ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2015, Vol. 89, No. 12, pp. 2254–2258. © Pleiades Publishing, Ltd., 2015.

STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Stability Constants of Ni(II)– and Cu(II)–N-Heterocycle Complexes According to Spectrophotometric Data[1]

Samata Badhe, Pradip Tekade*, Sonal Bajaj, and Shrikant Thakare

Department of Chemistry, Jankidevi Bajaj College of Science, Jamnalal Bajaj Marg, Civil Lines, Wardha, India

**e-mail: pradiptekade@gmail.com*

Received October 24, 2014

Abstract—The interaction of Ni(II) and Cu(II) with ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate [Ligand 1], 4-(1H-benzimidazol-2-yl)phenol [Ligand 2], and 2-(3-phenylamino-4,5-dihydro-1,2-oxazol-5-yl)phenol [Ligand 3] have been studied by spectrophotometric technique at 0.01 M ionic strength and 28°C in 70% dioxane—water mixture. The data obtained were used to estimate the stability constant of these ligands. Spectrophotometric investigation of Ni(II) and Cu(II) complexes with these ligands shows 1 : 1 complex formation. The formation of complexes has been studied by Job's variation method. The values of conditional stability constants of Cu(II) complexes are greater than the corresponding Ni(II) complexes. The greater value of stability constant of Cu(II) complexes may be due to the fact of more stable nature of Cu(II). The value of stability constant of Cu(II)—Ligand 2 complex is greater than that of Cu(II)—Ligand 1 and Cu(II)—Ligand 3. The same of Ni(II)—Ligand 3 complex is greater than that of Ni(II)—Ligand 1 and Ni(II)—Ligand 2.

Keywords: nickel complexes, copper complexes, heterocyclic ligands, Job's variation method.

DOI: 10.1134/S0036024415120250

INTRODUCTION

Rowland and Meloan [1] investigated cinnamohydroxamic acid chelates spectrophotometrically and reported the composition and the molar extinction coefficients of these chelates. Khobragade et al. [2] have investigated the metal-ligand stability constants of UO_2(II) and Cu(II) complexes with some substituted sulfonic acids. Narwade et al. [3] have studied Fe (III) complexes with substituted chalcones spectrophotometrically. Narwade et al. [4] investigated the stability constants of some lanthanide ions with sulphonic acid spectrophotometrically. The metal chelates of hydrazo-dimedone dyes are studied by Atef et al. [5]. Sunita and Gupta [6] have worked on spectrophotometric determaination of cyanide in biological complex. Manimekalai et al. [7] have determined the stability constants and composition of 3-(2-furanyl)-2-propenhydroxamic acid chelates by Job's method at continuous variations in 30% ethanol-water medium. Chavan and Joshi [8] have studied the spectrophotometric determination of micro amounts of gold (III) using cyclopentane-spiro-2'-(l'-methyl-2',4'-dithio)-5-triazine. Sawalakhe [9] also determined stability constant and composition of the Fe(III)–l-(2-hydroxyphenyl-3-phenyl-l,3-propandione) chelates by Job's method in 70% dioxane-water mixture. Bhargava and Tondon [10] determined the metal-ligand stability constant of Pt(IV) with substituted alkyl/aryl thiourea complexes spectrophotometrically. Sawalakhe et al. [11] studied the interaction of metals with 1,3-diketone, pyrazole and pyrazolines spectrophtometrically. Raghuwanshi et al. [12] studied the conditional stability constant of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. Conditional stability constants of transition metal ions with some amino acid peptides have been studied by Sondawale and Narwade [13]. Raut et al. [14] studied the conditional stability constants of transition metal ion complexes with the antibiotic drug captopril. Mixed ligand Cu(II) complexes of 2-aminobenzamide and amino acids viz., glycine, L-alanine, L-valine, and L-phenylalanine have been synthesized and characterized by various physico-chemical and spectral techniques [15]. Spectrophotometric study of triethylenetetramine dihydrochloride interaction with Cu(II) and Zn(II) have been reported by Nurchi et al. [16]. Spectrophotometric study of stability constants of Cr(III), Ni(II) and Cu(II) complexes with a Schiff bases in different solvents have been studied by Lere et al. [17].

