

## CHEMOMETRIC SPECIATION STUDY OF Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>-COMPLEXES OF TEREPHTHALIC ACID DIHYDRAZIDE IN AQUEOUS MEDIUM

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### ABSTRACT

The Chemical speciation and solution equilibrium study of Terephthalic acid dihydrazide (TPDH) with Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions was carried out using a pH-potentiometric method of data acquisition followed by chemometric modelling methods of analysis. TPDH acts as a ditopic ligand, as two coordinating units present on either side of the benzene ring. Speciation analysis of the metal ion M<sup>2+</sup>-TPDH systems of different homo nuclear and homo binuclear species was carried out. Several protonated and deprotonated species of the type M<sub>m</sub>L<sub>l</sub>H<sub>h</sub> (m= 1or 2, l=1or 2 and h varies from 2 to -1 depending on m and l) were observed to be present in the solution. The corresponding formation constants (303 K, and 0.01M ionic strength) were calculated with the application of MINIQUAD-75 program. HySS program was used to generate concentration distribution diagrams. The best-fit chemical models were chosen based on statistical parameters like Standard deviation (SD), sum of the residual squares in mass balance equations (U), chi-square test etc.

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### INTRODUCTION

Metal ions and their complexes play an inevitable role in most of the biological reactions, such as metal-activated enzymes and substrates. The reaction mechanism explains the formation of an enzyme-metal ion-substrate species, which probably occurs in biological fluids that contain several ligands as well as different metal ions. The field of ditopic ligands and their complexes is a developing part of coordination chemistry, encouraging various biological and industrial applications (Parab *et al.*, 2013; Matsutomi., 1973; Roewer *et al.*, 1977; Bunichiro *et al.*, 1989). Biochemically, there is a requirement of non-toxic ditopic ligands that are efficient at sequestering metal ions with high atom efficiency. Dihydrazides belong to a group of nitrogenous organic compounds that find extensive application in chemotherapy, synthetic chemistry, agriculture and chemical analysis. Terephthalic acid dihydrazide (TPDH) or benzene-1, 4-dicarboxylic acid dihydrazide, is a symmetrical molecule with a benzene ring between two –CONHNH<sub>2</sub> complexing groups on either side of the molecule (Fig.1) and two metal ions can be accommodated in two different coordination pockets of the same molecule which makes it a ditopic ligand.

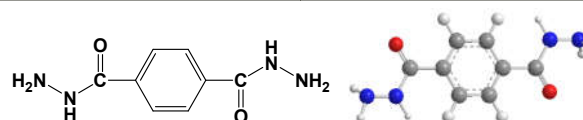


Fig 1 Terephthalic acid dihydrazide

This leads to form supramolecular like structures to impersonate metallo proteins and to recognize their DNA binding, structure-reactivity relationship, (Thomas., 1999) and specific and selective catalysis (Sankara Papavinasanam *et al.*, 1991). TPDH and its derivatives have been established for coatings of epoxy resins and in varnishes. TPDH forms several mono nuclear and binuclear complexes involves many interesting and important applications. Dihydrazides were proved to be non-genotoxic *in vitro* and *in vivo* tests. Food and Drug Administration (FDA) approved (Claudia *et al.*, 2015; FDA., 1994) the use of dihydrazides like coatings (Adrian *et al.*, 2012) on food package materials to avoid direct food contact.

Majority of the reports found in literature (Bakir *et al.*, 2014; Miminoshvili., 2009; Adeniyi *et al.*, 1999; Gogorishvili *et al.*, 1977) are on the synthesis and structural elucidation of the metal complexes of dihydrazides by elemental analyses, magnetic moments, molar conductance, ESR, IR, electronic and X-ray diffraction studies. We report here the results of our study on the chemical speciation of binary Terephthalic acid

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dihydrazide (TPDH) with Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions in aqueous medium.

