the protonation reaction of the ligand. (II) Often, at the same pH of titration, the color of the complex solution differs from that of free ligand.

$$\text{Log}_{10} K = - \Delta H / (2.303R) 1/T + \Delta S / (2.303R) \quad (7)$$

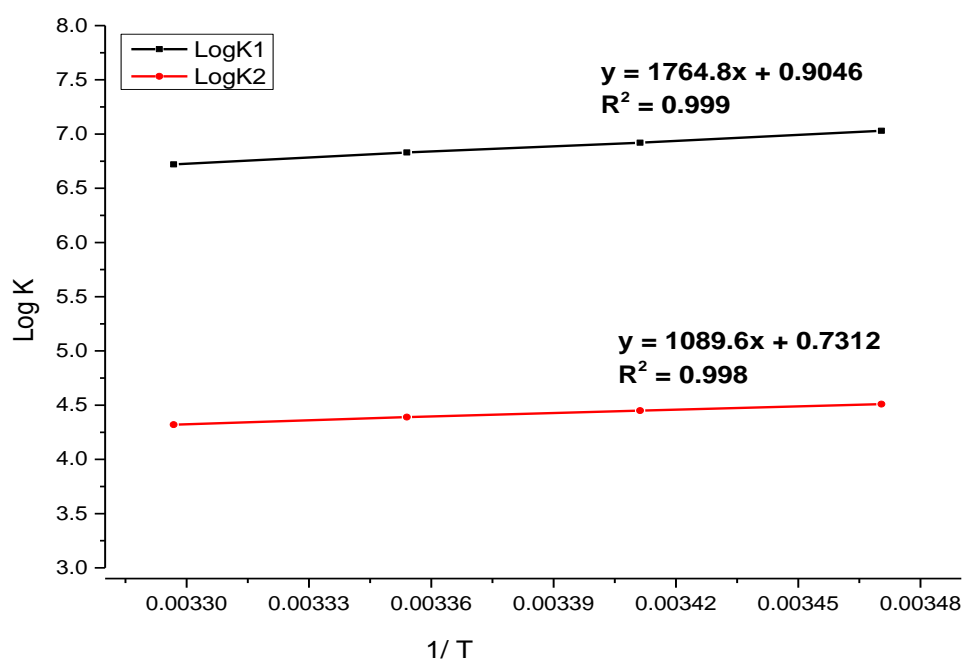
**Table 3.** Stepwise stability constants for ML and MHL complexes of EDAP-Schiff base ligand in DMSO-water mixtures and I = 0.1 M at different temperatures.

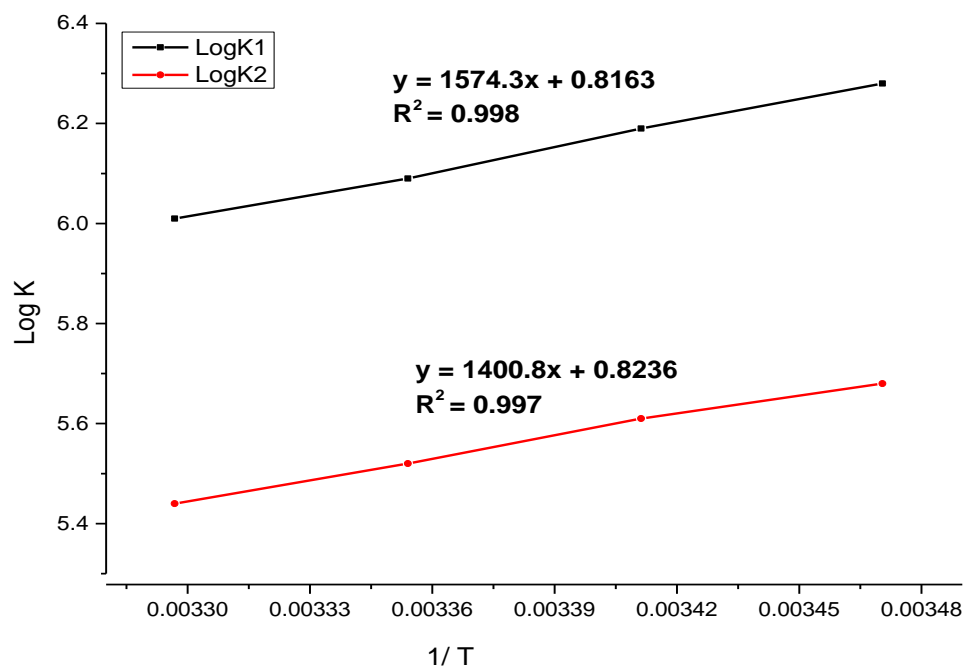
$M^{n+}$	20 °C		25 °C		30 °C		35 °C	
	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>1</sub>	logK <sub>1</sub>	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>1</sub>	logK <sub>2</sub>
Zn <sup>2+</sup>	4.71	6.15	4.66	6.12	4.60	6.05	4.55	6.01
Co <sup>2+</sup>	5.66	5.24	5.61	5.19	5.55	5.14	5.49	5.08
Ni <sup>2+</sup>	5.83	5.29	5.75	5.22	5.69	5.14	5.58	5.07
Cu <sup>2+</sup>	6.27	5.69	6.19	5.60	6.10	5.52	6.01	5.45

