

## Chemical speciation studies on complexation of ditopic ligands: Interaction of adipic acid dihydrazide with Mg(II) and Ca(II) in aqueous medium

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**Abstract:** A chemical speciation study on the interaction of adipic acid dihydrazide (AADH) with Mg(II) and Ca(II) (M) was carried out in aqueous medium at a temperature of  $30.0 \pm 0.1^\circ\text{C}$  and  $0.1 \text{ mol.dm}^{-3}$  ionic strength. The ditopic ligand, AADH possesses a number of potential donor atoms and is able to form both mono-nuclear and binuclear species in protonated, unprotonated and deprotonated forms. Best-fit chemical models representing the systems of different compositions were obtained using the Miniquad-75 computer program. Mononuclear species of the type MLH, ML, MLH<sub>-1</sub>, ML<sub>2</sub>H<sub>2</sub>, ML<sub>2</sub>H, ML<sub>2</sub>, ML<sub>2</sub>H<sub>-1</sub> and binuclear M<sub>2</sub>L, M<sub>2</sub>LH<sub>-1</sub> (L=AADH) were found to exist in solution. The species distribution diagrams were generated using HYSS program.

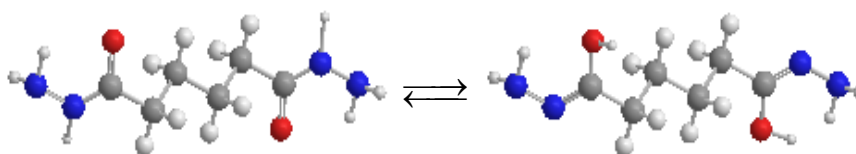
**Key words:** adipic acid dihydrazide, ditopic ligand, formation constant, speciation, Mg (II), Ca(II)

### I. Introduction

The field of polytopic ligands and their complexes is a developing part of coordination chemistry promising various biological and industrial applications [1]. These ligands can accommodate metal ions in different coordination pockets leading to the formation of multinuclear complexes. The formation of multinuclear species has special significance. The presence of more than one metal ion in the same species linked by small units of the ligand leads to several interesting and important applications. They possess unusual magnetic [2] and electrical properties and have been used as molecular switches [3], monitoring guest exchange and to mimic metalloproteins for understanding the structure- reactivity relationships [4]. The metal centres are found to act synergistically in catalysing reactions [5, 6].

In continuation of our study [7, 8] on the solution equilibria of metal ion complexes of ditopic ligands, we report here, a specimetric study on the metal-ligand equilibria of adipic acid dihydrazide (AADH) with Mg<sup>2+</sup> and Ca<sup>2+</sup>. Most of the studies reported in the literature on metal complexes of adipic acid dihydrazides were aimed at the synthesis and elucidation of structures by physicochemical methods [9-20]. Chemical modelling study, which gives the nature and extent of formation of various species in solution, is an essential pre-requisite to understand their behaviour in biological and other systems. Relatively a few reports that too with first row divalent transition metal ions [21-26] were found in the literature on the solution equilibria of the metal complexes of AADH. No reports were found on complexing tendencies of AADH in solution towards Mg<sup>2+</sup> and Ca<sup>2+</sup>. These metal ions were selected as they are of great biological concern and physiologically desirable. Magnesium and calcium are most abundant intracellular cations in the human body that work synergistically on not only the bones and nervous system but also on the muscles. Dihydrazides exhibit no toxicity, making them safe for industrial applications in the manufacturing of materials used in direct food contact [27]. Therefore, it is desirable to investigate the complexing properties of dihydrazides towards essential metal ions.

AADH possesses two hydrazide groups (-CO.NH.NH<sub>2</sub>) separated by four - (CH<sub>2</sub>) - links. Each hydrazide group can exist [Fig. (1)] in solution either in ketonic or enolic form. Under acidic conditions, the terminal amino groups of the neutral ligand may be protonated. These ligands may also lose protons from enolic form either at higher pH or on interaction with metal ions.



