# The Synthesis of New Triazole Ligands and Determination of Complex Stability Constants with Transition Metal Cations in Aqueous Media

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**Abstract** Six new triazole compounds were synthesized. These compounds containing the substituted benzylidenamino group were obtained by reaction of 3-(pyridine-4-yl)-5*p*-tolyl-4-amino-4H-1,2,4-triazole **1** with the corresponding aldehyde. The reduced forms were prepared with NaBH<sub>4</sub> in methanol. The structures of the compounds were determined by IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectral data, and their interaction with cations such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup> were investigated by using UV-visible spectrophotometry. Of the tested metal cations, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup> complexed with the ligands. The complex stability constants (log<sub>10</sub> K) were measured in slightly acidic aqueous media at 25.0 ± 0.1 °C. These stability constants were determined by measuring the increase in solubility of the nearly insoluble ligand molecule due to complex formation with a soluble cation, and this method is discussed. It was found that the position of chlorine atoms on the benzene ring strongly affects the complexation of Cu<sup>2+</sup> ion with these ligands.

Keywords Triazole · Synthesis · Complexes · Stability constant · Ligand solubility

## 1 Introduction

A large number of heterocyclic compounds containing the 1,2,4-triazole ring are associated with diverse pharmacological properties, such as antiinflammatory, antifungal, antimicrobial, anticonvulsant, antidepressant, antiviral and antitumor activity [1-10]. Some synthetic thiazoles also exhibit a range of biological activities. In addition, it is well known that Schiff

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bases possess potent activities including antimicrobial, anticonvulsant, antiviral and antiinflammatory [11–14]. Recently, a series of thiazolyl Schiff bases bearing the 1,2,4-triazole ring were synthesized and investigated for their antitumor activity against three human cancer cell lines, HL-60 (leukemia), BGC-823 (stomach) and HEP-2 (larynx cancer) [15].

It has been found that metal-ligand complexes of some thiosemicarbazone ligands have increased biological activity [16]. Forming the palladium complex of a Schiff base bearing the thiosemicarbazone moiety enhances the ligand's antitumor activity [17]. Similarly, the antioxidant effect of thiosemicarbazone derivative Schiff bases and their metal complexes was studied on rats, and it was shown that the zinc complex behaved as an antioxidant [18]. Similarly, the influences of metal complexes with 1,2,4-triazoles on biological activity are the subject of great interest in clinic chemistry [19].

In view of this, several articles devoted to the syntheses and biological activity of 4-arylidenamino-4H-1,2,4-triazoles have been published recently [8–10]. Due to their structural features, the 4-arylidenamino-4H-1,2,4-triazoles are important as being potential biologically active compounds [8–10]. The synthesis of certain 4-arylidenamino-4H-1,2,4-triazoles **2–4** was carried out in the present study by treating 3-(pyridine-4-yl)-5-*p*-tolyl-4-amino-4H-1,2,4-triazole 1 with selected aldehydes. Compound **1** was obtained from the reaction of ethyl *p*-tolylbenzoate (pyridine-4-yl) hydrazone with hydrazine by using a published method [9]. In general, reduction of an imine-type compound is possible [8–10, 20]. However, attempts to reduce the imines **2–4** may also result in reduction of the hetero ring. For this reason, selective reduction of only the imino group of compounds **2–4**, without affecting the hetero ring, was carried out in the present study. Thus, a general and convenient method was established for the synthesis of 4-arylmethylamino-4H-1,2,4-triazoles **5–7** in good yields by using NaBH<sub>4</sub> as a selective reducing agent.

Recently, metal complexes of Schiff base containing triazole ligands have been studied in the solid state by X-ray crystallography [21]. The copper(I) complex of N-benzylidene-3,5-di(2'-pyridyl)-4-amino-1,2,4-triazole was characterized by UV-vis, luminescence, and <sup>1</sup>H NMR spectroscopy and by cyclic voltammetry in a dichloromethane solution [22]. In the present study we investigated the complexation behavior between novel 1,2,4-triazole ligands with a substituted benzylideneamino group and various transition metal cations, and also with Pb<sup>2+</sup>, in aqueous solution. The extent of complexation was evaluated by measuring the stability constants.

