

## New Tetraaza Schiff Base Ligands and Their Complexes: Synthesis, Characterization and Thermodynamic Studies

A. Zamanpour<sup>a,b,\*</sup>, M. Asadi<sup>a</sup> and G. Absalan<sup>a</sup>

<sup>a</sup>Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, I. R. Iran

<sup>b</sup>Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, I.R. Iran

(Received 23 October 2014, Accepted 3 May 2016)

Some new symmetrical tetraaza Schiff base ligands containing 2-quinolinecarboxaldehyde moiety formed from condensation reaction of 2-quinolinecarboxaldehyde and *o*-phenylenediamine derivatives, such as N,N'-bis(2-quinolylmethylidene)-4-methoxy-1,2-phenylenediimine (L<sup>1</sup>), N,N'-bis(2-quinolylmethylidene)-4-methoxy-1,2-phenylenediimine (L<sup>2</sup>), N,N'-bis(2-quinolylmethylidene)-4-chloro-1,2-phenylenediimine (L<sup>3</sup>), N,N'-bis(2-quinolylmethylidene)-4-carboxylic-1,2-phenylenediimine (L<sup>4</sup>), N,N'-bis(2-quinolylmethylidene)-4-nitro-1,2-phenylenediimine (L<sup>5</sup>), and their Ni(II), Cu(II), Zn(II) complexes, have been synthesized. The ligands and their metal complexes have been characterized by molar conductance, elemental analysis, IR, <sup>1</sup>H NMR and UV-Vis spectroscopy. The formation constant and the free energy of the complexes were determined using electronic spectroscopic titration at constant ionic strength 0.1 M (NaClO<sub>4</sub>), at 25 °C in MeOH solvent. The comparison of the formation constants and the thermodynamic parameters show that the trend of complex formation toward a given ligand is as follows: L<sup>2</sup> > L<sup>1</sup> > L<sup>3</sup> > L<sup>5</sup> > L<sup>4</sup>. The trend for complex formation of the metal ions with a given ligand is as follows: Zn(II) > Cu(II) > Ni(II).

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

### INTRODUCTION

Schiff base tetraaza ligands have received special attention because of their versatile coordination behavior, and their biological activities, *i.e.*, toxicity against bacterial growth, anticancerous and other biochemical properties. Schiff base ligands differ from other noncyclic ligands due to the structural factors such as the cavity size, stereochemical rigidity, flexibility and ability to coordination in neutral form [1]. Schiff base ligands have played an integral role in the development of coordination chemistry [2,3]. Tetraaza molecules, based on quinolinecarboxaldehyde and their complexes received considerable attention because of their pharmacological properties. Particularly first row transition metal complexes with such ligands have a wide range of biological properties

[4-6].

The imino tetraaza ligands have been derived by condensation reaction between dicarbonyls and primary diamines. A dramatic progress in the chemistry of tetraaza complexes has received particular attention due to their mimicry with biologically significant molecules invoking a variety of catalytic, biochemical and industrial applications [7,8]. Schiff bases and their structural analogues, as ligating compounds containing acyclic and cyclic imine C=N bonds, are of great importance in modern coordination chemistry [9].

In our previous work [10], we reported synthesis and characterization of some N<sub>4</sub> Schiff base ligands and their complexes of Co(II), Ni(II), Cu(II) and Zn(II). As an extension in this paper, we report the synthesis, thermodynamics and physical properties of complexation of some new N<sub>4</sub> Schiff base ligands having 2-quinolinecarboxaldehyde moiety with Ni(II), Cu(II) and

\*Corresponding author. E-mail: zamanpour.a@gmail.com

Zn(II) metal ions. The compounds were characterized by molar conductance, elemental analysis, IR, NMR, and UV-Vis techniques. Also the formation constant,  $K_f$ , and the free energy,  $\Delta G^\circ$ , at 25 °C for the complexes were determined spectrophotometrically. The electronic effects of the cyclic amines on the Schiff base type ligand upon the formation constant and the free energy of the complexes were studied.

