A CHEMOMETRIC STUDY ON THE LIGATIONAL BEHAVIOUR OF DITOPIC ISOPHTHALIC ACID DIHYDRAZIDE TOWARDS Ni^{2+} AND Cu^{2+} METAL IONS

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Abstract

The H^+-ligand and M^{2+}-ligand equilibria (M^{2+}=Ni^{2+} or Cu^{2+}) of isophthalic acid dihydrazide were investigated potentiometrically using meticulous data acquisition and chemometric analytical techniques. Isophthalic acid dihydrazide possesses hydrazide groups on both sides of a benzene ring and is therefore capable of forming homo-and hetero-bimetallic species. The best-fit chemical models obtained through the Miniquad-75 program showed the existence of several mononuclear and binuclear complexes in different protonated, unprotonated, and deprotonated forms. The diagrammatic concentration distributions of the complexes against the pH of the solution were produced.

Keywords: Isophthalic acid dihydrazide, benzene 1, 3-dicarbxylic acid dihydrazide, ditopic ligand, divalent nickel, divalent copper, bimetallic complexes, Miniquad-75, HYSS.

Introduction

Ditopic ligands that contain multiple binding sites in their structures, enabling the formation of binuclear complexes, are of recent interest[1] as they allow the creation of well-ordered extended complexes containing the same or different cations. This has been the basis for the emphasis placed on the study of the interaction of ditopic ligands with metal ions for their probable use in the sequestration of offending metal ions. Dihydrazides act as ditopic ligands. These compounds and their metal complexes have ample commercial[2,3] and biological[4] applications. They are used in therapy, agronomy, analytical, and synthetic chemistry. Commercially, dihydrazides are used in the production of epoxy resins, acrylics, and polyurethanes.

Isophthalic acid (IPADH) or benzene 1,3-dicarboxylic acid dihydrazide is an aromatic ditopic ligand. As shown in Figure 1, the ligand possesses two hydrazide groups that are capable of coordinating with the metal ions through carbonyl and amino groups.

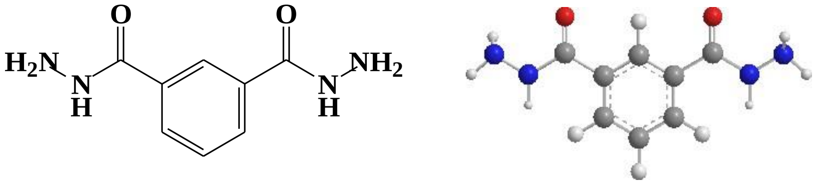


Figure 1: Isophthalic acid dihydrazide (IPADH)

Due to its ditopic nature, the ligand, in the presence of metal ions, may form homo- or hetero-bimetallic species, in addition to mononuclear complexes. Physicochemical studies of the divalent metal ion-IPADH complexes in the solid state[5] indicated the bidentate nature of the hydrazide group of the ligand. However, the characterization of metal complexes in the solid state is specific to isolated species and may be irrelevant to their behaviour in solutions where multiple species coexist. Despite the importance of dihydrazides in various fields, only a few reports[6-17] on chemical speciation in solution were found in the literature. No solution-phase studies were found in the literature on the proton-ligand or metal-ligand interactions of isophthalic acid dihydrazide. Therefore, it is worthwhile to have a detailed understanding of the chemical speciation of IPADH complexes in solution.

Experimental

Reagents

All the chemicals used were of analytical grade. Decimolar stock solutions of Co^{2+} and Ni^{2+} chlorides were prepared in 0.01 mol dm^{-3} hydrochloric acid to repress the hydrolysis of the metal ions, and their concentrations were determined[18] by complexometric titrations with EDTA. Isophthalic acid dihydrazide, obtained from TCI Co., Ltd., Japan, was recrystallized from aqueous ethanol and a 0.05 mol dm^{-3} solution of it was prepared in 0.15 mol dm^{-3} HCl, freshly before its use. The pH correction factor, K_W, and fortuitous carbonate content of the NaOH solution were determined using Gran's method[19].

