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Complexation studies of Cu^{2+} ion with four new synthesized triazene ligands by spectrophotometric and conductometric methods

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ABTRACT

Four new symmetric and asymmetric triazene ligands, ((E)-1,3-bis (2-ethoxyphenyl) triaze-1-ene (L_1), (E)- 3-(4-chlorophenyl)1-(2-methoxyphenyl)triaze-1-ene (L_2), (E)-1-(2-ethoxyphenyl)-3-(3- nitrophenyl) triaze-1-ene (L_3) and (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaze-1-ene (L_4)) have been synthesized and k_f value of it's complexes with Cu^{2+} ion have been determined spectrophometric and conductrometric methods. Comprise of the k_f data indicate that the stability of the complexes to vary in the order $L_1 > L_2 > L_3 > L_4$.

INTRODUCTION

Aryl triazenes have been interested for their structural, anticancer and reactivity properties[1]. They have been used in medicinal and as organometallic ligands. The first extensive investigation of the coordination chemistry of a triazene derivative (1,3-di phenyl triazene) was carried out in 1887 by Meldola[2]. Triazene compounds characterized by having a diazoamino group (-N=N-NH-), with two cis and trans conformers, can be have like microelectronic switch[3].

Triazenes have attracted chemist,s attentions in various regards. For example diphenyl triazene (DPT) derivative are utilized as ligands specific organometallic complexes synthesis[4]. Triazenes can bind to metals in both a monodentate and bidentate manner (Figure 1). The products are air and moisture stable and are easily prepared. The fact that there is the possibility of either mono- or bidentate binding of the triazene to the metal has exciting implication both for catalysis and also for application as polymer-supported metal complexes.

The study of transition metal complexes containing 1, 3-diaryltriazenide [RN=N-NR] ligands has increased greatly in the past few years, because their potential reactivity in relation to their several coordination modes[5-10]. Application of these compound as a selective ligand for determination of toxic metal ions[11-14], potentiometric sensor[15-16], Hg (II) and Pt (II) ion selective electrodes[17-18], have been reported. Since these ligands have the very good potential for analytical application and the nature of solvent may strongly influence the stoichiometry and complexation of metalic complexes in solution, we synthesized four new symmetric and asymmetric triazene compounds, (E)-1,3-bis (2-ethoxyphenyl) triaze-1-ene (L_1), (E)- 3-(4-chlorophenyl)1-(2-methoxyphenyl)triaze-1-ene (L_2), (E)-1-(2-ethoxyphenyl)-3-(3- nitrophenyl) triaze-1-ene (L_3), (E)-1-(2-ethoxyphenyl)-3-(4-nitrophenyl) triaze-1-ene (L_4), (Figure 2) and decided to study the complexation reaction of them with copper metal ion in acetonitrile solution.

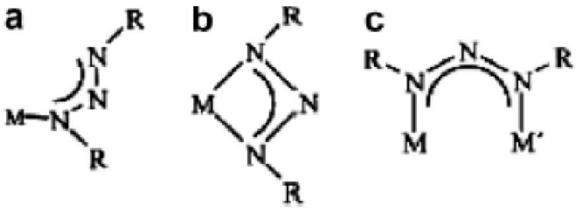

Figure 1 : Three mode coordination of triazene ligands, monodentate (a), chelating (b) (generating highly strained, four-membered rings), or a bridging ligand between two metal centers (c)

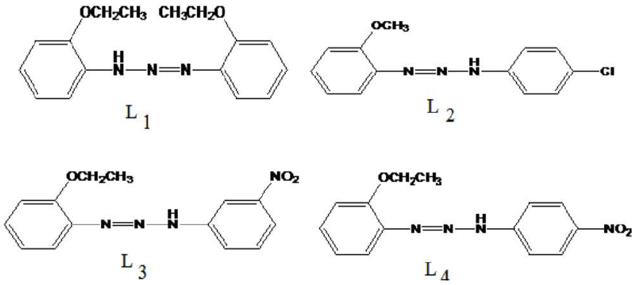

Figure 2 : Molecular structure of the triazine ligands

In this work we have reported spectrophotometric and conductometric studies of the stochiometry, complexation reaction of triazene ligands with Cu^{2+} ion in acetonitrile.

EXPERIMENTAL

Reagent grade copper nirtate and acetonitrile (AN) all from Merck and recently synthesized four triazene ligands synthesized, purified and dried as it has been described elsewhere[8] and were of highest purity available and were used without any further purification.

