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Conductometric, spectrophotometric, ^{1}HNMR and quantum chemical studies of the thermodynamics complexation of some transition metal ions with aza-15-crown-5 ligands in acetonitrile solution

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ABSTRACT

In this paper, the complexation reactions between aza-15-crown-5 (A15C5) ligand with Zn^{2+}, Hg^{2+}, Co^{2+}, Ag^+ and Cd^{2+} ions has been studied by conductometric and spectrophotometric methods in acetonitrile solution at various temperatures. The formation constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. At 25°C, the order of stability of the 1:1 complexes of the A15C5 ligand with different cations are as $Hg^{2+} > Co^{2+} > Cd^{2+} > Zn^{2+} > Ag^+$. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants. In addition, ^{1}HNMR study of complexes of nitrate salt of Cd^{+2} in acetonitrile with A15C5 ligand at 25°C has been also undertaken to compare the results with those obtained by conductivity and UV measurements, which have been found to be in good agreement with each other. Finally, ab initio studies of the level of HF/lanl2dz have been done to investigate the binding energies of the ligand with Ag^+ and Hg^{2+}. All theoretical data are in line with the experimental ones.

KEYWORDS

Conductometry;
Spectrophotometry;
NMR;
Complexation;
Formation constant;
Aza-15-crown-5.

INTRODUCTION

Macrocyclic polyethers (crown ethers), first prepared in the 1960[1], constitute an important class of “host” molecules that have been found broad application to studies of molecular recognition and inclusion phenomena[2]. They are macrocycles capable of ion encapsulation due to their cage like structures. The metal ion is held in the crown ether cavity by electrostatic attraction between the charged cation and dipoles created by the nonbonding electrons of donor atoms[3,4]. The selectivity and stability of crown ethers are also influenced by their structural flexibility, the number and type of donor atoms on the cavity of the crown, and the solvation energy of the metal ion. Thus, compounds of this type have been used extensively for selective complexation and transport of cations, anions and neutral molecules[5]. Macrocyclic crown compounds have gained a great deal of attention due to their wide applications in chemistry, microanalysis, sensing and separation of metal ion, biology, biophysics and ecology[6].

Aza-crown ethers have especially been focused on as useful ligands because of their versatility and applicability. The property of aza-crown ether can be modified by altering its side arms as well as macrocycle itself[7]. It was of interest to us to study the interaction of the various cations with aza crown ethers. Since the nature of these compounds and the size of cavity by the oxygen atoms in their ring may strongly influence the stoichiometry and complexation of transition metal complexes in solution[8], the complexation reactions between aza-15-crown-5 (A15C5) ligand (Figure 1) with Zn^{2+}, Hg^{2+}, Co^{2+}, Ag^{+} and Cd^{2+} ions were studied by conductometric and spectrophotometric methods in acetonitrile solution at various temperatures. The formation constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance (absorbance)-mole ratio data at different temperatures.

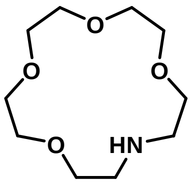

Figure 1 : Structure of 1-aza-15-crown-5 (A15C5) ligand

EXPERIMENTAL

Reagents

Reagent grade nitrate salts of Cobalt, Zinc, Cadmium, Mercury, and Silver were all from Merck. A15C5 from Fluka were of the highest purity available and used without any further purification. Spectroscopic grade acetonitrile (AN) from Merck was purified and dried by the previously described method[9]. The conductivity of the solvent was less than 1×10^{-7} S cm^{-1} at 25° C.