**MATERIALS AND METHODS**

TPDH purchased from Tokyo Chemical Industry Co., Ltd. (TCI), Japan, were re crystallized from ethanol before use. Solution of ~0.05 mol dm<sup>-3</sup> of TPDH was prepared freshly in ~0.1 mol dm<sup>-3</sup> hydrochloric acid just before use. All the other chemicals such as metal chlorides, hydrochloric acid, potassium chloride and potassium hydroxide were of analytical grade. Double distilled and de ionized water was used for the preparation of all solutions. Hydrolysis can be suppressed by maintaining Hydrochloric acid of ~0.01 mol dm<sup>-3</sup> in metal chloride solutions. Volumetric and complexometric (Schwarzenbach *et al.*, 1957) procedures were implemented to standardize metal ion solutions using standard EDTA solution. Ionic product of water, Carbonate content present in the potassium hydroxide solution, pH correction factor were determined using Gran method (Gran, 1950, 1952) before carrying out each and every potentiometric titration.

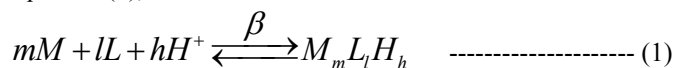
**Equipment**

Metrohm-877 titrinoplus auto titrator equipped with 801-stirrer (Switzerland) which is attached with a combined glass electrode of LL-Unitrode type (6.0259.100; 0-14 pH range) is used for all the potentiometric titrations. This instrument has readability and accuracy up to 0.001pH or 0.1mv. The experimental solution is kept under thermo stated water bath to maintain the temperature of 303 K and nitrogen gas is expelled continuously through it to prevent carbon dioxide content in the experimental solution.

**RESULTS AND DISCUSSION**

**Data acquisition and analysis**

The IUPAC (Braibanti *et al.*, 1987) recommendation requires electrode calibration in terms of hydrogen ion concentrations for the determination of equilibrium constants with the combined glass electrode. Consider a system containing a metal ion (M<sup>2+</sup>), and a ligand (L) involved in the formation of a generalized species represented by the equilibrium in equation (1),



and equation (2) represents the overall formation constant

$$\beta_{mlh} = \frac{[M_m L_l H_h]_i}{[M^{2+}]_i^m [L]_i^l [H^+]_i^h} \text{ ----- (2)}$$

m, l, and h represents Stoichiometric coefficients which specify the composition of the formed species. Positive, zero and negative values of h indicate, the formation of protonated, unprotonated and deprotonated (or hydroxyated) species respectively. The free concentrations of the metal ion, ligand and proton are represented by [M], [L], and [H] respectively. Bjerrum's potentiometric titration technique (Bjerrum, 1957) accompanied with Calvin and Wilson (Calvin and Wilson, 1945) was used for the investigation of protonation equilibria of the selected ligands in aqueous medium. A mixture of required volumes of hydrochloric acid (0.02 - 0.05 mol.dm<sup>-3</sup>), potassium chloride (I, ionic strength = 0.1 mol.dm<sup>-3</sup>) and water including and excluding the ligand in an entire volume of 50.0 cm<sup>3</sup> was analyzed with ~0.2 mol. dm<sup>-3</sup> potassium hydroxide.

The ligand concentration was maintained (0.004 to 0.015 mol.dm<sup>-3</sup>) for various compositions in different experiments. Freshly prepared solutions of ligands were used in all the titrations. The pH correction factor and ionic product of water were calculated using Gran method (Gans *et al.*, 1976). Titrations were conducted until the arrival of turbidity due to precipitation leading to a falling drift in the solution pH. It is compulsory to approach computer algorithms in conjunction with mathematical models known as chemometric algorithms consisting of complete data given, such as volumes and concentrations of metal, ligand, acid, approximate stability constants for the probable species and volume - pH data as input for the program. The data from different experiments with different metal to ligand ratios were analysed using the Miniquad-75 program (Sabatini *et al.*, 1974) and species distribution diagrams were generated using HySS program (Alderighi *et al.*, 1999) The selection of best fit models were on the basis of U (sum of the residual squares in mass balance equations), SD (standard deviations) in formation constants and  $\chi^2$  test which tests the distribution of errors against a normal one.