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 triazene ligand in AN (5×10^{-3} -1.0×10^{-2} mol L^{-1}) was added in a stepwise manner using a 10 μl Hamilton syringe. The conductance of the solution was measured after each addition. The triazene ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

All UV-Vis Spectra recorded on a computerized double-beam shimadzu 2550 spectrophotometer, using two matched 10.0 mm quartz cell. In a typical experiment, 2.0 ml of ligand solution (5.0×10^{-5}mol L^{-1}) in AN was placed in the spectrophotometer 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 a 10 μl Hamilton syringe. The absorbance of the solution was measured after each addition. The metal ions solution was continually added until the desired ligand to metal ion mole ratio was achieved.

In order to have a better understanding of the thermodynamics of complexation between rtiazene ligands and copper 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 Von't Hoff Equation (Equation 1).

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

The formation constant ($K_{ß}=K_1\times K_2$) and the molar absorptivity (ε) of the resulting 1:1 and 1:2 (metal ion to ligand) complexes between the triazene ligands and copper ion at 25ºC were calculated by fitting the observed absorbance, A_{obs}, at various Cu^{2+} / ligand mole ratios to the previously derived equations[19-20], 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[21].

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 copper 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 square of the residuals between calculated and observed molar conductance for all experimental points was minimized. The output of the KINFIT program comprises the refined parameters, the sum of squares and the standards deviation of the data[22].

RESULT AND DISCUSSION

Conductometric studies

The molar conductance of the nitrate salt of Cu^{2+} in acetonitrile solvent was monitored as a function of the triazenes ligands 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 Cu^{2+} ions complexes with four triazene ligans is shown in Figure 3 and at different temperatures for L_1 ligand is shown in Figure 4, and it is evident that ML and ML_2 complexes are formed in solution. As it is seen while the ligand solution possesses a negligible conductance, its addition to all metal ion solutions in acetonitrile caused a rather large and continuous increased in molar conductance. This could be due to the lower mobility of the solvated cation and existence of some ion pairing in the initial salt. This might indicate that the complexes formed are more mobile than the solvated metals ions. It is well known that transition copper ion strongly is complexed with acetonitrile and such a solvated ion will be highly ordered and sluggish.

The first addition of triazene ligand to copper ion solution wills complex with metal ion 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 ion 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 ML_2 complexes in solutions.

The formation constants of the resulting complexes were obtained by molar conductance measurements of solutions in which varying concentrations of ligand (5.0×10^{-3} mol L^{-1}) were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of metal ion solution. The entire resulting molar conductance – mole ratio data were best fitted to the previously derived equations[19-20], which further support the formation of mixed complexes in solution.

TABLE 1 : Conductometric formation constants for triazene ligands complexes with Cu^{2+} ion at different temperature and it's thermodynamics parameters

Ligands	$Logk_\beta$				ΔH Kj.mol^{-1}	ΔS j.mol^{-1}.K^{-1}
	5ºC	15ºC	25ºC	35ºC		
L_1	8.07±0.05	8.08±0.09	8.09±0.02	8.10±0.01	2.84±0.23	71.88±0.78
L_2	8.05±0.04	8.05±0.05	8.06±0.05	8.07±0.01	-0.75±0.11	65.80±0.37
L_3	8.03±0.08	8.04±0.06	8.05±0.07	8.06±0.26	-0.685±0.23	65.89±0.88
L_4	8.02±0.04	8.03±0.08	8.04±0.01	8.05±0.34	1.06±0.23	67.93±1.16

