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Conductometric and Spectrophotometric Studies of Thermodynamics of Complexation of Zn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} and Cu^{2+} Ions With 2,2'-Dimethyl-4,4'-bithiazole in Acetonitrile Solution

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In this work, the complexation reactions between 2,2'-dimethyl-4,4'-bithiazole (DMDTZ) and Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+} ions were studied conductometrically and spectrophotometrically in acetonitrile solution at various temperatures. The formation constants of the resulting 1:2 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. At 25 ºC, the stability of the resulting complexes varied in the order $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants.

Key Words: Conductometric, Spectrophotometric, Stability constants, Thermodynamics, Complexation, 2,2'-Dimethyl-4,4'-bithiazole.

INTRODUCTION

The first 2,2'-bithiazoles and 4,4'-bithiazoles have synthesized by Erlenmeyer and Uberwasser and then other bithiazoles and it's derivatives have have been synthesized[1-3]. In recent years the bithiazole derivatives have been used for many application[4-8]. Bleomycins are antitumour agents[9,10] and the effect of bithiazoles for binding of bleomycin to DNA has caused the design and synthesis of different compounds of these ligands has done by researchers. The bithiazole moiety, one domain of bleomycin, was shown to be responsible for binding of bleomycin to DNA, which caused such great interest that there has been an explosion in the research effort directed toward the design and synthesis of model compounds that can specifically recognize and cleave DNA. A number of bithiazole derivatives, however, indicated that many of these derivatives uniformly inhibit breakage of DNA by bleomycin. The bithiazole derivatives examined only promote helix unwinding and overwinding (positive supercoiling). Recently, Sasaki[11] found that the bithiazole derivative 2,2´-*bis*(2-aminoethyl)-4,4´-bithiazole demonstrates Co^{2+}-activated DNA cleaving activity.

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In recent years, the complexation of transition metal complexes with several multidentate non-cyclic and macrocyclic ligands in nonaqueous and mixed solvents has been investigated[12-21]. Since the study of complexation reaction in solution is very important and the nature of solvent may strongly influence the stoichiometry and thermodynamics of transition metal complexes in solution, it is decided to study the complexation reaction between a recently synthesized bithiazole ligand (Fig. 1) and some transition metal ions in acetonitrile. Consequently, we reported the stoichio-metry and thermodynamic parameters (log k_f, ΔH^o and ΔS^o) for the interaction of metallic ions (Co^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+} and Ni^{2+}) with DMDTZ ligand (L) by conducto-metric and spectrophotometric methods[22,23].

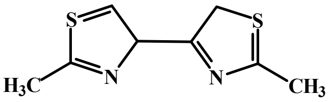

Fig. 1. Structure of 2,2'-dimethyl-4,4'-bithiazole (DMDTZ)

EXPERIMENTAL

Reagent grade nitrate salts of cobalt, copper, zinc, nickel and lead (all from Merck) and recently DMDTZ ligand (L) synthesized were of highest purity available[24] (> 99 %) and used without any further purification except for vacuum drying over P_2O_5. Reagent grade acetonitrile (Merck) was purified and dried by the previously described method[24]. The conductivity of the solvent was less than 1×10^{-7} S cm^{-1}.

Conductivity measurements were carried out with a Metrohm712 conductometer equipped with circulator model grant. In all measurements, cell was thermostated at desired temperature ± 0.1 ºC. The cell constant at the different temperature was determined by measuring the conductivity of a 1×10^{-2} mol cm^{-3} solution of analytical grade KCl (Merck) in triply distilled deionized water. The specific conductance of this solution at various temperatures has been reported in the literature[25]. The corresponding cell constant at 15, 25, 35 and 45 ºC were 0.834, 0.832, 0.829 and 0.820 cm^{-1}, respectively. A dip-type conductivity cell made of platinum blak.

All UV-Vis absorbance spectra were collected using a Shimadzu 2550 UV-Vis double-beam spectrophotometer using two matched 10 mm quartz cell.

