



Complexation reaction and thermodynamic of a recently synthesized Schiff base ligand, 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio) ethylimino)methyl) -4-bromophenol (PYTABr)

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Abstract

The complex-formation reactions between Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} ions with 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio)ethylimino)methyl)-4-bromophenol(PYTABr) has been studied by spectrophotometric and conductometric methods in acetonitrile at various temperatures. Formation constants of the 1:1 and 1:2 (metal ion to ligand) complexes were evaluated from computer fitting of the absorbance-mole ratio data, and molar conductance-mole ratio data at different temperatures, and found that complexes to vary in the order of $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. The enthalpy and entropy changes of the complexation reaction were determined from the temperature dependence of the formation constants.

Keywords: Conductometric, spectrophotometric, formation constants, schiff bases, complexation.

INTRODUCTION

The condensation of an amine with an aldehyde, forming what is called a Schiff base, is one of the oldest reactions in chemistry (Schiff and Suppl, 1864). Schiff base ligands coordinate to a metal through the imine nitrogen and another group, usually oxygen, situated on the origin aldehyde. When a diamine was first combined with two equiv of salicylaldehyde, the Salen ligands came into being (Atwood et al., 2001; Holm et al., 1966). These ligands are quite familiar as tetradentate ligands in metal complexes (Granovskii et al., 1993; Jacobson et al., 1991; Giacomelli et al., 1985). These ligands with N_2O_2 donor atom set are very well known to coordinate to inorganic and organic cations to give rise to chelate complexes (Carbouaro et al., 1999). Diamine Schiff bases are different from monoamine Schiff bases in having two chromophores bridged by a methylene chain in a molecule, and thus the mutual interactions between the chromophores appears to affect their chemical and physical properties (Carbouaro et al., 1999).

Therefore interesting optical properties derived from the interaction between the two chromophores in the diamine

Schiff bases could be expected. Some of optical properties of diamine Schiff base ligands have been reported in literature (Alizadeh et al., 1999), but the complexation reaction of these complexes in nonaqueous solvents has not been reported. Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are well known to form very stable complexes with transition metal ions (Rihter et al., 1993). Salen complexes of transition metals have been frequently used as catalysts in such diverse processes as oxygen and atom-transfer (Zhang et al., 1990), enantioselective epoxidation (Li et al., 1993), azidation (Aurangzeb et al., 1992), mediating organic redox reactions and recently as ionophores in ion-selective studies (Shamsipur et al., 2001).

Since the nature of solvent may strongly influence the stoichiometry and complexation of transition metal complexes in solution, we decided to study the complexation reaction and thermodynamic of a recently synthesized Schiff base ligand, 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio) ethylimino)methyl) -4-bromophenol (PYTABr), (Figure 1) (Daneshvar et al., 2003) with some transition metal ion

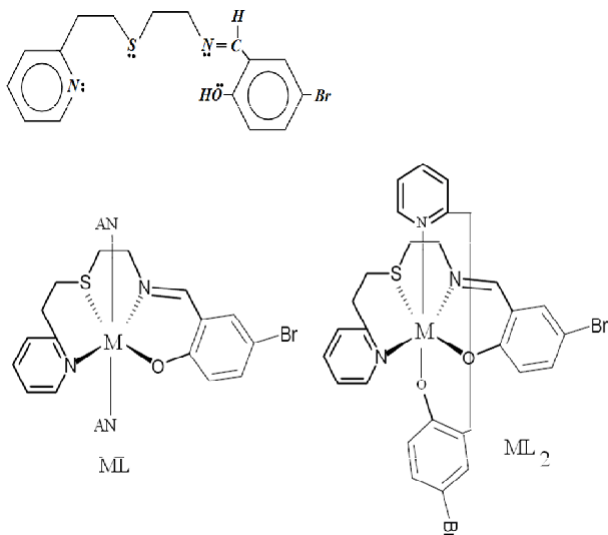


Figure 1. The new Schiff base ligand (PYTABr) and eventual structure of ML and ML₂ complexes in acetonitrile (AN) solution.

in acetonitrile solutions. In this paper we report the conductometric and spectrophotometric studies of the stoichiometry, complexation reaction and thermodynamics of PYTABr Schiff base ligand with Zn²⁺, Cu²⁺, Co²⁺, Ni²⁺ and Cd²⁺ ions in acetonitrile.