$\log K_1 = \log K_{110} = \log [ML] / [M][L]$ ;  $\log K_2 = \log K_{111} = \log [MHL] / [ML][H]$

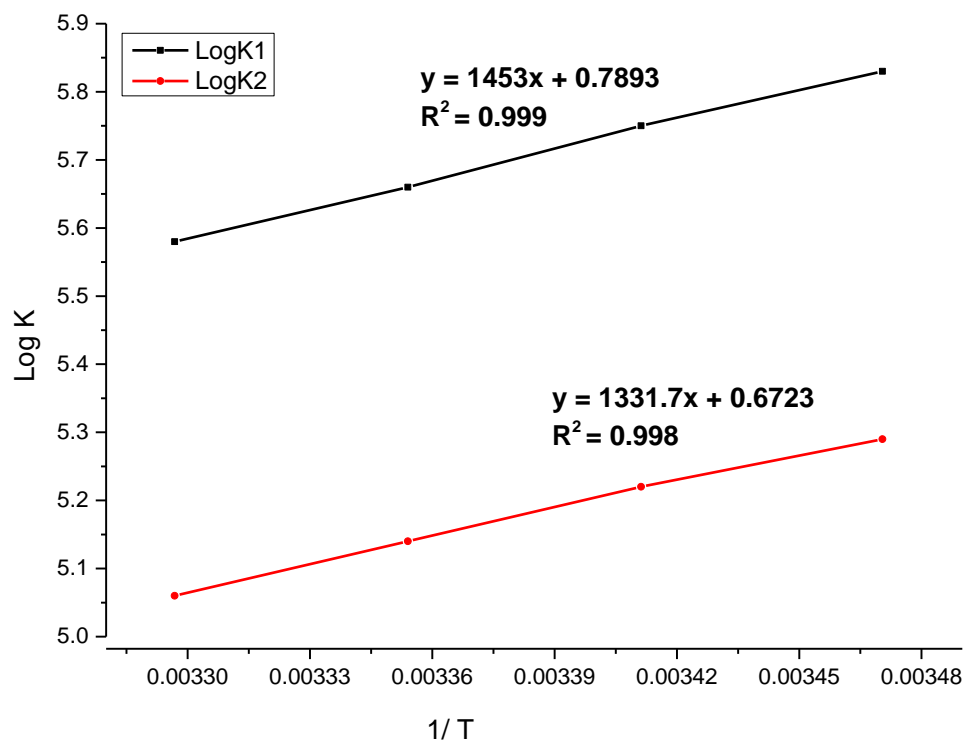
**Table 4.** Thermodynamics for the association of EDAP Schiff base ligand in 50% DMSO-50% H<sub>2</sub>O(v/v).

System	$\Delta H^\circ$ (kJmol <sup>-1</sup> )	$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\circ$ (kJmol <sup>-1</sup> )
EDAP			
$L^- + H^+ \rightleftharpoons LH$	-34.3	17.7	-39.5
$HL + H^+ \rightleftharpoons H_2L^+$	-20.8	15.6	-25.4

