Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (3): 909-917

(International Peer Reviewed Journal)

Speciation of Some Divalent Essential Metal Ion Complexes with Bidentate Ligand in Low Dielectric Media

Hadgu Hailekiros Belay, Budati Bala Venkata Sailaja and Gollapalli Nageswara Rao*

*Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam-530 003, **INDIA**

Email: gollapallinr@yahoo.com

Accepted on 27th April 2015

ABSTRACT

Chemical speciation of binary complexes of Co(II), Ni(II) and Cu(II) with ethylenediamine was studied pH-metrically in the concentrations range of 0-60% v/v DMSO-water mixtures maintaining an ionic strength of 0.16 mol L^{-1} at 303K. Alkalimetric titrations were carried out in different relative concentrations of metal and ethylenediamine. Stability constants of various models of binary complexes were refined with MINIQUAD75. The best-fit chemical models were selected based on statistical parameters and residual analysis. The species detected are ML, ML_2, and ML_3 for all the metals studied. The chemical speciation, metal bioavailability and transportation are explained based on the distribution diagrams drawn using HYSS HYPERQUAD.

Keywords: Binary Complexes, Stability constants, Ethylenediamine, DMSO.

INTRODUCTION

Ethylenediamine (en) is used in the manufacture of EDTA, carbamate fungicides, surfactants and dyes. It is involved in the synthesis of seven-membered ring components with β-ketoesters resulting secondary amines and β-enaminoesters [1]. It also plays an important role in the synthesis of Schiff base compounds [2].

Cobalt is an essential trace element for all multicellular organisms at the active center of cobalamins [3]. Nickel is an essential nutrient. It is a component of urease and hydrogenase [4,5]. Copper is an essential element for life and it has antibacterial properties [6]. Congenital inability to excrete copper can result in toxic levels of copper accumulation, which leads to Wilson's disease [7, 8].

Dimethylsulfoxide (DMSO) is a dipolar aprotic solvent that dissolves both polar and non-polar compounds and is miscible in a wide range of organic solvents. It is used as a cryoprotectant, added to cell media in order to prevent the cells from dying as they are being frozen [9]. Hence, the binary complexes of Co(II), Ni(II) and Cu(II) with en in DMSO-water mixtures have been studied. The purpose of this study is to confirm the species formed under the present experimental conditions and to validate the models by statistical treatment of the data. The effect of dielectric constant of the medium on the chemical speciation

of the complexes and the influence of errors in ingredients the magnitude of stability constants are also studied.

MATERIALS AND METHODS

Chemicals: DMSO (Qualigens, India) was used as received. Aqueous solutions of en, sodium chloride (Finar, India) and Metal solutions of Co(II), Ni(II) and Cu(II) chlorides were prepared using tripled distilled water. To increase the solubility of en and to suppress the hydrolysis of metal salts, the mineral acid concentration in the above solutions was maintained at 0.05 M. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one way classification (ANOVA) [10]. The strength (concentration) of alkali was determined using the Gran plot method [11,12].

Apparatus: The titrimetric data were obtained with an ELICO (Model LI-120) pH meter (readability 0.01). The pH meter was calibrated with a 0.05 M potassium hydrogen phthalate solution in the acidic region and a 0.01 M borax solution in the alkaline region. The glass electrode was equilibrated in a well-stirred DMSO–water mixture containing an inert electrolyte. All the solutions were carried out in the medium containing varying concentrations of DMSO (0-60% v/v) maintaining an ionic strength of 0.16 M with sodium chloride at 303.0 ± 0.1 K. The effects of variations in the asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of the glass electrode were accounted for in the form of correction factor [13].

The emf of the cell may be expressed by the equation $E = K + (RT/F) \ln a_{H^+}$ or $E = K + 0.0591$ pH at 25 ^{0}C, where K is a constant partly dependent upon the nature of the glass used for making the membrane. The value of K may vary slightly with time, and it is related to the existence of an asymmetry potential in a glass electrode [14]. Owing to the asymmetry potential, if a glass electrode is inserted into a test solution which is identical with the internal hydrochloric acid solution, the electrode shall have a small potential which is found to vary with time. Hence, glass electrode is standardized frequently using a buffer of known hydrogen activity.