EXPERIMENTALS

Reagents

Reagent grade metals nitrates and acetonitrile (AN) all from Merck and recently synthesized PYTABr Schiff base were of highest purity available and were used without any further purification.

Spectrophotometric study

All UV- Vis Spectra recorded on a computerized double-beam Shimadzu 2550 spectrophotometer, using two matched 10 mm quartz cell. Absorption measurements were carried out with a single-beam Jenway 6305 spectrophotometer equipped with a Jenway Heated Cell Block Controller. In a typical experiment, 2.0 ml of ligand solution (5.0×10^{-5} - 1.0×10^{-4} mol L⁻¹) in AN was placed in the spectro-photometer cell and the absorbance of solution was measured. Then a known amount of the concentrated solution of metal ions in AN (1.3×10^{-3} - 1.3×10^{-2} mol L⁻¹) was added in a stepwise manner using an IO 1 Hamilton syringe. The absorbance of the solution was measured after each addition. The metal ions solution was continually added until the desired metal to ligand mole ratio was achieved.

Conductometric study

Conductometric measurements were carried out by Metrohm 712 conductometer equipped with a Haake D1 circulator. In a typical experiment, 10.0 ml of metal ion solution (5.0×10^{-5} - 1.0×10^{-4} mol L⁻¹) in AN was placed in the two wall conductometer glass cell and the conductance of solution was measured. Then a known amount of the concentrated solution of Schiff base ligand in AN (5.0×10^{-3} -

1.0×10^{-2} mol L⁻¹) was added in a stepwise manner using an IO 1 Hamilton syringe. The conductance of the solution was measured after each addition. The Schiff base ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

Stability constants of metal ions-ligand system

The formation constant ($K_{\beta} = K_1 + K_2$) and the molar absorptivity (ϵ) of the resulting 1:1 and 1:2 (metal ion to ligand) complexes between the Schiff base and different cations at 25°C were calculated by fitting the observed absorbance, A_{obs} , at various metal ion/ ligand mole ratios to the previously derived equations (Ghasemi et al., 1995; Khajehsharifi et al., 1995) 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 (Nicely and Dye, 1971).

For evaluation of the formation constant from molar conductance (Λ) vs C_L/C_M mole ratio data, the KINFIT program was also used. Adjustable parameters are the K_f , molar conductance of free metal ion, and molar conductance of complex.

The free metal ion concentration, [M] was calculated by a Newton-Raphson procedure. When the value of [M] had been obtained, the concentration of all other species involved are calculated from the mass balance equations by using the estimated value of the formation constant at the current interaction step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed molar conductance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum of squares and the standards deviation of the data (Shamsipur et al., 2001).

Thermodynamic parameters of metal ions-ligand system

In order to have a better understanding of the thermodynamics of complexation between Schiff base and metal ions in acetonitrile, it is useful to consider the enthalpic and entropic contributions to these reactions. The enthalpy and entropy of the complexation reactions were determined by measuring the formation constants of the resulting complexes as a function of temperature with Van't Hoff Equation;

$$2.303 \log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

RESULTS AND DISCUSSION

Spectrophotometric study

The electronic absorption spectra of PYTABr ligand and its Cu²⁺, Zn²⁺, Co²⁺, Ni²⁺ and Cd²⁺ complexes in acetonitrile are shown in Figure 2, and for Co²⁺ in the increasing concentration of cations were recorded Figure 3 in acetonitrile at 25°C. All of the resulting complexes are distinguished by a strong spectral shift of about 70 nm toward longer wavelength, in comparison to the free ligand. The stoichiometry of the metal complexes was examined by the mole ratio method at λ_{max} of complexes. A sample of the resulting plots is shown in Figure 4 and it is evident that 1:1 and 1:2 (metal ion to ligand) complexes are formed in solution. As it can be seen from Figure 3, no pre-set of the sharp isobestic points in absorption spectra of