Equipment

The pH of the experimental solution in the potentiometric titrations was probed to 0.001 pH units (accuracy: ±0.002) using a combined electrode of type LL-Unitrode (6.0259.100; 0-14 pH range) attached to a Titrino Plus-877 auto-titrator and an 801-Stirrer (Metrohm, Switzerland). Potentiometric titrations were carried out in the nitrogen atmosphere at 30.0 ±0.1 ^{0}C.

Data collection and analysis

The experimental investigation consisted primarily of a series of potentiometric titrations, in which a solution containing a strong acid and IPADH with or without a metal salt was titrated by a strong base. The ionic strength was maintained at 0.1 mol dm^{-3} using sodium chloride solution. The total volume of the solution was 50.0 dm^3. The concentrations of metal and ligand were varied in different experiments. Various models containing the estimated values of the formation constants of different sets of chemically plausible species were refined using the Miniquad-75 program[20].

The model that gave the minimum sum of the squares of residuals (U) in mass balance equations, low standard deviations in the formation constants, and a good statistical fit was selected as the best-fit model. The stability constant of a jth complex in the best-fit model with stoichiometric coefficients m_j, l_j, and h_j corresponding to equilibrium at the ith experimental point,

$$m_j[M^{2+}]_i + l_j[L]_i + h_j[H^+]_i \overset{\beta_{m_j l_j h_j}}{\Leftrightarrow\!=\!=\!=\!=\!=\!=\!\Rightarrow} [M_{m_j} L_{l_j} H_{h_j}]_i \text{ -------(1)}$$

is given by the equation,

$$\beta_{m_j l_j h_j} = \frac{[M_{m_j} L_{l_j} H_{h_j}]_i}{[M^{2+}]_i^{\,m}[L]_i^{\,l}[H^+]_i^{\,h}} \quad \text{------ (2)}$$

The coefficients *m, l,* and *h* have varying values for various species in the solution. Protonated, unprotonated, and deprotonated (or hydroxylated) species are indicated by positive, zero, and negative values of *h*, respectively.

Results and Discussion

IPADH-H^+ system

The two $-NH_2$ groups of isophthalic acid dihydrazide (L) may be protonated in acid solutions forming both single and doubly protonated species. Further, the keto-enol tautomerism of the dihydrazide groups may lead to the formation of mono- and dianions by the loss of enolic protons in the basic medium. Therefore, the plausible models to be submitted for refinement should contain, LH^+, LH_2^{2+}, L, LH_{-1}, and LH_{-2} species as shown in Figure 2.

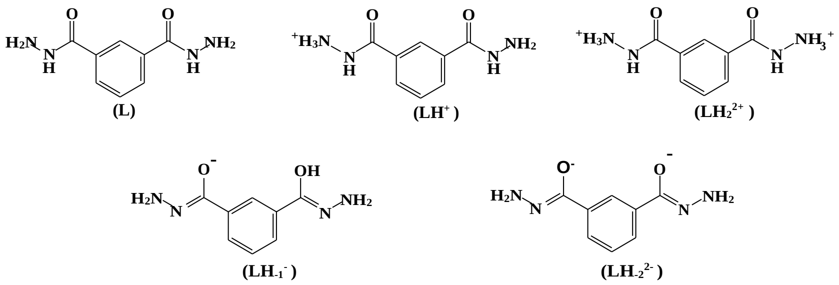


Figure 2: Possible protonation states of IPADH (L) in the aqueous medium

The predicted chemically plausible models were analysed using the Miniquad-75 program, and the refined formation constants are shown in Table 1.