Substituted isoxazolines, pyrimidines, and benzimidazoles are good complexing agents due to the presence of electron donor oxygen. Dihydropyrimidinone are known to exhibit a wide range of biological activities such as antiviral, antitumour, antibacterial,

---

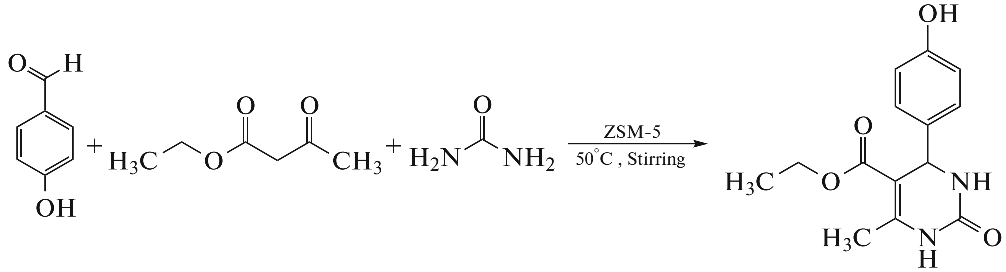
[1] The article is published in the original.

and anti-inflammatory properties [18]. In addition, these compounds have emerged [19] as potential calcium channel blockers, antihypertensive, α_1-adrenergic antagonists and neuropeptide antagonists. Isoxazoline derivatives have been reported to possess biological activity [20, 21]. Benzimidazole derivatives are known to have numerous antimicrobial [22, 23], anti-inflammatory [24] and anti-tumour [25] properties. Therefore, it was thought of interest to study the chelating properties of *N*-heterocycles viz. ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate [Ligand 1], 4-(1H-benzimidazol-2-yl)phenol [Ligand 2], and 2-(3-phenylamino-4,5-dihydro-1,2-oxazol-5-yl)phenol [Ligand 3] with Ni(II) and Cu(II) metal ions by Job's variation method under suitable conditions spectrophotometrically.

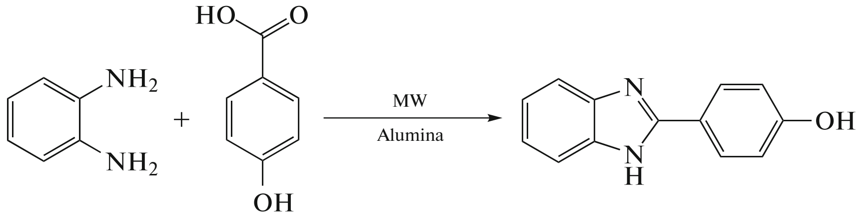
EXPERIMENTAL

All the chemicals used are of laboratory grade and used without further purification. The ligands were prepared by known methods [26–28]. Compounds were recrystallized before use.

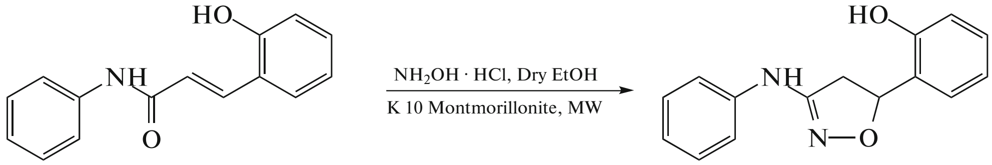
The preparation of ligands is described by the scheme:



Ligand 1



Ligand 2



2-(3-phenylamino-4,5-dihydro-1,2-oxazol-5-yl)phenol

Ligand 3

Distilled water used was free from carbon dioxide and pH of this water was about 6.80. Ni(II) (0.01 M) and Cu(II) (0.01 M) ionic solutions were prepared from nickel nitrate and copper nitrate (AR grade) and were standardized by standard methods. The solution of potassium nitrate was prepared (0.01 M) and used for maintaining ionic strength constants. Ligands are insoluble in water, hence ligand solutions of 0.01 M were prepared in 70% dioxane–water (v/v). 0.01 M solutions of ligand were prepared separately by dissolving 0.255, 0.214, and 0.278 g of ligand 1, 2, and 3 respectively in 100 mL of 70% dioxane.

Contech digital balance CA 224 having accuracy 0.001 g was used for weighing of samples. Systronics 108 UV–Visible spectrophotometer with 0.01 unit accuracy was used for absorbance measurements. IR spectra were recorded on Bruker Alpha IR spectrometer (Germany). ^{1}H NMR and ^{13}CNMR spectra of the compounds were recorded on Bruker DRX 300 NMR instrument using TMS as internal standard.

