

## Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes with New Tetraaza Schiff Base Ligands: Synthesis, Characterization and Thermodynamic Studies

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New complexes of Co(II), Ni(II), Cu(II) and Zn(II) with four new tetraaza Schiff base ligands, N,N'-bis(2-quinolylmethylidene)-1,2-ethanediimino ( $L^1$ ), N,N'-bis(2-quinolylmethylidene)-1,2-propanediimino ( $L^2$ ), N,N'-bis(2-quinolylmethylidene)-1,3-propanediimino ( $L^3$ ), N,N'-bis(2-quinolylmethylidene)-4-nitro-1,2-phenylenediimine ( $L^4$ ), were synthesized and characterized by elemental analysis, IR,  $^1\text{H}$  NMR, and UV-Vis spectroscopy. The thermodynamic formation constants of the complexes were measured spectrophotometrically, at the constant ionic strength 0.1 M ( $\text{NaClO}_4$ ), at 25 °C in MeOH solvent. The trend of the complex formation of a given metal ion with the ligands was found to be as follows  $L^2 > L^1 > L^3 > L^4$  and the trend of a given ligand with the metal ions was  $\text{Co(II)} > \text{Ni(II)} > \text{Cu(II)} > \text{Zn(II)}$ .

**Keywords:** Complexes, Formation constants, Thermodynamic parameters, Tetraaza Schiff base

### INTRODUCTION

Quinoline derivatives represent the major class of heterocyclics, and a number of preparations have been known since the late 1980s [1]. Quinolines are very important compounds due to their pharmacological properties which include wide applications in medicinal chemistry notably antimaterial drugs, anti-inflammatory agents, antiasthmatic, antibacterial, antihypertensive and tyrosine kinase inhibiting agents [2]. In addition, quinolines have been used for the preparation of nano and mesostructures with enhanced electronic and photonic properties [3,4]. The chemistry of multidentate Schiff base ligands with quinoline moieties and their complexes has been a fascinating area of research, though tetraazamacrocycles are the most extensively studied, due to their biological relevance [5].

The imino macrocyclic ligands have been derived from condensation reaction between dicarbonyls and primary

diamines. A dramatic development in the chemistry of tetraazamacrocyclic complexes has received particular attention due to their mimicry with biologically significant molecules invoking a variety of catalytic, biochemical and industrial applications [6,7]. The interactions of aromatic moieties are known to form charge transfer complexes with a variety of guests, which provide new insights into non-covalent interactions, chiefly cation- $\pi$  interactions which led to the stabilization of a positive charge by the face of an aromatic ring [8].

Schiff bases and their structural analogues, as ligating compounds containing acyclic and cyclic imine  $\text{C}=\text{N}$  bonds, are of great importance in modern coordination chemistry [9,10]. Among them, we note luminescent complexes [11] and liquid crystal [12] chemosensors [13]. Bioinorganics and biomimetics, containing a  $\text{C}=\text{N}$  bond, are widely represented [14,15]. In ion-pair extractive separation of metal cations using a neutral chelation reagent and a counter anion, the selection of the chelation reagent is the most important factor to facilitate the separation process. Moreover, investigation of

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the effect of steric structure around electron donor atoms in the reagent on the separation ability is very important for the development of novel reagents having high separation performance [16]. Schiff base ligands have gained importance because of the physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordinating metal ions given complexes which serve as models for biological systems [17].

As an extension of our previous work on Schiff base ligands and their complexes with transition metals, now we report the synthesis and spectroscopic properties of some new tetraaza Schiff base ligands with quinoline moieties and their nickel(II), copper(II), cobalt(II) and zinc(II) complexes. The compounds were characterized by elemental analysis, IR, NMR and UV-Vis techniques. The formation constant,  $K_f$ , and the free energy,  $\Delta G^\circ$ , at 25 °C for the complexes were determined spectrophotometrically. The electronic and steric effects of the linear and cyclic amines on the Schiff base type ligand upon the formation constant and the free energy of the complexes formed was studied.