Table 1: Refined protonation constants of Isophthalic acid dihydrazide, T= 30.0 ^{0}C and I= 0.1mole/dm^3

Species *mlh*	Log β_{0lh} (SD)	Experimental points analysed (NP)	Error square-sum in the mass balance equations, (U/NP)	χ^2
011	3.16 (0.01)	86	4.068 10^{-10}	2.51
012	5.54 (0.01)			
01-1	-11.42 (0.01)			

As expected, the best-fit model obtained contained the refined formation constants of the species LH_2^{2+}, LH^+, and LH_{-1}^- with structures as shown in Figure 2. The absence of the doubly deprotonated species, LH_{-2}^{2-} in the best-fit model infers that its equilibrium is outside the reliably measurable pH range of the glass electrode. But in the presence of a metal ion, on complexation, there is a chance of deprotonation of even the second enolic proton. β_{011} and β_{012} are the stability constants for the formation of mono- and biprotonated species of IPADH from its neutral form. The species distribution diagram of the IPADH-H^+ system shown in Figure 3 indicates that at lower pH (i.e., below ~2.4 pH), the biprotonated form, LH_2^{2+}, of IPADH dominates.

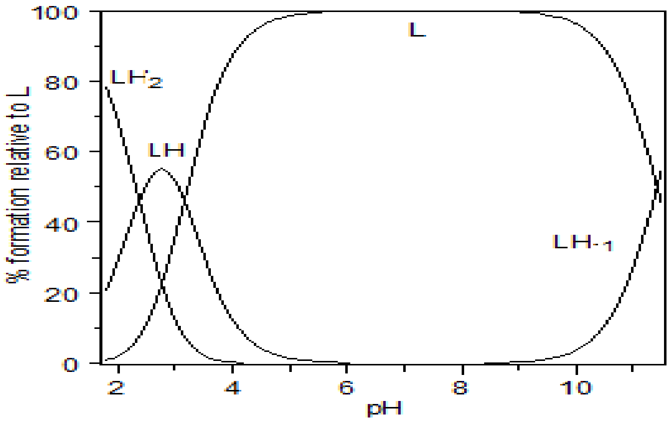
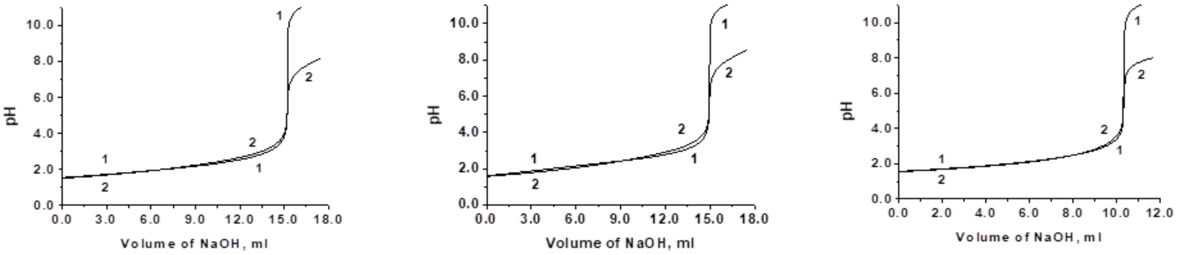


Figure 3: Species distribution of the Proton-IPADH system

As the pH of the solution increases, the biprotonated species undergo deprotonation, forming mono-protonated and neutral forms of IPADH with overlapping equilibria. β_{01-1} is the formation constant of the LH_{-1} species for its formation from the neutral L form by dissociation of the enolic proton.

IPADH-M^{2+} systems

The probed pH-metric data for metal ion-IPADH systems were initially analysed using classical methods[21] to determine the stability constants of simple mono-nuclear complexes, ML and ML_2. Using these constants, the titration data were reproduced using the computer program SOPHD[22] for comparison with the probed data to see whether these species alone would fit the experimental data. The simulated and experimental titration curves were drawn together, as shown in Figure 4, to identify the pH regions where these differ.