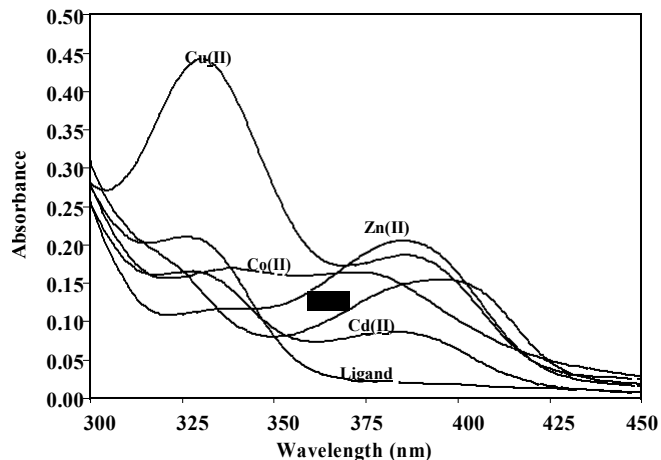


Figure 2. Spectra of PYTABr ligand and its complexes with Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} ions.

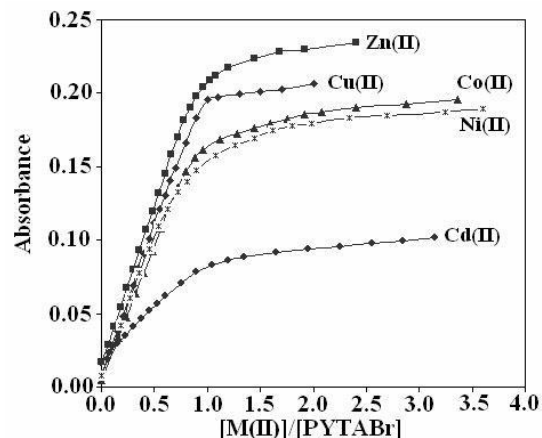


Figure 4. Mole ratio plots of the PYTABr ligand ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) with metal ions at max of its complexes at 25°C .

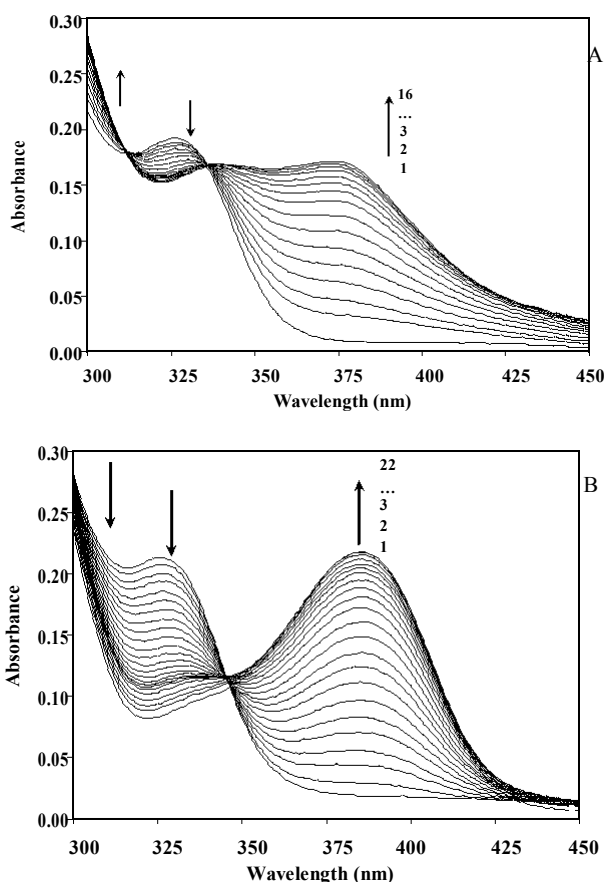


Figure 3. Electronic absorption spectra of PYTABr ligand ($5 \times 10^{-5} \text{ mol L}^{-1}$) in the presence of increasing concentration of Co^{2+} (A) and Zn^{2+} (B) ions at 25°C . The molar ratio of $[\text{Co}^{2+}]/[\text{L}]$ from down to up equal to: 0.0, 0.16, 0.24, 0.32, 0.40, 0.48, 0.56, 0.64, 0.72, 0.80, 0.88, 0.96, 1.12, 1.28, 1.44, 1.60 and $[\text{Zn}^{2+}]/[\text{L}] = 0.0, 0.12, 0.18, 0.24, 0.30, 0.36, 0.42, 0.48, 0.54, 0.60, 0.66, 0.72, 0.78, 0.84, 0.90, 0.96, 1.02, 1.08, 1.20, 1.44, 1.68, 1.92$.