Procedure: For the determination of stability constants of binary species, initially titrations of strong acid with alkali were carried out at regular intervals to check whether complete equilibration was achieved. Then, the calomel electrode was refilled with DMSO-water mixture of equivalent composition as that of the titrand. In each of the titrations, the titrand consisted of approximately 1.0 mmol mineral acid in a total volume of 50 mL. Titrations with different metal-to-ligand ratios (1:2.5, 1:3.75 and 1:5.0) were carried out with 0.4 mol L^{-1} sodium hydroxide. Other experimental details are given elsewhere [15].

Modeling Strategy: The computer program SCPHD [16] was used to calculate the correction factor. The binary stability constants were calculated with the computer program MINIQUAD75 [17] from the pH metric titration data. Species distribution diagrams for all the systems were generated with HYSS HYPERQUAD suite program [18]. The correction factor and protonation constants of en were fixed during the refinement of binary systems. The variation of stability constants with the dielectric constant of the medium was analyzed on the basis of electrostatic/non-electrostatic, solute-solute and solute-solvent interaction

RESULTS AND DISCUSSION

Interpretation of Systematic Errors: In order to rely upon the best chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was made by introducing pessimistic errors in the influential parameters like concentrations of alkali, mineral acid, ligand and metal (Table 1). The sensitivity of the stability constants to these errors is in the order: alkali > acid > ligand > metal. Some species were even rejected when errors were introduced in the concentrations. The rejection of some species and increased standard deviations in the

stability constants on introduction of errors confirm the appropriateness of the experimental conditions (concentrations of ingredients) and choice of the best fit models. This study also indicates the relative sensitivities of the model parameters.

Table 1: Effect of errors in influential parameters on Co(II)-en complex stability constants in 10% v/v DMSO-water mixture.

Ingredient	% error	log β_{mlh}(SD)		
		ML	ML_2	ML_3
Alkali	0%	5.62(07)	10.59(07)	14.46(09)
	-5	Rejected	Rejected	Rejected
	-2	Rejected	9.50(27)	22.32(20)
	2	6.51(29)	11.33(07)	15.37(21)
	5	7.88(17)	12.44(10)	Rejected
Acid	-5	9.37(26)	13.72(19)	17.(15)
	-2	6.94(12)	11.74(8)	15.79(01)
	2	Rejected	8.67(99)	Rejected
	5	7.08(19)	11.79(18)	15.70(04)
Ligand	-5	5.21(12)	9.00(81)	14.03(04)
	-2	5.90(06)	9.99(10)	14.10(26)
	2	5.96(11)	10.90(07)	15.16(07)
	5	6.56(13)	11.13(12)	15.79(21)
Metal	-5	5.60(08)	10.63(07)	14.44(09)
	-2	5.66(08)	10.60(07)	14.47(09)
	2	5.65(10)	10.61(07)	14.48(08)
	5	5.64(10)	10.60(08)	14.45(10)

Best Fit Models: The best fit models that contain the stoichiometry of the complex species and their overall formation constants along with some of the important statistical parameters are given in table 2. The formation constants for different metal ions were found to obey the Irving-William order [19, 20]. Very low standard deviation in overall stability constants (log β) signifies the precision of these constants. The small values of U_{corr} (sum of squares of deviations in concentrations of ligand and hydrogen ion at all experimental points) corrected for degrees of freedom, small values of mean, standard deviation and mean deviation for the systems are validated by the residual analysis [21].

In data analysis with least squares methods, the residuals (the differences between the experimental data and the data simulated based on model parameters) are assumed to follow Gaussian distribution. When the data are fit into the models, the residuals should ideally be equal to zero. If statistical measures of the residuals and the errors assumed in the models are not significantly different from each other, the model is said to be adequate. Further, a model is considered adequate only if the residuals do not show any trend. Respecting the hypothesis that the errors are random and follow normal distribution in the least squares analysis, the residuals are tested for normal distribution using χ^2, skewness, kurtosis and R-factor. These statistical parameters show that the best fit models portray the metal-ligand species in DMSO-water mixtures, as discussed below.