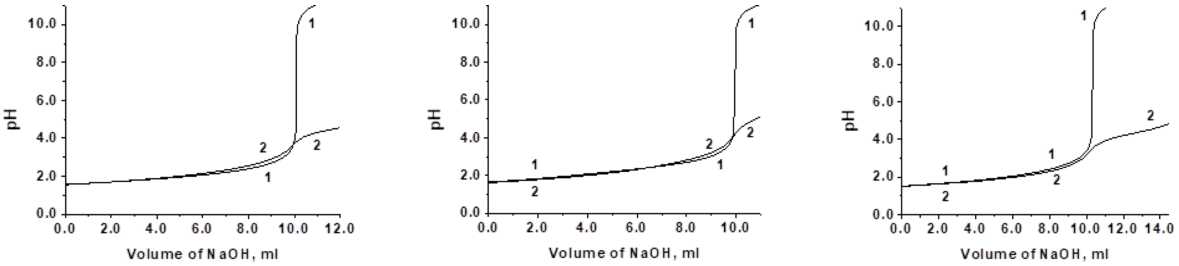


[IPADH]= 0.02000 mol dm^{-3}
[Ni^{2+}] = 0.02000 mol dm^{-3}
[HCl] = 0.06208 mol dm^{-3}
[NaOH] = 0.2040 mol dm^{-3}
Total Volume= 50.0 cm^3
1:1 (M:L)

[IPADH] = 0.02000 mol dm^{-3}
[Ni^{2+}] = 0.01000 mol dm^{-3}
[HCl] = 0.06104 mol dm^{-3}
[NaOH] = 0.2040 mol dm^{-3}
Total Volume= 50.0 cm^3
1:2 (M:L)

[IPADH] = 0.01000 mol dm^{-3}
[Ni^{2+}] = 0.02000 mol dm^{-3}
[HCl] = 0.04200 mol dm^{-3}
[NaOH] = 0.2032 mol dm^{-3}
Total Volume= 50.0 cm^3
2:1 (M:L)

Ni^2-IPADH



[IPADH] = 0.01000 mol dm^{-3}
[Cu^{2+}] = 0.01000 mol dm^{-3}
[HCl] = 0.04096 mol dm^{-3}
[NaOH] = 0.2032 mol dm^{-3}
Total Volume = 50.0 cm^3
1:1 (M:L)

[IPADH] = 0.01000 mol dm^{-3}
[Cu^{2+}] = 0.00500 mol dm^{-3}
[HCl] = 0.04044 mol dm^{-3}
[NaOH] = 0.2032 mol dm^{-3}
Total Volume = 50.0 cm^3
1:2 (M:L)

[IPADH] = 0.01000 mol dm^{-3}
[Cu^{2+}] = 0.02000 mol dm^{-3}
[HCl] = 0.04200 mol dm^{-3}
[NaOH] = 0.2032 mol dm^{-3}
Total Volume = 50.0 cm^3
2:1 (M:L)

Cu^{2+}-IPADH

Figure 4: Simulated and Experimental potentiometric titration curves

The differences between the curves, spreading over a wide pH range, evince the presence of other species in addition to simple mononuclear complexes. Keeping in mind the pH regions of differences between the curves, the available bonding centres of the protonated, unprotonated, or deprotonated forms of IPADH in those regions, and the coordination behaviour of the metal ion, various speciation models containing the formation constants of the chemically probable complexes were selected for refinement. The best-fit models obtained using the Miniquad-75 software are shown in Table 2.