PYTABr ligand in the presence of Co^{2+} and Zn^{2+} indicates that there are more than one species in equilibrium in solution. The eventual structure of ML and ML_2 complexes in acetonitrile (AN) solution have been shown in Figure 1. The formation constants of the resulting complexes were obtained at 25°C by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts ($5.0 \times 10^{-5} - 1.0 \times 10^{-4} \text{ mol l}^{-1}$) of PYTABr solution, at max of complexes. All the resulting absorbance-mole ratio data were best fitted to Equation 2, which further supports the formation of ML and ML_2 complexes in solution.

$$K_1 K_2 [L]^3 + K_1 (1 + K_2 (2C_M - C_L)) [L]^2 + (1 + K_1 (C_M - C_L)) [L] - C_L = 0$$

(2)

For evaluation of the formation constants and molar absorptivity coefficients from absorbance vs. $[\text{M}]/[\text{L}]$ mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the absorbance-mole ratio data for Cd^{2+} ion and PYTABr at 25°C is shown in (Figure 5). The resulting K_f of the PYTABr complexes at 25°C are listed in Table 1. The data given in Table 1 revealed that, at 25°C , the stability of the complexes of the PYTABr Schiff base ligand with different cations decrease in the order $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.

Conductometric study

The molar conductance of the nitrate salts of Zn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , and Cd^{2+} in acetonitrile solvent was monitored as a function of the PYTABr to metal ion mole ratio, and the stoichiometry of the complexes in acetonitrile was examined by the mole ratio method at variable temperatures. A sample of the resulting plots for Zn^{2+} and Cu^{2+} ions complexes is shown in Figure 6, and it is evident that

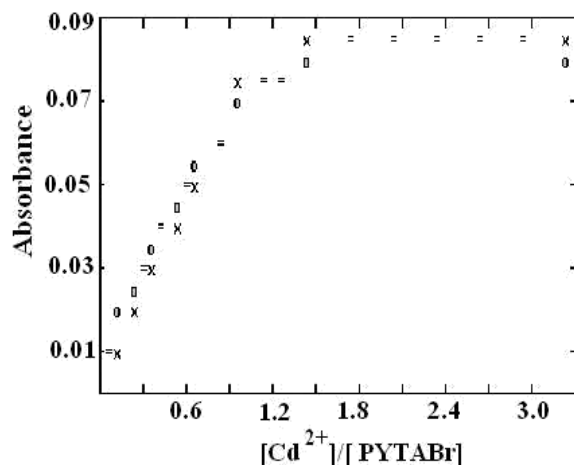


Figure 5. Computer fit of absorbance vs. $[Cd^{2+}]/[PYTABr]$ mole ratio plot in AN at 25°C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

Table 1. Spectrophotometric formation constant for M (PYTABr)₂ complex at 25°C.

$\log K_{\beta} \pm SD$		$\log K_{\beta}(\log K_1 + \log K_2)$
Cation	Co^{2+}	10.30 ± 0.01
	Ni^{2+}	11.02 ± 0.01
	Cu^{2+}	10.28 ± 0.02
	Zn^{2+}	9.81 ± 0.01
	Cd^{2+}	8.39 ± 0.02

Note: SD=standard deviation

ML and ML₂ complexes are formed in solution. As can be seen in AN solvent, addition of the ligand to the metal ions solutions cause a continuous increase in molar conductance of the solutions. This might indicate that the complexes formed are more mobile than the solvated metals ions. It is well known that transition metals ions strongly are complexed with acetonitrile (Strehlow et al., 1958) and such a solvated ions will be highly ordered and sluggish (Marji et al., 1998).

The first addition of PYTABr ligand will complex with metals ions resulting in a more mobile system with relatively high conductivity. Further additions of ligand to the relatively mobile system will cause a gradual increase in conductivity. However, the slope of the corresponding molar conductance- mole ratio plots change at the point where the ligand to ions ratio are one, and further additions of the ligand cause no or very slight changes in the molar conductance. Such a conductance behavior is indicative of the formation of ML and ML₂ complexes in solutions.