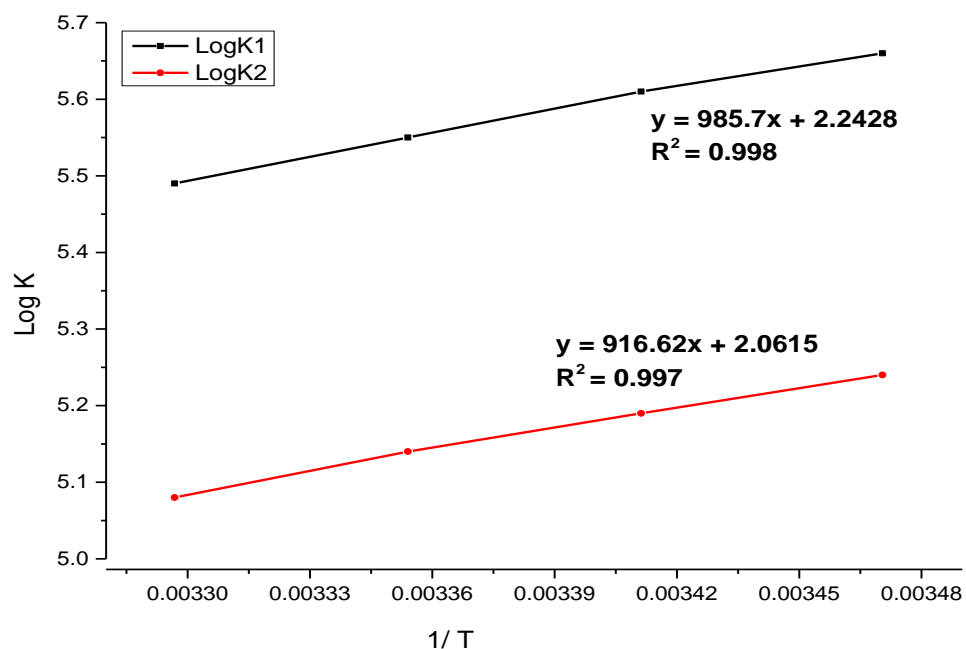
**Figure 5.** Effect of temperature on the protonation constants (log K<sub>1</sub> and log K<sub>2</sub>) of EDAP Schiff base ligand (EDAP = 1.25 M, T = 25 °C, I = 0.1 M).



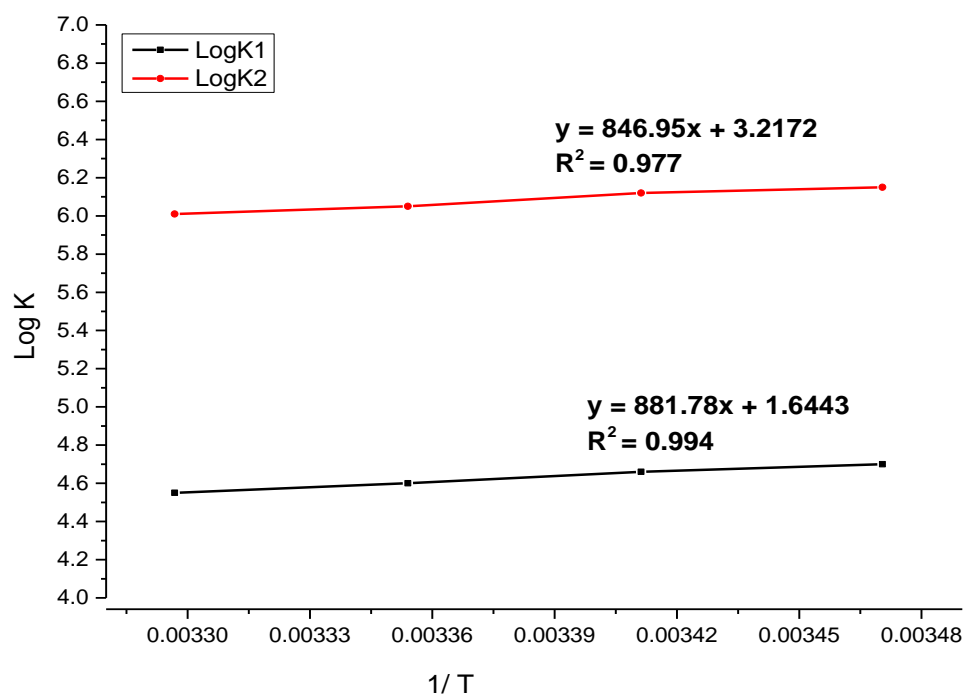
**Figure 6.** Effect of temperature on the formation constants of Cu(II)-EDAP complexes (Cu-EDAP = 1.25 M, T = 25 °C, I = 0.1 M).