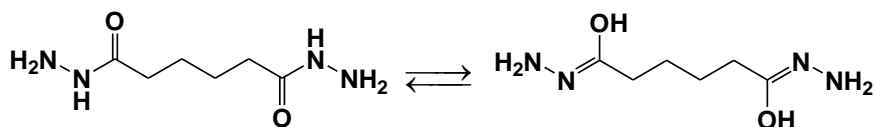


Fig.(1): Ketonic and enolic forms of Adipic acid dihydrazide

Each hydrazide group is capable of bonding to metal ions through terminal amino nitrogen and carbonyl or enolic oxygen. Hence there is a chance of formation of a variety of coexisting mononuclear and binuclear species in protonated, unprotonated and deprotonated forms [20,28].

## II. Experimental

### 2.1 Reagents

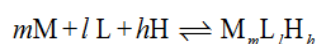
Solutions were prepared using doubly glass distilled water through which nitrogen gas was purged to expel any dissolved oxygen or carbon dioxide. Adipic acid dihydrazide (Fluka) was recrystallized twice from the water, dried at 100 °C and a ~0.05 mol dm<sup>-3</sup> solution was prepared freshly in 0.1 mol dm<sup>-3</sup> hydrochloric acid just before its use. All other chemicals used were of analytical grade. Metal ion solutions (Mg<sup>2+</sup> and Ca<sup>2+</sup>) were prepared from the corresponding chlorides and were standardized by conventional complexometric titrations [29]. An overall 0.01 mol dm<sup>-3</sup> acid was maintained in all the metal ion solutions to repress the hydrolysis [30]. A ~0.2 mol dm<sup>-3</sup> solution of sodium hydroxide was prepared and standardized against potassium hydrogen phthalate. It was then preserved under a nitrogen atmosphere and regularly Gran-titrated [31, 32] to check the absence of carbonates. Solution of ~0.2 mol dm<sup>-3</sup> hydrochloric acid, prepared by successive dilutions was standardized against a standard solution of sodium hydroxide. All potentiometric titrations were carried out in aqueous medium at an ionic strength of 0.1 mol dm<sup>-3</sup> using sodium chloride as the background electrolyte.

### 2.2 Equipment

A Control Dynamics pH-meter model APX 175 E/C in conjunction with a combination electrode (0-14 pH range) was used for pH measurements. The correction factor to convert the pH meter dial reading into logarithm of the reciprocal of hydrogen ion concentration was calculated before each set of experimental titrations by performing an acid base titration at the chosen ionic strength and analysing the data by Gran method<sup>32</sup>. Purified nitrogen gas was passed through the experimental solution both before and during titration to expel carbon dioxide.

### 2.3 Data acquisition and analysis

Chemical speciation studies involve the determination of composition and extent of formation of various species present in the solution containing metal ion(s) and ligand(s) under specified conditions of temperature, ionic strength and pH. The equilibria involved in a system containing a metal ion (M) and ligand (L) in the presence of a protic solvent may be represented as;



The overall formation constant for the species is represented by the equation;

$$\beta_{mlh} = \frac{[M_m L_l H_h]}{[M]^m [L]^l [H]^h}$$

Where, [M]<sub>i</sub>, [L]<sub>i</sub> and [H]<sub>i</sub> are the free concentrations of metal, ligand and hydrogen ion respectively at i<sup>th</sup> experimental point. Different species in solution possess different values of stoichiometric coefficients *m*, *l* and *h*. Positive value of *h* indicates protonated species and negative value indicates either deprotonated or hydroxylated species.

Calvin-Wilson titration technique as modified by Irving and Rossotti [33, 34] was used for the study of protonation and complex equilibria of the ligand (AADH). Requisite volumes of hydrochloric acid (to give an overall concentration of 4.0-5.0×10<sup>-2</sup> mol dm<sup>-3</sup>), sodium chloride (to maintain ionic strength at 0.1 mol dm<sup>-3</sup>) and ligand (0.005 to 0.015 mol dm<sup>-3</sup> in different experiments) in the absence and presence of a metal ion, in a total volume of 50.0 cm<sup>3</sup> was titrated with ~ 0.2 mol dm<sup>-3</sup> sodium hydroxide at 30.0 ±0.1°C. The initial metal to ligand molar concentration ratio was maintained at 1:1, 1:2 and 2:1 in different experiments. After the addition of each aliquot of sodium hydroxide, the pH-meter dial reading was recorded at regular intervals of time until two successive readings do not differ in more than 0.01 pH units.

