REDVET - Revista electrónica de Veterinaria - ISSN 1695-7504
Vol 25, No. 1 (2024)
http://www.veterinaria.org
Article Received: 08 July 2024 Revised: 04 August 2024 Accepted: 29 August 2024

Potentiometric Determination Of Proton-Ligand Dissociation Constant Of 2-({(2E)-[(3E)-3-(Hydroxyimino)Butan-2-Ylidene]Hydrazinylidene}Methyl) Phenol And Formation Constants Of Its Complexes With Cobalt, Nickel, And Copper In Dioxane-Water System

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Abstract
The first report of a newly synthesized ligand, 2-({(2E)-[(3E)-3-(hydroxyimino)butan-2-ylidene]hydrazinylidene}methyl) phenol (HDMH*m*HB), has been prepared. Coordination with metal ions of the transition element series piqued interest in this ligand because of its ambidenticity and likely multidenticity. Despite the ligand's likely two dissociable protons, our research shows that it is monobasic. We used a Calvin-Bjerrum potentiometric technique modified by Irving and Rassotti in a KCl and 60:40(V/V) 1,4-dioxane - water system at room temperature in an inert, nitrogen atmosphere to determine the proton ligand dissociation constant of HDMH*m*HB and the stability constants of its complexes with cobalt, nickel, and copper. The experiment was conducted under variable ionic strengths. The complex is formed in stages, with the complexed species' stepwise formation constants increasing in order of Co^{2+}, Ni^{2+}, and Cu^{2+} for both species. The ML_2 species is the most stable.

K**eywords:** Ionic Strength, Stability constants, Metal ion Complexes, Stepwise Formation Constants, Potentiometry.

INTRODUCTION:

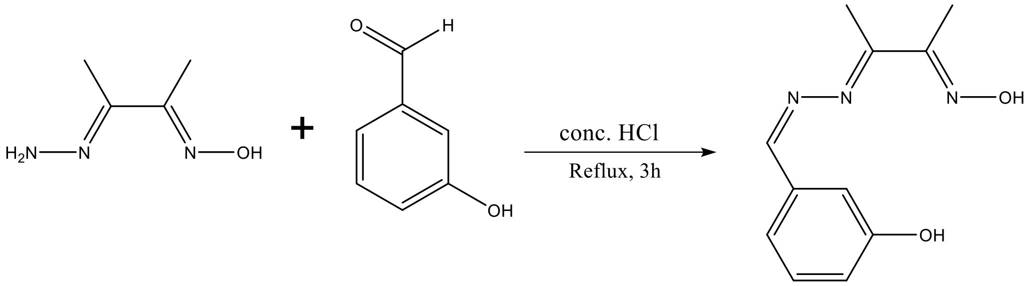
In the past several years, oximino ketones and their derivatives have garnered a lot of interest as coordination complexes. This is because these compounds are easy to synthesize and can undergo a variety of structural modifications. They also have many practical uses in fields such as analysis, bioinorganic systems, medicine, catalysts, and more. This is mainly due to the ambidentate nature of the ligand, the presence of the >C=N-group (a physiologically significant group since it indicates microbial activity), and the different locations of the likely donor atoms. Therefore, these ligands can report metal complexes with a wide range of shapes, stabilities, and uses. According to the literature review, no research has been conducted on the stability constants of the metal complexes containing the aforementioned organic ligand or its proton dissociation constant. Co^{2+}, Ni^{2+}, and Cu^{2+} complexes of the aforementioned organic ligand were studied, and the dissociation constant and stability constant were found to be affected by changes in ionic strength.

EXPERIMENTAL:

All of the chemicals used were AR grade. Other compounds, if used, were purified using normal techniques before use. The organic solvents employed were purified using conventional techniques. Vogel's conventional procedure for producing carbonate-free bidistilled water was followed. Before each use, volumetric glassware was calibrated. The titrations were conducted using an Equiptronicsp H-meter (EQ-610, accuracy ±0.01 unit) with an integrated magnetic stirrer. It was calibrated with buffer solutions at pH 4.0, 7.0, and 9.2 produced with buffer tablets (A.R.). The pH was measured with a combination glass electrode. The pH meter readings in the non-aqueous medium were adjusted [8]. All titrations were performed using a thermostat at room temperature and an inert atmosphere, with nitrogen gas bubbling through the solution. This served to keep the environment inert while also stirring the solution during titration.