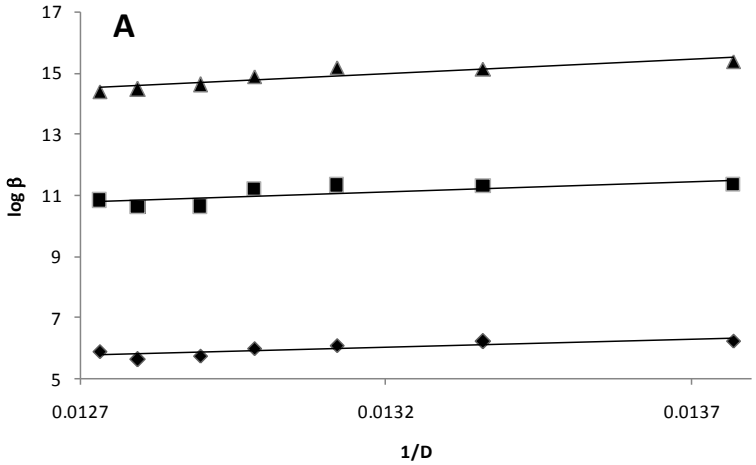
χ^2 distribution measures the probability of residuals forming a part of standard normal distribution with zero mean and unit standard deviation. If the χ^2 calculated is less than the table value, the model is accepted. Hamilton's R-factor ratio test is applied in complex equilibria to decide whether inclusion of more species in the model is necessary or not [22]. The low crystallographic R-values given in table 2 indicate the sufficiency of the model. The values of skewness are between -1.33 and 2.22. These data evince that the residuals form a part of normal distribution and hence, least-squares method can be applied to the data. Kurtosis is a measure of the peakedness of the error distribution near a modal value. For an

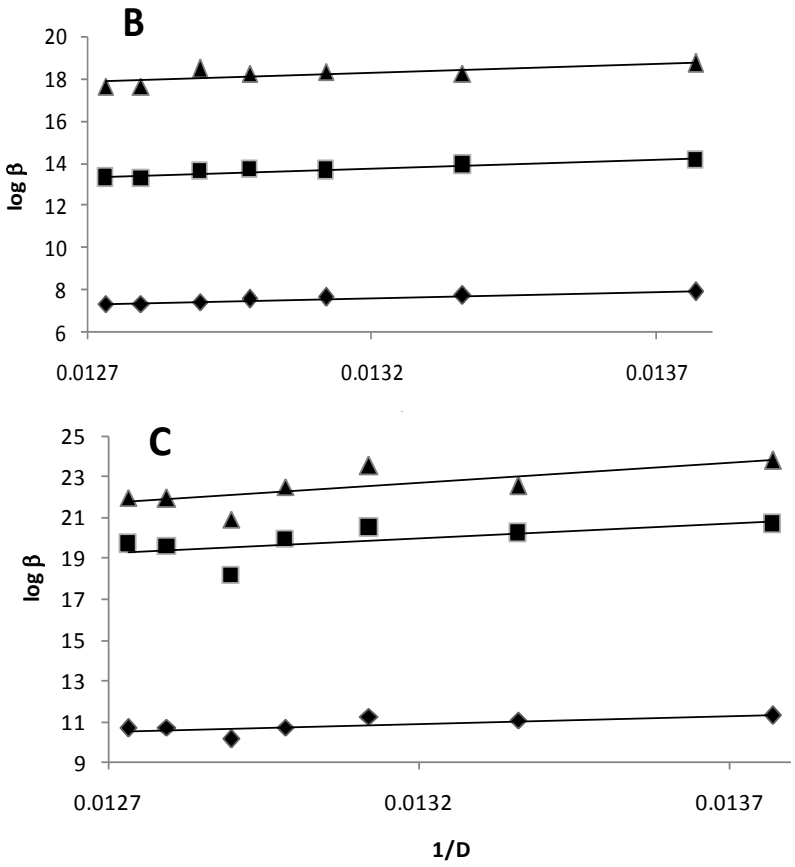
ideal normal distribution kurtosis value should be three (mesokurtic). If the calculated kurtosis is less than three, the peak of the error distribution curve is flat (platykurtic) and if the kurtosis is greater than three, the distribution shall have sharp peak (leptokurtic). The kurtosis values in the present study indicate that the residuals form leptokurtic pattern in majority of the systems.