### III. Results and discussion

#### 3.1 Proton-ligand equilibria of AADH

The pH-metric titration curve of hydrochloric acid + AADH is above that of the free acid curve (Fig. (2a)) indicating the association of protons to the ligand. In the basic region the ligand curve is slightly below that of free acid indicating ionization of the ligand.

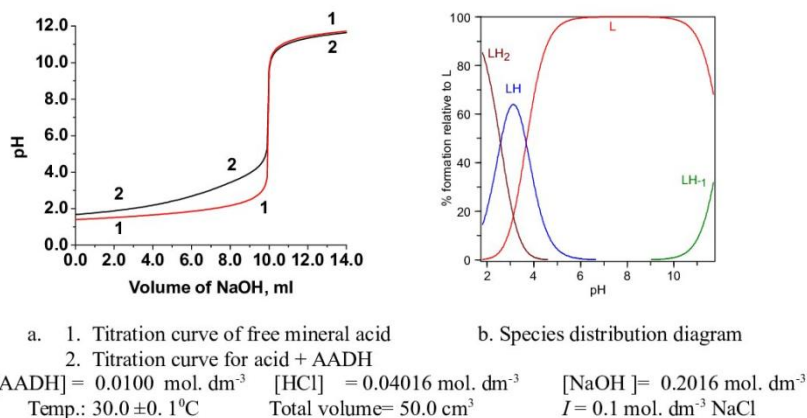


Fig.(2): Proton-Ligand system of AADH

The experimental data were subjected to analysis by the Miniquad-75 program [35]. The best-fit model obtained and the corresponding protonation and deprotonation equilibria of AADH are shown in Table 1 and Fig. (3) respectively.

**Table 1:** Best fit chemical model for acido-basic equilibria of adipic acid dihydrazide in aqueous medium. Temp. = 30.0 ± 0.1 °C and ionic strength, I = 0.1 mol dm<sup>-3</sup> (NaCl)

Species <i>mlh</i>	Log $\beta_{0lh}$ (SD)	No. of experimental points analysed	Sum of the squares of residuals, U/NP	$\chi^2$
011	3.67 (3)	75	4.099 X 10 <sup>-8</sup>	11.92
012	6.24 (2)			
01-1	-12.03 (3)			

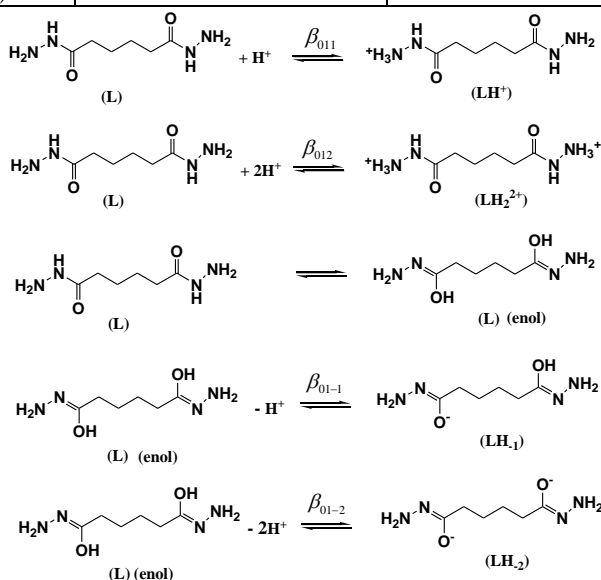


Fig.(3): Protonation and deprotonation equilibria of AADH

The best-fit model of AADH (L) indicates the formation of LH<sub>2</sub><sup>2+</sup>, LH<sup>+</sup> and LH<sub>-1</sub> species in aqueous medium. At lower pH (below ~3.0), AADH mostly exists (Fig. (2b)) in its biprotonated form, LH<sub>2</sub><sup>2+</sup>, and with an increase in pH, undergoes successive deprotonation to form the mono-protonated (LH<sup>+</sup>) and neutral species (L).  $\beta_{011}$  and  $\beta_{012}$  are the formation constants (Fig.(3)) of mono and biprotonated forms of AADH. The