Spectrophotometric titrations

All UV-Vis Spectra recorded on a computerized double-beam shimadzu 2550 spectrophotometer, using two matched 10 mm quartz cell. In a typical experiment, 2.0 ml of ligand solution (5.0×10^{-5} mol L^{-1}) 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} mol L^{-1}) was added in a stepwise manner using an l0ìl 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 titrations

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} mol L^{-1}) in acetonitrile was placed in the titration cell, thermostated to the desired temperature and the conductance of solution was measured. Then a known amount of the concentrated solution of ligand in acetonitrile (5.0×10^{-3} mol L^{-1}) was added in a stepwise manner using an l0 ìL Hamilton syringe. The conductance of the solution was measured after each addition. The ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

In all measurments, cell was thermostated at desired temperature ±0.1ºC; the cell constant at the different temperature used was determined by measuring the conductivity of 1×10^{-2} mol L^{-1} solution of analytical grade KCl in triply distilled deionized water. The specific conductances of this solution at various temperatures have been reported in the literature[10]. The corresponding cell constant at 15°, 25°, 35°, and 45° C were 0.834, 0.832, 0.829 and 0.820 cm^{-1}, respectively. A dip-type conductivity cell made of platinum black was used.

NMR titrations

All ^{1}HNMR Spectra recorded on a computerized Bruker Avance 300, in field of 300.13 megahertz using 5 mm cell. In a typical experiment, 0.5 ml of ligand solution (2×10^{-2} mol L^{-1}) in deuteriated acetonitrile was placed in the cell and the spectra of solution was measured. Then the concentrated solution of metal ion (2.0×10^{-1} mol L^{-1}) was added in a stepwise manner using an l0 ìL Hamilton syringe. The spectra of the solution were measured after each addition. The metal ion solution was continually added until the desired metal to ligand mole ratio was achieved.

Stability constants of metal ion-ligand systems

The formation constant (K_f) and the molar absorptivity (å) of the resulting 1:1 complexes between the ligand (A15C5) and different metal ions in acetonitrile at 25°C were calculated by fitting the observed absorbance, A_{obs}, at various metal ion / ligand mole ratios to the previously derived equations[11-12], 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[13].

For evaluation of the formation constant from molar conductance *vs.* C_L/C_M mole ratio data, the KINFIT program was also used. Adjustable parameters are the K_f, 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.

Thermodynamic parameters of metal ion- ligand systems

In order to have a better understanding of the thermodynamics of complexation between A15C5 ligand with 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 ML and ML_2 complexes as a function of temperature with Van't Hoff Equation (Equation 1).

$$2.3031\log K_f = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (1)$$

RESULTS AND DISCUSSION

Spectrophotometric studies

The electronic absorption spectra of A15C5 ligand and its Ag^+, Cd^{2+}, Hg^{2+}, Zn^{2+} and Co^{2+} complexes in acetonitrile are shown in Figure 2, and absorption spectra of A15C5 ligand (5×10^{-5} mol L^{-1}) in the presence of increasing concentration of Co^{2+} ions were recorded (Figure 3) in acetonitrile at 25°C. The resulting complexes of Ag^+, Cd^{2+}, Zn^{2+} and Co^{2+} with A15C5 are distinguished by a spectral shift of about 40 nm toward shorter wavelength, and for Hg^{2+}about 30 nm toward shorter wavelength in comparison to the free ligand.

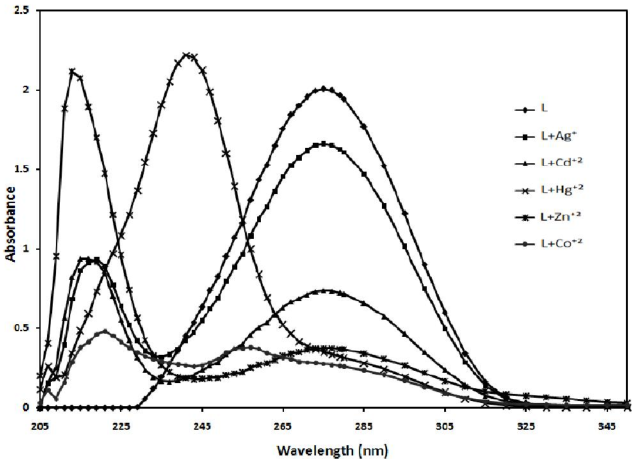

Figure 2 : Spectra of A15C5 ligand and it's complexes with Ag^+, Cd^{2+}, Hg^{2+}, Zn^{2+} and Co^{2+} ions in acetonitrile