Metal–ligand stability constants and confirmation of complexes have been studied by McBryde [29] and Banerjee [30]. The composition of the complexes are confirmed by Job's method as modified by Vosburgh and Gold [31]. Solutions of metal salt and ligand of equimolar concentration (1.00×10^{-2} M) are mixed pairwise in different ratios to prepare Job's solutions. Final volume of each solution was made 10 ml after adjusting the appropriate pH and maintaining the constant ionic strength (0.1 M sodium perchlorate). In addition to the wavelength of maximum (λ_{max}) some other wavelength were selected as proposed by Vosburgh and Gold.

RESULTS AND DISCUSSION

Spectral data for the prepared ligands are in good agreement with literature [26–28].

The concentration of complex (x) in any metal-ligand solution is obtained by Job's curve. Initial concentrations of metal and ligand in a particular solution are considered a and b and the equilibrium constant was determined by the law of mass action.

$$k = \frac{x}{(a-x)(b-x)}$$

or

$$k = \frac{x}{(a_1-x)(b_1-x)}\frac{x}{(a_2-x)(b_2-x)}.$$

The composition of metal ion solution (1×10^{-2} M) and ligand (1×10^{-2} M) were prepared in ten series. λ_{max} was determined using one of the compositions at which there is maximum absorption. The absorptions for all the compositions were recorded at constant wavelength (λ_{max}). Each solution is diluted up to 15 mL and absorptions are recorded at same λ_{max}. The data of absorption and percentage composition of metal ion and ligand solutions at constant pH are used and the curves are constructed. The conditional stability constants obtained by spectrophotometric techniques are presented in the table.

Conditional stability constants of complexes

System	K	$\log K$	$\log K'$ mean
Ni(II)–L1	0.02758	1.4406	1.8217
Cu(II)–L1	0.18674	2.2712	
Ni(II)–L2	0.01065	1.0274	
Cu(II)–L2	0.2774	2.4431	
Ni(II)–L3	0.03849	1.5853	
Cu(II)–L3	0.14559	2.1631	

It can be seen from table that for Ligands 1 and 2, the values of conditional stability constants of Cu(II) complexes are greater than the corresponding Ni(II) complexes. The greater value of stability constant of Cu(II) complexes may be due to the fact of more stable nature of Cu(II).

The value of stability constant of Cu(II)–Ligand 2 complex is greater than that of Cu(II)–Ligand 1 and Cu(II)–Ligand 3. The same of Ni(II)–Ligand 3 complex is greater than that of Ni(II)–Ligand 1 and Ni(II)–Ligand 2.

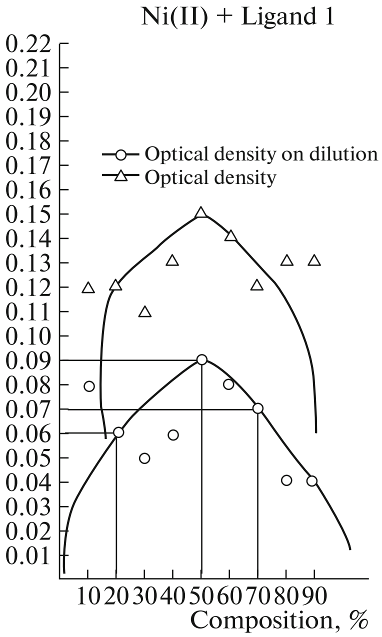


Fig. 1. Plot of optical density vs. composition (%) of system Ni(II)–Ligand 1.

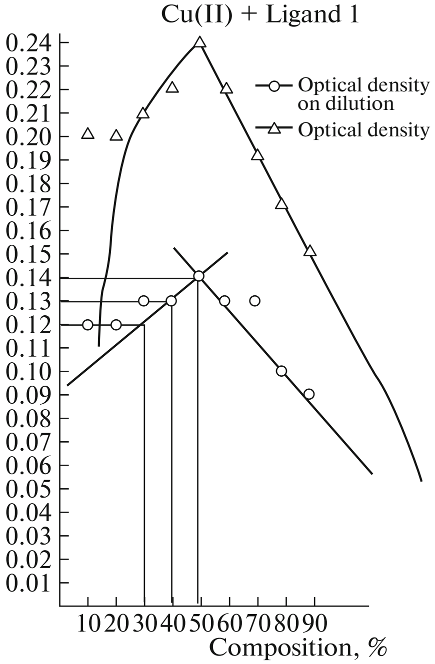


Fig. 2. Plot of optical density vs. composition (%) of system Cu(II)–Ligand 1.