## EXPERIMENTAL

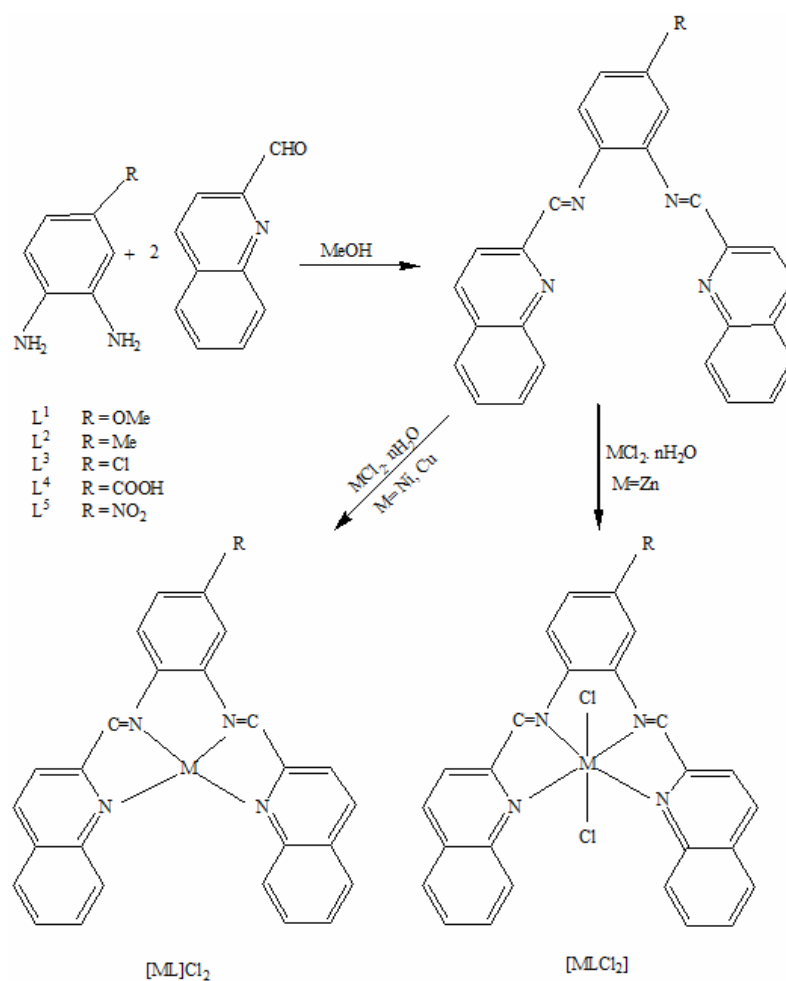
### Materials

2-Quinolinecarboxaldehyde, 4-nitro-1,2-phenylenediamine, 4-methoxy-1,2-phenylenediamine, 4-chloro-1,2-phenylenediamine, 4-methyl-1,2-phenylenediamine, 3,4-

diaminobenzoic acid, methanol, ethanol, acetonitrile, toluene, chloroform, copper chloride dihydrate, nickel chloride tetrahydrate, zinc chloride tetrahydrate, were commercially obtained from either Merck or Fluka and used without further purification. Spectrograde solvents were used for spectral measurements.

### Physical Measurements

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



Scheme 1

Termo fininngan-Flash-1200. Conductivity measurements were carried out by Metrohm 660 Conductometer.

### Synthesis of Tetraaza Ligands ( $L^1$ , $L^2$ , $L^3$ )

To an ethanolic solution of 2-quinolinecarboxaldehyde (9 mmol) was added a ethanolic solution of 4-methoxy-1,2-phenylenediamine ( $L^1$ ), 4-methyl-1,2-phenylenediamine ( $L^2$ ), 4-chloro-1,2-phenylenediamine ( $L^3$ ) (4.5 mmol), and stirred for 24 h under 0 °C. After one night evaporating of solvent, a light brown precipitate formed. The obtained crude product was recrystallized from ethanol and then washed with cold ethanol (See Scheme 1).

### Synthesis of Tetraaza Ligands ( $L^4$ , $L^5$ )

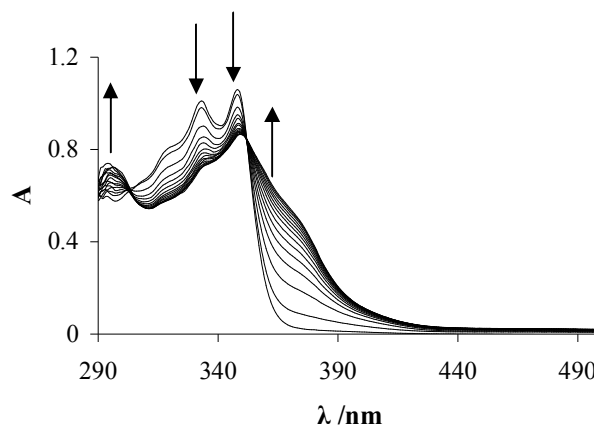
To an ethanolic solution of 3,4-diaminobenzoic acid ( $L^4$ ), 4-nitro-1,2-phenylenediamine ( $L^5$ ) [11] (4.5 mmol) was added a solution of 2-quinolinecarboxaldehyde (9 mmol) in ethanol and stirred for 2 h. The yellow raw product was then filtered off and washed with ethanol and petroleum ether. Then 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 (See Scheme 1).