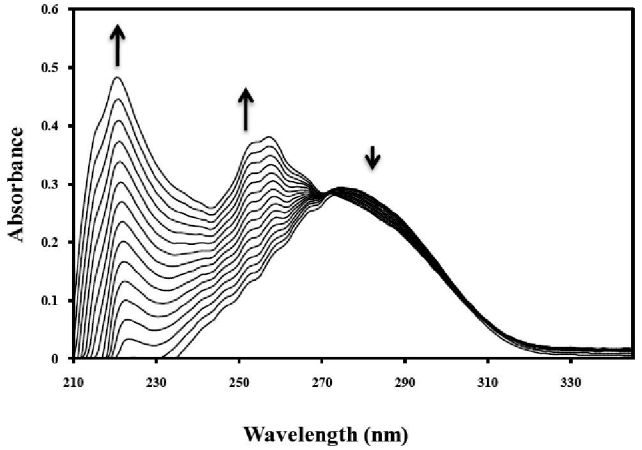

Figure 3 : Electronic absorption spectra of A15C5 ligand (5×10^{-5} mol L^{-1}) in the presence of increasing concentration of Co^{2+} ion at 25°C. The molar ratio of $[Co^{2+}]/[L]$ from down to up equal to: 0.0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16, 0.18, 0.2, 0.22, 0.24, 0.26, 0.28, 0.3

The stoichiometry of the metal complexes was examined by the mole ratio method. Sample of the resulting plot for Cd^{2+} - A15C5 complex is shown in Figure 4 at 275 nm, and it is evident that 1:1 (metal ion to ligand) complex are formed in solution. The formation constants of the resulting 1:1 metal ions to A15C5 complexes were obtained at 25°C by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts (5.0×10^{-5} mol L^{-1}) of A15C5 solution. All the resulting absorbance-mole ratio data were best fitted to Equation 2, which further supports the formation of ML in solution.

$$K_f[L]^2 + (1 + K_f C_M - K_f C_L)[L] - C_L = 0 \qquad (2)$$

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 was used. The resulting K_f of the A15C5 complexes at 25°C are listed in TABLE 1. The data given in TABLE 1 revealed that, at 25ºC, the order of stability of the 1:1 complexes of the A15C5 ligand with different cations are as $Hg^{2+} > Co^{2+} > Cd^{2+} > Zn^{2+} > Ag^{+}$.

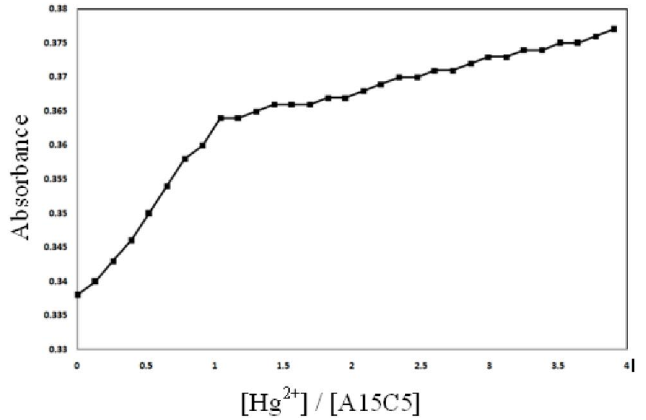

Figure 4 : Mole ratio plot of the A15C5 ligand (5.0×10^{-5} mol L^{-1})with Cd^{2+} at 275 nm at 25°C

TABLE 1 : Formation constants for M^{n+}-A15C5 complexes at 25°C in acetonitrile solution from spectrophotometric data

	Log K_f ± SD*				
Cation→ Ligand↓	**Ag^+**	**Cd^{2+}**	**Zn^{2+}**	**Co^{2+}**	**Hg^{2+}**
A15C5	3.34±0.10	4.96±0.10	4.84±0.20	5.15±0.20	5.16±0.10