## EXPERIMENTAL

### Materials

The materials used were 2-quinolinecarboxaldehyde, 4-nitro-1,2-phenylenediamine, ethylenediamine, 1,3-diaminopropane, 1,2-diaminopropane, methanol, ethanol, acetonitrile, toluene, chloroform, copper chloride tetrahydrate, nickel chloride tetrahydrate, cobalt chloride tetrahydrate and zinc chloride tetrahydrate all of which were commercially obtained from either Merck or Fluka and used without further purification. Spectrograde solvents were used for spectral measurements.

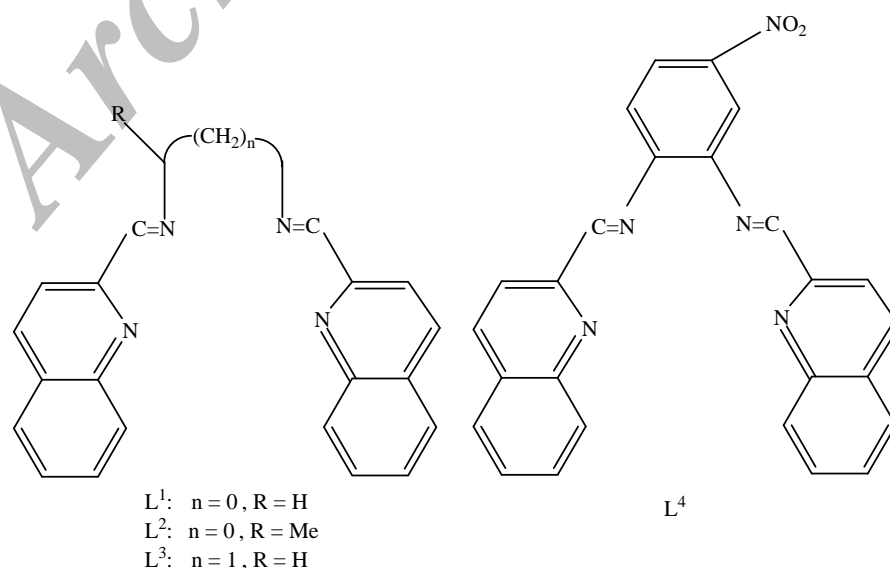
opropane, 1,2-diaminopropane, methanol, ethanol, acetonitrile, toluene, chloroform, copper chloride tetrahydrate, nickel chloride tetrahydrate, cobalt chloride tetrahydrate and zinc chloride tetrahydrate all of which were commercially obtained from either Merck or Fluka and used without further purification. Spectrograde solvents were used for spectral measurements.

### Apparatus

UV-Vis measurements were carried out on a JASCO V-530 and perkin Elmer (LAMBDA 2) UV-Vis spectrophotometers. The NMR spectra were recorded by Buker Avance Dpx 250 MHz spectrometer. IR spectra were recorded by Shimadzu FTIR 8300 infrared spectrophotometer. Elemental analyses were carried out by Termo finningan-Flash-1200

### Synthesis of Ligands

(1) **N,N'-Bis(2-quinolylmethylidene)-1,2-ethanediimino ( $L^1$ )**. To an ethanolic solution of 2-quinolinecarboxaldehyde 9 mmol (1.41 g) was added ethylenediamine 4.5 mmol (30 ml) in ethanolic solution and stirred for 2 h. After one night and the evaporation of the solvent, a light yellow precipitate formed. The obtained crude product was recrystallized from ethanol and then washed with cold ethanol [18] (see Scheme 1).



Scheme 1

(2) **N,N'-Bis(2-quinolylmethylidene)-1,2-propanedi-imino ( $L^2$ )**. To an ethanolic solution of 2-quinoline-carboxaldehyde 9 mmol (1.41 g) was added a solution of 1,2-diaminopropane 4.5 mmol (0.04 ml) in ethanol and stirred for 3 h. After one night and the evaporation of the solvent, a light brown precipitate formed. The obtained crude product was recrystallized from n-hexane and then washed with cold ethanol (see Scheme 1).