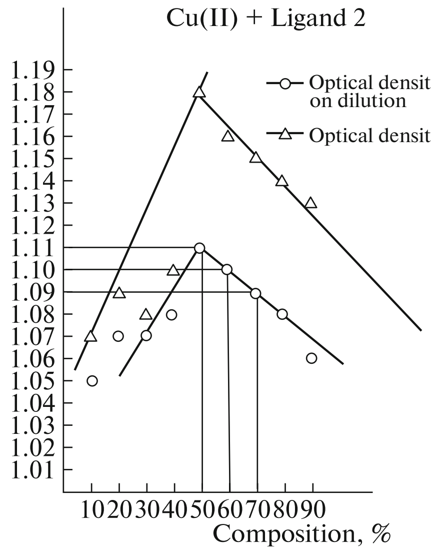


Fig. 3. Plot of optical density vs. composition (%) of system Cu(II)–Ligand 2.

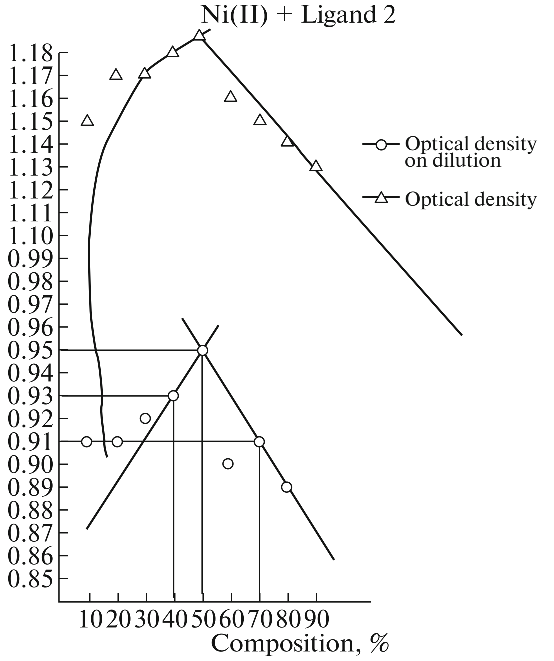


Fig. 4. Plot of optical density vs. composition (%) of system Ni(II)–Ligand 2.

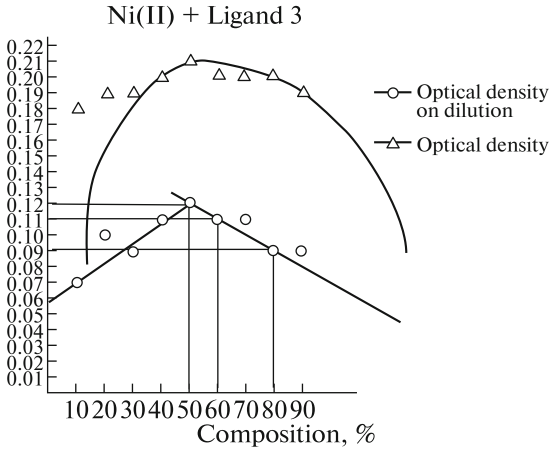


Fig. 5. Plot of optical density vs. composition (%) of system Ni(II)–Ligand 3.

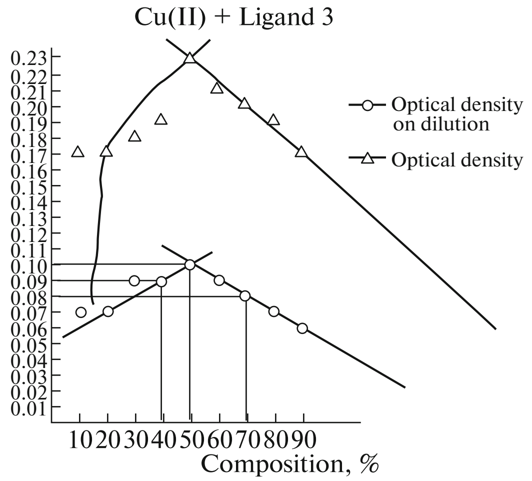


Fig. 6. Plot of optical density vs. composition (%) of system Cu(II)–Ligand 3.

Order of Stability Constants:
Cu(II)–Ligand 2 > Cu(II)–Ligand 1 > Cu(II)–Ligand 3,
Ni(II)–Ligand 3 > Ni(II)–Ligand 1 > Ni(II)–Ligand 2.

The curves are constructed between the values of optical density and percentage composition of metal ion as shown in Figs. 1–6.

CONCLUSION

In the present study spectrophotometric investigation of stability constant of complexes of the ligands with Ni(II) and Cu(II) metal ions was done. The formation of complexes (1 : 1) has been studied by Job's variation method.