formation constant,  $\beta_{01-1}$  corresponds to the deprotonation of one of the enolic protons at higher pH leading to the formation of  $LH_1$  species. The other ( $\beta_{01-2}$ ), corresponding to the formation of  $LH_2$  species, was not observed as its equilibrium may lie well above the pH range of study.

### 3.2 Metal-AADH systems

In a solution containing a metal ion and AADH, depending on the pH there is a possibility of formation of protonated, unprotonated and deprotonated mono and binuclear metal-ligand species. This is possible as the ligand is ditopic and exists in  $LH_2^{2+}$ ,  $LH^+$ ,  $L$  and  $LH_1$  forms depending on the pH of the solution as evidenced from a study of the proton-ligand equilibria. The potentiometric data for the metal-ligand systems was first analysed by classical procedures [33,34] and the formation constants of simple mono and binuclear species ( $ML$ ,  $ML_2$  and  $M_2L$ ) thus obtained were used to simulate the titration data using the program SOPHD [36] developed in our laboratory. The simulated and experimental titration data were then plotted together to see whether the assumption of formation of only simple complexes satisfies the experimental data. Titration curves for 1:1, 1:2 and 2:1 molar compositions (metal to ligand) of  $Ca^{2+}$ -AADH and  $Mg^{2+}$ -AADH systems are shown in Fig.(4) and Fig. (5) respectively. The differences between the two curves indicate the formation of other species in addition to simple complexes.