The formation constants of the resulting complexes were obtained by molar conductance measurements of

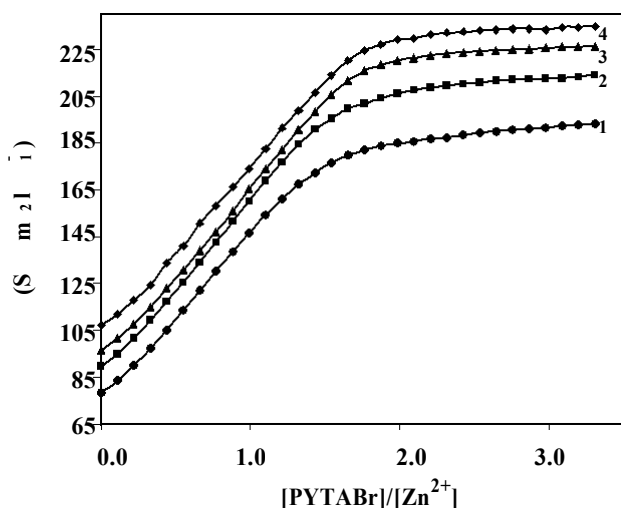
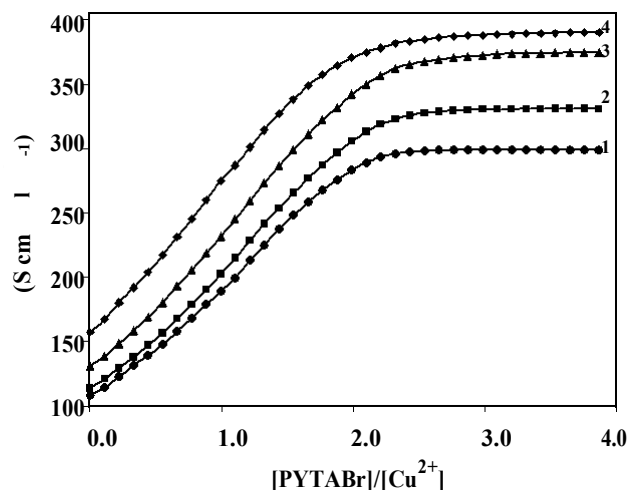


Figure 6. Mole ratio plots of PYTABr and its complexes with Cu^{2+} and Zn^{2+} ions at various temperatures: 1) 15°C, 2) 25°C, 3) 35°C, 4) 45°C.

solutions in which varying concentrations of ligand ($5.0 \times 10^{-3} \text{ mol L}^{-1}$) were added to fixed amounts ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) of metals ions solution. The entire resulting molar conductance-mole ratio data were best fitted to Equation 1, which further supports the formation of mixed complexes in solution.

For evaluation of the formation constants from molar conductance vs. C_L/C_M mole ratio data, a non-linear least complexes at 25°C is listed in Table 2.

All of the $\log K_{\beta}$ values evaluated from the computer fitting of the corresponding molar conductance-mole ratio data are listed in Table 2. Van't Hoff plots of $\log K_{\beta}$ vs. $1/T$, for metals complexes in acetonitrile were linear and are shown in Figure 8. H^0 and S^0 values were determined from Van't Hoff Equation 1 in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also listed in Table 2. Comparison of the data given in Table 2 indicate that the stability of the

Table 2. Formation constant values and thermodynamic parameters for M (PYTABr)₂ complexes at different temperatures.

Temperature		15°C	25°C	35°C	45°C
Log $k_{\beta} \pm SD$		log k_{β}	log k_{β}	log k_{β}	log k_{β}
Metal	Co ²⁺	10.32 ± 0.01	10.37 ± 0.01	10.36 ± 0.03	10.38 ± 0.01
	Ni ²⁺	11.10 ± 0.01	11.03 ± 0.02	10.97 ± 0.02	10.92 ± 0.01
	Cu ²⁺	10.30 ± 0.01	10.34 ± 0.02	10.23 ± 0.02	10.12 ± 0.01
	Zn ²⁺	9.89 ± 0.02	9.84 ± 0.01	10.09 ± 0.02	10.12 ± 0.01
	Cd ²⁺	7.24 ± 0.01	7.15 ± 0.02	7.79 ± 0.01	7.81 ± 0.02
Thermodynamic parameters		Complex			
		H (kJmol ⁻¹)	S (Jmol ⁻¹ k ⁻¹)		
Metal	Co ²⁺	3 ± 1	208 ± 4		
	Ni ²⁺	-10 ± 0.5	175 ± 2		
	Cu ²⁺	-11 ± 4	159 ± 15		
	Zn ²⁺	16 ± 7	245 ± 22		
	Cd ²⁺	41 ± 17	279 ± 55		

