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Spectrophotometric and Thermodynamic Studies of 1,3-*Bis*-(2-cyanobenzene)triazene Complexes with Hg^{2+} and Cd^{2+} Ions

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The complexation reactions between 1,3-*bis*(2-cyanobenzene)-triazene (CBT) with Hg^{2+} and Cd^{2+} ions have been studied using spectrophotometry in acetonitrile at various temperatures. The formation constants of the resulting 1:1 and 1:2 (metal ion to ligand) complexes were calculated from the computer fitting of the absorbance mole ratio data. At 25 °C the stability constant of the Hg^{2+} complex is higher than the Cd^{2+} complex. The enthalpy and entropy changes of the complexation reactions were also evaluated from the temperature varied formation constants.

Key Words: 1,3-*Bis*(2-cyanobenzene)triazene, Hg^{2+}, Cd^{2+}, Spectrophotometry, Stability constant, Enthalpy, Entropy.

INTRODUCTION

Aryl triazene have been studied over 140 years for their interesting structural, anticancer and reactivity properties[1]. They have been used in medicinal[2] and combinatorial chemistry[3], in natural product synthesis[4], as organometallic ligands[5] and as precursors to heterocyclic compounds. The first extensive investigation of the coordination chemistry of 1,3-diphenyltriazene was carried out by Meldola[6].

The study of transition metal complexes containing 1,3-diaryltriazenide (R-N=N-N-R) ligands has increased rapidly in the past few years, because of their potential reactivity in relation to their several modes of coordination[7,8]. This anion is a 'smallbite', three-atom donor ligand that can act as a monodentate group (a), a chelating ligand (b) (generating highly strained 4-membered rings) or a bridging ligand between two metal centers (c) (Fig. 1)[9,10].

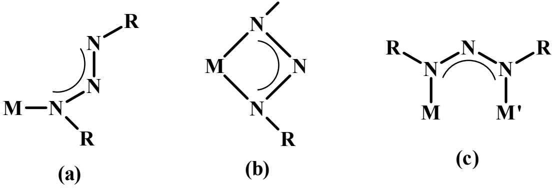

Fig. 1. Different moieties of triazene ligands

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In recent years, linear triazenes have been attracted considerable biological interest. Although QSAR studies by Hansch indicate little separation between toxicity and antitumor activity for this class of compounds[11], chemical and biological interest continues[12-14]. Antifungal[15] antitrypanosomal[16] have been described to certain triazene derivatives. Triazene are well important and interesting substances on the basis of their structures and biological activity. Many chemotherapeutic treatments of tumors are based on the combination of drugs, having a different mechanism of action, among which is often an alkylating agent. A class of alkylating agents is represented by triazene compounds, which continue to be a subject of interest for some research groups. These compounds are able to alkylate the DNA molecule[17].

The synthesis and crystal structure of 1,3-*bis*(2-methoxybenzene)triazene (MBT) ligand[18], structural and solution studies of a novel tetranuclear silver(I) cluster of it was reported[19]. Recently, the structure of 1,3-*bis*(2-cyanobenzene)triazene (CBT) is reported[20] (Fig. 2) and in present paper solution complexation of it with Hg^{2+} and Cd^{2+} metal ions have been investigated.

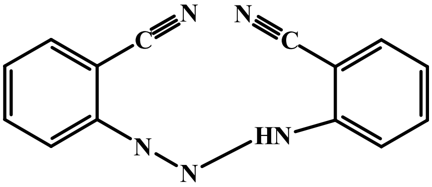


Fig. 2. Molecular structures of 1,3-*bis*(2-cyanobenzene)triazene (CBT) ligand

EXPERIMENTAL

Reagent grade mercury(II) perchlorate, cadmium acetate and acetonitrile (all from Merck) were of the highest purity and used without any further purification except for vacuum drying over P_2O_5. Recently synthesized 1,3-*bis*(2-cyanobenzene)-triazene (CBT) ligand of highest purity were used.

All UV-Vis spectra is 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 Philips PU8750 spectrophotometer equipped with a Philips cell temperature controller. In all measurements, the cell was thermostated at the desired temperature ± 0.02 °C.