(3) **N,N'-Bis(2-quinolylmethylidene)-1,3-propanedi-imino ( $L^3$ )**. To an ethanolic solution of 2-quinolinecarboxaldehyde 9 mmol (1.41 g) was added a solution of 1,3-diaminopropane 4.5 mmol (0.04 ml) in ethanol and stirred for 3 h. After one night evaporating of solvent, a light brown precipitate formed. The obtained crude product was recrystallized from n-hexane and then washed with cold ethanol. (see Scheme 1)

(4) **N,N'-Bis(2-quinolylmethylidene)-4-nitro-1,2-phenylenediimine ( $L^4$ )**. To an ethanolic solution of 4-nitro-1,2-phenylenediamine 4.5 mmol (0.69 g) was added a solution of 2-quinolinecarboxaldehyde 9 mmol (1.41 g) in ethanol and stirred for 2 h. The yellow raw product was then filtered out and washed with ethanol and petroleum ether. After recrystallization from ethanol, the product was dissolved in toluene and refluxed for 3 h. The solvent was evaporated after one night and the orange product was collected and dried in vacuum at 90 °C [19] (see Scheme 1).

### Synthesis of Complexes

The metal complexes were prepared by the following general procedure: To a hot magnetically stirred methanolic solution (20 ml) of ligands ( $L^1$ - $L^4$ ), was added methanolic solution of metal (II) chloride tetrahydrate salts in equimolar values. The solution was stirred at 50 °C for 24 h. Then the volume of the solution was reduced, the complex separated was filtered, dried and further purified by recrystallization from hot methanolic solution and dried in vacuum desiccator.

### Thermodynamic Studies

The formation constant measurements were carried out by spectrophotometric titration at the constant ionic strength 0.1 M ( $\text{NaClO}_4$ ) at 25 °C ( $\pm 0.1$  °C). In a typical measurement, 2.5 ml solution of the ligand ( $3.5 \times 10^{-5}$  M) in methanol was titrated with various concentrations of the metal chloride ( $3.5$ -

$5 \times 10^{-6}$  M) in methanol. UV-Vis spectra were recorded in the range 250-500 nm about 1 min after each addition. The formed product showed different absorptions from the free ligand, while the metal ion solution showed no absorption at those wavelengths. As an example, the variation of the electronic spectra for  $L^1$  titrated with various concentrations of Zn(II) chloride at 25 °C in methanol is shown in Fig. 1. The same change is valid for other systems. The electronic spectra of the complexes formed during the titration were the same as those of the separately synthesized complexes (Fig. 2).

## RESULTS AND DISCUSSION

### Spectral Studies

Some new ligands and their complexes were prepared and characterized by elemental analyses, IR, UV-Vis and  $^1\text{H}$  NMR spectroscopy. The elemental analyses and physical constants are shown in Table 1. All the ligands and their complexes displayed satisfactory elemental analysis.

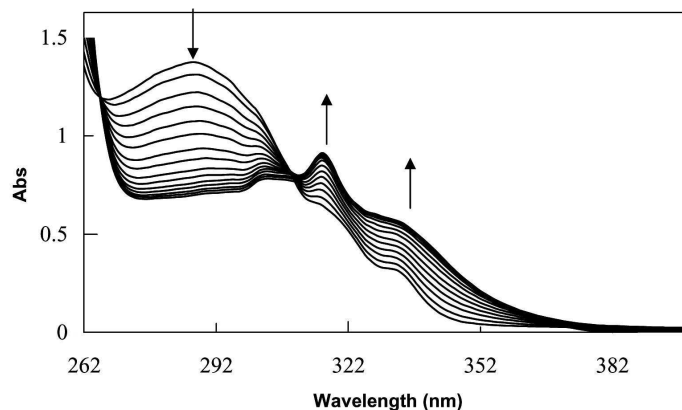
The IR spectra of complexes were compared with those of the free ligands to determine the changes that might have taken place during complexation. The important bands assignments of the ligands and their complexes are summarized in Table 2. The free ligands exhibit strong bands between 1635-1645  $\text{cm}^{-1}$  corresponding to  $\nu(\text{C}=\text{N})$ . In the IR spectrum of complexes, these bands were shifted to higher frequencies, which signify the coordination of the metal to the nitrogen donor atoms [20].

The strong and sharp absorption bands appearing in the regions 2835-2970  $\text{cm}^{-1}$  may be due to C-H stretching vibrations [21].