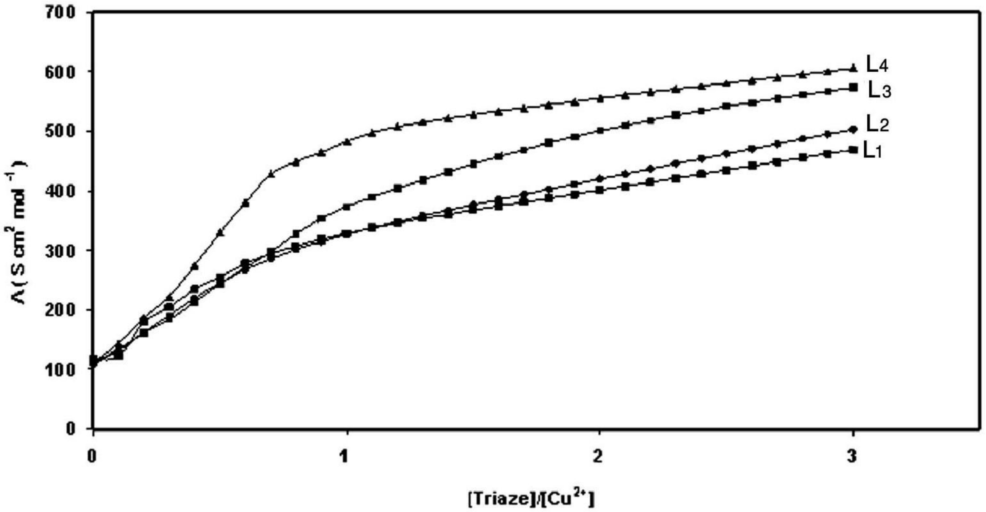

Figure 3 : Mole ratio plots of triazene ligands with Cu^{2+} ion complexes at 25ºC

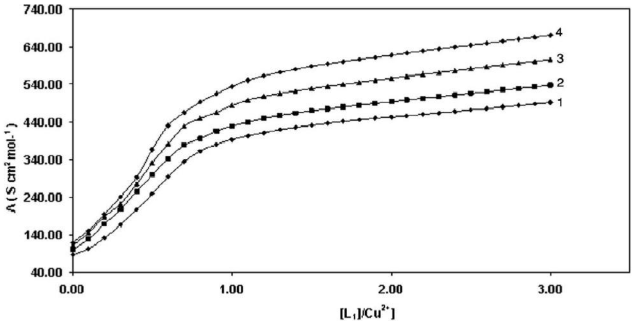

Figure 4 : Mole ratio plots of L_1 ligand Cu^{2+} ion at various temperatures: 1) 5ºC, 2) 15ºC, 3) 25ºC, 4) 35ºC

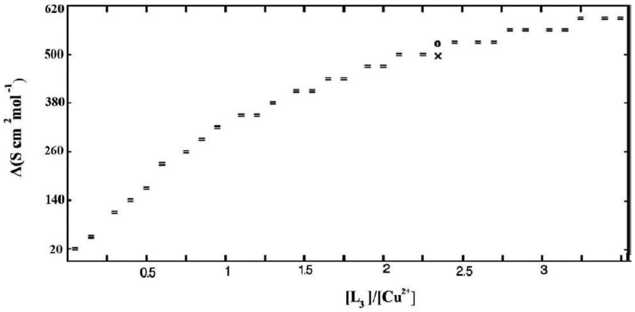

Figure 5 : Computer fit of molar conductance *vs* $[L_3]$ / $[Cu^{2+}]$ mole ratio plot in AN at 25ºC, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

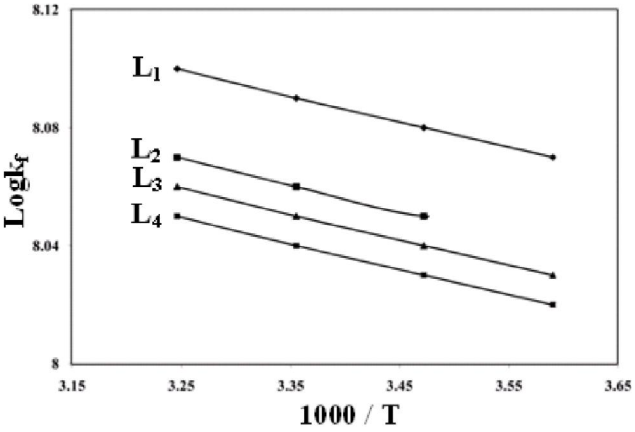

Figure 6 : Log k_f vs.1/T for Cu^{2+} ion complexes with four triazene ligands (L_1, L_2, L_3, L_4)

For evaluation of the formation constants from molar conductance *vs.* C_L/C_M mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the molar conductance-mole ratio data for Cu^{2+} and L_3 at 25ºC is shown in Figure 5. All of log $K_ß$ values evaluated from the computer fitting of the corresponding molar conductance-mole ratio data are listed in TABLE 1. Van't Hoff plots of log $K_ß$ *vs.* 1/T, for metal complexes in acetonitrile were linear and are shows in Figure 6. ΔH^0 and ΔS^0 determined from Van't Hoff Equation in the usual manner from the slops and intercept of the plots, respectively, and the results are also listed in TABLE 1.

