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Der Pharma Chemica, 2015, 7(12):232-240
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Chemical speciation of some divalent essential metal ion complexes of L-ornithine in DMSO-water mixtures

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ABSTRACT

Chemical speciation of binary complexes of Co(II), Ni(II) and Cu(II) with L-ornithine 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 L-ornithine. 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, MLH and ML_2H_2 for of Co(II), Ni(II) and Cu(II). The chemical speciation, metal bioavailability and transportation are explained based on the distribution diagrams drawn using HYSS HYPERQUAD.

Keywords: Binary Complexes, Stability constants, L-ornithine, Speciation, DMSO.

INTRODUCTION

Speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ion. Hence, the chemical speciation of biologically important ligands with some essential and toxic metal ions has been studied in this laboratory [1-5]. They can be used to mimic metalloproteins [6]. L-Ornithine (Orn) is a tridentate amino acid containing nitrogen donor group in the side chain in addition to the nitrogen donor group found on the α-carbon. The nitrogen donor atoms can associate with hydrogen ions in the physiological pH range. Hence, there is often significant competition between hydrogen and metal ions for these donor sites which leads to the existence of a number of equilibria. This phenomenon may result in successively protonated complexes.

Cobalt is an essential trace element for all multicellular organisms at the active center of cobalamins [7]. Nickel is an essential nutrient. It is a component of urease and hydrogenase [8,9]. Copper is an essential element for life and it has antibacterial properties [10]. Congenital inability to excrete copper can result in toxic levels of copper accumulation, which leads to Wilson's disease [11, 12].

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 [13]. Hence, the results of a speciation study on the interaction of Orn with Co(II), Ni(II) and Cu(II) in DMSO-water mixtures are reported in this paper.

MATERIALS AND METHODS

2. 1. Chemicals

DMSO (Qualigens, India) was used as received. Aqueous solutions of Orn and sodium chloride (Merck, India) were prepared. Metal solutions of Co(II), Ni(II) and Cu(II) chlorides were prepared. To increase the solubility of Orn 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) [14]. The strength (concentration) of alkali was determined using the Gran plot method [15,16].

2.2 Apparatus

The titrimetric data were obtained with a calibrated ELICO (Model LI-120) pH meter (readability 0.01), which can monitor changes in the H^+ ion concentration. 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 [17].

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 [18] in a glass electrode. 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.

2.3 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 [19].

2.4 Modeling Strategy

The computer program SCPHD [20] was used to calculate the correction factor. The binary stability constants were calculated with the computer program MINIQUAD75 [21] from the pH metric titration data. Species distribution diagrams for all the systems were generated with HYSS HYPERQUAD suite program [22]. The correction factor and protonation constants of Orn were fixed during the refinement of binary systems. During modeling study, as the number of species increased, the model gave better statistics denoting the better fit. This indicates that the final models appropriately fit the experimental data. 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 interactions.

RESULTS AND DISCUSSION

3.1 Exhaustive modeling

Existence of species was determined by performing exhaustive modeling [24] and the results of some typical system (Co(II)-Orn system in 10% DMSO) are given in Table 1. The models were evaluated assuming the simultaneous existence of different combinations of species. Models containing various number and combinations of species were generated using an expert system package CEES [24] and these models were refined using MINIQUAD75 [21]. As the number of species increased, the models gave better statistics denoting better fit. The table contains the stiochiometric coefficients and stability constants of the complex species, standard deviations in the stability constants and residual statistics of the models.

Table 1: Exhaustive modeling study performed on Co(II)-L-Orn system in 10% v/v DMSO in 4.0-10.0 pH range (number of experimental points, NP=60)