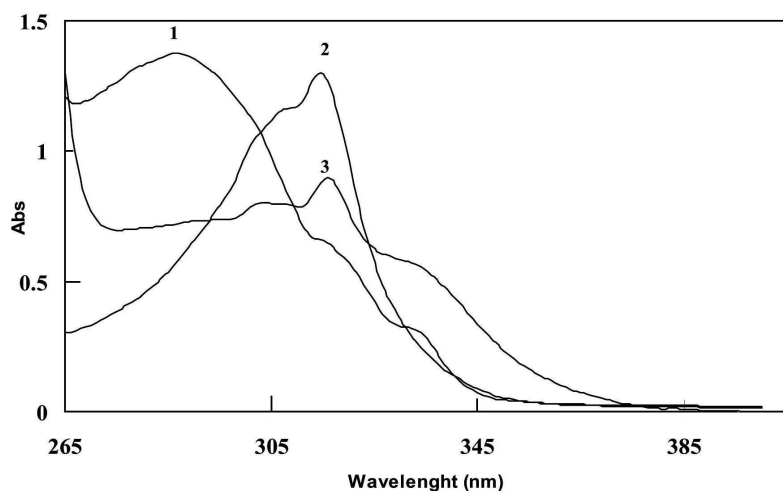
The presence of several bands of medium intensity around 1419-1472  $\text{cm}^{-1}$  could be assigned to the aromatic skeletal vibration  $\nu(\text{C}=\text{C})$ , and  $\nu(\text{C}=\text{N})$  pyridine has been identified around 1502-1596  $\text{cm}^{-1}$  regions [22]. The new bands in the region 400-500  $\text{cm}^{-1}$  due to  $\nu(\text{M}-\text{N})$  vibrations, suggest that the imide nitrogen is coordinating with the metal ions [23].

In the  $^1\text{H}$  NMR spectra of the nickel and zinc complexes, the hydrogen of imine ( $\text{HC}=\text{N}$ ) exhibits a shift relative to the free ligands. The multiples of the aromatic protons appeared within the range 7.16-8.73 ppm [24].

The absorption spectra of  $L^1$  at 286, 316, 332 nm;  $L^2$  at 283, 316 nm;  $L^3$  at 287, 314 nm and  $L^4$  at 254, 300, 378 nm



**Fig. 1.** The variation of the electronic spectra of  $L^1$  titrated with various concentration of Zn(II) chloride at 25 °C in  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ) and in MeOH.



**Fig. 2.** UV-Vis spectra of the ligand  $L^1$  (1), the synthesized  $\text{ZnL}^1$  (2) in MeOH and the end point of the titration of the ligand with  $\text{Zn}^{2+}$  (3).

show intra-ligand charge transfer bands. These bands appear at 302-364 nm for  $\text{NiL}^{1-4}$  complexes and at 301-378 nm for  $\text{CoL}^{1-4}$  and at 301-363 nm for  $\text{CuL}^{1-4}$  and at 302-362 nm for  $\text{ZnL}^{1-4}$ . All data demonstrate the coordination of the metal ions with the ligands [25,29].

#### Formation Constants and Thermodynamic Free Energy Calculations for Schiff Bases with $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ , $\text{Zn}^{2+}$ Ions in MeOH Solvent

The formation constants were determined by UV-Vis

absorption spectroscopy through titration of the ligands with various concentrations of the metal ions at constant ionic strength 0.1 M ( $\text{NaClO}_4$ ) and at 25 °C. The interaction of  $\text{NaClO}_4$  with the ligands in MeOH was negligible. The complex formation constants,  $K_f$ , were calculated using SQUAD computer program [26-28].

Also, the free energy change,  $\Delta G^\circ$ , of the complexes were determined by  $\Delta G^\circ = -RT \ln K_f$ , at 25 °C where  $K_f$  is the complex formation constant, R is the gas constant and T is the temperature in Kelvin.