Conductometry recommended procedure: In a typical experiment 10 mL of the corresponding metal nitrate solution (5×10^{-5} M) in acetonitrile was placed in the two-wall conductometer glass cell equipped with a magnetic stirrer, thermostated at the desired temperature and the conductance of the solution was measured and in order to keep the ionic strength constant during the experiment the solution in the titration vessel was mixed by means of a magnetic stirrer. Then a known amount of the concentrated solution of ligand (DMDTZ) in acetonitrile (5×10^{-3} M) was added in a step wise manner using a 10 µL Hamilton syringe. The conductance of the solution was measured after each addition. Addition of the ligand was continued until the desired ligand to cation mole ratio was achieved.

Spectrophotometry recommended procedure: In a typical experiment, 2 mL of ligand solution (5×10^{-5} M) in acetonitrile was placed in the quartz cell and the absorbance of solution was measured. Then with an 10 µL Hamilton syringe a known amount of the concentrated solution of corresponding metal nitrate (Co^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Ni^{2+}) in acetonitrile (1.25×10^{-3} M) was added in a stepwise manner. The absorbance of the solution was measured after each addition. The salt solution was continually added until the desired metal ion to ligand mole ratio was achieved.

The formation constant (K_f) and the molar absorptivity (ε) of the resulting 1:1 and 1:2 (metallic ion to DMDTZ) complexes between the DMDTZ and different cations at 25 ºC were calculated by fitting the observed absorbance, A_{obs}, at various metal ion/ligand mole ratios to the previously derived equations[17,27], which express the A_{obs} as a function of the free and complexed metal ions and the formation constant evaluated from a non-linear least-squares program KINFIT[28].

RESULTS AND DISCUSSION

The resulting molar conductance (Λ) *vs.* [DMDTZ]/metallic ions mole ratio plots at 25 ºC is shown in Fig. 2 and at different temperatures for nickel(II) has been recorded (Fig. 3). As can be seen in Fig. 2, it is found that: I) in some cases, there is a gradual decrease in the molar conductance with adding of the DMDTZ concentration. This behaviour indicates that the complexed ions are less mobile than the corresponding solvated ions. II) Plots begin to level off at a mole ratio about two, indicating the formation of a stable 2:1 (DMDTZ to metallic ion) complex. III) as expected, the corresponding molar conductance increased rapidly with temperature, due to the decreased viscosity of the solvent and consequently, the enhanced mobility of the charged species present. IV) for each cation, the curvature of the corresponding mole ratio plot decreased with increasing temperature, indicating the formation of weaker complexes at elevated temperatures[29-31].

The 1:1 complexation of M^{2+} ion with DMDTZ ligand can be expressed by the following equilibrium

$$M^{2+} + L = ML^{2+} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

$$k_f = \frac{[ML^{2+}]}{[M^{2+}][L]} \times \frac{f(ML^{2+})}{f(M^{2+})f(L)} \tag{2}$$

where $[ML^{2+}]$, $[M^{2+}]$, [L] and f represent the equilibrium molar concentrations of the complex, free cation, free ligand and the activity coefficients of the species indicated, respectively. Under the highly diluted conditions, we used the activity coefficient of uncharged ligand, f(L), can be reasonably assumed as unity[32-34]. The use of Debye-Huckel limiting law[32] leads to the conclusion that $f(Mn^{+}) \approx f(ML^{n+})$, so the activity coefficients in eqn. 2 can be canceled. Thus, the complex formation constant in terms of the molar conductance can be expressed as[2,29-31]:

$$K_f = \frac{[ML^{2+}]}{[M^{2+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{3}$$