Table 2: Best-Fit Chemical Models of M^{2+}-IPADH systems

Composition (M: L)	**Species mlh**	**log β_{mlh} (SD)**	
		Ni^{2+}- IPADH	**Cu^{2+} - IPADH**
1:1	111	5.53 (0.01)	6.49 (0.01)
	110	3.30 (0.01)	4.16 (0.01)
	11-1	-4.83 (0.01)	-1.15 (0.02)
	11-2	-	-5.09 (0.01)
	U/NP	4.567×10^{-09}	2.689×10^{-10}
	NP	154	99
	χ^2	8.72	16.62
1:2	122	10.80 (0.01)	11.48 (0.01)
	121	8.37 (0.01)	8.97 (0.01)
	120	5.45 (0.01)	6.05 (0.01)
	12-1	-2.55 (0.01)	0.92 (0.01)
	12-2	-11.28 (0.02)	-4.12 (0.03)
	U/NP	3.672×10^{-09}	4.137×10^{-10}
	NP	119	82
	χ^2	8.20	28.80
2:1	111	5.53	-
	210	5.60 (0.01)	6.43 (0.01)
	21-1	-2.79 (0.01)	1.57 (0.05)
	21-2	-10.83 (0.02)	-2.22 (0.02)
	U/NP	1.218×10^{-08}	7.336×10^{-09}
	NP	89	65
	χ^2	8.27	5.41

In systems containing equimolar concentrations of IPADH and metal, the formation of mono-protonated (MLH), unprotonated (ML), and deprotonated (MLH_{-1} and MLH_{-2}) species was observed. In the protonated species, MLH, one of the two hydrazide groups may be participating in bonding, leaving the other free. With the increase in the pH of the solution, the MLH species is converted to ML. The Δ log β (= log β_{111}- log β_{110}) values for this deprotonation as shown in Row-1 of Table 3, are less than the proton binding constant 3.16 of IPADH. This is expected as metal binding at one centre in the molecule may affect proton binding at the other centre.

Table 3: Deprotonation constants of metal complexes of IPADH

Δ log β		Ni^{2+}	Cu^{2+}
1	log β_{111}- log β_{110}	2.23	2.33
2	log β_{122}- log β_{121}	2.43	2.51
3	log β_{121}- log β_{120}	2.92	2.92

In solutions with a 1:2 metal-to-ligand mole ratio, the formation of the simple ML_2 complex along with the protonated ML_2H_2, ML_2H, and deprotonated, ML_2H_{-1} and ML_2H_{-2} species was observed. The Δ log β (= log β_{122}- log β_{121} and log β_{121}- log β_{120}) values for the successive deprotonation of ML_2H_2 range from 2.43 to 2.92 (Table 3: Rows 2 and 3) evincing that the protons attached to the species are due to the protonation of unbound –NH_2 groups of IPADH. In solutions of C_M/C_L=2.0 mole ratio, the formation of unprotonated and deprotonated bimetallic complexes of the types, M_2L, M_2LH_{-1}, and M_2LH_{-2} was noticed. In all these species, IPADH binds metal ions at both the hydrazide groups.

The deprotonation of the complexes leading to the formation of MLH_{-1}, MLH_{-2}, ML_2H_{-1}, ML_2H_{-2}, M_2LH_{-1}, and M_2LH_{-2}, may be attributed to the hydroxylation or loss of the enolic protons. The anticipated bonding modes of isophthalic acid dihydrazide in various complexes backed by the solid-state studies [5, 23-25], are depicted in Figure 5.