Model no	log βmlh (SD)				Ucorr x10^8	χ2	Skew ness	Kurto sis	R –factor
	ML	ML_2	MLH	ML_2H_2					
1	14.17(19)	-----	----	-----	4.11	43.66	-1.75	4.763	0.0088
2	----	8.32(8)	----	-----	4.59	23.95	-1.32	4.50	0.0103
3	-----	-----	14.03(15)	-----	3.45	28.44	-1.25	5.22	0.0062
4	-----	-----	-----	29.05(32)	12.88	35.98	-1.20	4.33	0.0070
5	5.51(48)	8.67(22)	-----	-----		14.62	-1.53	4.71	0.0067
6	6.55(13)	-----	15.22(24)	-----	12.09	43.22	-1.45	4.44	0.0075
7	Rejected	-----	-----	Rejected	------	------	------	------	------
8	-----	8.13(7)	14.00(66)	-----	0.65	90.14	-1.11	4.75	0.0082
9	----	8.76(14)	----	26.81(8)	13,75	105.45	-0.55	7.00	0.0079
10	----	----	14.00(18)	28.33(2)	0.43	22.34	-0.56	6.00	0.0071
11	6.13(8)	8.43(13)	14.29(19)	----	85.45	55.66	-1.45	5.49	0.0063
12	6.61(12)	----	15.33(143)	28.61(7)	12.76	34.12	-1.33	5.83	0.0056
13	6.30.(8)	8.23(11)	----	27.22(13)	0.43	7.55	-0.50	5.90	0.0058
14	----	8.72(19)	14.81(21)	27.94(14)	0.74	7.76	0.04	13.11	0.0047
15	5.92(8)	8.53(11)	14.19(17)	27.55(6)	0.02	12.63	-0.01	2.57	0.0046

3.2 Model validation

3.2.1 Retrieval of protonation constants

Protonation constants were retrieved from the metal-ligand titration data and compared with those obtained from proton-ligand titration data. The proximity of the two values confirms the existence of the reported metal-ligand species only and the accuracy of the titration data. Such comparisons for some typical systems are given in Table 2. Then simultaneous refinement of all the constants revealed that when the approximate constants are very close to the true values, either fixing some of the species or ingredient concentrations do not have any ill-effects on modeling studies.

Table 2. Retrieval of protonation constants from proton-ligand and Co(II)-Orn titration data

DMSO % v/v	From proton-ligand titration data			From metal-ligand titration data		
	log β1	log β2	log β3	log β1	log β2	log β3
0.0	10.57	18.93	20.80	10.57	18.95	20.78
10.0	10.08	18.54	20.55	10.10	18.57	20.54
20.0	10.01	18.48	20.80	09.98	18.49	20.80
30.0	09.97	18.20	20.44	10.01	18.21	20.42
40.0	09.86	18.07	20.41	09.82	18.10	20.44
50.0	09.74	17.65	20.24	09.71	17.70	20.27
60.0	09.62	17.44	20.08	09.64	17.41	20.10

Table 3: Effect of errors in influential parameters on Co(II)-Orn complex stability constants in 10% v/v DMSO-water mixture

Ingredient	% error	log β_{mlh}(SD)			
		ML	ML_2	MLH	ML_2H_2
	0%	5.92(8)	8.53(11)	14.19(17)	27.55(6)
Alkali	-5	Rejected	7.56(28)	13.55(49)	30.04(31)
	-2	rejected	7.94(27)	14.76(27)	28.45(27)
	2	6.33(29)	8.90(38)	15.33(34)	28.33(12)
	5	4.44(32)	9.12(37)	Rejected	26.10(19)
Acid	-5	6.45(30)	6.77(30)	15.22(25)	28.33(39)
	-2	7.17(35)	6.19(30)	13.44(56)	28.22(25)
	2	Rejected	8.00(17)	15.73(30)	29.13(8)
	5	04.49(19)	5.55(38)	16.37(44)	26.26(10)
Ligand	-5	6.90(16)	9.07(11)	14.19(48)	27.33(26)
	-2	6.29(02)	8.56(10)	14.10(26)	27.40(15)
	2	5.92(25)	8.25(11)	14.09(22)	27.30(03)
	5	5.77(26)	7.93(13)	14.19(38)	28.17(17)
Metal	-5	6.90(5)	8.55(11)	14.18(18)	27.54(03)
	-2	5.91(09)	8.57(10)	14.18(16)	27.50(7)
	2	5.91(25)	8.56(10)	14.19(17)	27.52(9)
	5	5.93(06)	7.58(13)	14.17(18)	28.51(6)

3.2.2. 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 3). 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.

3.3 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 4. The formation constants for different metal ions were found to obey the Irving-William order [25, 26]. 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 [1].

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. Such tests are 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.