Table 2: Parameters of best fit chemical models of binary complexes of en with Co(II), Ni(II) and Cu(II) in DMSO-water mixtures

DMSO % v/v	log β_{mlh}(SD)			NP	U_{corr} x10^8	χ^2	Skewness	Kurtosis	R-factor
	ML	ML_2	ML_3						
Co(II) (pH 5.5-9.0)									
10.0	5.62(7)	10.59(7)	14.46(19)	52	2.12	11.33	-1.10	3.66	.0034
20.0	5.73(24)	10.63(37)	14.60(64)	45	3.32	10.19	2.22	4.01	.0012
30.0	5.99(12)	11.19(11)	14.89(29)	56	4.87	10.15	-0.57	2.17	.0225
40.0	6.10(11)	11.32(12)	15.18(30)	50	4.63	13.09	-0.16	3.90	.0201
50.0	6.21(6)	11.28(7)	15.12(17)	33	3.44	12.82	-1.22	4.70	.0114
60.0	6.23(12)	11.33(14)	15.37(36)	47	3.89	15.35	-1.33	3.15	.0211
Ni(II) (pH 5.0-9.0)									
10.0	7.29(3)	13.25(4)	17.61(9)	51	0.80	16.65	1.06	3.19	.0061
20.0	7.42(18)	13.60(19)	18.45(61)	44	4.00	12.41	1.03	3.47	.0022
30.0	7.53(9)	13.71(11)	18.22(38)	45	9.77	12.05	0.07	4.02	.0145
40.0	7.61(4)	13.65(6)	18.34(10)	58	7.22	14.22	0.32	2.16	.0057
50.0	7.70(3)	13.92(4)	18.23(15)	39	0.43	10.40	1.07	3.07	.0060
60.0	7.89(10)	14.10(14)	18.7(24)	50	3.51	18.23	0.78	4.40	.0124
Cu(II) (pH 3.0-9.0)									
10.0	10.69(2)	19.59(2)	21.92(9)	50	0.10	07.66	-0.11	4.04	.0021
20.0	10.11(15)	18.13(16)	20.90(44)	45	2.34	05.54	1.04	3.33	.0037
30.0	10.68(9)	19.90(14)	22.51(37)	51	5.44	6.37	0.47	2.19	.015
40.0	11.25(7)	20.51(9)	23.52(22)	53	6.69	13.40	-0.09	2.04	.0120
50.0	11.02(5)	20.24(7)	22.53(20)	49	9.39	12.05	-0.33	3.45	.0007
60.0	11.26(7)	20.69(9)	23.77(21)	47	7.29	14.58	-0.37	3.15	.0029

Effect of Dielectric Constant Of Medium: The DMSO-water mixture influences microscopic dynamics of solvated ions [23, 24] and dye molecules [25, 26] so that these solutes exhibit a quantitatively different behavior compared to the behavior in other solvents. The linear variation of log β values with 1/D (D is the dielectric constant of the medium) of DMSO-water mixtures (Fig. 1) indicates that the electrostatic forces are dominating the equilibrium processes of complex formation under the experimental conditions. It also indicates that the dialectic constant or long range interactions are responsible for the stability trend.





Distribution Diagrams

Fig. 1: Variation of stability constant values of metal-en complexes with reciprocal of dielectric constant (1/D) of DMSO-water mixture. (A) Co(II); (B) Ni(II); (C) Cu(II) (♦) log β ML; (■) log β ML_2; (▲) log β ML_3.

Ethylenediamine has two associable protons. The different forms of en are LH_2^{2+}, LH^+, and L in the pH ranges 5.0-8.0, 7.0-10.0 and 8.0-10.4, respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the existence of ML, ML_2 and ML_3 for Co(II), Ni(II) and Cu(II). The formation of various binary complex species is shown in the following equilibria.

Typical species distribution diagrams of complexes are given in fig. 2. ML species is formed for Co(II), Ni(II) and Cu(II) according to Equilibria 1 and 2 at low pH. ML_2 species is formed as per Equilibria 3-6. In the case of Cu(II) ML_2 species is the most dominating species due to Jahn-Teller effect, where distorted octahedral or tetragonal complex is expected [27, 28]. ML_3 species is formed as per Equilibria 7-12. In the case of Co(II) and Ni(II) ML_3 is the most dominating species because they form octahedral complexes and three bidentate ligands are required to form such complexes. The distribution diagrams indicate the relative abundance of various forms of metal (chemical speciation) at different pH and dielectric conditions. A weak binary metal complex makes the essential metals bioavailable and the strong complexes make them transport easily in biofluids.