Synthesis of 1,3-*bis*(2-cyanobenzene)triazene (CBT): The compound was prepared by the following method: a 1 L flask was charged with 100 g of ice and 150 mL of water and then cooled to 0 °C in an ice-bath. To this was added 11.80 g (0.10 mol) of *o*-cyanoaniline and 13 g (0.36 mol) of hydrochloric acid (d = 1.18 g/mL). To this solution was added a solution of $NaNO_2$ containing 4.10 g (0.06 mol) in 25 mL of water during a 15 min period. After mixing for 15 min a solution containing

14.76 g (0.18 mol) of sodium acetate in 45 mL of water was added. After mixing for 45 min the yellow product was filtered and dissolved in Et_2O. After evaporation of Et_2O a purified sharp yellow powder (Fig. 2) was produced. Yield, 62 %, 7.66 g, m.p. 128-130 °C.

Spectrophotometric titrations and determination of stability: In a typical experiment, 2.0 mL of ligand solution (5.0×10^{-5} M) in acetonitrile 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 acetonitrile (1.3×10^{-3} M) was added in a stepwise manner using an l0 µL 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.

The formation constant (K_f) and the molar absorptivity (ε) of the resulting 1:1 and 1:2 (metal ion to ligand) complexes between CBT ligand with Hg^{2+} and Cd^{2+} at various temperature were calculated by fitting the observed absorbance, A_{obs}, at various metal ion/ligand mole ratios to the previously derived equations[21-23]. The formation constant evaluated from a non-linear least-squares program KINFIT[24]. The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique[25] or the Powell procedure[26].

Thermodynamic studies: In order to have a better understanding of the thermodynamics of complexation between CBT and metal ions (Hg^{2+} and Cd^{2+}) in acetonitrile, it is helpful 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 1:1 and 1:2 complexes as a function of temperature. ΔH° and ΔS° values were determined from Van't Hoff equation (eqn. 1) in the usual manner from the slopes and intercepts of the plots, respectively.

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

RESULTS AND DISCUSSION

The electronic absorption spectra of CBT ligand and its Cd^{2+} and Hg^{2+} complexes, in the increasing concentration of cadmium(II) acetate and mercury(II) perchlorate, in acetonitrile are shown in Figs. 3 and 4, respectively at 25 °C. The absent of isobestic point shows that more than one complexes are formed. The stoichiometry of the Cd^{2+} complex was examined by the mole ratio method at 340 nm (λ_{max} of ligand) and 420 nm (λ_{max} of its Cd^{2+} complex) and for Hg^{2+} complex at 360 nm in acetonitrile. A sample of the resulting plots is shown in Fig. 5 for cadmium and Fig. 6 for mercury respectively and it is evident that 1:1 and 1:2 (metal ion to ligand) complexes are formed in solution.

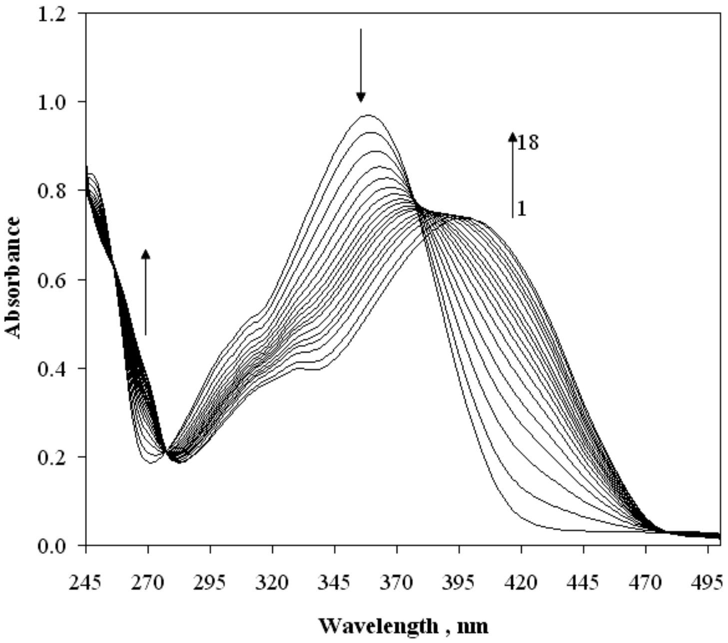


Fig. 3. Electronic absorption spectra of CBT ligand (4.8×10^{-5} M) in the presence of increasing concentration of $Cd(C_2H_3O_2)_2$ at 25 ºC in acetonitrile, at different [Cd]]/[CBT] mole ratio, (1) spectrume of ligand, (2) 0.08, … (18) 2.48