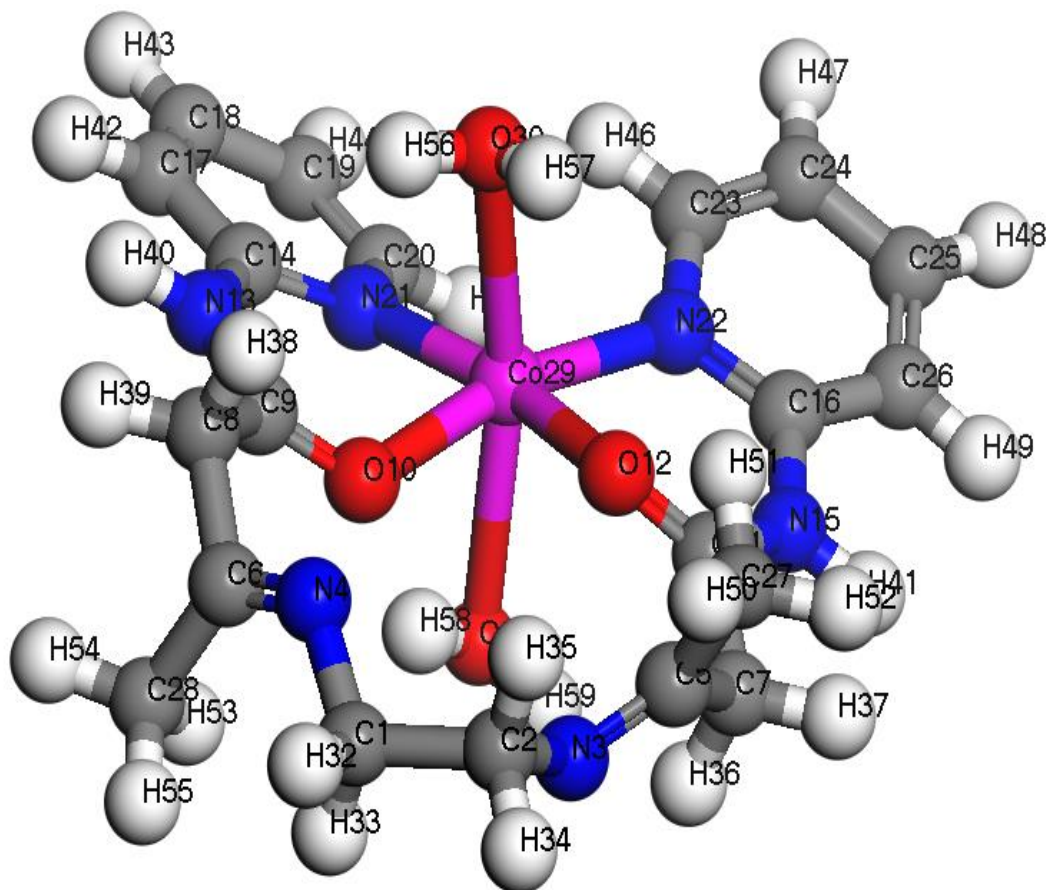
**Figure 7.** Effect of temperature on the formation constants of Ni(II)-EDAP complexes (Ni-EDAP = 1.25 M, T = 25 °C, I = 0.1 M).



**Figure 8.** Effect of temperature on the formation constants of Co(II)–EDAP complexes (Co-EDAP = 1.25 M, T = 25 °C, I = 0.1 M).



**Figure 9.** Effect of temperature on the formation constants of Zn(II)–EDAP complexes (Zn-EDAP = 1.25 M, T = 25 °C, I = 0.1 M).

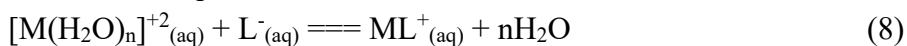


**Figure 10.** The molecular structure of Co-EDAP complex along with the atom numbering scheme.

The stability constants of the metal complexes have been computed at different temperatures and the following remarks have been summarized as follow:

- a) Values of formation constant decrease with rising of temperatures, suggesting that the complex formation is exothermic process and this is also agree with the (-ve) values of ( $\Delta H$ ).
- b) As it is known, the divalent metal ions are surrounded by six water molecules in an octahedral symmetry [68]. Therefore, the obtained values of entropy and enthalpy are probably the sum of the contributions of both bond broken and bond formation reactions.
- c) Inspection of the data reveals that M(II)-complexes (ML) as well as the protonated complexes (MHL) are formed in 1:1 molar ratio while 1:2 complexes ( $ML_2$ ) were not observed. This may owe to the steric effect of the second bulky ligand which prevents formation of the (1:2) complex species.
- d) At constant temperature, the stability order of the Schiff base complexes obeys the stability order of the binary complexes as well as Irving–Williams order [69–71].
- e) The spontaneous process of the complex formation reactions is demonstrated by the negative sign of ( $\Delta G$ ).
- f) According to the data recorded in Table 5, the abnormal higher (+ve) values of  $\Delta S$  for all the metal complexes demonstrate that the reactions are entropically favorable and this is in agreement with the principal suggesting that displacement of water molecules (bond breaking) by coordinated

ligand [72-76] increase in the number of particles liberated in solution and hence the randomness of the system as shown in Eq. 8.