The most common experimental techniques for determining stability constants of complexes are potentiometry, conductometry, polarography, UV-vis and fluorescence spectroscopy, NMR spectroscopy, mass spectrometry, kinetic measurement and calorimetry [23–29]. Due to the low solubility of triazoles, no common experimental methods can be used to study their complex formation in aqueous solution. Some years ago a technique was developed to study reactions between nearly insoluble ligands and salts [30]. Thus, it was shown that it is possible to calculate the stability constants of the complexes formed between nearly insoluble ligands and cations under certain conditions, based on the increase in solubility of these ligands in aqueous solution [31, 32]. We applied this method to the complexation of novel triazole ligands with cations in aqueous media. Revealing the complexation properties of the novel Schiff bases bearing a triazole ring, with metal cations in aqueous media, is important for the further investigation of the biological activity of these ligands.

#### 2 Experimental

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#### 2.1 Chemicals and Apparatus

All chemicals used in the synthesis of the ligands were purchased from Merck and Fluka. The starting compound **1** was synthesized by the method reported earlier [9]. The anhydrous salts LiCl, NaCl, KCl, RbCl, CsCl, BaCl<sub>2</sub>, SrCl<sub>2</sub>, CoCl<sub>2</sub>, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, CaCl<sub>2</sub>, NiCl<sub>2</sub>, CdCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, CrCl<sub>3</sub>, and AgNO<sub>3</sub> (all from Merck) were of the highest purity available and were used without further purification. Doubly distilled water was used as the solvent.

Melting points were determined on a Büchi oil-heated melting-point apparatus and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian 200 A spectrometer using tetramethylsilane as the internal reference. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer using KBr pellets. Absorption spectra of the solutions were recorded using a Varian Cary 5E spectrophotometer.

#### 2.2 Measurements

The solid ligands were added to slightly acidic aqueous solutions of the salts  $(2 \times 10^{-3} \text{ to } 2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})$ . The amount of ligand added was high enough to ensure formation of saturated solutions. The solutions were thermostatted at 25 °C and shaken at intervals. Samples of the solutions were analyzed after three days. The solutions were centrifuged and the resulting clear solutions were filtered through a membrane filter (polycarbonate, 0.4 µm) to remove the undissolved ligand. The absorption spectra of the solutions were then recorded. Changes in the absorption of the solutions due to complex formation were evaluated at the absorbance maximum wavelength. The wavelengths used for the measurement of the stability constants were 264, 575, 511, 394, 300, 302, 300 and 301 nm for Cu<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup>, respectively, with all of the ligands.

## 2.3 Synthesis

## 2.3.1 General Method for the Synthesis of Compounds 2-4

The corresponding aldehyde (0.005 mole) was added to a solution of compound **1** (0.005 mole) in 20 mL of glacial acetic acid and the mixture was refluxed for 4 h. After cooling, the mixture was poured into a beaker containing 100 mL of ice water. The formed precipitate was separated by filtration. After being dried in vacuo, the product was recrystallized from an appropriate solvent to give the desired compound.

3-(Pyridin-4-y1)-5-(*p*-tolyl)-4-(2-chlorobenzylidenamino)-4H-1,2,4-triazole **2** was recrystallized from ethanol. The yield was 75%, m.p. 161–162 °C; IR (KBr): 1608 and 1590 cm<sup>-1</sup> ( $v_{2C=N}$ ); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  = 2.38 (s, 3H, CH<sub>3</sub>), Ar-H: [7.37 (d, 3H), 7.54–7.74 (m, 6H), 7.86 (s, 1H), 8.10–8.16 (m, 1H), 8.45 (d, 1H)], 8.80 (s, 1H, N=CH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  = 165.97 (N=CH),  $\delta$  = 150.34 (triazole C<sub>3</sub>), 150.01 (triazole C<sub>5</sub>), Ar-C: [142.73 (CH), 139.90 (CH), 139.54 (C), 135.10 (C), 130.27 (C), 129.99 (CH), 129.38 (2CH), 129.05 (2CH), 128.82 (2CH), 128.37 (2CH), 128.22 (CH), 127.33 (CH), 123.60 (C), 122.10 (C)], 20.85 (ar-CH<sub>3</sub>).