$$M(II) + LH_2 \rightleftharpoons ML + 2H^+ \quad (1)$$

$$M(II) + LH \rightleftharpoons ML + H^+ \quad (2)$$

$$M(II) + 2LH_2 \rightleftharpoons ML_2 + 4H^+ \quad (3)$$

$$M(II) + 2LH \rightleftharpoons ML_2 + 2H^+ \quad (4)$$

$$ML + LH_2 \rightleftharpoons ML_2 + 2H^+ \quad (5)$$

$$ML + LH \rightleftharpoons ML_2 + H^+ \quad (6)$$

$$M(II) + 3LH_2 \rightleftharpoons ML_3 + 6H^+ \quad (7)$$

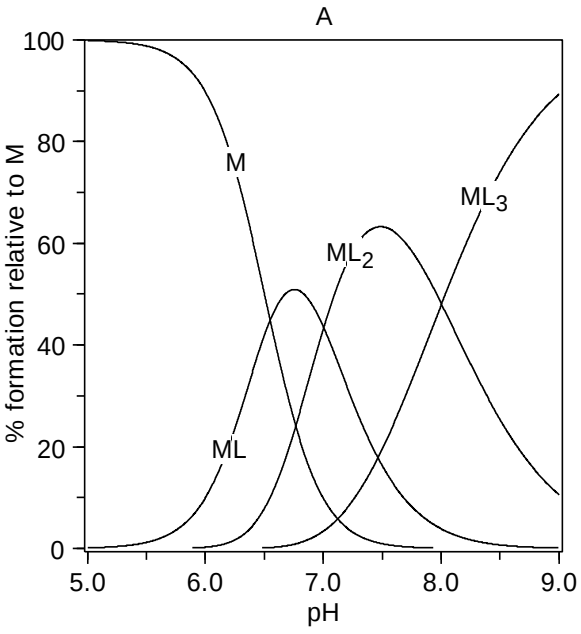
$$M(II) + 3LH \rightleftharpoons ML_3 + 3H^+ \quad (8)$$

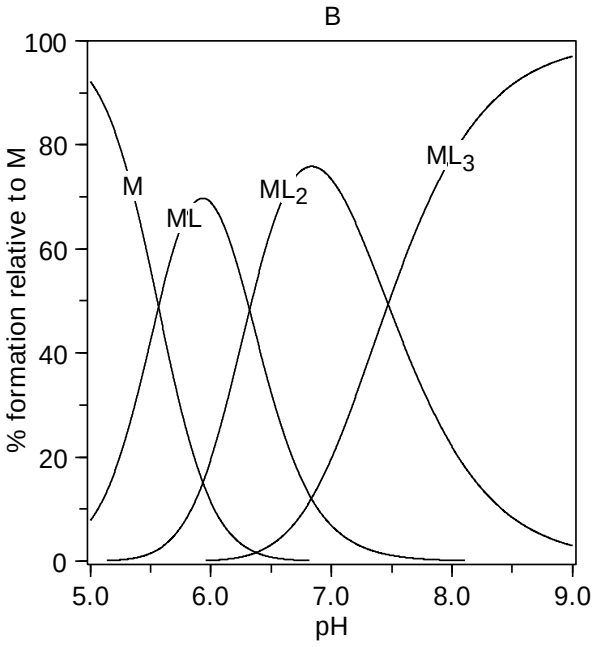
$$ML + 2LH_2 \rightleftharpoons ML_3 + 4H^+ \quad (9)$$

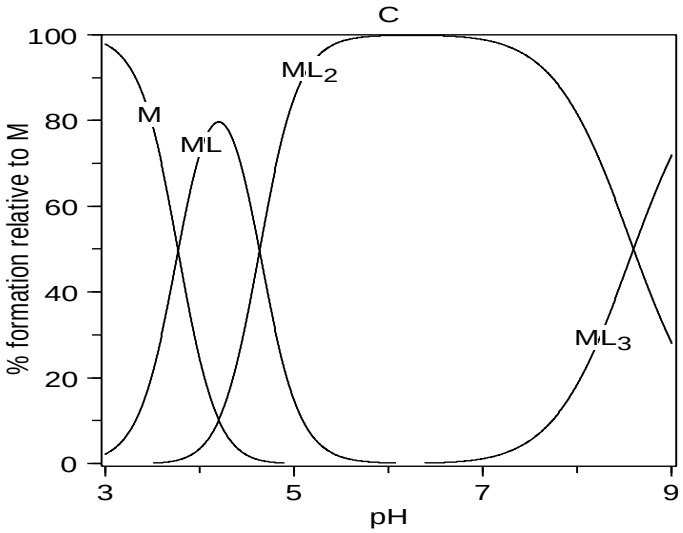
$$ML + 2LH \rightleftharpoons ML_3 + 2H^+ \quad (10)$$

$$ML_2 + LH_2 \rightleftharpoons ML_3 + 2H^+ \quad (11)$$

$$ML_2 + LH \rightleftharpoons ML_3 + H^+ \quad (12)$$







Structures of Complexes

Fig. 2: Distribution diagrams of binary complexes of en in 10% v/v DMSO-water mixture. (A) Co(II), (B) Ni(II), and (C) Cu(II).