**Acid-base equilibria of proton-TPDH system**

In solution at low pH, TPDH (L) exists as a biprotonated species, the protonation being at the two amino groups. Hydrazides are prone to lose enolic protons in basic medium by keto-enol tautomerism. The proton-ligand equilibria of TPDH contains three formation constants,  $\beta_{011}$ ,  $\beta_{012}$  and  $\beta_{01-1}$  with log  $\beta$  values 3.12, 5.24 and -10.85 respectively, corresponding to the formation of mono-protonated, biprotonated and deprotonated forms of TPDH. The formation constant,  $\beta_{01-2}$  corresponding to the formation of LH<sub>2</sub> in which TPDH loses both the enolic protons was not converged, as its equilibrium may not be accessible pH metrically. But in the sight of a metal ion this dissociation may take place leading to the formation of MLH<sub>2</sub> type of species. The ligand-proton equilibria of TPDH represented in (Fig.2) indicates the existence of TPDH in solution as LH<sub>2</sub><sup>2+</sup>, LH<sup>+</sup>, L and LH<sub>1</sub> may interact with a metal ion depending on pH.

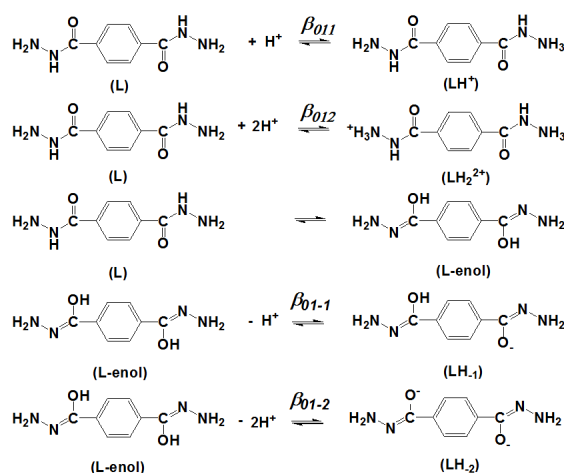


Fig 2 Protonation and deprotonation equilibria of TPDH (L) in aqueous medium

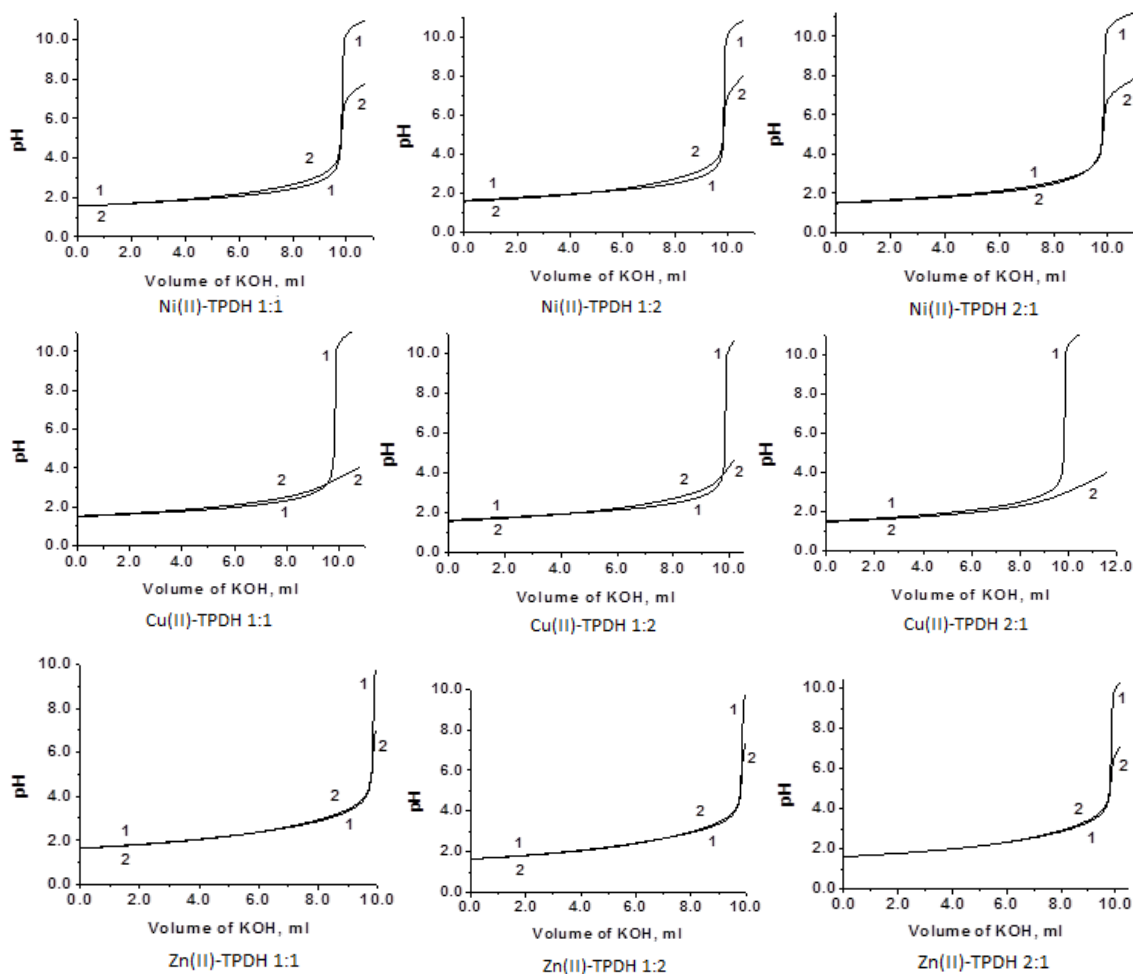


Fig 3 Simulated (1) and Experimental (2) titration curves of  $M^{2+}$ -TPDH systems