**Table 5.** Thermodynamic functions for ML and MHL complexes of EDAP Schiff base in DMSO-water mixture and I = 0.1 M.

M <sup>n+</sup>	T/K	Gibbs energy/kJ.mol <sup>-1</sup>		Enthalpy/kJ.mol <sup>-1</sup>		Entropy/J.mol <sup>-1</sup> .K <sup>-1</sup>	
		$\Delta G_1$	$\Delta G_2$	$\Delta H_1$	$\Delta H_2$	$\Delta S_1$	$\Delta S_2$
Zn <sup>2+</sup>	293	-26.4	-34.5	-18.7	-16.9	26.4	59.9
	298	-26.6	-34.9				
	303	-26.7	-35.1				
	308	-26.9	-35.5				
Co <sup>2+</sup>	293	-31.2	-28.9	-19.7	-18.3	41.2	37.7
	298	-31.5	-29.1				
	303	-31.7	-29.3				
	308	-31.9	-29.5				
Ni <sup>2+</sup>	293	-32.7	-29.6	-27.7	-25.6	17.3	14.0
	298	-32.8	-29.7				
	303	-32.9	-29.8				
	308	-33.0	-29.9				
Cu <sup>2+</sup>	293	-35.2	-31.9	-30.1	-27.7	17.5	14.4
	298	-35.3	-32.0				
	303	-35.4	-32.1				
	308	-35.5	-32.2				

### 3.5. The relationship between the ionic strength and the protonation constants of Schiff base.

The ionic strength of the solution (I) is given by Eq. 9

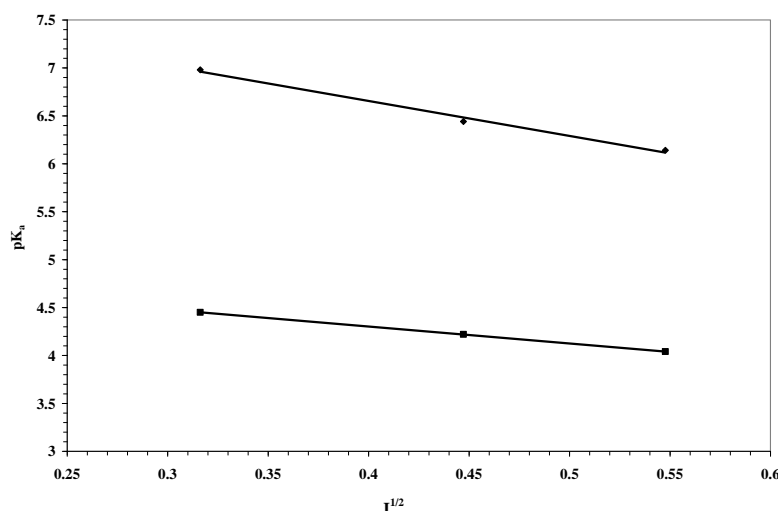
$$I = 1/2 \sum Z_i^2 M_i \quad (9)$$

Where, M<sub>i</sub> is the molar concentration of the ions and Z<sub>i</sub> is the charge of an ion. The relation between ionic strength and the activity coefficients of the ions in solution is given by Eq. 10.

$$\log \gamma_{\pm} = -\alpha Z_+ |Z_-| I^{1/2} \quad (10)$$

Where  $\gamma_{\pm}$  is the activity coefficient of cations and anions,  $\alpha$  is the degree of dissociation, and  $Z_+|Z_-|$  is the positive product of the cations and anions. At very low concentration the value of  $\gamma_{\pm} \approx 1$  and therefore the ions behave independently. At higher concentrations, the value of  $\gamma_{\pm} \neq 1$  and the oppositely charged ions attract each other [70].





**Figure 11.** Plot of  $\log_{10}K$  versus  $I^{1/2}$  at 25 °C (EDAP = 1.25 M,  $I = 0.1, 0.2$  and  $0.3$  M,  $r = 0.98-0.99$ ).