***SD= Standard deviation**

Conductometric studies

The molar conductance of the nitrate salts of Zn^{2+}, Cd^{2+}, Co^{2+}, Hg^{2+}, and Ag^+ in acetonitrile solvent was monitored as a function of the A15C5 ligand to metal ion mole ratios, 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 all metal ions with A15C5 at 25ºC are shown in Figure 5, and for Zn^{2+} complexes is shown in Figure 6 at different temperatures. It is evident that 1:1 (metal to ligand) complexes are formed in solution. As it is seen, while the ligand solution possesses a negligible conductance, its addition to all metal ions caused a rather large and continuous increase in molar conductance except for silver ion that a decrease in Ë values was observed. This could be due to the lower mobility of the solvated cation and existence of some ion pairing in the initial salt[14-16].

This might indicate that the complexes formed are more mobile than the solvated metals ions. It is well known that transition metal ions strongly are complexed with acetonitrile and such a solvated ions will be highly ordered and sluggish[17].

Also this has been explained on the basis of a solvation sphere, the divalent metal ions have a high charge-to-radius ratio on account of which they are highly solvated but on complexation, the crown ether molecule replaces the salvation sheath around the metal ion and as a result the moving entity becomes less bulky and more mobile[18]. The silver ions, on the other hand, are relatively larger and have lower charge-to-radii ratio. Hence, they are solvated to a lesser extent. When complexed with crown ether it becomes bulkier causing a decrease in its mobility and also in the Ë values[19,20].

The first addition of A15C5 ligand, causes that the complexes be formed 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 complexes in solutions.

The formation constants of the resulting ML 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 ions solution. The entire resulting molar conductance-mole ratio data were best fitted to Equation 2, which further supports the formation of ML complexes in solution.

For evaluation of the formation constants from molar

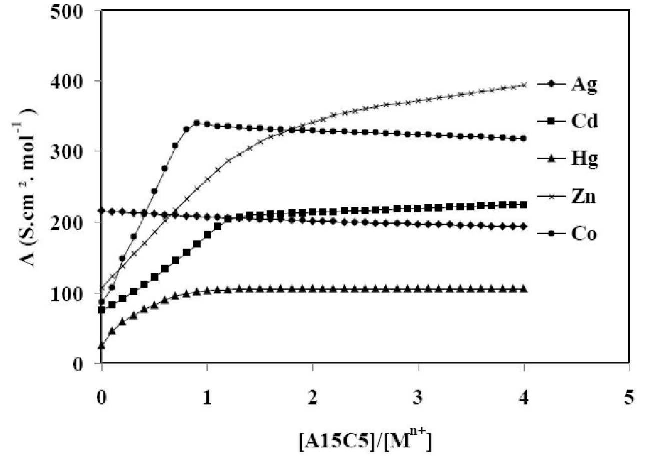

Figure 5 : Molar conductance (S cm^2 mol^{-1}) *vs.* [A15C5]/[M^{n+}] plots in AN at 25ºC

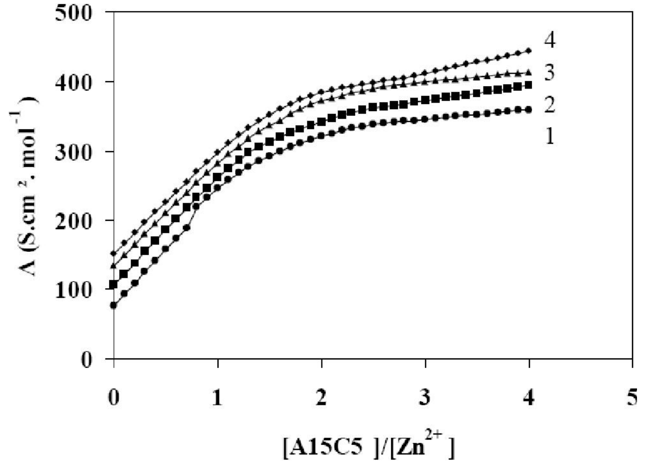

Figure 6 : Molar conductance (S cm^2 mol^{-1}) *vs.* [A15C5]/[Zn^{2+}] plots in AN at various temperatures: 1) 15°C, 2) 25°C, 3) 35°C and 4) 45°C

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 Zn^{2+} and A15C5 at 25ºC is shown in Figure 7. The resulting K_f of the A15C5 complexes at 25°C are listed in TABLE 2.