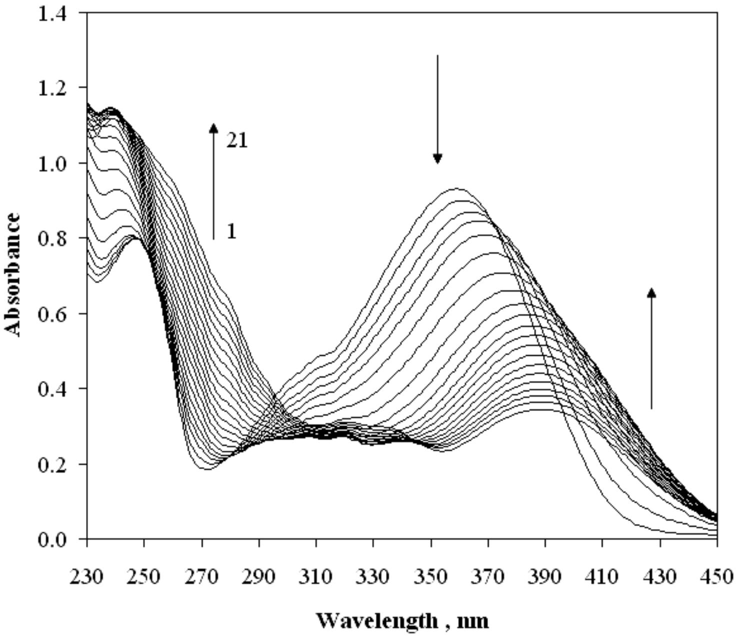


Fig. 4. Electronic absorption spectra of CBT ligand (4.8×10^{-5} M) in the presence of increasing concentration of $Hg(ClO_4)_2$ at 25 ºC in acetonitrile, at different [Hg]/[CBT] mole ratio, (1) spectrum of ligand, (2) 0.09, … (12) 1.02, … (21) 2.79

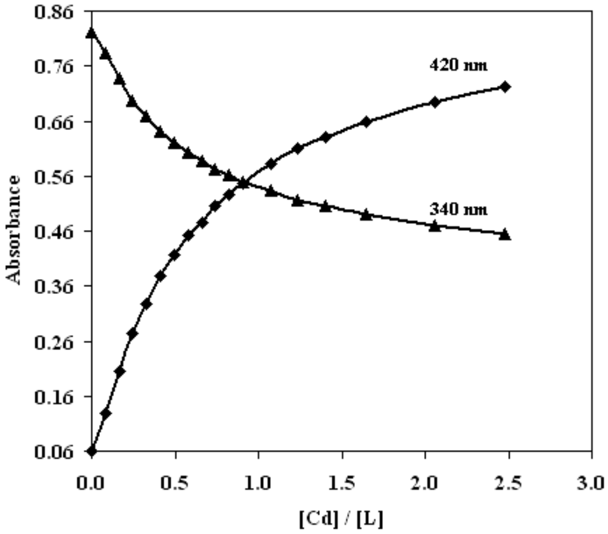


Fig. 5. Mole ratio plots of CBT ligand (4.8 × 10^{-5} M) with $Cd(C_2H_3O_2)_2$ solution in acetonitrile at 25 ºC

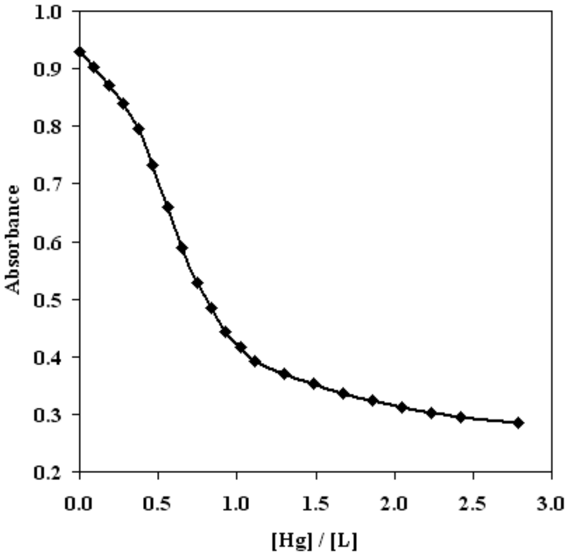


Fig. 6. Mole ratio plots of CBT ligand (4.8 × 10^{-5} M) with $Hg(ClO_4)_2$ solution in acetonitrile at 25 ºC

The formation constants of the resulting 1:1 and 1:2 (metal ion to ligand) complexes were obtained, in which varying concentrations of metal ions was added to fixed amounts of ligand solution. All the resulting absorbance-mole ratio data were best fitted to eqn. 2, which further supports the formation of mixed complexes in solution.