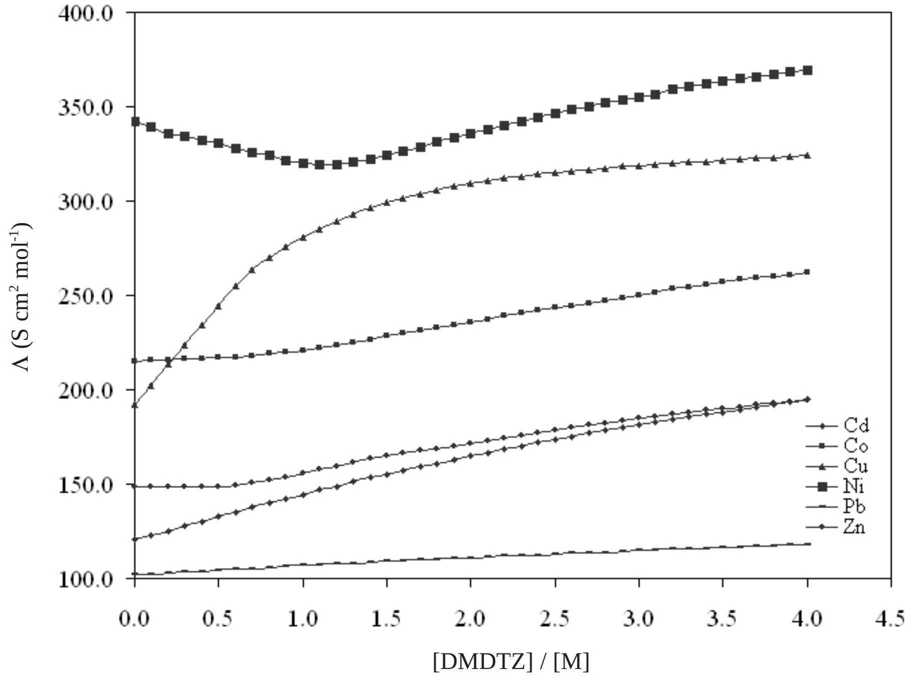

Fig. 2. Molar conductance *vs.* [DMDTZ] / [M^{2+}] plots at 25 ºC

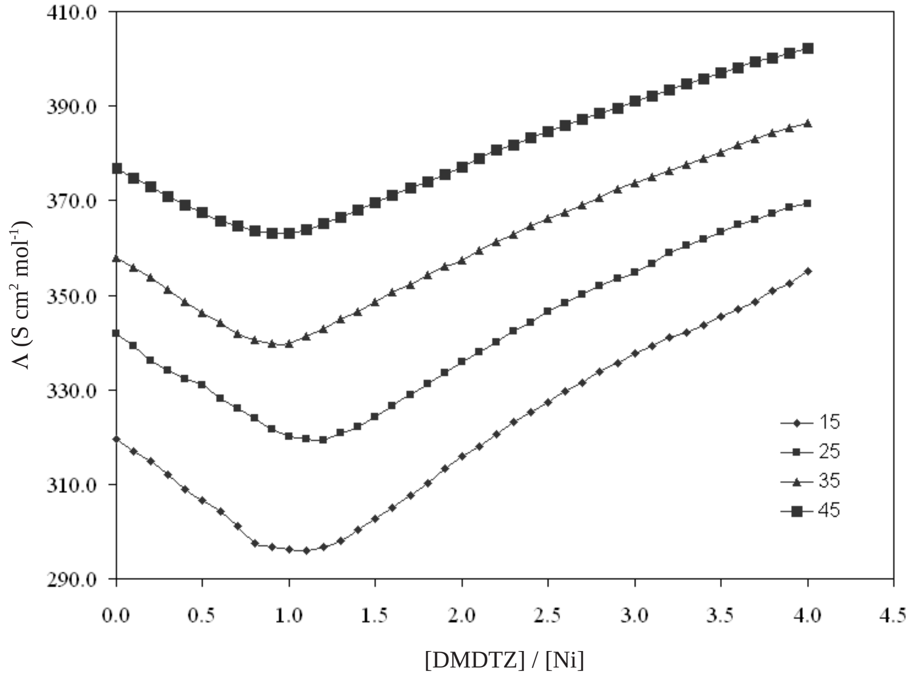

Fig. 3. Molar conductance *vs.* [DMDTZ]/[Ni^{2+}] plots at 15, 25, 35 and 45 ºC

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \tag{4}$$

Λ_M, Λ_{obs}, Λ_{ML}, C_L and C_M are molar conductance of the metal nitrate before addition of the ligand, the molar conductance of solution during titration, the molar conductance of the complex, the analytical concentration of the ligand added and the analytical concentration of the metal nitrate respectively.