REFERENCES

1. R. Rowland and C. E. Meloan, Anal. Chem. **42**, 1261 (1970).

2. B. G. Khobragade and M. L. Narwade, Acta Cienc. Ind. **9C**, 32 (1983).
3. M. L. Narwade, S. W. Sathe, and M. M. Chincholkar, J. Ind. Chem. Soc. **62**, 194 (1985).
4. M. L. Narwade, A. S. Wankhade, and B. G. Khobragade, J. Ind. Chem. Soc. **63**, 360 (1986).
5. A. Atef and T. Ramdas, Asian J. Chem. **4**, 457 (1992).
6. S. Sunita and V. K. Gupta, J. Ind. Chem. Soc. **64**, 431 (1987).
7. A. Manimekalai and V. Thanikachalam, J. Ind. Chem. Soc. **68**, 403 (1991).
8. J. D. Chavan and V. P. Joshi, Asian J. Chem. **4**, 360 (1992).
9. P. D. Sawalakhe, PhD Thesis in Chemistry (Amravati Univ., Amaravati, 1992).
10. C. Bhargava and V. K. Tondon, Asian J. Chem. **4**, 664 (1992).
11. P. D. Sawalakhe, in *Proceedings of the Colloquium Spectroscopium International, Laughborough, UK, June 29, 1993.*
12. P. B. Raghuwanshi and A. G. Doshi, Asian J. Chem. **8**, 211 (1996).
13. P. J. Sondawale and M. L. Narwade, Orient. J. Chem. **13**, 41 (1997).
14. A. R. Raut, S. N. Irfan Quazi, A. D. Khambre, S. A. Ikhe, and M. L. Narwade, Ultra Sci. **16**, 203 (2004).
15. J. Dharmaraja, Th. Esakkidurai, P. Subbaraj, and S. Shobana, Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. **114**, 607 (2013).
16. V. M. Nurchi, G. Crisponi, M. Crespo-Alonso, J. I. Lachowicz, Z. Szewczuk, and G. J. S. Cooper, Dalton Trans. **42**, 6161 (2013).
17. I. L. Lere, M. G. Beyene, M. Chekol, and R. K. Upadhyay, Orient. J. Chem. **29**, 1111 (2013).
18. C. O. Kappe, Tetrahedron **49**, 6937 (1993).
19. K. S. Atwal, B. N. Swanson, S. E. Unger, S. Floyed Moreland, A. Hedberg, and B. C. O'Reilly, J. Med. Chem. **34**, 806 (1991); C. O. Kappe, W. M. F. Fabian, and M. A. Semones, Tetrahedron **53**, 2803 (1997); K. S. Atwal, G. C. Roonyak, B. C. O'Reilly, and A. Schwartz, J. Org. Chem. **54**, 5898 (1989).
20. N. Rao, R. Kumar, and Y. Srivastava, Rasayan J. Chem. **2**, 716 (2009).
21. S. Dawane, G. Konda, M. Shaikh, S. Chobel, T. Khandare, T. Kamble, and B. Bhosale, Int. J. Pharm. Sci. Rev. Res. **1** (2), 09 (2010).
22. S. K. Gupta, S. S. Pancholi, M. K. Gupta, D. Agarwal, and M. P. Khinchi, J. Pharm. Sci. Res. **2**, 228 (2010).
23. B. Vijaya, K. Rajeev, G. Varadaraj, and G. Gautham, Asian J. Res. Chem. **2**, 162 (2009).
24. J. T. Leonard, O. S. Rajesh, L. Jeyaseeli, and K. Murugesh, Asian J. Chem. **19**, 116 (2007).
25. *Vogel's Textbook of Practical Organic Chemistry* (Dorling Kindersley, 2006), p. 1162.
26. Sonal Dilip Bajaj, O. A. Mahodaya, and P. V. Tekade, Pharmaceut. Chem. J. **48**, 10 (2014).
27. K. Niknam and A. Fatehi Raviz, J. Iran. Chem. Soc. **4**, 438 (2007).
28. S. D. Bajaj, O. A. Mahodaya, and P. V. Tekade, Heterolett. **3**, 219 (2013).
29. W. A. F. McBryde, Canad. J. Chem. **42**, 1917 (1964).
30. S. K. Banerjee, J. Inorg. Nucl. Chem. **32**, 686 (1970).
31. K. R. Gold and W. C. Vosburgh, J. Am. Chem. Soc. **64**, 1630 (1942).