3-(Pyridin-4-yl)-5-(*p*-toly1)-4-(2,4-dichlorobenzylidenamino)-4H-1,2,4-triazole **3** was recrystallized from ethanol. The yield was 86%, m.p. 162–163 °C; IR (KBr): 1601 and 1583 cm<sup>-1</sup> ( $\nu_{2C=N}$ ); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  = 2.37 (s, 3H, CH<sub>3</sub>), Ar-H: [7.21–7.39 (m, 3H), 7.62–7.83 (m, 6H), 8.05–8.21 (m, 1H), 8.35–8.45 (m, 1H)], 8.75 (s, 1H, N=CH);

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  = 164.92 (N=CH),  $\delta$  = 150.70 (triazole C<sub>3</sub>), 150.33 (triazole C<sub>5</sub>), Ar-C: [148.18 (CH), 139.94 (CH), 139.58 (C), 138.63 (C), 135.91 (C), 133.76 (CH), 129.91 (C), 129.52 (2CH), 129.40 (2CH), 128.49 (2CH), 127.63 (2CH), 127.35 (CH), 123.02 (C), 122.13 (C)], 20.86 (ar-CH<sub>3</sub>).

3-(Pyridin-4-yl)-5-(*p*-tolyl)-4-(2,6-dichlorobenzylidenamino)-4H-1,2,4-triazole **4** was recrystallized from ethanol. The yield was 82%, m.p. 162–163 °C; IR (KBr): 1601 and 1583 cm<sup>-1</sup> ( $\nu_{2C=N}$ ); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta = 2.37$  (s, 3H, CH<sub>3</sub>), Ar-H: [7.33–7.39 (m, 2H), 7.63–7.70 (m, 3H), 7.77–7.85 (m, 2H), 8.06–8.18 (m, 2H), 8.69–8.75 (m, 2H)], 8.78 (s, 1H, N=CH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta = 164.92$  (N=CH),  $\delta = 150.69$  (triazole C<sub>3</sub>), 150.33 (triazole C<sub>5</sub>), Ar-C: [139.93 (CH), 139.57 (CH), 138.64 (C), 135.92 (C), 133.75 (C), 129.92 (CH), 129.63 (C), 129.52 (2CH), 129.39 (2CH), 128.55 (2CH), 128.48 (2CH), 128.85 (CH), 123.53 (C), 122.14 (C)], 20.86 (ar-CH<sub>3</sub>).

#### 2.3.2 General Method for the Synthesis of Compounds 5–7

The corresponding compound **2–4** (0.005 mole) was dissolved in 50 mL of dried methanol and NaBH<sub>4</sub> (0.005 mole) was added in small portions to this solution. The mixture was refluxed for 20 min and then allowed to cool. After concentration at 25 to 30 °C under reduced pressure, the resulting solid residue was washed with cold water. After drying in vacuo, the solid product was recrystallized from an appropriate solvent to yield the desired compound.

3-(Pyridin-4-yl)-5-(*p*-tolyl)-4-(2-chlorobenzylamino)-4H-1,2,4-triazole **5** was recrystallized from ethyl acetate. The yield was 89%, m.p. 162–163 °C; IR (KBr): 3309 ( $\nu_{NH}$ ), 1619 and 1608 cm<sup>-1</sup> ( $\nu_{2C=N}$ ); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta = 2.38$  (s, 3H, CH<sub>3</sub>), 3.86 (d, 2H, CH<sub>2</sub>), 6.83 (t, 1H, NH) Ar-H: [7.05–7.34 (m, 4H), 7.37–7.43 (m, 4H), 7.75–7.94 (m, 4H)]; <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta = 150.34$  (triazole C<sub>3</sub>), 150.01 (triazole C<sub>5</sub>), Ar-C: [142.73 (CH), 139.90 (CH), 139.54 (C), 135.10 (C), 130.27 (C), 129.99 (CH), 129.38 (2CH), 129.05 (2CH), 128.82 (2CH), 128.37 (2CH), 128.22 (CH), 127.33 (CH), 123.60 (C), 122.10 (C)], 51.39 (CH<sub>2</sub>), 20.85 (ar-CH<sub>3</sub>).

3-(Pyridin-4-yl)-5-(*p*-tolyl)-4-(2,4-dichlorobenzylamino)-4H-1,2,4-triazole **6** was recrystallized from ethyl acetate. The yield was 86%, m.p. 162–163 °C; IR (KBr): 3329 ( $\nu_{\rm NH}$ ), 1602 and 1598 cm<sup>-1</sup> ( $\nu_{2C=N}$ ); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  = 2.39 (s, 3H, CH<sub>3</sub>), 3.85 (d, 2H, CH<sub>2</sub>), 6.80 (t, 1H, NH), Ar-H: [7.07 (d, 1H), 7.22–7.47 (m, 6H), 7.76–7.88 (m, 4H)]; <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  = 153.64 (triazole C<sub>3</sub>), 151.84 (triazole C<sub>5</sub>), Ar-C: [149.66 (CH), 139.87 (CH), 139.25 (C), 134.45 (2CH), 133.80 (2CH), 133.11 (2CH), 132.34 (2CH), 129.19 (CH), 128.89 (C), 128.35 (2CH), 127.71 (C), 126.85 (C), 124.07 (C), 123.56 (C)], 50.92 (CH<sub>2</sub>), 20.85 (ar-CH<sub>3</sub>).