For evaluation of the formation constants from absorbance *vs.* C_M/C_L mole ratio data, a non-linear least squares curve fitting program KINFIT was used. Sample computer fits of the absorbance-mole ratio data for Cd^{2+} at 340 nm and Hg^{2+} at 360 nm with CBT are shown in Fig. 7a and b, respectively. The formation constant (log K_f) of complexes were evaluated and are listed in Table-1.

TABLE-1
FORMATION CONSTANTS OF Cd^{2+}-CBT AND Hg^{2+}-CBT COMPLEXES IN ACETONITRILE AT 25 ºC

Cation	λ (nm)	log K_1	log K_2
Cd^{2+}	420	4.03 ± 0.02	2.94 ± 0.04
	340	3.91 ± 0.02	2.69 ± 0.02
Hg^{2+}	360	4.31 ± 0.02	3.87 ± 0.02

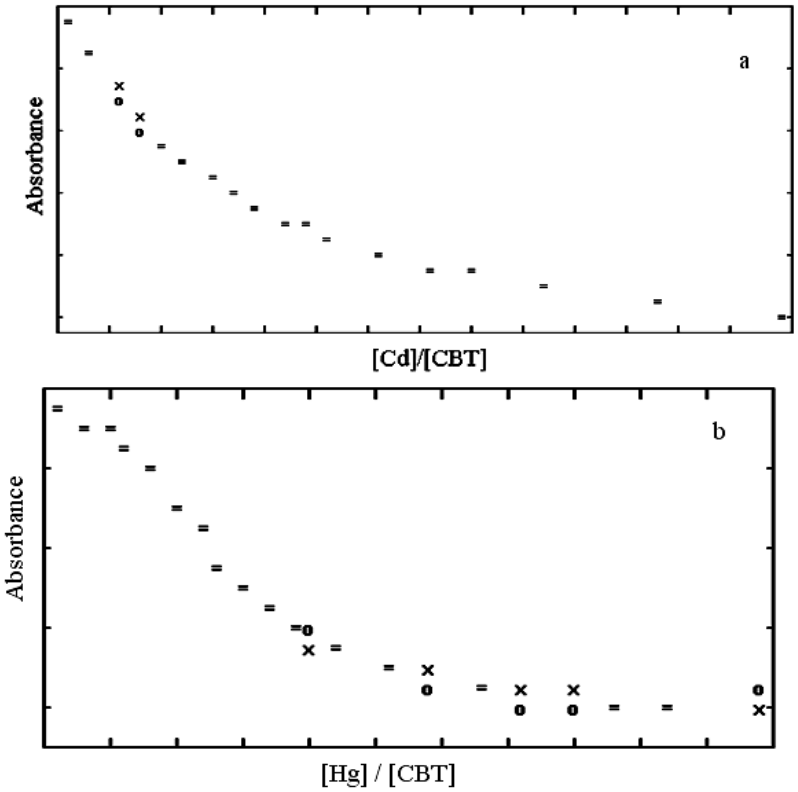


Fig. 7. Computer fits of absorbance *vs.* (a) $[Cd^{2+}]$/[CBT] at 340 nm and (b) $[Hg^{2+}]$/[CBT] at 360 nm mole ratio plots in acetonitrile at 25 °C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

For evaluation of the thermodynamics of complexation between CBT with Hg^{2+} and Cd^{2+} metal ions in acetonitrile, varying concentrations of metal ions was added to fixed amounts of ligand solution at variable temperature and the mole ratio plots are shown in Figs. 8 and 9 for cadmium and mercury, respectively. The enthalpy and entropy of the complexation reactions were determined by measuring the formation constants of the resulting 1:1 and 1:2 complexes as a function of temperature. The log K_f values evaluated from the computer fitting of the corresponding absorbance - mole ratio data are listed in Table-2. Van't Hoff plots of log K_f *vs.* 1/T, for metals complexes in acetonitrile were linear and is shows in Fig. 10. ΔH° and ΔS° values were determined from Van't Hoff equation (eqn. 3) and the results are listed in Table-3.