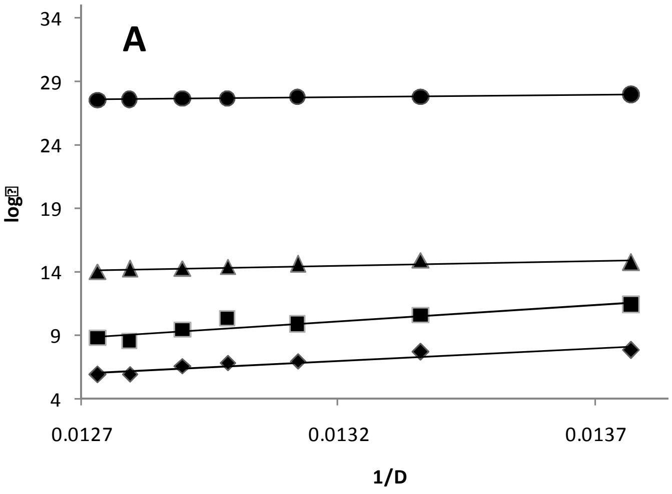
χ^2 distribution measures the probability of residuals forming a part of standard normal distribution with zero mean and unit standard deviation. If the χ^2 calculated is less than the table value, the model is accepted. Hamilton's R-factor ratio test is applied in complex equilibria to decide whether inclusion of more species in the model is necessary or not [27]. The low crystallographic R-values given in Table 4 indicate the sufficiency of the model. The values of skewness are between -1.03 and 1.04. 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.

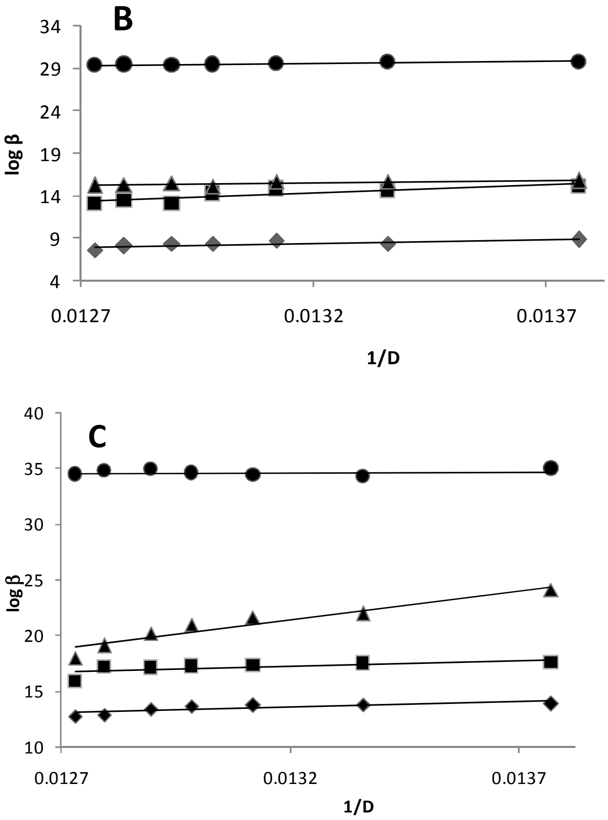
Table 4: Parameters of best fit chemical models of Co(II), Ni(II), and Cu(II) binary complexes of Orn in DMSO – water mixtures