3-(Pyridin-4-yl)-5-(*p*-tolyl)-4-(2,6-dichlorobenzylaınino)-4H-1,2,4-triazole **7** was recrystallized from ethyl acetate. The yield was 84%, m.p. 162–163 °C; IR (KBr): 3327 ( $\nu_{\text{NH}}$ ), 1601 and 1598 cm<sup>-1</sup> ( $\nu_{2\text{C}=\text{N}}$ ); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  = 2.41 (s, 3H, CH<sub>3</sub>), 3.86 (d, 2H, CH<sub>2</sub>), 6.80 (t, 1H, NH), Ar-H: [7.05–7.10 (m, 1H), 7.23–7.36 (m, 4H), 7.40–7.48 (m, 1H), 7.77–7.89 (m, 5H)]; <sup>13</sup>C NMR (DMSO-d<sub>6</sub>) :  $\delta$  = 153.64 (triazole C<sub>3</sub>), 151.83 (triazole C<sub>5</sub>), Ar-C: [149.66 (CH), 139.87 (CH), 139.25 (C), 134.45 (2CH), 133.78 (2CH), 133.31 (2CH), 132.62 (2CH), 129.19 (CH), 128.90 (C), 128.35 (2CH), 127.75 (C), 126.85 (C), 124.07 (C), 121.66 (C)], 50.92 (CH<sub>2</sub>), 20.93 (ar-CH<sub>3</sub>).

#### 3 Results and Discussion

#### 3.1 Treatment of the Experimental Data

The formation of a 1:1 complex between a ligand L and a cation  $M^{n+}$  can be described by:

$$\mathbf{L} + \mathbf{M}^{n+} \rightleftharpoons \mathbf{L} \mathbf{M}^{n+} \tag{1}$$

The corresponding stability constant is defined as:

$$K = \frac{[\mathrm{LM}^{n+}]}{[\mathrm{L}][\mathrm{M}^{n+}]} \tag{2}$$

If only the ligand and the complex formed absorb at a given wavelength, then the experimentally measured absorptivity A' for an optical path length d is given by Eq. 3:

$$A = (A'/d) = \varepsilon_1[L] + \varepsilon_2[LM^{n+}]$$
(3)

The molar absorptivities of the ligand and complex are  $\varepsilon_1$  and  $\varepsilon_2$ , respectively. The salt solution is saturated with the ligand so the first term in Eq. 3 is constant. As a result one gets:

$$A_{\rm o} = \varepsilon_1 [L]_{\rm sat} \tag{4}$$

where  $[L]_{sat}$  denotes the solubility of the ligand in the pure solvent. Equations 5 and 6 describing the material balances,

$$c_{\rm M} = [{\rm M}^{n+}] + [{\rm L}{\rm M}^{n+}],$$
 (5)

$$c_{\rm L} = [\mathrm{L}]_{\rm sat} + [\mathrm{L}\mathrm{M}^{n+}] \tag{6}$$

where  $c_{\rm M}$  and  $c_{\rm L}$  are the total concentrations of the ion and the ligand in solution, respectively. Equation 3 can be transformed into Eq. 7 using Eq. 2:

$$(A/A_{o}) - 1 = [(\varepsilon_{2}/\varepsilon_{1})Kc_{salt}]/(1 + K[L]_{sat})$$

$$\tag{7}$$

Plotting  $(A/A_o) - 1$  as a function of the total salt concentration  $c_{salt}$ , one gets a straight line with the slope *b*. From this slope the stability constant of the complex can be calculated according to Eq. 8:

$$K = b/[(\varepsilon_2/\varepsilon_1) - b[\mathbf{L}]_{\text{sat}}]$$
(8)

If both molar absorptivities are nearly equal and the solubility of the ligand is low, then the stability constant *K* is given by the slope *b*. The correctness of these assumptions has already been established for some macrocyclic ligands such as cryptands, cucurbit[n]urils, aza crown ethers and benzo crown ethers [26, 30–35].