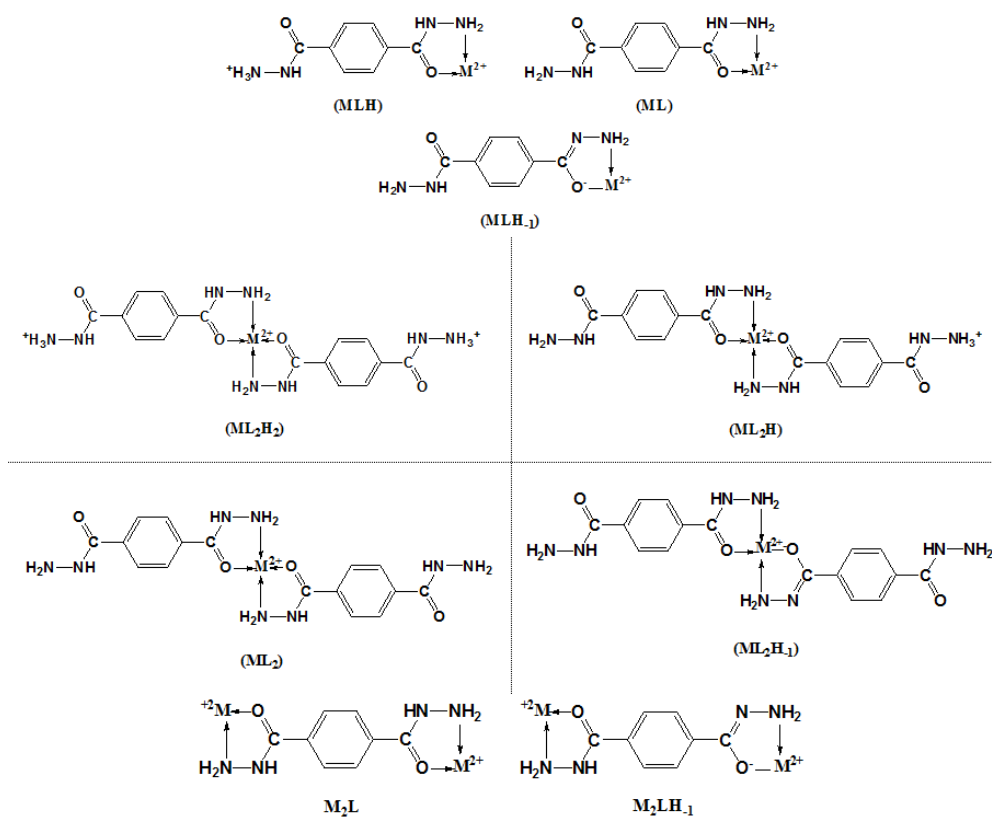