The mass balance equations are given by:

$$C_M = [M^{2+}] + [ML^{2+}] \tag{5}$$

$$C_L = [L] + [ML^{2+}] \tag{6}$$

where C_M and C_L are the initial analytical concentration of M^{2+} and the DMDTZ ligand, respectively. The mass balance equations for the 1:1 model can be solved in order to obtain an equation for the ligand concentration, [L], as:

$$K_f[L]^2 + (1 + K_fC_M - K_fC_L)[L] - C_L = 0 \tag{7}$$

when the reaction between M^{2+} and ligand produce ML_2 complex, the mass balance equations are given by:

$$C_M = [M^{2+}] + [ML^{2+}] + [ML_2] \tag{8}$$

$$C_L = [L] + [ML^{2+}] + 2[ML_2] \tag{9}$$

The mass balance equations for the 1:2 models can be solved in order to obtain an equation for the ligand concentration:

$$K_1K_2[L]^3 + K_1(1 + K_2(2C_M - C_L))[L]^2 + (1 + K_1(C_M - C_L))[L] - C_L = 0 \tag{10}$$

The formation constant (K_f) and the molar conductance (Λ_{ML}) of the resulting 1:1 and 1:2 (metal ion to ligand) complexes between the DMDTZ and different cations were calculated at different temperatures by fitting the observed conductance, Λ_{obs}, at various metal ion/ ligand mole ratios to the 7 and 10 equations, which express the Λ_{obs} as a function of the free and complexed ligand. The formation constant evaluated from a non-linear least-squares program KINFIT[28].

Sample computer fit of the mole ratio data for Ni-DNDTZ systems are shown in Fig. 4. The assumption of 1:1 and 1:2 (metallic ion to ligand) stochiometry for the resulting complexes of metallic ions was further supported by excellent agreement between the observed and calculated molar conductances in the process of computer fitting of the mole ratio data.

It is noteworthy that in the process of calculation of formation constants, the association between metal and NO_3^- ions was considered negligible under the highly dilute experimental conditions (5×10^{-5} M). Since the concentration of ligand was kept below (5×10^{-3} M) during the experiments, correction for the viscosity changes was also neglected.

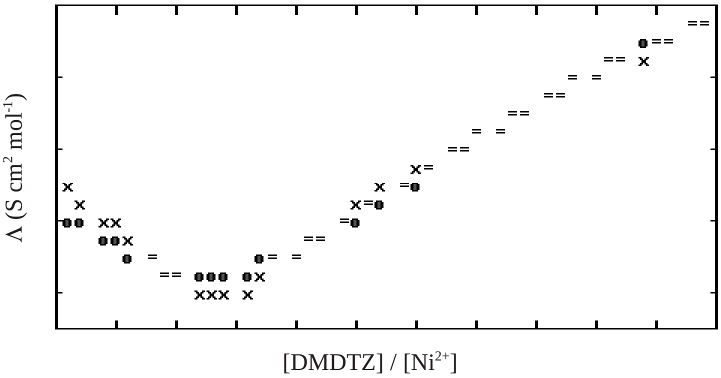

Fig. 4. Computer fit of molar conductance *vs.* [DMDTZ]/[Ni^{2+}] mole ratio plot in acetonitrile at 25 ºC, (×) experimental point, (•) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

In order to have a better understanding of the thermodynamic of the complexation reactions of M^{2+} ions with the DMDTZ ligand, it is useful to consider the enthalpic and entropic contributions to these reactions. The ΔH and ΔS values for the complexation reactions were evaluated from the corresponding log K_f and temperature data by applying a linear least squares analysis according to the eqn. 11.

$$2.303 \log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

Plots of log K_f *vs.* 1/T for different metal ions-DMDTZ system were linear for all cases, (Fig. 5, K_β value have been used). The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots and the results are included in Table-1. Comparison of the data given in Table-1 indicate that the stability of the $MLML_2$ complexes vary in the order of $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$.