## 3.2 The Synthesis and Characterization of Ligands

The synthetic pathways to the new ligands (2–7) are summarized in Scheme 1. Many substituted 4-amino-3,5-diaryl-4H-1,2,4-triazoles have been prepared by using known methods [8–10]. 4-Amino-3-phenyl-5-pyridinyl-4H-1,2,4-triazole 1 was synthesized according to a



Scheme 1 The synthetic pathways for the triazole ligands used in the present study

literature method [9]. Schiff bases 2–4 were prepared by the condensation of 4-amino-3phenyl-5-pyridinyl-4H-1,2,4-triazole 1 with various aldehydes in acetic acid. During the reduction of compounds 2–4, formation of multiple products was possible since reduction of the hetero ring might occur. However, the reductions were performed on the imino group of 5–7 without affecting the hetero ring by using NaBH<sub>4</sub> as a selective reducing agent.

IR spectra showed C=N bands of 2-4 in the 1583–619 cm<sup>-1</sup> region. The <sup>1</sup>H NMR characteristic signals of 2-4 were observed at  $\delta = 8.55-8.80$  ppm (s, 1H, N=CH). The <sup>13</sup>C NMR signals for the -N=CH- group of compounds 2-4 were recorded at  $\delta = 164-166$  ppm. Arylmethylamino derivatives 5-7 showed IR absorption bands around 3309–3290 cm<sup>-1</sup> ( $\nu_{NH}$ ). The <sup>1</sup>H NMR characteristic signals of 5-7 were observed as a triplet at  $\delta = 6.80-6.83$  ppm (t, 1H, NH) and as a doublet at  $\delta = 3.85-3.86$  ppm (d, 2H, CH<sub>2</sub>); the -NH-CH<sub>2</sub>- carbon signal of compounds 5-7 were recorded between  $\delta = 50$  and 52 ppm.

#### 3.3 The Stability Constants of Metal-Ligand Complexes

Any experimental method for the determination of the total concentration of a ligand in a salt solution, e.g. UV-Vis spectroscopy or TOC measurements, allow the determination of the stability constant of the complex formed in solution. It is not necessary to know the exact relation between the measured signals and the ligand concentrations, and the intensities of the signals only need to be directly proportional.

In the present study Cu<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup> cations caused a small change in the absorption spectra of all the ligands. Therefore, we can say that the molar absorptivities of the ligand and complex,  $\varepsilon_1$  and  $\varepsilon_2$ , are nearly the same. The measurements were carried out at an appropriate wavelength in which the increments of absorbance are regular functions of increasing metal concentration. There was no regular correlation between  $(A/A_0) - 1$  and  $c_{salt}$  in the case of other tested metal ion such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup>. Because of this, the corresponding stability constant could not be calculated for those cations.

For the Cu<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup> cations, straight lines were found in accordance with Eq. 7 for all of the studied ligands. Owing to complex formation, the total concentration of the dissolved ligand in solution increased. The change in the total concentration of the dissolved ligand was monitored with spectrophotometric measurements. The complex stability constant (*K*) was calculated according to the present method, which was previously used for various macrocyclic ligands [30–35]. The quantity  $(A/A_0) - 1$  is plotted versus  $c_{salt}$ , and the stability constant is given by the slope. For example, the linear response of  $(A/A_0) - 1$  versus  $c_{Cu2+}$  for ligand **7** with Cu<sup>2+</sup> is represented by the equation y = 3546.2x - 6.43 with a correlation coefficient of 0.9913.

Cation	$\log_{10} K^{a}$					
	2	3	4	5	6	7
Cu <sup>2+</sup>	$2.46\pm0.07$	$2.53\pm0.06$	$3.13\pm0.02$	$3.42\pm0.04$	$2.82\pm0.05$	$3.80 \pm 0.04$
Cr <sup>3+</sup>	$3.12\pm0.01$	$3.11\pm0.01$	$3.22\pm0.02$	$3.31\pm0.01$	$3.23\pm0.01$	$3.16\pm0.01$
Co <sup>2+</sup>	$3.17\pm0.01$	$3.09\pm0.01$	$3.04\pm0.01$	$3.08\pm0.01$	$2.83\pm0.01$	$3.02\pm0.01$
Ni <sup>2+</sup>	$3.14\pm0.01$	$3.08\pm0.01$	$3.09\pm0.01$	$3.04\pm0.01$	$3.10\pm0.01$	$3.18\pm0.01$
$Zn^{2+}$	$2.49\pm0.01$	$2.73\pm0.01$	$2.75\pm0.01$	$3.04\pm0.03$	$2.76\pm0.01$	$2.75\pm0.01$
$Cd^{2+}$	$2.60\pm0.02$	$2.66\pm0.01$	$2.78\pm0.01$	$2.84\pm0.01$	$2.91\pm0.01$	$2.87\pm0.01$
$Pb^{2+}$	$2.61\pm0.02$	$2.69\pm0.01$	$2.77\pm0.01$	$2.88\pm0.01$	$2.95\pm0.01$	$2.92\pm0.01$
Ag <sup>+</sup>	$2.65\pm0.02$	$2.65\pm0.02$	$2.66\pm0.01$	$2.46\pm0.01$	$2.89\pm0.01$	$2.76\pm0.01$