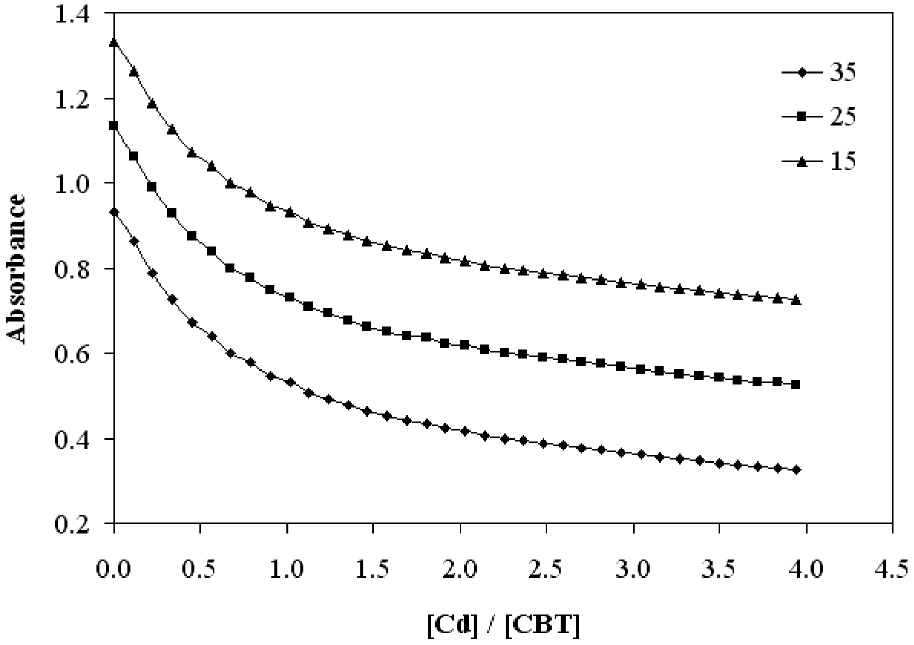


Fig. 8. Mole ratio plots of the CBT (5.0×10^{-5} M) with $Cd(C_2H_3O_2)_2$ solution in acetonitrile at various temperatures (15, 25, 30 and 35 °C)

TABLE-2
FORMATION CONSTANTS OF Cd^{2+}- CBT AND Hg^{2+}- CBT COMPLEXES IN ACETONITRILE AT VARIABLE TEMPERATURES

Cation	15 ºC		25 ºC		35 ºC	
	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
Cd^{2+}	4.07 ± 0.01	2.85 ± 0.03	3.91 ± 0.02	2.69 ± 0.02	3.68 ± 0.02	2.41 ± 0.02
Hg^{2+}	4.42 ± 0.02	3.99 ± 0.02	4.31 ± 0.02	3.87 ± 0.02	4.17 ± 0.02	3.74 ± 0.02

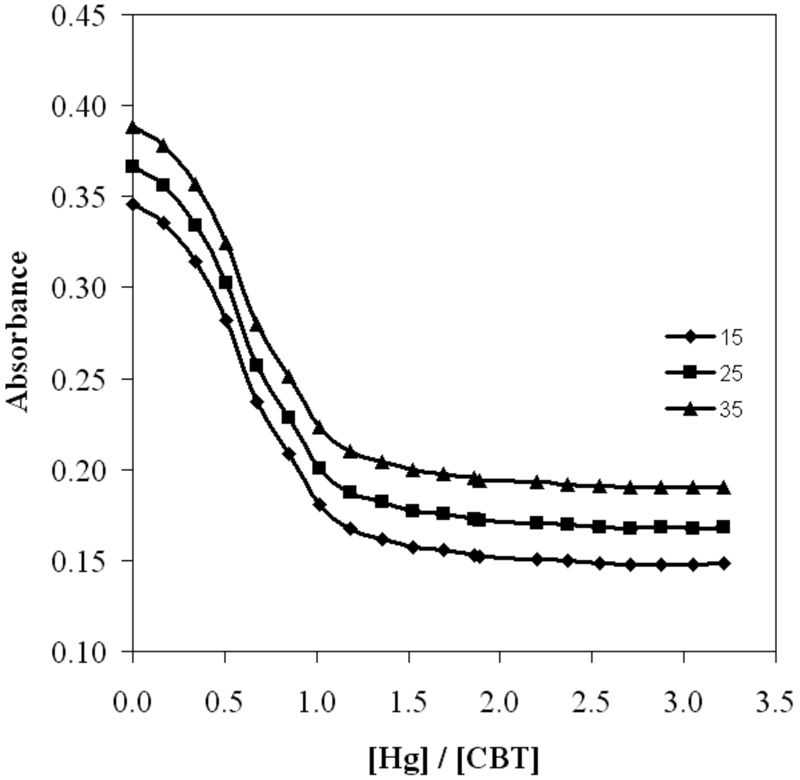
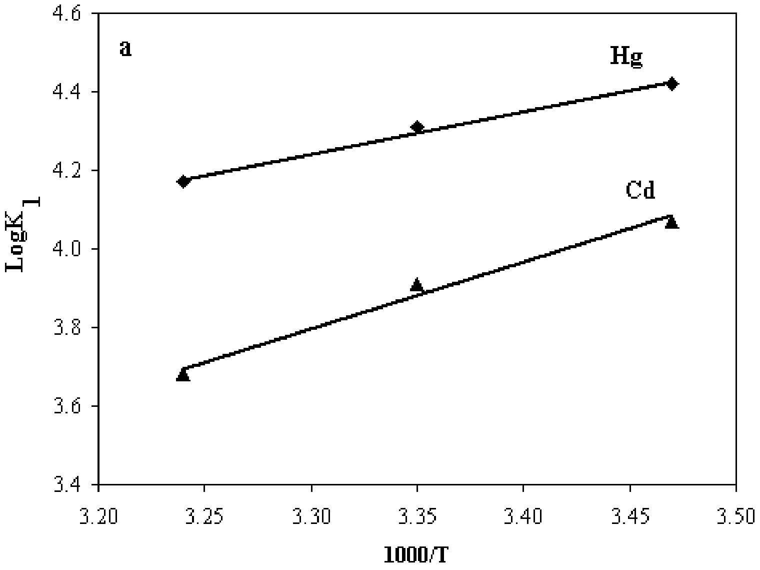