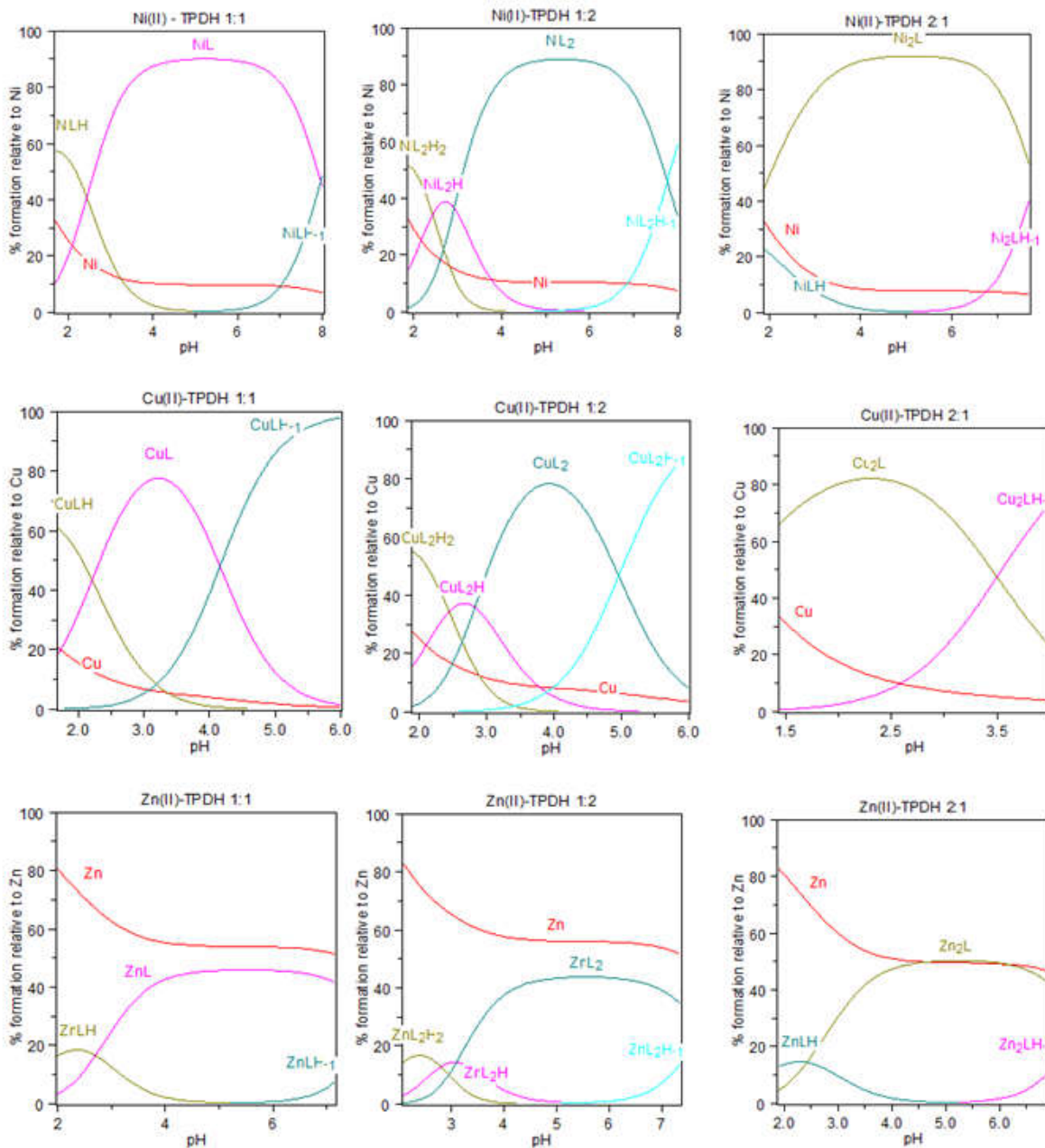