### Synthesis of the Tetraaza Complexes

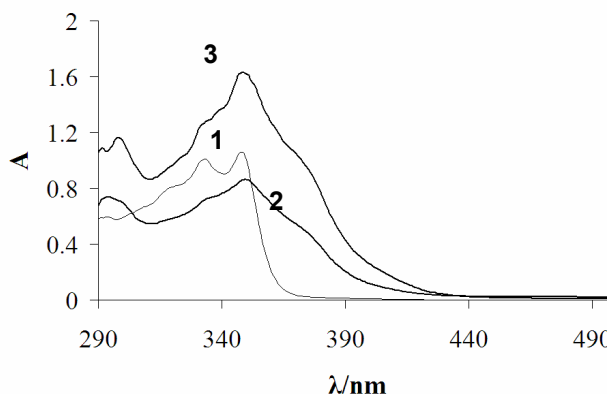
A warm methanolic (10 cm<sup>3</sup>) solution of the corresponding metal chloride (1 mmol) was added to a warm ethanolic solution (10 cm<sup>3</sup>) of the ligand ( $L^1$ - $L^5$ ) (1 mmol). The mixed solution was stirred at 50 °C for 24 h. Then the volume of the solution was reduced, the complex separated was filtered, dried and further purified by recrystallization from hot methanolic solution and dried in vacuum desiccator (See Scheme 1).

### Thermodynamic Studies

The formation constant measurements were carried out by spectrophotometric titration at constant ionic strength 0.1 M (NaClO<sub>4</sub>) at 25 °C ( $\pm 0.1$  °C). In a typical measurement, 2.5 cm<sup>3</sup> solution of the ligand ( $3.5\text{--}8 \times 10^{-5}$  M) in methanol was transferred in to thermodynamic cell compartment of UV-Vis instrument and titrated by the metal chloride ( $3.5\text{--}8 \times 10^{-6}$  M) in methanol. UV-Vis spectra were recorded in the range 250-600 nm about 1 min after each addition. The formed product showed different absorption from the free



**Fig. 1.** The variation of the electronic spectra of  $L^3$  titrated with various concentration of  $\text{Cu}^{2+}$  chloride at 25 °C in I = 0.1 M (NaClO<sub>4</sub>) and in MeOH.



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

ligand, while the metal ion solution shows no absorption at those wavelengths. As an example, the variation of the electronic spectra for  $L^3$  titrated with various concentration of Cu(II) chloride at 25 °C in methanol is shown in Fig. 1. The electronic spectra of the complexes formed during the titration were the same as of the separately synthesized complexes (Fig. 2).