Fig. 9. Mole ratio plots of the CBT (5.0×10^{-5} M) with $Hg(ClO_4)_2$ solution at 300 nm in acetonitrile at various temperatures (15, 25, 30 and 35 °C)



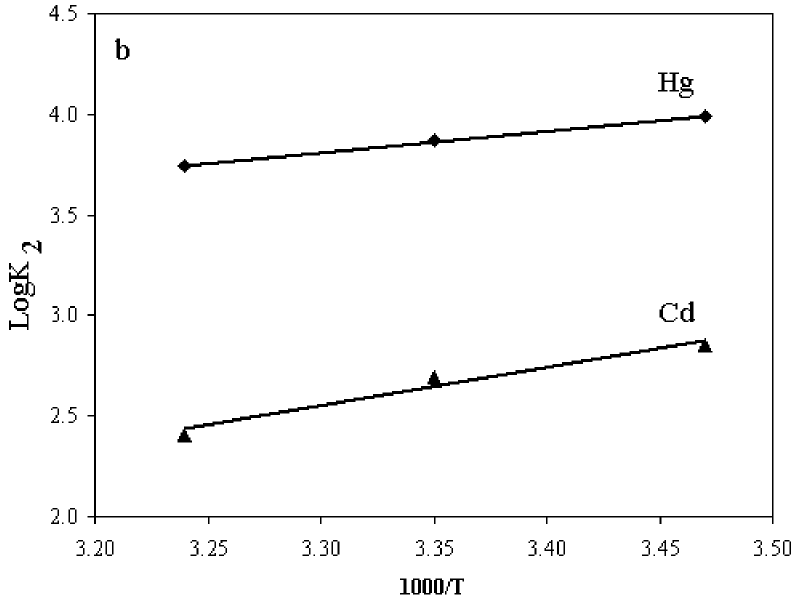


Fig. 10. Van's Hoff plots for the CBT system with Cd^{2+} and Hg^{2+} ion, (a) for K_1 and (b) for K_2 in acetonitrile

TABLE-3
ENTHALPY AND ENTROPY VALUES FOR Cd^{2+}-CBT AND Hg^{2+}-CBT COMPLEXES IN ACETONITRILE SOLUTION

Cation	ML complex		ML_2 complex	
	ΔH° (KJ/mol)	ΔS° (J/mol K)	ΔH° (KJ/mol)	ΔS° (J/mol K)
Cd^{2+}	-32.4 ± 4.2	-34.1 ± 14.0	-36.5 ± 6.7	-71.5 ± 22.4
Hg^{2+}	20.8 ± 1.9	12.8 ± 6.6	20.8 ± 1.0	4.3 ± 3.3

Conclusion

The complexes between 1,3-*bis*(2-cyanobenzene)triazene (CBT) with Hg^{2+} and Cd^{2+} ions in acetonitrile are ML and ML_2 mixture. The stability constant of the mercury complex is higher than the cadmium complex.

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