% v/v DMSO	log β_{mlh} (SD)				NP	U_{Corr} x10^8	χ^2	Skewness	Kurtosis	R-Factor
	ML	ML_2	MLH	ML_2H_2						
Co(II) (pH 4.0-10.0)										
0.00	5.86(8)	8.72(2)	14.02(9)	27.53(12)	59	2.53	11.53	-0.19	3.02	0.0013
10.00	5.92(8)	8.53(11)	14.19(17)	27.55(6)	60	0.02	12.63	-0.01	2.57	0.0046
20.00	6.54(13)	9.43(12)	14.27(6)	27.59(10)	45	0.32	4.47	0.53	3.31	0.0134
30.00	6.85(19)	10.27(17)	14.39(18)	27.63(11)	50	2.01	14.96	0.13	4.15	0.0020
40.00	6.93(5)	9.87(19)	14.59(14)	27.78(15)	55	1.96	12.02	0.11	2.59	0.0510
50.00	7.68(10)	10.55(9)	14.92(15)	27.74(11)	59	3.54	8.31	-0.44	3.41	0.0126
60.00	7.81(11)	11.39(8)	14.73(10)	27.90(16)	40	4.90	10.03	0.08	4.39	0.0033
Ni(II) (pH 2.0-9.3)										
0.00	7.68(9)	13.09(17)	15.21(7)	29.31(7)	73	2.24	29.70	-0.16	3.72	0.0139
10.00	8.10(11)	13.45(7)	15.34(29)	29.43(22)	49	2.29	10.64	-1.03	2.78	0.0039
20.00	8.36(19)	13.01(11)	15.47(13)	28.82(29)	68	3.09	9.13	-0.25	4.03	1.0143
30.00	8.39(9)	14.28(7)	15.15(22)	29.44(24)	60	1.07	7.78	1.04	3.19	0.0107
40.00	8.70(10)	14.86(6)	15.68(25)	29.51(9)	69	2.39	14.00	0.51	3.09	0.0060
50.00	8.38(14)	14.55(12)	15.73(18)	29.69(15)	65	3.86	16.70	0.14	4.30	0.0178
60.00	8.87(21)	15.10(8)	15.79(9)	29.74(15)	70	2.83	14.22	0.37	3.55	0.0026
Cu(II) (pH 1.9-10.0)										
0.00	12.71(13)	15.79(4)	17.91(11)	34.42(5)	67	1.13	13.00	-0.37	3.17	0.0123
10.00	12.81(13)	17.10(16)	19.05(17)	34.72(12)	43	1.63	11.07	0.06	4.48	0.0012
20.00	13.39(17)	17.09(12)	20.13(16)	34.89(22)	80	1.25	14.14	0.81	3.19	0.0014
30.00	13.62(21)	17.2(10)	20.93(22)	35.55(8)	79	1.23	9.51	0.03	4.99	0.0018
40.00	13.70(14)	17.29(10)	21.56(24)	34.34(32)	59	0.74	12.33	-0.04	1.91	1.0114
50.00	13.78(15)	17.46(4)	21.88(17)	34.20(8)	56	1.22	13.00	0.33	3.22	0.0044
60.00	13.82(29)	17.53(5)	22.06(20)	34.95(6)	40	1.48	10.50	-0.11	3.12	0.0058

3.4 Effect of dielectric constant of medium

The water-DMSO mixture influences microscopic dynamics of solvated ions [28, 29] and dye molecules [30, 31] so that these solutes exhibit a quantitatively different behavior compared to the behavior in other solvents The linear variation log β values with variation of 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.





$$M(II) + LH_3 \rightleftharpoons MLH + 2H^+ \quad (1)$$

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

$$M(II) + 2LH_2 \rightleftharpoons ML_2H_2 + 2H^+ \quad (3)$$

$$MLH + LH_2 \rightleftharpoons ML_2H_2 + H^+ \quad (4)$$

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

$$MLH \rightleftharpoons ML + H^+ \quad (6)$$

$$ML_2H_2 \rightleftharpoons ML_2 + 2H^+ \quad (7)$$

$$MLH + LH \rightleftharpoons ML_2 + 2H^+ \quad (8)$$

$$ML + LH \rightleftharpoons ML_2 + H^+ \quad (9)$$

Fig. 1: Variation of stability constant values of metal-Orn complexes with reciprocal of dielectric constant (1/D) of DMSO (A) Co(II); (B) Ni(II); (C) Cu(II)-(♦) log β ML; (■) log β ML_2; (▲) log β MLH; (●) log βML_2H_2

3.5 Distribution Diagrams

Orn has one dissociable proton and two amino groups which can associate with two protons. It exists as LH_3^{2+} at low pH and gets deprotonated with the formation of LH_2^+, LH and L^-, successively, with increasing pH, in the ranges 1.9-4.1, 1.9-9.8 and above 8.0, respectively. The binary metal-ligand complexes confirmed under the experimental conditions are ML, ML_2, MLH and ML_2H_2 for Co(II), Ni(II) and Cu(II) in the pH range 4.0-10.0. The protonated forms of species like MLH and ML_2H_2 are prevalent at lower pH. The neutral form of Orn forms unprotonated complexes (ML and ML_2) as shown in the following equilibria:

Typical distribution diagrams are shown in Fig. 2. in the pH range 3.8-10.0. MLH species is formed for Co(II), Ni(II) and Cu(II) according to Equilibria 1 and 2 at low pH and it is deprotonated to ML (Equilibrium 6) with increasing pH. ML_2H_2 species is formed as per Equilibria 3 and 4. Fig. 2B reveals the simultaneous formation of ML_2H_2 and ML. ML is formed as per Equilibria 5 and 6. ML_2 is formed by the deprotonation of M_2H_2 (Equilibrium 7) and as per Equilibria 8 and 9. But ML_2 is not formed through Equilibrium 8 in Cu-Orn system (Fig. 2C).