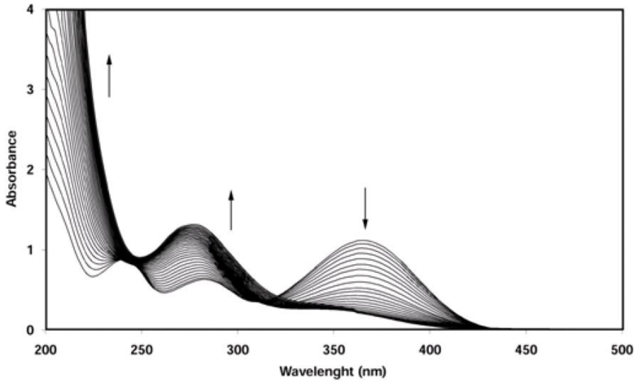

Figure 7 : Electronic absorption spectra of L_2 ligand (5×10^{-5} mol L^{-1})) in the presence of Cu^{2+} ion. $[Cu^{2+}]/[L_2]$ from down to up equal to: 0.0, 0.13, 0.26, 0.39, 0.52, 0.65, 0.78, 0.91, 1.04, 1.17, 1.3, 1.43, 1.56, 1.69, 1.82, 1.95, 2.08, 2.21, 2.34, 2.47, 2.6, 2.73, 2.86, 2.99, 3.12, 3.25, 3.38, 3.51, 3.64, 3.77, 3.9

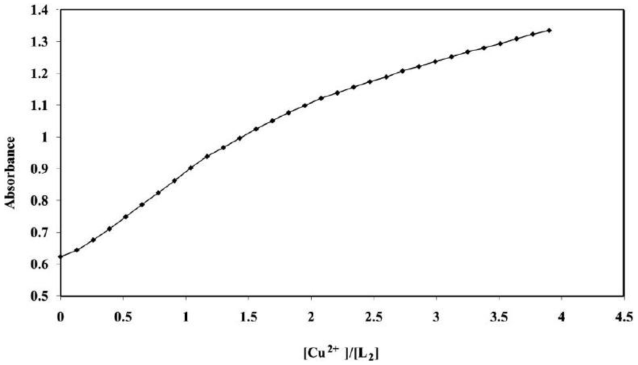

Figure 8 : Mole ratio plots of the L_2 ligand (5.0×10^{-5} mol L^{-1}) with Cu^{2+} ion at 277 nm at 25ºC

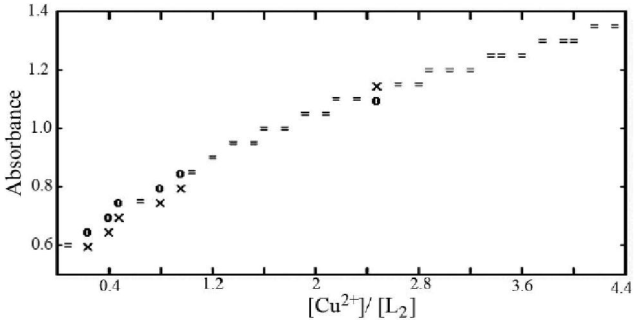

Figure 9 : Computer fit of absorbance versus$[Cu^{2+}]/[L_2]$ mole ratio plot in AN at 25ºC, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

Comprise of the data given in TABLE 1 indicate that the stability of the complexes to vary in the order $L_1 > L_2 > L_3 > L_4$. The thermodynamic data in TABLE 1 reveal that, enthalpy for formation of complexes for L_1,

TABLE 2 : Spectrophotometric formation constant for Cu^{2+} - Triazene ligands complexes at 277 nm

Ligands	Log k_β
L_1	8.01
L_2	7.80
L_3	6.97
L_4	6.65

L_4 positive and for L_2, L_3 is negative. It means that formation of these complexes is enthalpy desired and in all cases the complexes are entropy stabilized.

Spectrophotometric studies

The electronic absorption spectra of L_4 ligand and its Cu^{2+} complexes in acetonitrile solvent are shown in Figure 7. The stoichiometry 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 Figure 8 and it is evident that 1:1 and 1:2 (metal ion to ligand) complexes are formed in solution. The formation constants of the resulting complexes were obtained at 25ºC by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of ligands solution, at λ_{max} of complexes.

For evaluation of the formation constants and molar absorptivity coefficient from absorbance vs. [M]/[L] mole ratio data, a nonlinear least squares curve fitting program KINFIT was used. A sample computer fit of the absorbance - mole ratio data for Cu^{2+} and L_4 at 25ºC is shown in Figure 9.

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