## RESULTS AND DISCUSSION

### Spectral Studies

The ligands ( $L^1$ - $L^5$ ) and their metal complexes were

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

Compounds	Empirical formula	Formula weight	Melting point (°C)	Molar conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Anal. Found (Calcd.) (%)		
					C	H	N
L <sup>1</sup>	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> O	416	175	-	77.50(77.87)	4.56(4.84)	13.73(13.45)
L <sup>2</sup>	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub>	400	50	-	80.76(80.98)	4.88(5.03)	14.33(13.99)
L <sup>3</sup>	C <sub>26</sub> N <sub>4</sub> H <sub>17</sub> Cl	420	95	-	73.89(74.09)	3.98(4.07)	13.55(13.31)
L <sup>4</sup>	C <sub>27</sub> N <sub>4</sub> H <sub>18</sub> O <sub>2</sub>	430	160	-	74.97(75.34)	4.36(4.21)	12.88(13.03)
L <sup>5</sup>	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub>	431	145	-	72.03(72.38)	3.63(3.97)	16.46(16.23)
[L <sup>1</sup> Ni]Cl <sub>2</sub>	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> ONiCl <sub>2</sub>	544	130	275	59.57(59.39)	4.13(3.88)	12.05(11.97)
[L <sup>2</sup> Ni]Cl <sub>2</sub>	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> NiCl <sub>2</sub>	528	172	281	61.35(61.18)	3.66(3.80)	10.85(10.57)
[L <sup>3</sup> Ni]Cl <sub>2</sub>	C <sub>26</sub> N <sub>4</sub> H <sub>17</sub> NiCl <sub>3</sub>	548	248	223	56.45(56.73)	3.38(3.11)	10.35(10.18)
[L <sup>4</sup> Ni]Cl <sub>2</sub>	C <sub>27</sub> N <sub>4</sub> H <sub>18</sub> O <sub>2</sub> NiCl <sub>2</sub>	558	>250	217	57.54(57.90)	3.38(3.24)	10.14(10.00)
[L <sup>5</sup> Ni]Cl <sub>2</sub>	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> NiCl <sub>2</sub>	559	>250	219	55.33(55.66)	3.44(3.05)	12.17(12.48)
[L <sup>1</sup> Cu]Cl <sub>2</sub>	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> OCuCl <sub>2</sub>	549	140	154	59.06(58.86)	4.05(3.77)	10.66(10.47)
[L <sup>2</sup> Cu]Cl <sub>2</sub>	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> CuCl <sub>2</sub>	533	>250	157	60.28(60.62)	4.45(4.14)	11.35(11.51)
[L <sup>3</sup> Cu]Cl <sub>2</sub>	C <sub>26</sub> N <sub>4</sub> H <sub>17</sub> CuCl <sub>3</sub>	553	>250	95	55.85(55.23)	3.48(3.09)	10.22(10.09)
[L <sup>4</sup> Cu]Cl <sub>2</sub>	C <sub>27</sub> N <sub>4</sub> H <sub>18</sub> O <sub>2</sub> CuCl <sub>2</sub>	563	>250	73	57.34(57.41)	3.43(3.21)	9.85(9.92)
[L <sup>5</sup> Cu]Cl <sub>2</sub>	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> CuCl <sub>2</sub>	564	>250	76	55.33(55.18)	3.26(3.03)	12.15(12.38)
[L <sup>1</sup> ZnCl <sub>2</sub> ]	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> OZnCl <sub>2</sub>	550	>250	41	58.37(58.67)	3.64(3.82)	12.05(11.80)
[L <sup>2</sup> ZnCl <sub>2</sub> ]	C <sub>27</sub> N <sub>4</sub> H <sub>20</sub> ZnCl <sub>2</sub>	534	>250	43	60.31(60.42)	4.05(3.76)	10.71(10.44)
[L <sup>3</sup> ZnCl <sub>2</sub> ]	C <sub>26</sub> N <sub>4</sub> H <sub>17</sub> ZnCl <sub>3</sub>	554	>250	19	55.78(56.05)	3.41(3.08)	10.15(10.06)
[L <sup>4</sup> ZnCl <sub>2</sub> ]	C <sub>27</sub> N <sub>4</sub> H <sub>18</sub> O <sub>2</sub> ZnCl <sub>2</sub>	564	>250	18	57.58(57.22)	3.34(3.25)	9.75(9.89)
[L <sup>5</sup> ZnCl <sub>2</sub> ]	C <sub>26</sub> N <sub>5</sub> H <sub>17</sub> O <sub>2</sub> ZnCl <sub>2</sub>	565	>250	20	55.25(55.18)	3.39(3.02)	12.25(12.34)

characterized by <sup>1</sup>H NMR, IR, UV-Vis, melting point and elemental analysis. The physicochemical properties of the ligands and their complexes are summarized in Table 1. The data of the metal chelates presented in Table 1 indicate that the Zn metal ion is coordinated to one ligand molecule and

two chloride ions and the Ni and Cu metal ions are coordinated to one ligand molecule.

#### Molar Conductivity

The molar conductivity ( $\Lambda_m$ ) of 1 mM solution of the

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

Compounds	C-H	C=N	C=N (Pyridine)	C=C	Substituted
L <sup>1</sup>	2924	1628	1597	1510	-
L <sup>2</sup>	2931	1658	1597	1504	-
L <sup>3</sup>	2862	1650	1597	1497	-
L <sup>4</sup>	2907	1618	1591	1504	1730
L <sup>5</sup>	2907	1645	1579	1482	1330,1570
[L <sup>1</sup> Ni]Cl <sub>2</sub>	2924	1632,1615	1584	1481	-
[L <sup>2</sup> Ni]Cl <sub>2</sub>	2912	1633,1614	1585	1457	-
[L <sup>3</sup> Ni]Cl <sub>2</sub>	2939	1620, 1604	1597	1504	-
[L <sup>4</sup> Ni]Cl <sub>2</sub>	2920	1620	1596	1504	1704(CO)
[L <sup>5</sup> Ni]Cl <sub>2</sub>	2920	1654,1632	1596	1434	1380,1550
[L <sup>1</sup> Cu]Cl <sub>2</sub>	2947	1620	1597	1435	-
[L <sup>2</sup> Cu]Cl <sub>2</sub>	2923	1604,1612	1597	1481	-
[L <sup>3</sup> Cu]Cl <sub>2</sub>	2932	1620,1604	1597	1504	-
[L <sup>4</sup> Cu]Cl <sub>2</sub>	2923	1620	1597	1504	1689(CO)
[L <sup>5</sup> Cu]Cl <sub>2</sub>	2923	1605	1597	1427	1334,1350
[L <sup>1</sup> ZnCl <sub>2</sub> ]	2923	1627	1597	1481	-
[L <sup>2</sup> ZnCl <sub>2</sub> ]	2923	1620	1597	1480	-
[L <sup>3</sup> ZnCl <sub>2</sub> ]	2939	1620	1589	1504	-
[L <sup>4</sup> ZnCl <sub>2</sub> ]	2953	1620	1597	1512	1736(CO)
[L <sup>5</sup> ZnCl <sub>2</sub> ]	2953	1653,1638	1587	1438	1358,1550