SD=standard deviation

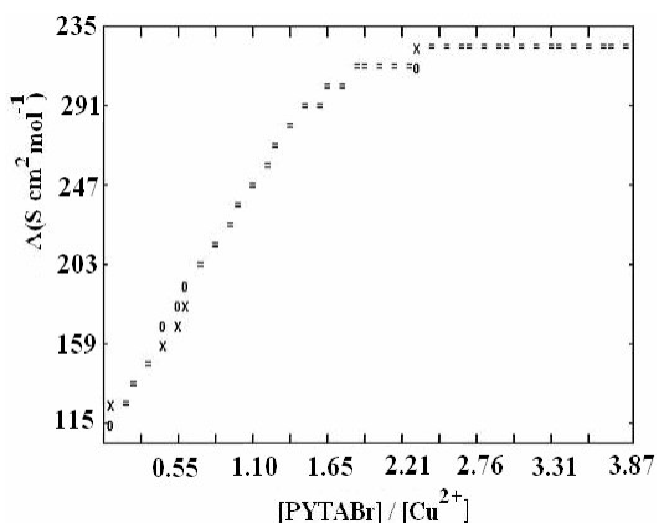


Figure 7. Computer fit of molar conductance vs. [PYTABr]/[Cu²⁺] mole ratio plot in AN at 25°C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

The complexes to vary in the order Ni²⁺>Co²⁺>Cu²⁺>Zn²⁺>Cd²⁺. The thermodynamic data in Table 2 reveal that, enthalpy for formation of complexes for Co, Zn, and Cd is positive. It means that formation of these complexes is enthalpy desirable and in all cases the complexes are entropy stabilized.

It is important to be noted that in spectrophotometric method, the addition of metal cations to ligand causes the formation of the ML₂ complexes due to presence of large amount of ligand in the first and then the formation of ML complexes in higher metal cation to ligand mole ratios.

The ML complexes are superior to ML₂ complexes and therefore, the mole ratio plots indicate weak curvature in

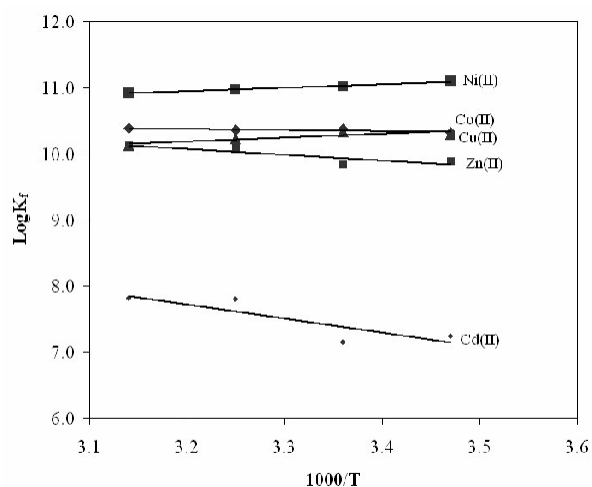


Figure 8. LogK_β vs. 1/T for metal ions complexes with PYTABr.

1:2 and strong curvature in 1:1 metal cation to ligand mole ratios (Figure 4). However, in contrast, in conductometric method, the addition of ligand to metal cations causes the formation of the ML complexes due to presence of less amount of ligand in the first and then the formation of ML₂ complexes in higher ligand to metal cation mole ratios. When ligand concentration increases, the solvent molecules that coordinated to metal ion replaced with another molecule of ligand. Thus the ML₂ complexes are superior to ML complexes and therefore, the mole ratio plots indicate weak curvature in 1:1 and strong curvature in 2:1 ligand to metal cation mole ratios (Figure 6)

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