Fig 4 Probable bonding nature of TPDH in metal complexes

The formation constants of the simple complexes, ML and  $ML_2$  were obtained by subjecting the experimentally probed data of metal ion-TPDH systems to analysis (Irving and Rosotti., 1954) The Simulated and experimental titration curves were plotted together using SOPHD (Satyanarayana *et al.*, 1984) program to identify the regions of pH where they differ. The Metal ion-TPDH, titration curves are shown in (Fig. 3).

The species converged for 1:1 metal to ligand mole ratio systems were, MLH, ML and  $MLH_{-1}$ . In MLH the ligand binds the metal ion at one of the hydrazide moieties, leaving the other non-bonding and protonated. With the raise in pH, MLH species lose this proton forming ML type of species. The values of the step-wise protonation constants  $\Delta \log \beta (= \log \beta_{111} - \log \beta_{110})$  for the formation of MLH from ML, as shown in row 'A' of (Table 2) are less than 3.12, the protonation constant of the ligand.



**Fig5** Species Distribution Diagrams of  $M^{2+}$ -TPDH systems  
 ([TPDH] = 0.0100 mol dm<sup>-3</sup>,  $[M^{2+}] = 0.0100$  mol dm<sup>-3</sup>, 0.0050 mol dm<sup>-3</sup>, 0.0200 mol dm<sup>-3</sup> for 1:1, 1:2 and 2:1 respectively)

Keeping in view of the (a) bonding nature of TPDH in different protonation states, (b) nature of the ( $M^{2+}$ ) metal ion and (c) the difference of pH region in the titration curves, different speciation models containing chemically plausible species were chosen for refinement using the Miniquad-75 program. The best-fit models obtained for all the metal ions in various compositions are presented in (Table 1).

This indicates that the complex formation at one end of the molecule affects the protonation at the other end.

**Table 1** Best - fit chemical models of M<sup>2+</sup>- TPDH systems in the aqueous medium at 303 K and ionic strength, I = 0.1 mol dm<sup>-3</sup> (SD= Standard Deviation)

Initial concentration of M:L	Species (M <sub>m</sub> L <sub>l</sub> H <sub>h</sub> )	log β <sub>mlh</sub> (SD)			
		Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	
1:1	111	6.42 (0.01)	6.83 (0.01)	4.90 (0.01)	
	110	3.98 (0.01)	4.62 (0.01)	2.20 (0.01)	
	11-1	-3.98(0.01)	0.46 (0.01)	-5.70 (0.04)	
	U/NP	3.508 e-09	9.089e-10	3.810e-09	
	χ <sup>2</sup>	27.26	6.85	70.93	
	122	12.29(0.03)	12.54 (0.01)	10.30(0.03)	
	121	9.85 (0.02)	10.10 (0.01)	7.50(0.02)	
	120	6.92 (0.02)	7.28(0.01)	4.40(0.02)	
	12-1	-0.83(0.02)	2.32 (0.01)	-3.34(0.04)	
	U/NP	2.900 e -09	5.400e-10	3.810e-09	
1:2	χ <sup>2</sup>	14.09	22.06	60.18	
	111	6.42	-	4.90	
	110	-	4.65	-	
	210	6.71 (0.01)	7.08(0.01)	4.02(0.01)	
	21-1	-1.11 (0.01)	3.58 (0.01)	-3.48(0.03)	
	U/NP	2.203e-08	2.740e-09	3.873e-08	
	χ <sup>2</sup>	33.49	13.50	147.14	
	2:1	111	6.42 (0.01)	6.83 (0.01)	4.90 (0.01)
		110	3.98 (0.01)	4.62 (0.01)	2.20 (0.01)
		11-1	-3.98(0.01)	0.46 (0.01)	-5.70 (0.04)
U/NP		3.508 e-09	9.089e-10	3.810e-09	
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12-1		-0.83(0.02)	2.32 (0.01)	-3.34(0.04)	
U/NP		2.900 e -09	5.400e-10	3.810e-09	