**Table 1.** Analytical and Physical Data of the Compounds

Compounds	Empirical formula	Formula weight	Anal. Found (Calcd.) (%)		
			C	H	N
L <sup>1</sup>	C <sub>22</sub> N <sub>4</sub> H <sub>18</sub> O <sub>2</sub>	338	77.96 (78.08)	5.43 (5.46)	16.23 (16.56)
L <sup>2</sup>	C <sub>23</sub> N <sub>4</sub> H <sub>18</sub>	352	78.03 (78.38)	5.56 (5.72)	16.11 (15.90)
L <sup>3</sup>	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub>	352	78.03 (78.38)	5.96 (5.72)	15.67 (15.90)
L <sub>4</sub>	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub>	431	72.03 (72.38)	4.26 (3.97)	16.40 (16.23)
[NiL <sup>1</sup> ]	C <sub>22</sub> N <sub>4</sub> H <sub>18</sub> NiCl <sub>2</sub>	466	56.13 (56.46)	4.13 (3.88)	12.05 (11.97)
[NiL <sup>2</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> NiCl <sub>2</sub>	480	57.01 (57.31)	4.45 (4.18)	11.86 (11.62)
[NiL <sup>3</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> NiCl <sub>2</sub>	480	56.93 (57.13)	4.41 (4.18)	11.37 (11.62)
[NiL <sup>4</sup> ]	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> NiCl <sub>2</sub>	559	55.33 (55.66)	3.44 (3.05)	12.17 (12.48)
[CoL <sup>1</sup> ]	C <sub>22</sub> N <sub>4</sub> H <sub>18</sub> CoCl <sub>2</sub>	467	56.05 (56.43)	3.64 (3.87)	12.05 (11.97)
[CoL <sup>2</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> CoCl <sub>2</sub>	481	56.91 (57.28)	4.45 (4.18)	11.35 (11.62)
[CoL <sup>3</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> CoCl <sub>2</sub>	481	56.98 (57.28)	4.41 (4.18)	11.35 (11.62)
[CoL <sup>4</sup> ]	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> CoCl <sub>2</sub>	560	55.33 (55.64)	3.34 (3.05)	12.27 (12.48)
[CuL <sup>1</sup> ]	C <sub>22</sub> N <sub>4</sub> H <sub>18</sub> CuCl <sub>2</sub>	471	56.05 (55.88)	3.64 (3.84)	12.05 (11.85)
[CuL <sup>2</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> CuCl <sub>2</sub>	485	56.92 (56.74)	4.45 (4.14)	11.35 (11.51)
[CuL <sup>3</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> CuCl <sub>2</sub>	485	56.38 (56.74)	4.41 (4.14)	11.35 (11.51)
[CuL <sup>4</sup> ]	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> CuCl <sub>2</sub>	564	55.33 (55.18)	3.34 (3.03)	12.17 (12.38)
[ZnL <sup>1</sup> ]	C <sub>22</sub> N <sub>4</sub> H <sub>18</sub> ZnCl <sub>2</sub>	472	56.03 (55.67)	3.64 (3.82)	12.05 (11.80)
[ZnL <sup>2</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> ZnCl <sub>2</sub>	486	56.91 (56.53)	4.45 (4.12)	1.35 (11.46)
[ZnL <sup>3</sup> ]	C <sub>23</sub> N <sub>4</sub> H <sub>20</sub> ZnCl <sub>2</sub>	486	56.90 (56.53)	4.41 (4.12)	11.47 (11.36)
[ZnL <sup>4</sup> ]	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> ZnCl <sub>2</sub>	565	55.33 (55.01)	3.34 (3.02)	12.17 (12.34)

**Table 2.** IR Characterization of the Ligands and their Complexes (in cm<sup>-1</sup> Unit)

Compounds	C-H	C=N	C=N (Pyridine)	C=C	Substituted
L <sup>1</sup>	2922	1642	1502	1462	-
L <sup>2</sup>	2835	1643	1595	1421	-
L <sup>3</sup>	2862	1635	1558	1419	-
L <sup>4</sup>	2907	1645	1572	1429	1330,1570
[NiL <sup>1</sup> ]	2933	1652,1618	1511	1467	-
[NiL <sup>2</sup> ]	2912	1633,1614	1571	1460	-
[NiL <sup>3</sup> ]	2923	1652,1618	1570	1423	-
[NiL <sup>4</sup> ]	2920	1654,1632	1596	1434	1380,1550
[CoL <sup>1</sup> ]	2936	1654,1620	1515	1469	-
[CoL <sup>2</sup> ]	2910	1640,1618	1580	1473	-
[CoL <sup>3</sup> ]	2940	1649,1623	1583	1436	-
[CoL <sup>4</sup> ]	2938	1662,1623	1583	1442	1333,1555
[CuL <sup>1</sup> ]	2940	1665,1636	1517	1473	-
[CuL <sup>2</sup> ]	2914	1642,1620	1578	1462	-
[CuL <sup>3</sup> ]	2932	1648,1633	1566	1460	-
[CuL <sup>4</sup> ]	2960	1653,1638	1575	1453	1330,1350
[ZnL <sup>1</sup> ]	2938	1668,1624	1518	1472	-
[ZnL <sup>2</sup> ]	2916	1650,1638	1566	1464	-
[ZnL <sup>3</sup> ]	2970	1641, 1632	1566	1458	-
[ZnL <sup>4</sup> ]	2953	1653, 1638	1587	1438	1358,1550