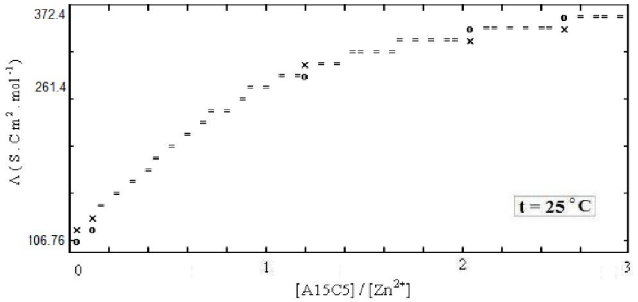

Figure 7 : Computer fit of molar conductance *vs.* [A15C5]/[Zn^{2+}] mole ratio plot in acetonitrile at 25°C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

The ÄH^0 and ÄS^0 values were determined from Van't Hoff Equation (Equation 1) in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also listed in TABLE 2. The Van't Hoff plots for A15C5 ligand are shown in Figure 8. Comparison of the data given in TABLE 2 indicates that the stability of the ML complexes of the A15C5 ligand with different cations decrease in the order $Hg^{2+} > Co^{2+} > Cd^{2+} > Zn^{2+} > Ag^+$.

TABLE 2 : Formation constants, enthalpies, and entropies for M^{n+}-A15C5 complexes in acetonitrile solution

Ligand	Cation	Log K$_f$ ± SD				ΔH^0 (kj mol $^{-1}$)	ΔS^0 (jmol^{-1}K^{-1})
		15ºC	25ºC	35ºC	45ºC		
A15C5	Cd^{2+}	5.36±0.01	5.27±0.01	5.25±0.01	5.21±0.01	-8 ± 2	73 ± 6
	Zn^{2+}	4.71±0.01	4.54±0.01	4.54±0.01	4.45±0.01	-14 ± 4	42 ± 13
	Co^{2+}	6.56±0.02	6.86±0.03	6.49±0.02	6.60±0.02	- 4 ± 15	113 ± 50
	Ag^+	3.63±0.01	3.64±0.04	3.34±0.01	3.71±0.01	- 1± 16	64 ± 52
	Hg^{2+}	6.72±0.01	6.70±0.01	6.33±0.01	6.68±0.10	-9 ± 17	97 ± 55

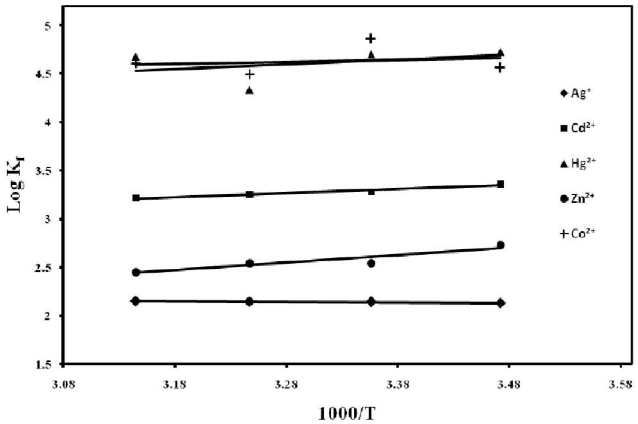

Figure 8 : logK$_f$ *vs.* 1/T plots for the 1:1 complexation of metal ions with A15C5 in AN

NMR studies

The ^{1}HNMR spectra of A15C5 ligand in the presence of increasing concentration of Cd^{2+} ion were recorded in deuteriated acetonitrile. The resulting complexes of Cd^{2+} with A15C5 are distinguished by a chemical shift of about 0.34 ppm toward longer chemical shift. The stoichiometry of the metal complexes was examined by the mole ratio method. The plot are shown in Figure 10 at 2.65-2.99 ppm. It is evident that 1:1 (metal ion to ligand) complexes are formed in solution.