The species ML<sub>2</sub>H<sub>2</sub>, ML<sub>2</sub>H, ML<sub>2</sub> and ML<sub>2</sub>H<sub>1</sub> were found to exist in solutions of 1:2 metal to ligand mole ratio. Again the protons associated with the species are due to the protonated –NH<sub>2</sub> groups of the non-bonding hydrazide moiety. The log K values (= log β<sub>122</sub>- log β<sub>121</sub> and log β<sub>121</sub>- log β<sub>120</sub>) are in between 2.44 and 3.10 (rows ‘B’ and ‘C’ of Table 2) evincing that the attached proton is due to the protonation of the free –NH<sub>2</sub> group.

**Table 2** Step-wise protonation constants of metal ion complexes of TPDH

		Δlog β		
		Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
A	log β <sub>111</sub> - log β <sub>110</sub>	2.44	2.21	2.70
B	log β <sub>122</sub> - log β <sub>121</sub>	2.44	2.44	2.80
C	log β <sub>121</sub> - log β <sub>120</sub>	2.93	2.82	3.10

Homo bimetallic species of the type M<sub>2</sub>L and M<sub>2</sub>LH<sub>1</sub> were observed in 2:1 metal to ligand mole ratio solutions in which the ligand binds two metal ions at the two hydrazide groups. The probable bonding nature of TPDH in different species, supported by solid-state studies (Kumbhar *et al.*, 1976, 1982; Yadav *et al.*, 1987; Shi *et al.*, 2000) is shown in (Fig. 4).

Due to the release of an enolic proton at one of the hydrazide groups or hydroxylation of the corresponding species the deprotonated species, MLH<sub>1</sub>, ML<sub>2</sub>H<sub>1</sub> and M<sub>2</sub>LH<sub>1</sub> may be observed. The concentration distribution diagrams generated using HySS program for all the systems under study are shown in (Fig.5). All the protonated species exist only below a pH of ~4.0. The bimetallic M<sub>2</sub>L type of complexes, depending on the metal ion, represents 50-92% of the total metal. With an increase in pH, these species lose an enolic proton and are converted to the M<sub>2</sub>LH<sub>1</sub> type of species. The stabilities of the complexes are in the order of Ni<sup>2+</sup> < Cu<sup>2+</sup> > Zn<sup>2+</sup>, satisfying, the well known Irving & William’s order (Irving *et al.*, 1953) of stability constants.

## CONCLUSIONS

1. Terephthalic acid dihydrazide TPDH is a ditopic ligand with two hydrazide groups on either side of the molecule.

2. The bonding nature ( ON donor through carbonyl oxygen and –NH<sub>2</sub> group, in neutral bidentate form & tetradentate form, mono negative or binate tetradentate bonding in enolic form ) of TPDH through solid state studies was taken into account and the behavior of it, towards transition metal ions, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> examined in aqueous solution using pH-potentiometric technique.
3. Miniquad-75 program was used for the data analysis and best-fit models were obtained consisting of protonated, unprotonated and deprotonated-mono and symmetric binuclear species depending on the metal-ligand concentration ratio.
4. The stability order of various metal-ligand-proton species was found to be Ni<sup>2+</sup><Cu<sup>2+</sup><Zn<sup>2+</sup> satisfying Irving & William’s order.

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