**Table 3.** UV-Vis Bands  $\lambda_{\max}$  (nm) of Compounds in MeOH

Compounds	$\lambda_{\max}$
L <sup>1</sup>	286, 316 (sh), 332 (sh)
L <sup>2</sup>	288, 316
L <sup>3</sup>	287, 314
L <sup>4</sup>	254, 300, 378
[NiL <sup>1</sup> ]	303 (sh), 316, 335 (sh)
[NiL <sup>2</sup> ]	303, 315, 334 (sh)
[NiL <sup>3</sup> ]	302 (sh), 315, 328 (sh)
[NiL <sup>4</sup> ]	364
[CoL <sup>1</sup> ]	302, 315, 333(sh)
[CoL <sup>2</sup> ]	300, 315, 335 (sh)
[CoL <sup>3</sup> ]	301 (sh), 315, 327 (sh)
[CoL <sup>4</sup> ]	305 (sh), 378
[CuL <sup>1</sup> ]	301, 315, 332
[CuL <sup>2</sup> ]	302, 314, 332 (sh)
[CuL <sup>3</sup> ]	301, 314, 335 (sh)
[CuL <sup>4</sup> ]	363
[ZnL <sup>1</sup> ]	303 (sh), 316, 335 (sh)
[ZnL <sup>2</sup> ]	302, 316, 331 (sh)
[ZnL <sup>3</sup> ]	302, 314, 330 (sh)
[ZnL <sup>4</sup> ]	362

**Table 4.** <sup>1</sup>H NMR Data of Schiff Bases and Their Complexes ( $\delta$ /ppm)

Compound	HC=N	Ar-H	Diamin protons
L <sup>1</sup>	8.61	7.56-8.2	4.17
L <sup>2</sup>	8.60	7.25-8.25	1.37, 3.41-4.04
L <sup>3</sup>	8.61	7.50-8.17	2.27, 3.90
L <sup>4</sup>	8.91	7.69-8.59	6.78-6.92
[NiL <sup>1</sup> ]	9.02	7.57-8.54	2.00-3.032
[NiL <sup>2</sup> ]	9.99	7.53-8.45	1.93, 2.01-4.29
[NiL <sup>3</sup> ]	8.18	7.50-8.60	2.46-3.44
[NiL <sup>4</sup> ]	8.63	7.16-8.59	6.00-6.72
[ZnL <sup>1</sup> ]	8.94	7.61-8.46	2.47-4.11
[ZnL <sup>2</sup> ]	9.16	7.18-8.50	1.13, 2.10-3.41
[ZnL <sup>3</sup> ]	8.55	7.58-8.73	2.48, 3.83
[ZnL <sup>4</sup> ]	8.70	7.45-8.39	6.59-6.76

The formation constants and the thermodynamic parameters are presented in Table 5. The formation constant of the complexes follow the sequence Co(II) > Ni(II) > Cu(II) > Zn(II).

The Irving-Williams series show that if the ligands and oxidation state of the metal ions are similar and constant, the smallest ion with the lowest radii has the highest stability, *i.e.* Co(II) > Ni(II) > Cu(II) > Zn(II).

On the other hand, the crystal field stabilization energy, CFSE, affected the stability of the produced complexes. Co(II) had the highest CFSE, hence, it has the highest formation constant.

The coordination around Ni was essentially square planer with a small distortion. The molecular structure of the same complex Ni(bqb) was determined previously and could be compared with the structure of the present complexes Ni(L<sup>1</sup>-L<sup>4</sup>) [29].