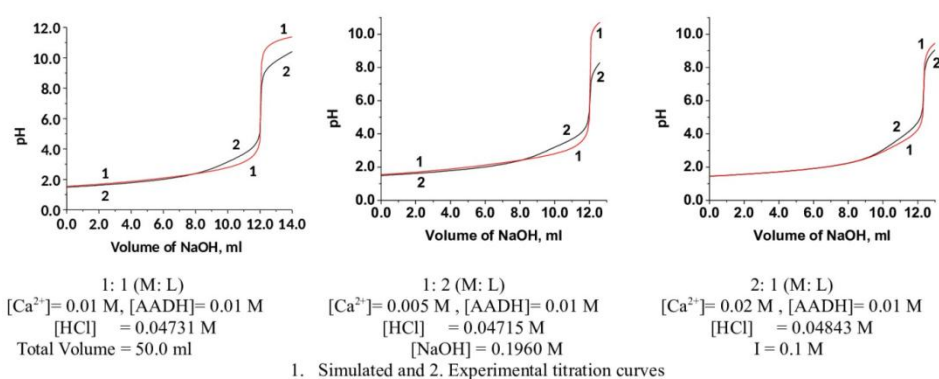


Fig.(4): Simulated and experimental titration curves of  $Ca^{2+}$ -AADH systems

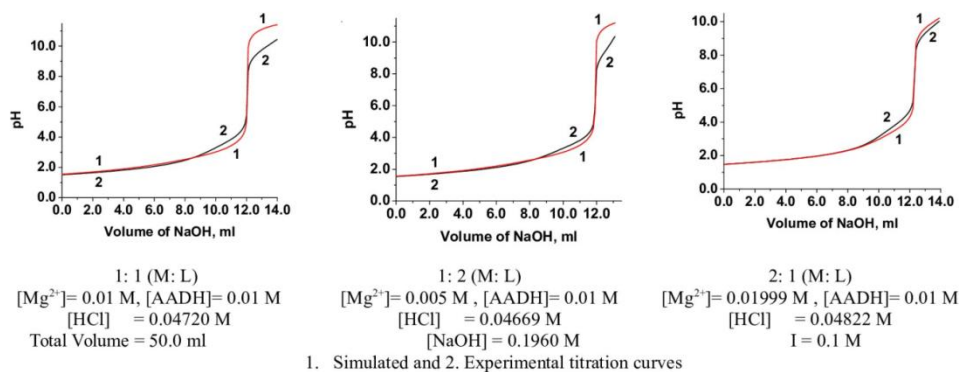


Fig.(5): Simulated and experimental titration curves of  $Mg^{2+}$ -AADH systems

Various models containing chemically plausible species were analysed using the Miniquad-75 program. The best-fit models obtained along with statistical parameters for both the metal ion systems with different metal to ligand molar compositions are shown in Table-2. The species converged include  $MLH$ ,  $ML$ ,  $MLH_1$  for 1:1 composition,  $ML_2H_2$ ,  $ML_2H$ ,  $ML_2$ ,  $ML_2H_1$ ,  $ML_2H_2$  for 1:2 composition and  $M_2L$ ,  $M_2LH_1$  for 2:1 composition. Inclusion of metal hydroxide species in the models resulted in a final rejection suggesting their absence or existence at undetectable low concentrations.

Table 2: Best fit chemical model for metal ion- adipic acid dihydrazide systems  
 (Temp. =  $30.0 \pm 0.1^\circ C$  and ionic strength,  $I = 0.1$  mol  $dm^{-3}$  (NaCl))

Composition (M: L)	$Ca^{2+}$ - AADH System			$Mg^{2+}$ - AADH System		
	Species mlh	Log $\beta_{mlh}$ (SD)	Statistical parameters	Species mlh	Log $\beta_{mlh}$ (SD)	Statistical parameters
1:1	CaLH CaL CaLH <sub>1</sub>	7.02 (5) 3.59 (6) -6.36 (12)	U/NP = $5.081 \times 10^{-7}$ NP=123 $\chi^2 = 38.96$ Skewness= 0.11	MgLH MgL MgLH <sub>1</sub>	6.52 (6) 2.90 (5) -6.89 (7)	U/NP = $5.609 \times 10^{-7}$ NP=123 $\chi^2 = 67.75$ Skewness= -0.24

			Kurtosis= 2.89			Kurtosis= 3.11
1:2	CaLH CaL CaL <sub>2</sub> H <sub>2</sub> CaL <sub>2</sub> H CaL <sub>2</sub> CaL <sub>2</sub> H <sub>1</sub> CaL <sub>2</sub> H <sub>2</sub>	7.02 3.59 13.96 (13) 10.63 (5) 7.07 (1) -1.20 (1) -10.83	U/NP = 2.032X 10 <sup>-9</sup> NP=69 $\chi^2$ = 16.11 Skewness= 0.02 Kurtosis=3.52	MgL <sub>2</sub> H <sub>2</sub> MgL <sub>2</sub> H MgL <sub>2</sub> MgL <sub>2</sub> H <sub>1</sub>	12.74 (2) 9.38 (7) 5.77 (1) -3.52 (4)	U/NP =4.490 X 10 <sup>-9</sup> NP=56 $\chi^2$ = 34.10 Skewness= -0.39 Kurtosis= 3.53
2:1	CaLH Ca <sub>2</sub> L Ca <sub>2</sub> LH <sub>1</sub>	7.02 5.52 (8) -3.88 (6)	U/NP =5.359 X 10 <sup>-7</sup> NP=133 $\chi^2$ = 6.47 Skewness= -0.76 Kurtosis= 3.51	MgLH Mg <sub>2</sub> L Mg <sub>2</sub> LH <sub>1</sub>	6.52 4.93(7) -4.62 (10)	U/NP = 5.301X 10 <sup>-7</sup> NP=36 $\chi^2$ = 36.52 Skewness= 0.29 Kurtosis= 3.74

[U is the sum of the squares of residuals in the mass balance equations. NP is number of experimental points analysed. Skewness and kurtosis indicate the symmetry of residual distribution.  $\chi^2$ , tests the distribution of errors against a normal one. Figures in the parenthesis represent the standard deviation in the least significant digit.]