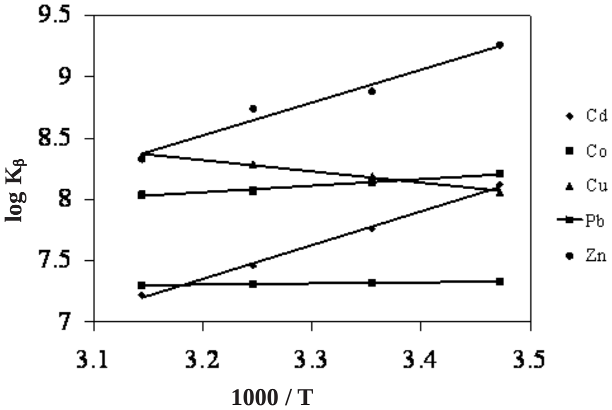

Fig. 5. log K_β *vs.* 1/T for different M^{2+}-DMDTZ complexes ($MLML_2$) in acetonitrile solution

TABLE-1
FORMATION CONSTANTS, ENTHALPIES, ENTROPIES FOR DIFFERENT M^{2+}-DMDTZ COMPLEXES IN ACETONITRILE SOLUTION, (SD = STANDARD DEVIATION)

	log K_β ± SD				$MLML_2$ Complex	
M^{2+}	Temperature (°C)				ΔH°	ΔS°
	15	25	35	45	(KJ/mol)	(J/mol K)
Co^{2+}	8.21 ± 0.01	8.14 ± 0.01	8.07 ± 0.01	8.04 ± 0.01	-10.2 ± 1.2	121.7 ± 4.0
Cu^{2+}	8.06 ± 0.01	8.19 ± 0.01	8.29 ± 0.01	8.36 ± 0.04	17.6 ± 1.6	215.6 ± 5.5
Zn^{2+}	9.26 ± 0.03	8.88 ± 0.02	8.74 ± 0.02	8.33 ± 0.02	-51.3 ± 2.3	-80.4 ± 0.9
Ni^{2+}	8.53 ± 0.07	8.62 ± 0.04	8.84 ± 0.02	8.92 ± 0.02	24.3 ± 1.3	247.5 ± 4.2
Pb^{2+}	7.33 ± 0.02	7.32 ± 0.06	7.31 ± 0.03	7.30 ± 0.02	-1.7 ± 0.5	134.3 ± 1.6
Cd^{2+}	8.12 ± 0.02	7.76 ± 0.04	7.46 ± 0.02	7.22 ± 0.05	-52.6 ± 2.3	-27.7 ± 0.9

Some of of ML complexes have been stable with increase of temperature, but all of them are entropy stable. At 25 °C, the stability of $MLML_2$ complexes (K_β value) are in the order of $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$. This stability order can be explained by Irving-Williams stability order for Zn^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+}. The DMDTZ is a medium base, thus can not interact with Cd^{2+} as a soft acid. The radius of Pb^{2+} ion is grater than other metal ions, thus have small stability than other ions.