So, the ionic strength of different solution affects the protonation behavior of ligand at constant temperature. In this study, the protonation constants of the Schiff base ligand (EDAP) have been estimated at different ionic strengths ( $I = 0.10, 0.20$  and  $0.30$  M) using  $\text{NaNO}_3$  as supporting electrolyte at 25 °C.

**Table 7.** Protonation constants of EDAP-Schiff base at 25 °C at different ionic strengths of  $\text{NaNO}_3$ .

System	$\log K \pm \sigma^a$	$\log K \pm \sigma^a$	$\log K \pm \sigma^a$
	$I = 0.10$ M	$I = 0.20$ M	$I = 0.30$ M
1) $L + H^+ \rightleftharpoons HL^+$	$6.98 \pm 0.05$	$6.64 \pm 0.07$	$6.14 \pm 0.04$
2) $HL^+ + H^+ \rightleftharpoons H_2L^{2+}$	$4.45 \pm 0.08$	$4.22 \pm 0.06$	$4.04 \pm 0.03$

<sup>a</sup>Standard deviation

The data reported in Table 7 shows that decreasing ionic strength of solution by dilution would increase the protonation constant of the Schiff base ligand which in a good agreement with Debye-Hückel equation [71]. For all systems, there is a linear relationship between the values of  $\log_{10}K$  and the square root of ( $I$ ) Fig. 11. The values of correlation coefficients for the calculated values ranges from 0.98-0.99.

### 3.6. Molecular computational calculation

Optimization of the metal(II) complexes was done to get the most stable structure formed in solution. Computational parameters include the energies of gas phase, frontier molecular orbitals ( $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ), electronegativity ( $\chi$ ), energy band gap ( $\Delta E$ ) which explains the probable charge transfer

interaction within the molecule, global hardness ( $\eta$ ), chemical potential ( $\mu$ ), global electrophilicity index ( $\omega$ ) and global softness ( $S$ ) [77-81] are listed in Table 6.

$$\begin{aligned}\chi \text{ (electronegativity)} &= -\frac{1}{2} (E_{LUMO} + E_{HOMO}) \\ \mu \text{ (potential)} &= -\chi = \frac{1}{2} (E_{LUMO} + E_{HOMO}) \\ \eta \text{ (hardness)} &= \frac{1}{2} (E_{LUMO} - E_{HOMO}) \\ S \text{ (softness)} &= \frac{1}{2} \eta \\ \omega \text{ (electrophilicity)} &= \frac{\mu^2}{2\eta}\end{aligned}$$

To understand the mode of chelation and stability of these complexes in solution, DFT method was used to give the most stable geometry of metal complexes and the energy parameters have been calculated for all these complexes to correlate the experimental values with the theoretical parameters obtained from computational calculations for all compounds.

The molecular structure along with atom numbering scheme of Co-EDAP complex as a representative example are represented in Fig.10 (Table 1S). From the analysis of the data calculated for the bond lengths and angles ( $\text{\AA}$ ), one can conclude the following:

In most of the cases, the actual bond lengths and bond angles are relatively close to the optimal values, and thus the proposed geometry of the complex is acceptable. The energies of both HOMO ( $\pi$  donor) and LUMO ( $\pi$  acceptor) are main parameters in quantum chemical studies. Where, HOMO is the orbital that acts as an electron donor, LUMO is the orbital that act as the electron acceptor and these molecular orbitals are known as the frontier molecular orbitals (FMOs). The HOMO–LUMO band gap is a good indication for the compound stability [82,83]. As HOMO–LUMO band gap increases the stability of compound increases accordingly and the chemical reactivity decreases. The values of band gap for the complexes have descending order as follow:

Cu-EDAP ( $\Delta E = 2.43$ ) > Ni-EDAP ( $\Delta E = 0.51$ ) > Co-EDAP ( $\Delta E = 0.29$ ) > Zn-EDAP ( $\Delta E = 0.17$ ). The significant higher value of Cu-EDAP complex ( $\Delta E = 2.43$ ) is agree with the obtained values compared to that of other complexes.

The higher values of hardness ( $\eta$ ) would attain a molecule higher stability according to the principle of hardness [84]. The global hardness ( $\eta$ ) has been calculated for the Metal complexes and was found to follow this sequence; Cu-EDAP ( $\eta = 0.61$ ) > Ni-EDAP ( $\eta = 0.13$ ) > Co-EDAP ( $\eta = 0.07$ ) > Zn-EDAP ( $\eta = 0.04$ ) which also supports the experimental results.