Synthesis of Schiff base HDMH*m*HB ligand:

Diacetylmonoximehydrazide (1.50 g, 0.10 mol) and 3-hydroxybenzaldehyde (13.4 g, 0.11 mol) were combined in a 50-ml methanol solution and refluxed for three hours while the mixture was agitated. Two rounds of washing with diethyl ether followed by two rounds of water (two x 15 ml) were used to filter and wash the solid that resulted. Schematic 1 depicts the process of recrystallization from methanol.



Scheme-1: Preparation of HDMH*m*HB ligand

Potentiometric measurements:

A solution of ligand (0.05 mol·dm^{-3}) was made by dissolving a precisely measured quantity of the solid in dioxane (A.R.). Metal ion solutions (0.01 mol·dm^{-3}) were prepared using the respective metal chlorides in distilled water and standardized by titration with E.D.T.A. Solutions of 0.01 mol·dm^{-3} HCl and 1.0 mol·dm^{-3} KCl were also prepared in distilled water. A potassium hydroxide solution free from carbonate in a 60% dioxane-water mixture (by volume) was standardized using a standard succinic acid solution and employed as the titrant. The subsequent mixtures were prepared and potentiometrically titrated at room temperature, i.e., 301 K, against a standard 0.1 mol·dm^{-3} KOH in a 60% dioxane-water mixture (by volume).

[1] 5.0 ml of 0.10 mol·dm^{-3} HCl + 30.0 ml Dioxane.
[2] 5.0 ml of 0.10 mol·dm^{-3} HCl +5.0 ml of 0.05 mol.dm^{-3} ligand + 25.0 ml Dioxane.
[3] 5.0 ml of 0.10 mol·dm^{-3} HCl + 5.0 ml of 0.05 mol.dm^{-3} ligand + 5.0 ml of 0.01 mol.dm^{-3} metal chloride + 25.0 ml Dioxane.

For each scenario, a suitable volume of 1.0 M KCl was added to uphold an ionic strength of 0.05 mol·dm^{-3}, and the total volume was adjusted to 50.0 ml with distilled water. The solution was then titrated against standardized 0.10 mol·dm^{-3} KOH solution until precipitation began or constant pH values were observed, whichever occurred first. Similar titrations were conducted for ionic strengths of 0.075 mol·dm^{-3} and 0.10 mol·dm^{-3}.

RESULTS AND DISCUSSION:

The mean number of protons bound to the ligand at various pH levels, denoted as $\overline{nA}$ was determined by analyzing the titration curves of the acid both with and without the ligand, using equation (1).

$$\bar{n}_A = \gamma - \frac{(V_2-V_1)(N^0+E^0)}{(V^0+V_1)TC_L^0} \qquad \text{.... Eq.1}$$

where Y is the number of ionizable protons in the ligand (Y = 1), and V_1 and V_2 represent the volumes of alkali needed to achieve the same pH on the titration curves of hydrochloric acid and the reagent, respectively. V_0 is the initial volume (50.0 ml) of the mixture, TC°_{L} is the total concentration of the reagent (ligand), $N°$ is the normality of the potassium hydroxide solution, and $E°$ is the initial concentration of the free acid. Thus, formation curves ($\overline{\overline{nA}}$ versus pH) for the proton-ligand systems were plotted, ranging between 0 and 1 on the $\overline{\overline{nA}}$ scale, indicating that the ligand has one ionizable proton. Formation curves for the metal complexes were generated by plotting the average number of ligands attached per metal ion ($\bar{n}$) against the free ligand exponent (pL), following the method of Irving and Rossotti [1]. The average number of reagent molecules attached per metal ion ($\bar{n}$) and the free ligand exponent, pL, can be calculated using equations (2) and (3) respectively:

$$\bar{n} = \frac{(V_3-V_2)(N^0+E^0)}{(V^0+V_2)\bar{n}_A+TC_M^0} \qquad \text{.... Eq. 2}$$

$$pL = \log(10)[\frac{\sum_{n=0}^{n=j}/\beta_n^H(1/antilog\ pH)^n}{TC_L^o - \bar{n}TC_M^o} . \frac{V^o+V3}{V^o}] \qquad \text{.... Eq. 3}$$