Ethylenediamine acts as bidentate ligand via two strong nitrogen donor sites and the chelation results a highly stable five membered ring. Although it is not possible to elucidate or confirm the structures of complex species pH metrically, it is possible to postulate structures based on comparison with known structures for related complexes. Literature shows that, Co(II), Ni(II) and Cu(II) ions typically form octahedral complexes, with Cu(II) normally being Jahn-Teller distorted [27,28]. Thus octahedral structures have been proposed tentatively as given in Fig. 3.

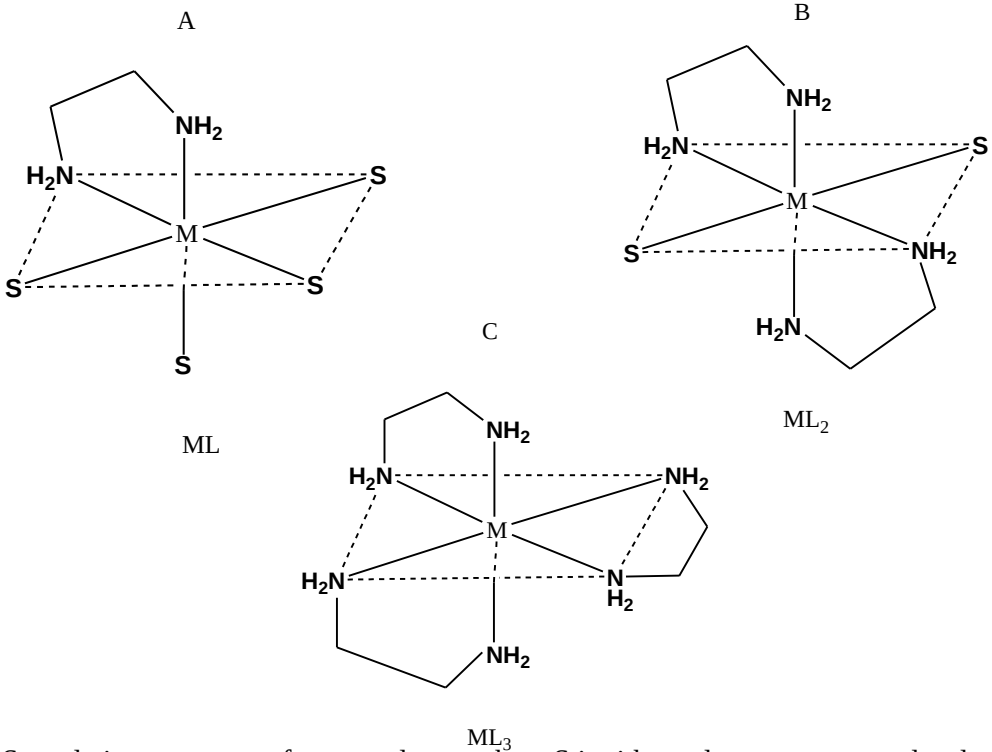


Fig. 3 Speculative structures of en complexes, where S is either solvent or water molecule and M is Co(II), Ni(II) or Cu(II).

APPLICATIONS

This study is to confirm the species formed under the present experimental conditions to validate the models by statistical treatment of the data.

CONCLUSIONS

1. The binary species detected are ML, ML_2 and ML_3 for M= Co(II), Ni(II) , Cu(II) and L= en. These models are validated by statistical treatment of data.
2. The linear trend in the step-wise stability constants with the dielectric constant of DMSO-water mixtures indicated the dominance of electrostatic forces in the metal-ligand equilibria.
3. The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > ligand > metal.
4. High concentrations of the complex chemical species indicate that metals are more amenable for transportation at biological pH.

ACKNOWLEDGMENTS

One of the authors (HHB) gratefully acknowledges the financial support provided to him by the Ministry of Education of the Federal Democratic Republic of Ethiopia.