The formation constants of the resulting 1:1 Cd^{2+} to ligand complexes were obtained at 25°C by chemical shift measurements of solutions in which varying concentrations of Cd^{2+} were added to fixed amounts of ligand solution. The entire resulting chemical shift -mole ratio data were best fitted to Equation 2, which further supports the formation of ML in solution. For evaluation of the formation constants and molar chemical shift coefficients from chemical shift *vs.* [M]/[L] mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the chemical shift-mole ratio data for Cd^{2+} ion and A15C5 in deuteriated acetonitrile at 25°C is shown in Figure 11. ^{1}HNMR formation constants for Cd^{2+}-A15C5 complexes at 25°C are listed in TABLE 3. The data given in all Tables revealed that, at 25ºC, the stability of the 1:1 complexes of the A15C5 ligand with Cd^{2+} obtained by ^{1}HNMR measurements[21-24], are in good agreement with other methods (UV-Vis and conductivity).

Quantum chemical calculations

Nowadays, quantum mechanical calculations are receiving a great deal of attention due to their roles in providing chemists detail information about intra- and inter-molecular interactions. In this paper, A15C5, and it;s complexes with different metal ions were optimized by HF/Lanl2dz level of theory in order to better understand the nature of interactions. Figure 12 shows the optimized geometries of the species. In our previous studies, almost all predictions of this level of theory were in good agreement with the experimental results. Another advantage of this level and basis set is that it is not very CPU time consuming.

All calculations were done by Gaussian 03 program[25]. To be sure that the optimized structures are true minima and not saddle points, number of imaginary frequency (NIMAG) were searched. In all calculations, NIMAG was equal to zero.

As was noted in the experimental section, the ligand A15C5 interacts with Hg2$^+$ more than Ag^+. In this section, the differences are explained by using ab initio calculations. TABLE 4 shows the electronic energy for metal ions, free ligand, and it;s complexes with Ag^+ and Hg^{2+}. The data have been collected for the gas phase calculations. Binding energy between an ion M^+ or M^{2+} and a ligand L is shown as:

$$\text{Ä}E_{LM}=E_{LM}-E_{M}-E_{L}$$

Theoretical data show that there is a tendency for A15C5 ligand to complex with Hg^{2+} and Ag^+. However, the interaction of ligand with Hg^{2+} is more than the interaction with Ag^+ (see TABLE 4 to compare binding energies between ligands and ions). This is true for the ligand A15C5. The charge density on the Hg^{2+} is higher than Ag^+, and this may cause difference in behaviors of ions. Hg^{2+} may interact more with solvent molecules.

TABLE 3 : ^{1}HNMR formation constants for Cd^{2+}-A15C5 complexes at 25°C

Log K_f ± SD	Chemical shift (ppm)	ligand
4.35 ± 0.02	2.65-2.99	A15C5

TABLE 4 : Electronic and binding energies for A15C5 ligand, Hg^{2+}, Ag^+, and it;s complexes in the gas phase. All data are in kcal mol^{-1}

Species	Electronic Energy	Binding Energy
A15C5	-467199.64	-
Hg^{2+}	-25410.35	-
Ag^+	-90774.98	-
A15C5-Hg^{2+}	-492887.69	-277.70
A15C5-Ag^+	-558061.67	-87.05