**Table 1** Stability constants  $(\log_{10} K)$  at infinite dilution for 1:1-complex formation of different new ligands with metal salts in aqueous solution at 25.0 °C

 $^a$  Average values and standard deviations calculated from five independent experiments. The confidence level is 95%

Table 1 shows the stability constants (as  $\log_{10} K$ ) determined by means of the present method for Cu<sup>2+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup> and Ag<sup>+</sup> ions with all of the ligands. As seen from the table, the stability constants increase when the ligand changes from 2 to 3 for  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions. These results show that the number of chlorine atoms has a strong effect on the complexation. Namely, increasing the number of chlorine atoms increases the stability constant for these cations. This situation may be explained by the increasing electron density on the azomethine bond that increases the electron donor properties of the nitrogen atom. Consequently, more stable complexes form with ligand 3 compared with ligand 2. Similarly, the stability constants increase when the ligand changes from 3 to 4 for all of the metal cations except for  $Co^{2+}$ . This result shows that the position of the second chlorine atom is also important for the complexation for these cations with the Schiff base ligands. In ligand 4 the second chlorine atom, which is located on the 6-position, increases the electron donor properties of the nitrogen atom because of its nearer position to the azomethine group that is attached to the benzene ring. This produces more stable complexes with the ligand having the 2-6-dichloro-phenyl group with the mentioned metal cations. The position effect of the second chlorine atom is observed most strongly for Cu<sup>2+</sup>. The value of  $\log_{10} K$  increases from 2.53 to 3.13 when the ligand changes from 3 to 4. The smallest position effect of the chlorine atom is seen on the complexation of Ni<sup>2+</sup> and Ag<sup>+</sup> cations for ligands, **3** and **4**. When the ligand changes from **3** to **4** the  $\log_{10} K$  value remains constant at 2.65–2.66 and 3.08–3.09 for Ag<sup>+</sup> and Ni<sup>2+</sup>, respectively.

As seen from Table 1, all of the Schiff base ligands and their reduced forms give stable complexes having  $\log_{10} K$  values that are higher than 3.04 with the  $Cr^{3+}$  and  $Ni^{2+}$  cations. A similar situation occurs for  $Co^{2+}$  except for ligands, **6** and **7**. However, the values of  $\log_{10} K$  for the  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Ag^+$  ions with all of the ligands are below 2.95. A similar situation occurs for  $Zn^{2+}$  except for ligand **5**. It is interesting to note that complexation with the  $Cu^{2+}$  cation is affected most by the structure of the ligands. It is clear that  $Cu^{2+}$  gives the most stable complex with ligand **7** among the ligands. The corresponding  $\log_{10} K$  value is 3.80 in this case. Consequently, Table 1 shows that moderately soft metal cations ( $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ) form more stable complexes with the triazole ligands compared to soft metal cations such as  $Cd^{2+}$  and  $Ag^+$ . We can say that the nitrogen atoms of the triazole ligands are effective for metal complexation. The nitrogen atom belonging to an azomethine group may also participate in complexation. As is known, the nitrogen atom is a moderately

soft donor atom in coordination compounds. Therefore, one expects that the present triazole ligands form more stable complexes with moderately soft transition metal cations such as  $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , compared with soft metal cations such as  $Cd^{2+}$  and  $Ag^+$ .

The results presented here clearly demonstrate the possibility of quantitatively studying complexation reactions between triazole ligands and metal cations even when the ligand is nearly insoluble in water. Due to the fact that nearly insoluble triazole ligands were used, very small samples of them are sufficient to perform these measurements. Therefore the present method requires only very small samples of the ligand for the study of complex formation. The method is rapid and simple. Moreover, the ligand sample can be recovered after the determination. Because of low solubility properties of triazole compounds in aqueous media, there is no convenient method described in the literature for measuring complexation properties of these types of ligands with metal cations. The presented method is therefore important in this respect.

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