tetraaza complexes was measured in DMSO at 25 °C and are collected in Table 1. The Ni(II) and Cu(II) complexes have molar conductivity of 73-281 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup> indicating the 1:2 ionic nature. These values are indicative of the presence two outer sphere chloride anions. The Zn(II) complexes were non-electrolytes with conductance values of 18-41 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup> in DMSO. Thus, the Ni(II) and Cu(II) complexes may be formulated as [ML]Cl<sub>2</sub> and [MLCl<sub>2</sub>] formula for Zn(II) complexes [12-15,21].

### Infrared Spectral Data

The IR spectra of the Schiff base M(II) [M = Ni(II), Cu(II), Zn(II)] complexes show a medium intensity band due to ν(C=N). This band was shifted compared to ligand spectra and appeared in the range of 1604-1653 cm<sup>-1</sup>. This supports the fact that the ligands are coordinated to the metal ions through the nitrogen of imine group in all the complexes. The new bands in the region 400-500 cm<sup>-1</sup> due to ν(M-N) vibrations, suggest that the imine nitrogen is

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

Compounds	Intra-ligand	Charge transfer
L <sup>1</sup>	316, 345	-
L <sup>2</sup>	290 (sh), 340, 350	-
L <sup>3</sup>	319 (sh), 332, 348	-
L <sup>4</sup>	319 (sh), 331, 347	-
L <sup>5</sup>	253, 302	-
[L <sup>1</sup> Ni]Cl <sub>2</sub>	315, 349	398
[L <sup>2</sup> Ni]Cl <sub>2</sub>	296 (sh), 351	374
[L <sup>3</sup> Ni]Cl <sub>2</sub>	317, 331, 346	370
[L <sup>4</sup> Ni]Cl <sub>2</sub>	318 (sh), 332, 346	365
[L <sup>5</sup> Ni]Cl <sub>2</sub>	256	364
[L <sup>1</sup> Cu]Cl <sub>2</sub>	316 (sh), 346	397
[L <sup>2</sup> Cu]Cl <sub>2</sub>	294, 355	378
[L <sup>3</sup> Cu]Cl <sub>2</sub>	295, 334 (sh), 348	374
[L <sup>4</sup> Cu]Cl <sub>2</sub>	316 (sh), 330, 346	379
[L <sup>5</sup> Cu]Cl <sub>2</sub>	255	363
[L <sup>1</sup> ZnCl <sub>2</sub> ]	314, 350 (sh)	396
[L <sup>2</sup> ZnCl <sub>2</sub> ]	294, 336 (sh), 350	370
[L <sup>3</sup> ZnCl <sub>2</sub> ]	331, 347	372
[L <sup>4</sup> ZnCl <sub>2</sub> ]	318 (sh), 331, 346	373
[L <sup>5</sup> ZnCl <sub>2</sub> ]	257	362

coordinating to the metal ions. The C-H stretching and bending vibrations appear at 2862-2953 cm<sup>-1</sup>, respectively [16-22]. The aromatic skeletal vibration  $\nu(\text{C}=\text{C})$  of the ligands and the complexes were in the region of 1427-1512 cm<sup>-1</sup> and  $\nu(\text{C}=\text{N})$  pyridine has been identified around 1579-1597 cm<sup>-1</sup> regions [23,24]. The main infrared bands and their assignments are collected in Table 2.

### Electronic Spectra

The electronic spectral data of the free ligands (L<sup>1</sup>-L<sup>5</sup>) and their tetraaza complexes in methanol solutions were

recorded and listed in Table 3. The spectra of the ligands exhibit bands at lower level than 360 nm range assigned to the intra-ligand  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. These bands do not shift much in the spectra of the tetraaza complexes. The bands above 360 nm are due to charge transfer transitions [25-28,30]. The d-d bands are not observed due to the low concentration of the complexes solution. This bands should be low intensity in the region of 600-700 nm.