Zn(II), with a d<sup>10</sup> configuration, had more potency to take a tetrahedral configuration hence, it has the smallest formation constant while Cu(II), with a d<sup>9</sup> configuration, tends to have a

distorted square planer geometry because of the Jahn-Teller effect [30].

### The Effect of Diamine Bridge

To investigate the effects of the electronic and the steric properties of diamine bridge on the formation constant of the Schiff base complexes giving N<sub>4</sub> coordination sphere, we effected the interaction of L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup> and L<sup>4</sup> with Co(II), Ni(II), Cu(II), Zn(II) in MeOH. The formation constants and the free energies data are shown in Table 5.

On the basis of the results, the formation of the complexes follows the sequence ML<sup>2</sup> > ML<sup>1</sup> > ML<sup>3</sup> > ML<sup>4</sup>.

The trimethylene derivatives (L<sup>3</sup>) are considered to produce a weaker ligand field than the dimethylene derivatives, since the strain caused by the trimethylene chain on the complex formation is higher. Therefore, L<sup>3</sup> would produce a weaker ligand field than L<sup>2</sup> and L<sup>1</sup>. Hence having the smallest K<sub>f</sub> constant [26,31].

The formation constants and the free energies data for L<sup>2</sup> were larger than that for L<sup>1</sup>. It was observed that the addition of

**Table 5.** The Formation Constants, logK<sub>f</sub>, and the Free Energy, ΔG°, for the Complexes of the Ligands with the M<sup>2+</sup> Ion at 25 °C, in MeOH

Complexes	M <sup>2+</sup>	
	logK <sub>f</sub>	ΔG° (kJ mol <sup>-1</sup> )
[NiL <sup>1</sup> ]	6.12 (0.23)	34.90 (0.57)
[NiL <sup>2</sup> ]	6.32 (0.57)	36.04 (1.33)
[NiL <sup>3</sup> ]	5.98 (0.01)	34.10 (0.02)
[NiL <sup>4</sup> ]	5.15 (0.62)	29.37 (1.53)
[CoL <sup>1</sup> ]	7.23 (0.12)	41.23 (0.29)
[CoL <sup>2</sup> ]	7.61 (0.42)	43.40 (1.04)
[CoL <sup>3</sup> ]	7.01 (0.04)	39.98 (0.09)
[CoL <sup>4</sup> ]	6.83 (0.28)	38.95 (0.64)
[CuL <sup>1</sup> ]	5.30 (0.30)	-30.22 (0.74)
[CuL <sup>2</sup> ]	5.90 (0.07)	33.64 (0.17)
[CuL <sup>3</sup> ]	5.08 (0.22)	28.97 (0.54)
[CuL <sup>4</sup> ]	4.80 (0.74)	27.37 (1.33)
[ZnL <sup>1</sup> ]	5.11 (0.41)	29.14 (1.01)
[ZnL <sup>2</sup> ]	5.36 (0.09)	30.57 (0.22)
[ZnL <sup>3</sup> ]	4.73 (0.48)	26.97 (1.19)
[ZnL <sup>4</sup> ]	4.20 (0.27)	23.95 (0.66)

methyl electron donation group to Schiff base ligands increases the formation constant of the complexes. In the L<sup>4</sup> ligand, the electron withdrawing group (NO<sub>2</sub>) on a cyclic bridge make the Schiff base a poor donor ligand and decrease the formation constant [26,31].

## CONCLUSIONS

Some new tetraaza Schiff base ligands (L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>, L<sup>4</sup>) were synthesized and their complexation capacity towards Cobalt(II), Nickel(II), Copper(II) and Zinc(II) was studied. The coordination behavior of the ligands and their complexes were determined using physical techniques. By considering the formation constants and the free energies data for Schiff base ligands as donors, and the metal ions as acceptors, the following conclusions have been drawn. The formation constants, K<sub>f</sub> and the free energy values for Co(II) were the highest, while for Zn(II), the values were the lowest. Ni(II) and Cu(II) values were intermediate, respectively. An electron donor group on the ligands increases the formation constant, while a withdrawing functional group decreases it. The trend of the formation constant is as follows: ML<sup>2</sup> > ML<sup>1</sup> > ML<sup>3</sup> > ML<sup>4</sup>, M = Co(II), Ni(II), Cu(II), Zn(II).

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