Spectrophotometric studies: The electronic absorption spectra of DMDTZ ligand and its Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} complexes in acetonitrile are shown in Fig. 6 and in the increasing of Cu^{2+} and Ni^{2+} are shown in Fig. 7 and 8, respectively. The stochiometry of the metal complexes was examined by the mole ratio method at λ_{max} of its complexes. A sample of the resulting plots is shown in Fig. 9 and it is evident that 1:2 (metal ion to ligand) complexes are formed in solution. The formation constants (K_β) of the resulting 1:1 and 1:2 metal ions to DMDTZ complexes

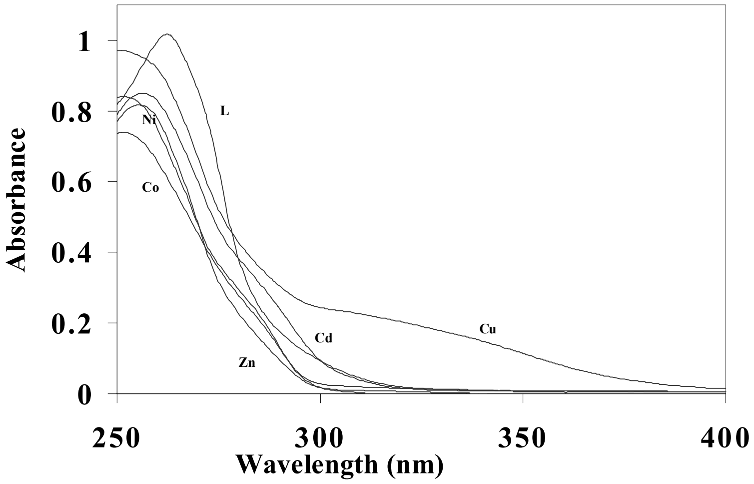

Fig. 6. Electronic absorption spectra of DMDTZ ligand and its metal complexes

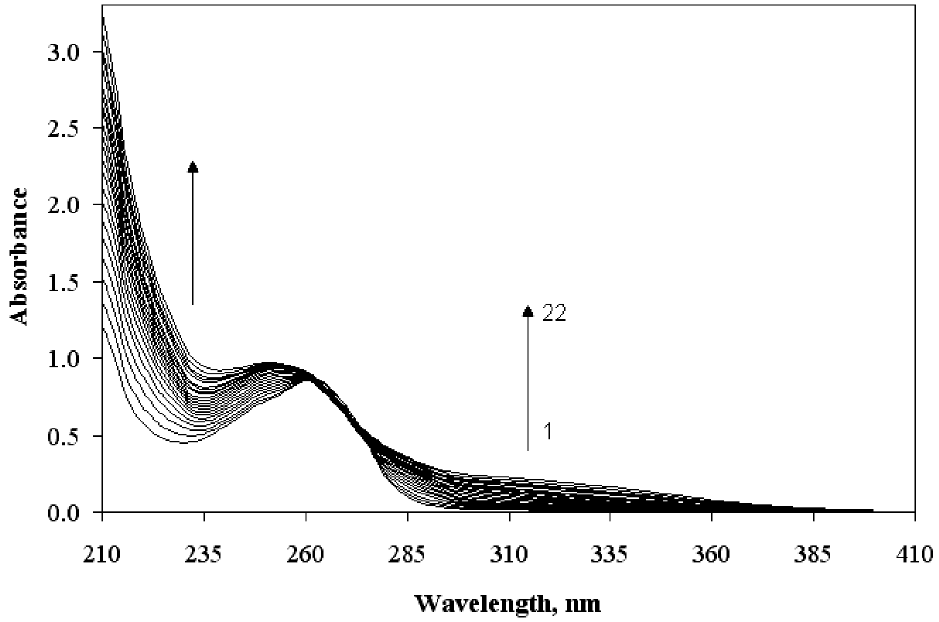

Fig. 7. Electronic absorption spectra of DMDTZ ligand in the presence of increasing concentration of Cu^{2+} ions at 25 ºC, $[Cu^{2+}]$/[DMDTZ] in 1 = 0 (only ligand), 22 = 3.0