### NMR Studies

<sup>1</sup>H NMR data and their assignments for the ligands and

**Table 4.**  $^1\text{H}$  NMR Data of Schiff Bases and their Complexes  $\delta$  (ppm)

Compounds	HC=N	Ar-H	Substituted protons
L <sup>1a</sup>	6.54	6.88-8.49	3.77
L <sup>2b</sup>	7.47	7.13-8.58	2.49
L <sup>3b</sup>	6.60	7.20-8.75	-
L <sup>4a</sup>	8.32	7.49-8.59	13.53
L <sup>5a</sup>	8.91	7.69-8.59	-
[L <sup>1</sup> Ni]Cl <sub>2</sub> <sup>a</sup>	6.51	7.11-8.49	~3.5
[L <sup>2</sup> Ni]Cl <sub>2</sub> <sup>a</sup>	8.35	6.58-8.16	2.44
[L <sup>3</sup> Ni]Cl <sub>2</sub> <sup>a</sup>	8.75	6.59-8.68	-
[L <sup>4</sup> Ni]Cl <sub>2</sub> <sup>a</sup>	7.51	7.38-8.71	13.89
[L <sup>5</sup> Ni]Cl <sub>2</sub> <sup>a</sup>	8.63	7.16-8.59	-
[L <sup>1</sup> ZnCl <sub>2</sub> ] <sup>a</sup>	7.16	7.18-8.59	3.82
[L <sup>2</sup> ZnCl <sub>2</sub> ] <sup>a</sup>	7.50	7.09-8.70	~3.6
[L <sup>3</sup> ZnCl <sub>2</sub> ] <sup>a</sup>	7.65	7.27-8.58	-
[L <sup>4</sup> ZnCl <sub>2</sub> ] <sup>a</sup>	8.27	7.63-8.61	13.6
[L <sup>5</sup> ZnCl <sub>2</sub> ] <sup>a</sup>	8.70	7.45-8.39	-

<sup>a</sup>DMSO-d<sub>6</sub>, <sup>b</sup>CDCl<sub>3</sub>.

their complexes are compiled in Table 4. The  $^1\text{H}$  NMR spectra of the ligands and their metal complexes show the imine resonance that demonstrates the equivalence of the two imine of Schiff base framework [29]. The  $^1\text{H}$  NMR spectra of the Schiff base complexes also exhibit shift of the imine protons because of the coordination of the ligands *via* the imine nitrogen atom. The quinoline ring protons also exhibit shifts in the complexes relative to that in the free ligands as a result of coordination *via* the quinoline ring nitrogen atom. The multiplet in the region 6.58-8.75 ppm may reasonably be assigned to aromatic protons of the quinoline and phenyl moiety of the tetraaza Schiff base framework [30-35].

#### The Formation Constant and the Thermodynamic Free Energy for the Complex Formation of the Schiff Bases with Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> Ions in MeOH Solvent

The formation constants have been 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 (NaClO<sub>4</sub>) and at 25 °C. The interaction of NaClO<sub>4</sub> with the ligands in MeOH was negligible. The complex formation constants,  $K_f$ , were calculated using SQUAD computer program [36,37].

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

**Table 5.** The Formation Constants,  $\log K_f$ , and the Free Energy,  $\Delta G^\circ$ , for the Complexes of the Ligands with the  $M^{2+}$  Ion at 25 °C, in MeOH

Complexes	$M^{2+}$	
	$\log K_f^a$	$\Delta G^\circ$ (kJ mol <sup>-1</sup> ) <sup>a</sup>
[L <sup>1</sup> Ni]Cl <sub>2</sub>	5.23 (1.23)	-29.9 (1.78)
[L <sup>2</sup> Ni]Cl <sub>2</sub>	5.63 (0.63)	-32.1 (1.56)
[L <sup>3</sup> Ni]Cl <sub>2</sub>	5.12 (0.45)	-29.2 (1.11)
[L <sup>4</sup> Ni]Cl <sub>2</sub>	4.09 (1.08)	-23.3 (1.85)
[L <sup>5</sup> Ni]Cl <sub>2</sub>	4.30 (0.62)	-24.5 (1.53)
[L <sup>1</sup> Cu]Cl <sub>2</sub>	5.77 (0.08)	-32.9 (0.19)
[L <sup>2</sup> Cu]Cl <sub>2</sub>	5.85 (0.85)	-33.36 (1.61)
[L <sup>3</sup> Cu]Cl <sub>2</sub>	5.51 (0.10)	-31.42 (0.24)
[L <sup>4</sup> Cu]Cl <sub>2</sub>	4.48 (1.11)	-25.55 (1.76)
[L <sup>5</sup> Cu]Cl <sub>2</sub>	4.80 (0.74)	-27.37 (1.83)
[L <sup>1</sup> ZnCl <sub>2</sub> ]	6.43 (1.20)	-36.67 (1.56)
[L <sup>2</sup> ZnCl <sub>2</sub> ]	6.75 (0.32)	-38.49 (0.79)
[L <sup>3</sup> ZnCl <sub>2</sub> ]	6.12 (0.75)	-34.90 (1.85)
[L <sup>4</sup> ZnCl <sub>2</sub> ]	5.38 (1.14)	-30.68 (1.46)
[L <sup>5</sup> ZnCl <sub>2</sub> ]	5.60 (0.04)	-31.93 (0.09)

<sup>a</sup>The figures in parentheses are the standard deviations.

the complex formation constant, R is the gas constant and T is the temperature in Kelvin.