**Table 6.** Some quantum chemical parameters of the M(II)-EDAP complexes.

Compound	-E <sub>H</sub> (eV)	-E <sub>L</sub> (eV)	ΔE (eV)	X (eV)	μ (eV)	η (eV)	S (eV) <sup>-1</sup>	ω (eV)	σ (eV) <sup>-1</sup>
<b>Cu-EDAP</b>	4.39	1.96	2.43	3.17	-3.17	0.61	0.30	8.29	1.65
<b>Ni-EDAP</b>	2.43	1.92	0.51	2.17	-2.17	0.13	0.06	18.45	7.83
<b>Co-EDAP</b>	1.82	1.53	0.29	1.68	-1.68	0.07	0.03	19.55	13.89
<b>Zn-EDAP</b>	1.89	1.71	0.17	1.80	-1.80	0.04	0.02	37.32	22.99

## 5. CONCLUSIONS

Complex formation constant of some bivalent metal ions with EDAP Schiff base ligand were studied in 50 % DMSO-H<sub>2</sub>O mixture. As well known, quantitative data obtained from the protonation and stability constants of EDAP ligand and its M(II) complexes contributes greatly by its active groups as (C=O), (C=N<sub>pyridine</sub>) and (C=N<sub>azomethine</sub>) in the biological systems. From our point of view, the data collected from this study would help researchers to understand the acid-base behavior as well as the chemical factors of Schiff base s in the common DMSO-water mixtures which are involved in more complicated biological processes. The protonation and complexation reactions are exothermic and spontaneous. Four factors affecting the stability of complexes in solution i) hardness and softness of the coordinating species; ii) size of the metal ions; iii) Basic character of the ligands and iv) Reaction temperature. DFT methods were used to have good data about the most optimum geometry and energy parameters to support the experimental results for complexes.

## SUPPLEMENTARY DATA:

**Table 1S.** Selected bond angles (°) and bond length (Å) of Co-EDAP using DFT-method.

Bond	Actual angles (°)	optimum angles (°)	Bond	Actual Length(Å)	Optimum Length(Å)
H(55)-C(28)-H(54)	107.826	109	C(6)-C(28)	1.521	1.497
H(55)-C(28)-C(6)	112.112	110	C(5)-C(27)	1.519	1.497
H(54)-C(28)-H(53)	107.7	109	C(26)-C(16)	1.406	1.42
H(54)-C(28)-C(6)	112.881	110	C(25)-C(26)	1.4	1.42
H(53)-C(28)-C(6)	109.66	110	C(24)-C(25)	1.424	1.42
H(52)-C(27)-H(51)	108.207	109	C(23)-C(24)	1.383	1.42
H(52)-C(27)-H(50)	108.224	109	N(22)-C(23)	1.388	1.358
H(52)-C(27)-C(5)	114.023	110	C(16)-N(22)	1.391	1.358
H(51)-C(27)-C(5)	109.646	110	N(21)-C(14)	1.389	1.358
H(50)-C(27)-C(5)	109.626	110	C(20)-N(21)	1.387	1.358
H(49)-C(26)-C(25)	120.931	120	C(19)-C(20)	1.384	1.42