The species distribution diagrams generated by HYSS [37] program are shown in Fig.(6). For 1:1 and 1:2 compositions at low pH, i.e. below 4.0, the protonated species MLH, ML<sub>2</sub>H and ML<sub>2</sub>H<sub>2</sub> are prevalent for both the metal ions under study. In the case of protonated species MLH and ML<sub>2</sub>H<sub>2</sub>, probably only one of the hydrazide groups of the AADH (L) is involved in bonding as a bidentate, bonding through carbonyl oxygen and terminal nitrogen [38, 39]. The other hydrazide group is protonated at the terminal nitrogen and is non-bonding. The species ML<sub>2</sub>H<sub>2</sub> loses a proton with increase in pH on non-bonding side and forms ML<sub>2</sub>H. Beyond pH 4.0 the neutral form of AADH participates in complexation and simple complexes like ML and ML<sub>2</sub> appear in the solutions of molar compositions 1:1 & 1:2 (M: L). The percentage of formation of these species reaches 70-85% of the total metal. With an increase in pH, ML and ML<sub>2</sub> species lose protons and form deprotonated species like MLH<sub>1</sub>, ML<sub>2</sub>H<sub>1</sub> and ML<sub>2</sub>H<sub>2</sub>. The formation of these species may be due to the participation of deprotonated enolic form, LH<sub>1</sub> of the ligand in bonding (Fig.(3)).

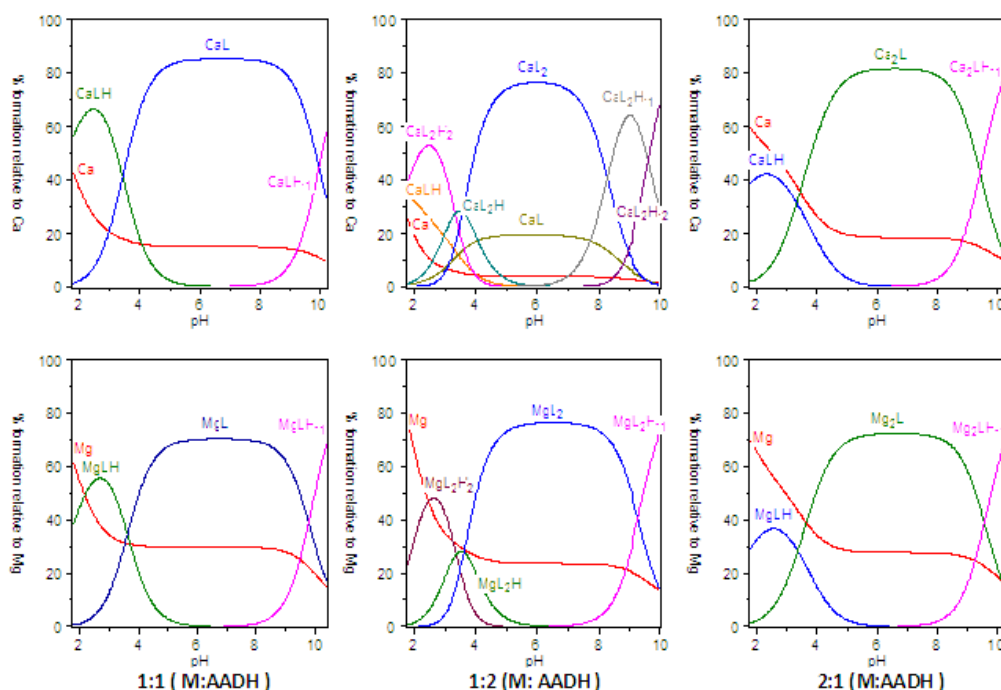


Fig.(6): Species distribution diagrams for 1:1, 1:2 and 2:1 (M: L) molar concentration ratios of binary systems of Ca<sup>2+</sup> and Mg<sup>2+</sup> with AADH.