### The Electronic Effect of the Ligands upon Complex Formation

In the substituted Schiff base ligands, the formation constants vary as could be expected according to the electronic effect of the substituents at the position 4. The formation constant complexes of the follows the sequence: Me > OMe > Cl > NO<sub>2</sub> > COOH

The COOH and NO<sub>2</sub> the electron withdrawing functional groups make the Schiff base a poor donor ligand therefore decreases the formation constant, while electron donor groups such as OMe and Me increases the formation

constant. The thermodynamic parameters are collected in Table 5 [36-38].

### The Metal Effect upon Complex Formation

The formation constant and the thermodynamic free energy parameter for the selected metal tetraaza Schiff base complexes are summarized in Table 5. On the bases of the results, the formation constants for M<sup>(II)</sup>(L<sup>1</sup>-L<sup>5</sup>) complexes follows the sequence : Zn(II) > Cu(II) > Ni(II) [39].

Based on the spectral and molar conductance data, an octahedral geometry was assigned for Zn(II) complexes, whereas square-planar and tetragonal geometry were proposed for the Ni(II) and Cu(II) complexes, respectively. Therefore Zn(II) complexes have the highest stability. The



complex formation and the free energy values for Cu(II) complexes are higher than for Ni(II) complexes, which may be attributed to its higher positive charge distribution and the ligand deformation geometry [40,12].

### The Effect of the Diamine Bridge in the Ligands

In continuation to our previous studies concerning linear and the cyclic diamines in the Schiff base ligands. The formation constants and the free energies data for the linear ligands [10] are larger than the cyclic ligands in the present work.

The phenyl ring in the 4-X-*o*-phenylenediamine bridge, (where X = COOH, NO<sub>2</sub>, Cl, OMe, Me) makes the complexes a poor donor relative to the complexes with ethylenediamine, 1,3-diaminopropane and 1,2-diaminopropane in the corresponding diamine bridge. So the complex formation of the Schiff base with aromatic bridge ligands are the least. The steric effect of the Schiff base ligand with cyclic bridge also contribute in decreasing the complex formation [41,42].

### CONCLUSIONS

Five new tetraaza symmetrical Schiff base ligands and their complexes with Ni(II), Cu(II) and Zn(II) has been synthesized and characterized. These ligands act as tetradentate and strongly conjugated to form solid complexes, [ML]Cl<sub>2</sub>, M = Ni, Cu and [MLCl<sub>2</sub>], M = Zn. By considering the formation constants and the free energy changes of tetraaza complexes; The following trend for ligands with a given metal are assessed : L<sup>2</sup> > L<sup>1</sup> > L<sup>3</sup> > L<sup>5</sup> > L<sup>4</sup>.

The trend for complex formation of metals with a given ligand are as follows: Zn (II) > Cu (II) > Ni(II)

### ACKNOWLEDGEMENTS

We are grateful to Shiraz University Research Council for their financial support.

### REFERENCES

[1] R. Sellappan, S. Prasad, P. Jayaseelan, R. Rajavel, *Ras. J. Chem.* 3 (2010) 556.

[2] I. Kim, Y. Sun Ha, D.F. Zhang, Ch.S. Ha, U. Lee, *Macro. Rapid Commun.* 25 (2004) 1319.

[3] R. Johari, G. Kumar, D. Kumar, S. Singh, *J. Ind. Council Chem.* 26 (2009) 23.

[4] S. Chandra, X. Sangeetika, *Spectrochim. Acta Part A* 60 (2004) 147.

[5] N. Iqbal, J. Iqbal, M. Imran, *J. Sci. Res.* 1 (2009) 15.

[6] H. Keypour, P. Arzhang, N. Rahpeyma, M. Rezaeivala, Y. Elerman, H.R. Khavasi, *Inorg. Chim. Acta* 367 (2011) 9.

[7] T.J. Hubin, *Coord. Chem. Rev.* 241 (2003) 27.

[8] C.A. Bosweel, X. Sun, W. Niu, G.R. Weisman, E.H. Wong, A.L. Rheingold, C.J. Anderson, *J. Med. Chem.* 47 (2004) 1465.

[9] C.A. Hunter, J.K.M. Sanders, *J. Am. Chem. Soc.* 112 (1990) 5525.

[10] M. Asadi, Gh. Absalan, A. Zamanpour, *J. Iran. Chem. Soc.* 8 (2011) 1073.

[11] K. Yliheikkila, K. Lappalainen, P.M. Castro, K. Ibrahim, A. Abu-Surrah, M. Leskea, T. Repo, *Eur. Poly. J.* 42 (2006) 92.

[12] S. Chandra, M. Tyagi, S. Agrawal, *J. Serb. Chem. Soc.* 75 (2010) 935.