H(49)-C(26)-C(16)	118.722	120	C(18)-C(19)	1.42	1.42
H(48)-C(25)-C(26)	120.547	120	C(17)-C(18)	1.398	1.42
H(48)-C(25)-C(24)	121.845	120	C(14)-C(17)	1.411	1.42
H(47)-C(24)-C(25)	121.606	120	N(15)-C(16)	1.403	1.345
H(47)-C(24)-C(23)	119.12	120	C(11)-N(15)	1.375	1.369
H(46)-C(23)-C(24)	120.898	120	N(13)-C(14)	1.398	1.345
H(46)-C(23)-N(22)	114.795	116.5	C(9)-N(13)	1.384	1.369
C(24)-C(23)-N(22)	124.257	123.5	C(11)-O(12)	1.278	1.208
H(45)-C(20)-N(21)	115.396	116.5	C(7)-C(11)	1.514	1.509
H(45)-C(20)-C(19)	119.926	120	C(9)-O(10)	1.287	1.208
N(21)-C(20)-C(19)	124.671	123.5	C(8)-C(9)	1.522	1.509
H(44)-C(19)-C(20)	119.437	120	C(6)-C(8)	1.535	1.497
H(44)-C(19)-C(18)	121.252	120	C(5)-C(7)	1.537	1.497
H(43)-C(18)-C(19)	122.056	120	N(4)-C(6)	1.299	1.26
H(43)-C(18)-C(17)	120.458	120	N(3)-C(5)	1.293	1.26
H(42)-C(17)-C(18)	121.097	120	C(2)-N(3)	1.471	1.47
H(42)-C(17)-C(14)	118.382	120	C(1)-C(2)	1.539	1.523
C(26)-C(16)-N(22)	122.5	120	C(1)-N(4)	1.465	1.47
C(26)-C(16)-N(15)	117.226	120	C(1)-H(32)	1.107	1.113
N(22)-C(16)-N(15)	120.155	120	C(1)-H(33)	1.103	1.113
H(41)-N(15)-C(16)	113.466	110	O(31)-H(59)	0.975	0.942
H(41)-N(15)-C(11)	114.952	117.4	O(31)-H(58)	0.975	0.942
N(21)-C(14)-C(17)	122.562	120	O(30)-H(57)	0.976	0.942
N(21)-C(14)-N(13)	120.82	120	O(30)-H(56)	0.972	0.942
C(17)-C(14)-N(13)	116.617	120	C(28)-H(55)	1.1	1.113
H(40)-N(13)-C(14)	112.942	110	C(28)-H(54)	1.096	1.113
H(40)-N(13)-C(9)	114.404	117.4	C(28)-H(53)	1.104	1.113
N(15)-C(11)-O(12)	123.665	122.6	C(27)-H(52)	1.095	1.113
N(15)-C(11)-C(7)	115.642	114	C(27)-H(51)	1.102	1.113
O(12)-C(11)-C(7)	120.665	122.5	C(27)-H(50)	1.104	1.113
N(13)-C(9)-O(10)	123.239	122.6	C(26)-H(49)	1.092	1.1
N(13)-C(9)-C(8)	114.641	114	C(25)-H(48)	1.089	1.1
O(10)-C(9)-C(8)	121.913	122.5	C(24)-H(47)	1.087	1.1
H(39)-C(8)-H(38)	108.291	109.4	C(23)-H(46)	1.088	1.1
H(39)-C(8)-C(9)	109.954	108.8	C(20)-H(45)	1.085	1.1
H(39)-C(8)-C(6)	110.692	109.41	C(19)-H(44)	1.089	1.1
H(38)-C(8)-C(9)	109.087	108.8	C(18)-H(43)	1.09	1.1
H(38)-C(8)-C(6)	109.293	109.41	C(17)-H(42)	1.09	1.1
C(9)-C(8)-C(6)	109.493	110.2	N(15)-H(41)	1.019	1.012
H(37)-C(7)-H(36)	106.199	109.4	N(13)-H(40)	1.018	1.012
H(37)-C(7)-C(11)	106.765	108.8	C(8)-H(39)	1.104	1.113
H(37)-C(7)-C(5)	108.425	109.41	C(8)-H(38)	1.097	1.113
H(36)-C(7)-C(11)	110.263	108.8	C(7)-H(37)	1.1	1.113
H(36)-C(7)-C(5)	107.866	109.41	C(7)-H(36)	1.102	1.113
C(11)-C(7)-C(5)	116.816	110.2	C(2)-H(35)	1.104	1.113

C(28)-C(6)-C(8)	116.013	117.2	C(2)-H(34)	1.101	1.113
C(28)-C(6)-N(4)	127.169	115.1			
C(8)-C(6)-N(4)	116.785	115.1			
C(27)-C(5)-C(7)	113.628	117.2			
C(27)-C(5)-N(3)	128.471	115.1			
C(7)-C(5)-N(3)	117.861	115.1			
C(6)-N(4)-C(1)	120.838	108			
C(5)-N(3)-C(2)	119.944	108			
H(35)-C(2)-H(34)	106.807	109.4			
H(35)-C(2)-C(1)	107.934	109.41			
H(34)-C(2)-C(1)	108.039	109.41			
H(33)-C(1)-H(32)	107.057	109.4			
H(33)-C(1)-C(2)	108.736	109.41			
H(32)-C(1)-C(2)	107.966	109.41			

#### 4. ABBREVIATIONS

EDAP: [(3E,3'E)-3,3'-(ethane-1,2-diylbis(azanylylidene))bis(N-(pyridin-2-yl)butanamide)]

DMSO: Dimethyl sulphoxide

Cu-EDAP: Copper(II) complex

Zn-EDAP: Zinc(II) complex

Ni-EDAP: Nickel(II) complex

Co-EDAP: Cobalt(II) complex

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