REFERENCES

[1] F. Hiromichi, M. Kenichi, Y. Kita, K. Ozora and O. Yuruke, *Org. Lett*., **2007,** 9, 1687.
[2] F. Hiromichi, M. H. Habibi, R. W. Harrington, M. Morteza and C. William, *J. Fluorine Chem*., **2006,** 127, 769.
[3] C. Sennett, L. E. G. Rosenberg and I. S. Millman. *Annu. Rev. Biochem*., **1981,** 50, 1053.
[4] R.A. Poellot, T.R. Shuler, E. O. Uthus and F. H. Nielsen, *Proc. Natl. Acad. Sci*., USA, **1990,** 44, 80.
[5] H. Kim and R. J. Maier, *J. Biol. Chem*., **1990,** 265, 18729.
[6] W. B. Schaap and D. L. McMasters, *J. Am. Chem. Soc*., **1961,** 83, 4699.
[7] K. D. Karlin and Z. Tyeklar (Eds.), "Bioinorganic Chemistry of Copper", Chapman and Hall, New York, **1993**, 506.
[8] W. Kaim and B. Schwederski (Eds.), "Inorganic Elements in the Chemistry of Life", Wiley, Chichester **1994**, 187.
[9] D.E. Pegg, Principles of Cryopreservation. *Methods Mol. Biol*. **2007,** 368, 39.
[10] G.N. Rao and R.S. Rao, Computer applications in chemistry, Himalaya Publishing House, Mumbai, **2005**, 277.
[11] G. Gran, *Analyst*, **1952,** 77, 661.
[12] G. Gran, *Anal. Chim. Acta*, **1988,** 206, 111.
[13] B.B.V. Sailaja, T. Kebede, G.N. Rao and M.S.P. Rao, *Proc. Nat. Acad. Sci. (India)* **2004,** 74, 399.
[14] G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, (Eds) Vogel's Text Book of Quantitative Chemical Analysis, 5th ed., Longman: London; **1991**, 557.
[15] N. Padmaja, M.S. Babu, G.N. Rao, R.S. Rao and K.V. Ramana, *Polyhedron* , **1990,** 9, 2497.
[16] G. N. Rao, Ph.D. Thesis, Andhra University, Visakhapatnam, India **1989**.
[17] P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, **1976,** 18, 237.
[18] L. Alderighi, P. Gans, A. Ienco, D. Peters and A. Sabatini, A. Vacca, *Coord. Chem. Rev.* **1999,** 184,311.
[19] H.M. Irving and R.J.P. Williams, *Nature* (London) **1948,**162, 746.
[20] H.M. Irving and R.J.P. Williams, *J. Chem. Soc.* **1953,** 167, 3192.

[21] G. N. Rao and R. S. Rao, Computer applications in Chemistry, Himalaya Publishing House, Mumbai, **2005,** 302.
[22] W.C. Hamilton, *Acta. Crystallogr.* **1965,** 18, 502.
[23] I.I. Vaisman, R.B. Lyalina, Y.M. Kessler, R.S. Kumeev and V.V. Gon-charov, *Zh. Fiz. Khim.* **1988,** 62, 838.
[24] Y.M. Kessler, R.S. Kumeev, I.I. Vaisman, R.B. Lyalina and R.H. Bra-tishko, Ber. Bunsenges. *Phys. Chem.* **1989,** 93, 770.
[25] E.F.G. Templeton and G.A. Kenny-Wallance, *J. Phys. Chem.*, **1986,** 90, 2896.
[26] J.D. Simon, *Acc. Chem. Res.*, **1988**, 2, 128.
[27] J. Sheals, P. Persson and B. Hedman, Inorg. Chem. **2001,** 40, 4302.
[28] J.K. Cherutoil, L.L. Cheruiyot and C.P. Kiprono, *Bull. Chem. Soc. Ethiop*, **2005,** 19, 295.

AUTHORS' ADDRESSES

1. **Prof. G. NAGESWARA RAO, Ph.D.**
Professor of Inorganic Chemistry
Director, School of Chemistry
Phone: 91-9849701527
E-mail: gollapallinr@yahoo.com
2. **Dr. B.B.V. Sailaja**
Assistant Professor
Phone: 91-9441328956
E-mail:saileja-bbv@yahoo.co.in
3. **Mr. Hadgu Hailekiros Belay**
Research scholar
Phone: 91-8143781411
E-mail:hadgu10@gmail.com