In the given context, the total concentration of the metal ion in the solution is denoted by TC_M^o, and the overall proton-reagent stability constant is denoted by β_n^H are significant. V_1, V_2, and V_3 represent the volumes of alkali needed to achieve equivalent pH levels on the titration curves of hydrochloric acid, organic ligand, and complex, respectively. Analysis of these curves enabled the determination of successive metal-ligand stability constants. The values of these stability constants (log K_1 and log K_2) can be found in **Tables 2, 3**, and **4**. Here are some general observations:

a. The maximum value of $\bar{n}$ was approximately 2, indicating the formation of 1:1 and 1:2 (metal: ligand) complexes exclusively.
b. The metal ion solution utilized in this study was highly diluted (1 × 10^{-3} mol·dm^{-3}); thus, the possibility of forming polynuclear complexes was eliminated.

c. The metal titration curves exhibited displacement towards the right-hand side of the ligand titration curves along the volume axis, signifying proton release during the complex formation of the metal ion with the ligand. The substantial decrease in pH for the metal titration curves compared to the ligand titration curves suggests the formation of strong metal complexes.
d. For the same ligand at a constant temperature, the stability of chelates follows the order Co^{2+}, Ni^{2+}, and Cu^{2+}. This order predominantly reflects that the stability of Cu^{2+} complexes surpasses those of other metals in the 3*d* series. Cu^{2+} receives additional stabilization due to the tetragonal distortion of octahedral symmetry in its complexes, influenced by both the polarizing ability of the metal ion and the ligand field. The greater stability of Cu^{2+} complexes may be attributed to the Jahn-Teller effect, which distorts the regular octahedral environment for the metal ion.

The dissociation constant (pK$_H$) for the ligand, as well as the stability constants of its complexes with Co^{2+}, Ni^{2+}, and Cu^{2+}, were evaluated at concentrations of 0.05 mol·dm^{-3}, 0.075 mol·dm^{-3}, and 0.1 mol·dm^{-3}, and are presented in **Tables 1-4**.

Table-1: Proton –ligand dissociation constants at R.T. (301K)

Sr. No.	Ionic Strength	Proton-Ligand Constants		pK$_H$
		By half integral method	By graphical method	
1	0.05	10.73	10.73	10.73
2	0.075	10.64	10.64	10.64
3	0.01	10.55	10.55	10.55

Table 2: Stepwise stability constants for ML$^+$ and ML$_2$ complexes in 60:40 (by volume) dioxane: water mixture and I = 0.05 mol/dm^{-3} at room temperature (301K)

	logK1		logK2		logβ= logK1+ logK2
M^{n+}	By graph	By calculations	By graph	By calculations	
Co^{2+}	9.39	9.35	6.84	6.86	16.22
Ni^{2+}	9.77	9.79	7.27	7.28	17.07
Cu^{2+}	10.37	10.36	9.38	7.36	19.77

Table 3: Stepwise stability constants for ML$^+$ and ML$_2$ complexes in 60:40 (by volume) dioxane: water mixture and I = 0.075 mol/dm^{-3} at room temperature (301K)

	logK1		logK2		logβ= logK1+ logK2
M^{n+}	By graph	By calculations	By graph	By calculations	
Co^{2+}	9.37	9.26	6.77	6.78	16.05
Ni^{2+}	9.70	9.69	7.17	7.16	16.87
Cu^{2+}	10.32	10.32	9.30	7.29	19.63

Table 4: Stepwise stability constants for ML$^+$ and ML$_2$ complexes in 60:40 (by volume) dioxane: water mixture and I = 0.10 mol/dm^{-3} at room temperature (301K)

	logK1		logK2		logβ= logK1+ logK2
M^{n+}	By graph	By calculations	By graph	By calculations	
Co^{2+}	9.26	9.26	6.77	6.78	16.05
Ni^{2+}	9.70	9.69	7.17	7.16	16.87
Cu^{2+}	10.32	10.32	9.30	7.29	19.63

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