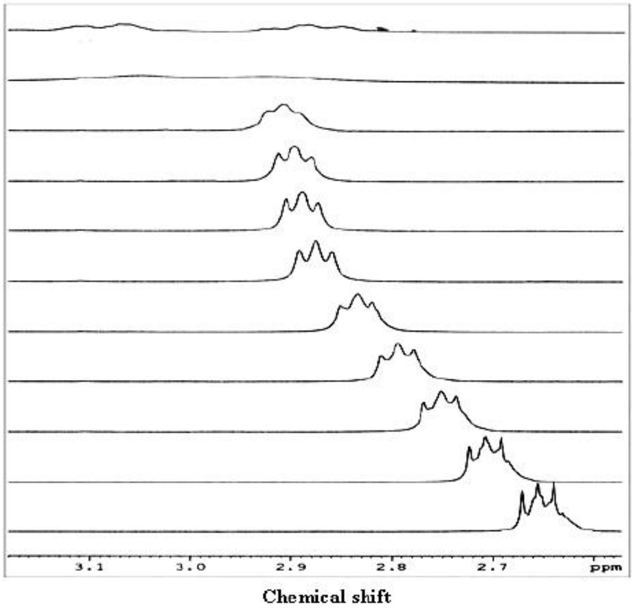

Figure 9 : The ^{1}HNMR spectra of A15C5 ligand in the presence of increasing concentration of Cd^{2+} ions in deuteriated AN at chemical shift of 2.65-2.99 ppm at 25°C

To test this idea, we have calculated electronic energy in the presence of implicit solvent molecules by PCM model of Tomasi and his co-workers[25-28]. The results have been summarized in TABLE 5. PCM results are compatible with experiments. Due to the CPU time needed for considering explicit solvent molecules, we have not calculated the binding energy by using micro-solvation approach. A detail study by micro-solvation model is in progress, and the results will be presented later.

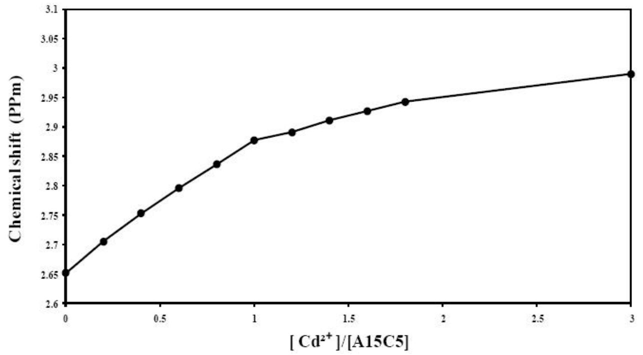

Figure 10 : Mole ratio plots of the Cd^{2+} ion with A15C5 ligand at 2.65-2.99 in deuteriated AN

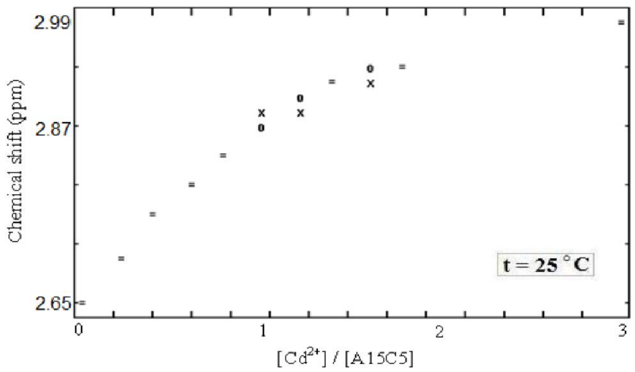

Figure 11 : Computer fit of the Chemical shift-mole ratio data *vs.* $[Cd^{2+}]/[A15C5]$ mole ratio plot in deuteriated AN at 25°C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot

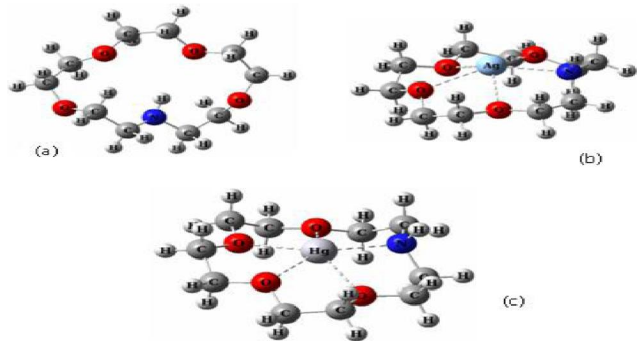

Figure 12 : The optimized structure for (a) free ligand A15C5, (b) A15C5-Ag^+, and (c) A15C5-Hg^{2+}

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