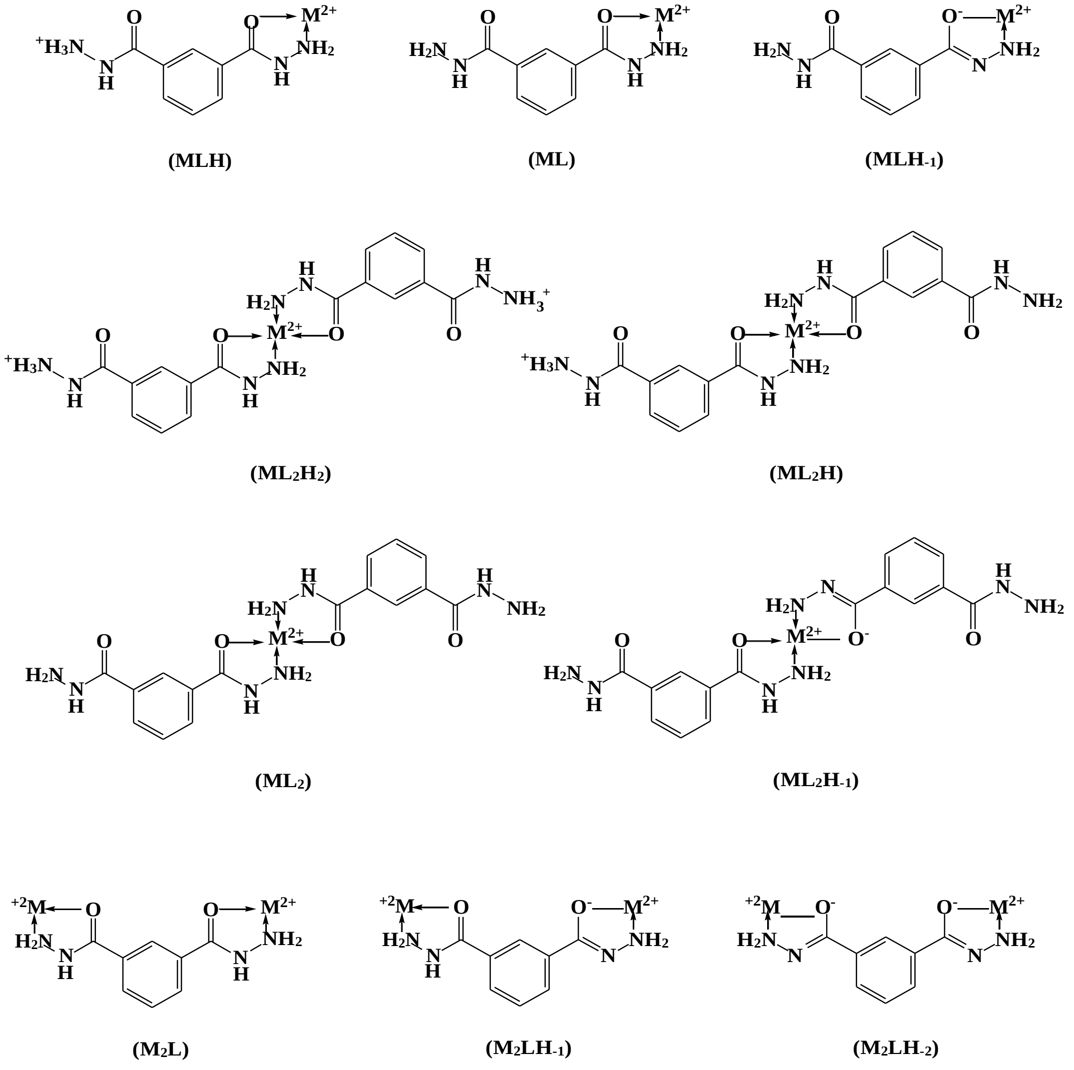
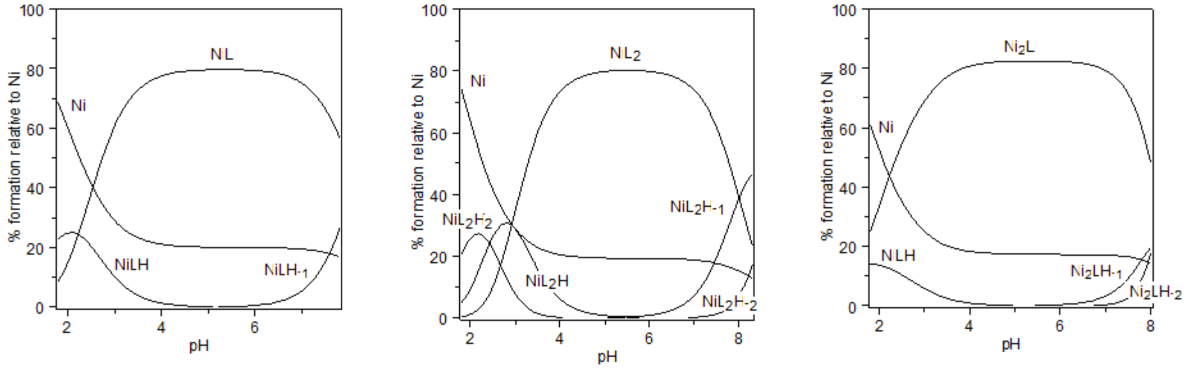
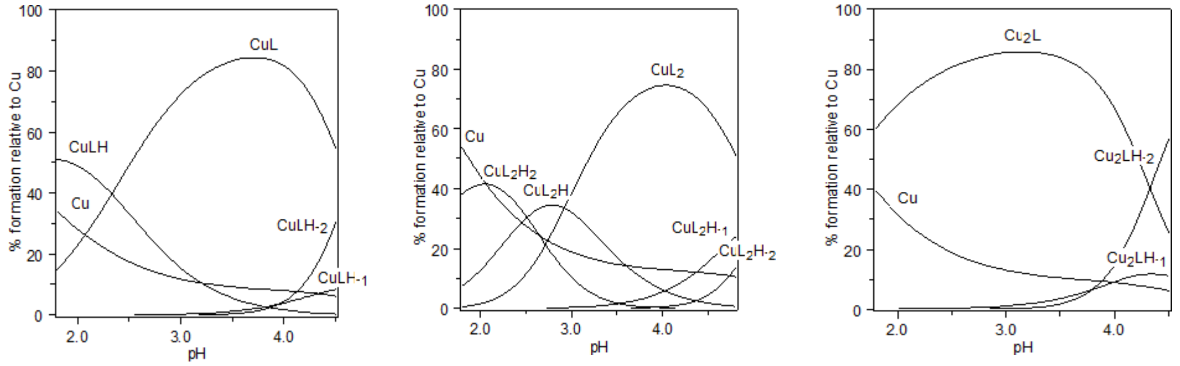