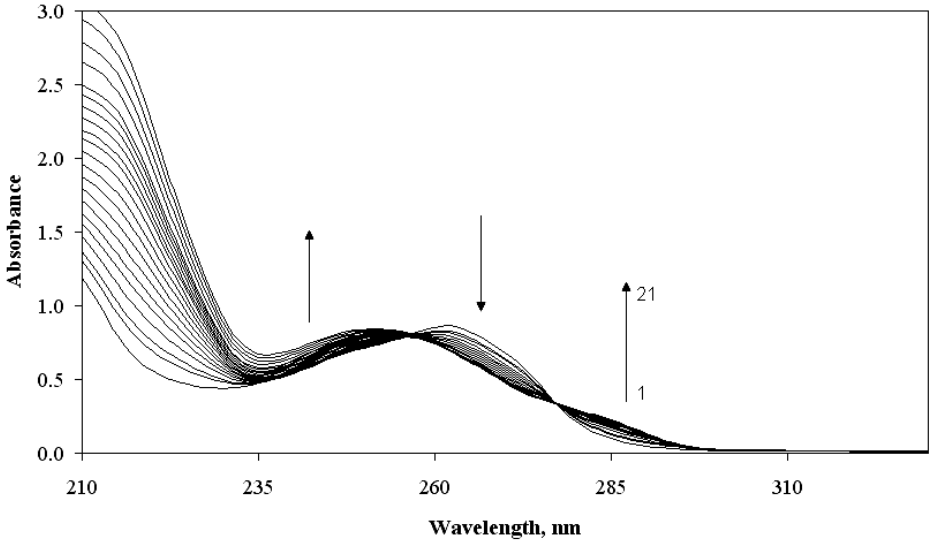

Fig. 8. Electronic absorption spectra of DMDTZ ligand in the presence of increasing concentration of Ni^{2+} ions at 25 ºC, $[Ni^{2+}]$/[DMDTZ] in 1 = 0 (only ligand), 21 = 3.0

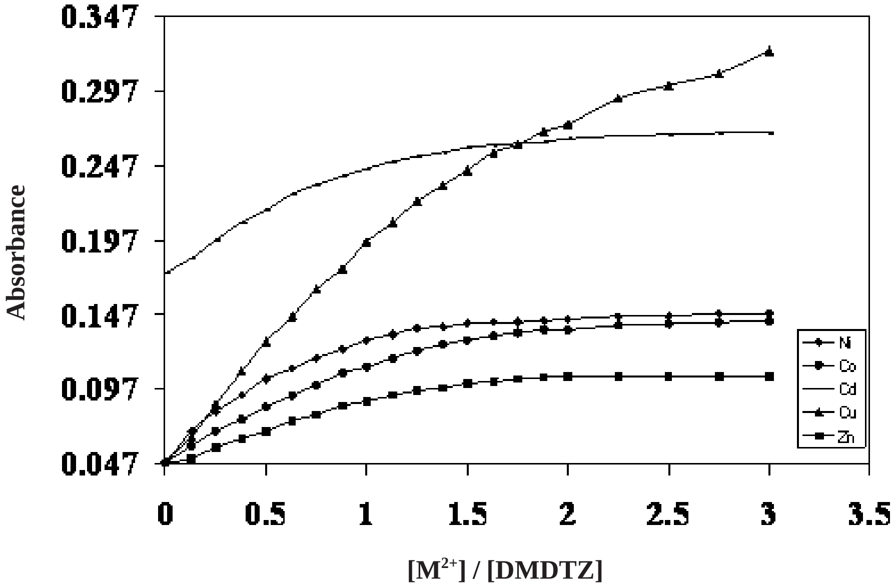

Fig. 9. Mole ratio plots of the DMDTZ ligand with metal ions at λ_{max} of complexes

were obtained at 25 ºC by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts (5×10^{-5} M) of DMDTZ solution, at λ_{max} of complexes. All the resulting absorbance-mole ratio data were best fitted to eqn. 10, which further supports the formation of $MLML_2$ complexes in solution.