In the case of 2:1 metal to ligand molar concentration ratio, both Ca<sup>2+</sup>-AADH and Mg<sup>2+</sup>-AADH systems exhibit the formation of homo binuclear complexes, where AADH acts as a ditopic ligand and is attached to two metal ions either in neutral or deprotonated enolic form. Although solution phase studies of speciation cannot give the exact structure of a complex, a probable bonding scheme of binuclear complexes supported by solid state studies [15, 20, 40, 41], excluding the participation of solvent molecules and other ions is shown in Fig.(7).

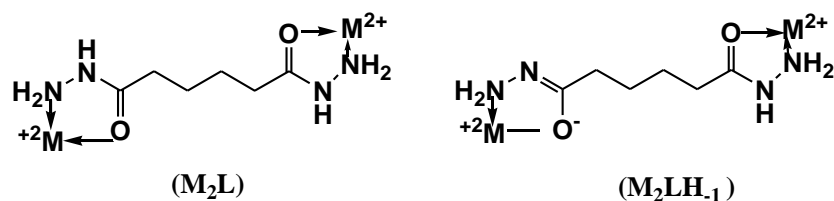


Fig.(7): Homo binuclear species of metal ion-AADH systems

The ligand acts as a bis bidentate coordinating through carbonyl oxygen and  $\text{-NH}_2$  groups forming five membered rings on both sides. This complex is the major species in a wide range of pH, i.e. 5.0 to 8.5 and accounts for nearly 70-80% of total metal. Beyond this range, deprotonation of  $\text{M}_2\text{L}$  takes place leading to the formation of a  $\text{M}_2\text{LH}_1$  type of species.

Stabilities of  $\text{Ca}^{2+}$  species are found to be greater than those of  $\text{Mg}^{2+}$ . Several characteristics of a metal ion such as ionic size, coordination number, hard & soft acid-base nature, geometric factors etc., affect the stabilities of the formed species. The nature of the bond between a metal ion and a ligand may vary from purely electrostatic to almost covalent. Alkaline earth metals  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are hard acids, not easily polarized, favour oxygen donors and show predominately electrostatic bonding in complexes.  $\text{Mg}^{2+}$  ion has relatively small size, high charge density and strong affinity for inner sphere water molecules. The relatively higher stability of  $\text{Ca}^{2+}$  complexes is therefore explicable in terms of smaller hydration energy [42] as the formation of metal-ligand bond requires the breakage of metal ion-solvent bonds. Another factor to be considered is the size of the chelate ring [43, 44] relative to the size of the metal ion. Small metal ions favour six membered rings while large ions prefer five membered rings. Therefore, the relative higher stabilities of  $\text{Ca}^{2+}$ -AADH complexes may be explicable on the basis of the above factors.

#### IV. Conclusions

Adipic acid dihydrazide contains two hydrazide groups at either end of the molecule connected by a flexible C-C bridge and is able to act as a ditopic ligand. Speciation studies on the proton-ligand equilibria of AADH (L) indicated the formation of biprotonated ( $\text{LH}_2^{2+}$ ), mono-protonated ( $\text{LH}^+$ ), unprotonated (L) and mono-deprotonated ( $\text{LH}_1^-$ ) species in aqueous medium. The protonation is at the two terminal amino groups and deprotonation is from one of the enolic groups. The dissociation of the second enolic group is out of the pH region of study. The ligand interacts with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions forming mononuclear  $\text{MLH}$ ,  $\text{ML}$ ,  $\text{MLH}_1$ ,  $\text{ML}_2\text{H}_2$ ,  $\text{ML}_2\text{H}$ ,  $\text{ML}_2$ ,  $\text{ML}_2\text{H}_1$ ,  $\text{ML}_2\text{H}_2$  and homo-binuclear,  $\text{M}_2\text{L}$ ,  $\text{M}_2\text{LH}_1$  type of species. In binuclear species the ligand is attached to two metal ions either in neutral or deprotonated enolic form acting as a bis bidentate bonding through terminal  $\text{-NH}_2$  groups and carbonyl or enolic oxygen, forming five membered rings on both the sides.

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