(MLH) (ML) (MLH_{-1})
(ML_2H_2) (ML_2H)
(ML_2) (ML_2H_{-1})
(M_2L) (M_2LH_{-1}) (M_2LH_{-2})

Figure 5: Probable bonding nature of IPADH in metal complexes.

The distribution curves of the various Ni^{2+} and Cu^{2+} binary complexes against the pH of the solution, drawn using the Hyperquad Simulation and Speciation (HySS) software[26] were shown in Figure 6.



Ni^{2+}-IPADH (1:1) system Ni^{2+}-IPADH (1:2) system Ni^{2+}-IPADH (2:1) system



Cu^{2+}-IPADH (1:1) system Cu^{2+}-IPADH (1:2) system Cu^{2+}-IPADH (2:1) system

Figure 6: Percentage concentration distribution vs pH of the solution of M^2-IPADH systems

Protonated complexes were found to exist only below a pH of 4.0. Depending on the metal ion, the bimetallic, M_2L type of complexes, account for 83-86% of the total metal. M_2L complexes with the increase in the pH of the solution, are converted to deprotonated M_2LH_{-1} and M_2LH_{-2} species by losing enolic protons.

Conclusions

A chemometric speciation study on the complex equilibria of isophthalic acid dihydrazide was conducted in an aqueous medium. IPADH is a ditopic ligand possessing hydrazide donor groups on both sides of a benzene ring. The SOPHD and Miniquad-75 programs were used to generate and analyse various models containing chemically plausible species. The species that converged include both mono-and bi-nuclear complexes with different extents of protonation or deprotonation. The anticipated bonding behaviour of IPADH in the complexes, based on the pH regions of their existence and literature reports on solid-state studies, was proposed.

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