[13] G.K. Patra, I. Goldberg, *New. J. Chem.* 27 (2003) 1124.

[14] M. Shakir, Y. Azim, H.T.N. Chishti, S. Parveen, *Spectrochim. Acta Part A* 65 (2006) 490.

[15] T.A. Khan, S. Naseem, S.N. Khan, A.U. Khan, M. Shakir, *Spectrochim. Acta Part A* 73 (2009) 622.

[16] K. Shanker, M. Ashok, P.M. Reddy, R. Rohini, V. Ravinder, *Int. J. Chem. Tec. Res.* 1 (2009) 777.

[17] F.M. Morad, M.M.E.L. Ajaily, S.B. Gweirif, *J. Sci. App.* 1 (2007) 72.

[18] N. Raman, C. Thangaraja, *Tran. Met. Chem.* 30 (2005) 317.

[19] M.A. Panchbhai, L.J. Paliwal, N.S. Bhave, *E-J. Chem.* 5 (2008) 1048.

[20] M.A. Ali, A.H. Mirza, M. Haniti, S.A. Hamid, P.V. Bernhardt, *Polyhedron* 24 (2005) 383.

[21] S. Khan, S.A.A. Nami, K.S. Siddiqi, *Spectrochim. Acta Part A* 68 (2007) 269.

[22] S. Ilhan, H. Temel, I. Yimaz, M. Sekerci, *Polyhedron* 26 (2007) 2795.

[23] M. Asadi, K. Mohammadi, K.A. Jamshid, A.H.

- Kyanfar, *Inorg. Chim. Acta* 360 (2007) 1725.
- [24] M. Salavati-Niasari, S.N. Mirsattari, *J. Mol. Catal. A: Chem.* 268 (2007) 50.
- [25] G.K. Karaoglan, U. Avetata, A. Gul, *Ind. J. Chem.* 46A (2007) 1273.
- [26] Y. Wei, Y. Cheng, H. Wei, *Chin. J. Inorg. Chem.* 26 (2010) 867.
- [27] M. Amirasr, A.H. Mahmoudkhani, A. Gorji, S. Dehghanpour, H.R. Bijanzadeh, *Polyhedron* 21 (2002) 2733.
- [28] S. Meghdadi, M. Amirasr, V. Langer, A. Zamanpour, *Can. J. Chem.* 84 (2006) 971.
- [29] F. Firdaus, K. Fatma, M. Azam, S.N. Khan, A.U. Khan, M. Shakir, *Spectrochim. Acta Part A* 72 (2009) 591.
- [30] M.A. Ali, A.H. Mirza, M.H.S.A. Hamid, F.H. Bujang, P.V. Bernhardt, *Polyhedron* 23 (2004) 2405.
- [31] M. Asadi, K.A. Jamshid, *Tran. Met. Chem.* (2007) 1.
- [32] M.R. Ganjali, M. Tavakoli, F. Faridbod, S. Riahi, P. Norouzi, M.S. Niassari, *Int. J. Elect. Sci.* 3 (2008) 1559.
- [33] M.F. Mahon, J.M. Ginley, A.D. Rooney, J.M.D. Walsh, *Inorg. Chim. Acta* 362 (2009) 2353.
- [34] T.R. Todorovic, A. Bacchi, N.O. Juranic, D.M. Sladic, G. Pelizzi, T.T. Bozic, N.R. Filipovic, K.K. Andelkovic, *Polyhedron* 26 (2007) 3428.
- [35] M. Amanullah, S.K. Sadozai, W. Rehman, Z. Hassan, A. Rauf, M. Iqbal, *Afr. J. Biotech.* 10 (2011) 209.
- [36] M. Asadi, K. Mohammadi, S. Esmailzadeh, B. Etemadi, H. Kun Fun, *Inorg. Chim. Acta* 362 (2009) 4913.
- [37] M. Asadi, S. Esmailzadeh, K. Mohammadi, *Acta Chim. Solv.* 56 (2009) 927.
- [38] [38] M. Asadi, K. Mohammadi, S. Esmailzadeh, B. Etemadi, H. Kun Fun, *Polyhedron* 28 (2009) 1409.
- [39] [39] M. Asadi, H. Sepehrpour, K. Mohammadi, *J. Serb. Chem. Soc.* 76 (2011) 1.
- [40] [40] M. Asadi, S. Esmailzadeh, K. Mohammadi, *Phosphorus, Sulfur, and Silicon* 185 (2010) 1445.
- [41] [41] M. Asadi, M. Mohammadikish, K. Mohammadi, *J. Iran. Chem. Soc.* 7 (2010) 195.
- [42] [42] M. Asadi, K. Mohammadi, A. H. Kyanfar, *Syn. React. Inorg. Metal-org. Nano-Met. Chem.* 37 (2007) 77.