For evaluation of the formation constants and molar absorptivity coefficients from absorbance *vs.* [M]/[L] mole ratio data, a non-linear least squares curve fitting program KINFIT[28] was used. Sample computer fits of the absorbance - mole ratio data for Cu^{2+}-DMDTZ and Co^{2+}-DMDTZ at 25 ºC are shown in Fig. 10 and 11, respectively. The resulting log K_f of the M^{2+}-DMDTZ complexes at 25 ºC are listed in Table-2. The data given in Table-2 revealed that the stability (K_β) of the complexes decrease in the order of $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$.

TABLE-2

SPECTROPHOTOMETRIC FORMATION CONSTANTS FOR M^{2+}-(DMDTZ) AT λ_{max} OF COMPLEXES, (SD = STANDARD DEVIATION)

Metallic ions	log K_β
Zn^{2+}	7.83 ± 0.01
Ni^{2+}	7.14 ± 0.01
Cu^{2+}	6.96 ± 0.01
Co^{2+}	6.90 ± 0.01
Cd^{2+}	6.77 ± 0.01

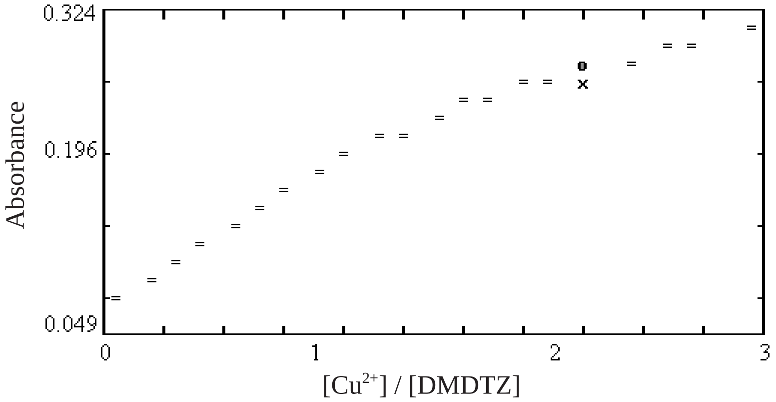

Fig. 10. Computer fit of absorbance *vs.* $[Cu^{2+}]/[DMDTZ]$ mole ratio plot in acetonitrile at the room temperature in wavelength 310 nm, (×) experimental point, (o) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

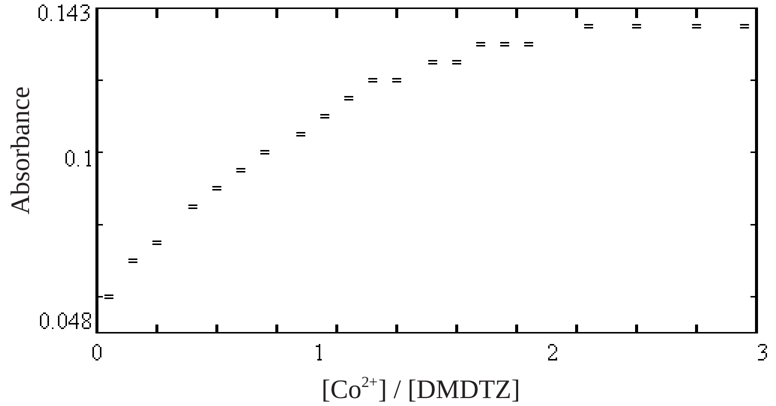

Fig. 11. Computer fit of absorbance *vs.* $[Co^{2+}]/[DMDTZ]$ mole ratio plot in acetonitrile at the room temperature in wavelength 310 nm, (×) experimental point, (o) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

Conclusion

The stoichiometry of 2,2'-dimethyl-4,4'-bithiazole (DMDTZ) ligand (L) with divalent metal ions in acetonitrile solution is ML and ML_2 mixture. At 25 ºC, the stability of the resulting complexes that have been determined by spectrophotometric and conductometric methods varied in the order $Zn^{2+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants and all of the complexation reactions are entropy stable.

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