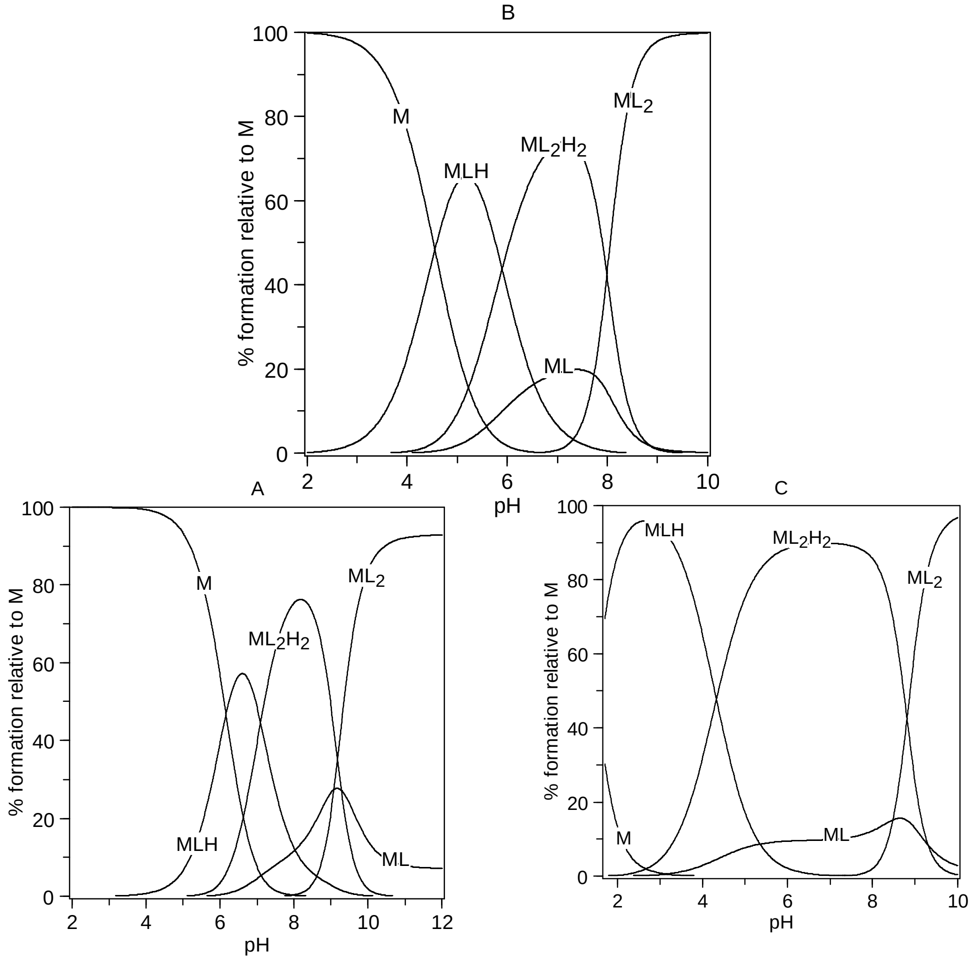


Fig. 2: Distribution diagrams of binary complexes of Orn in 10% v/v DMSO-water mixture. (A) Co(II), (B) Ni(II), and (C) Cu(II)

3.6. Structures of complexes

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 [32, 33]. Thus octahedral structures have been proposed tentatively as given in Fig. 3. Orn is coordinated to the metal ions as (O, N) donor to form MLH and ML_2H_2, which have eight-membered rings and protonated ά-amino groups (structures A and B). They are deprotonated to form ML and ML_2 (structures C and E) where Orn still acts as (O, N) donor. In the case of ML and ML_2 two structures are possible, based on whether eight or seven-membered ring is formed. According to Baeyer strain Theory [34] Structure C may rearrange itself to give Structure D where Orn acts as (N, N) donor through both the amino groups. Similarly, Structure E may rearrange itself to give Structure F.

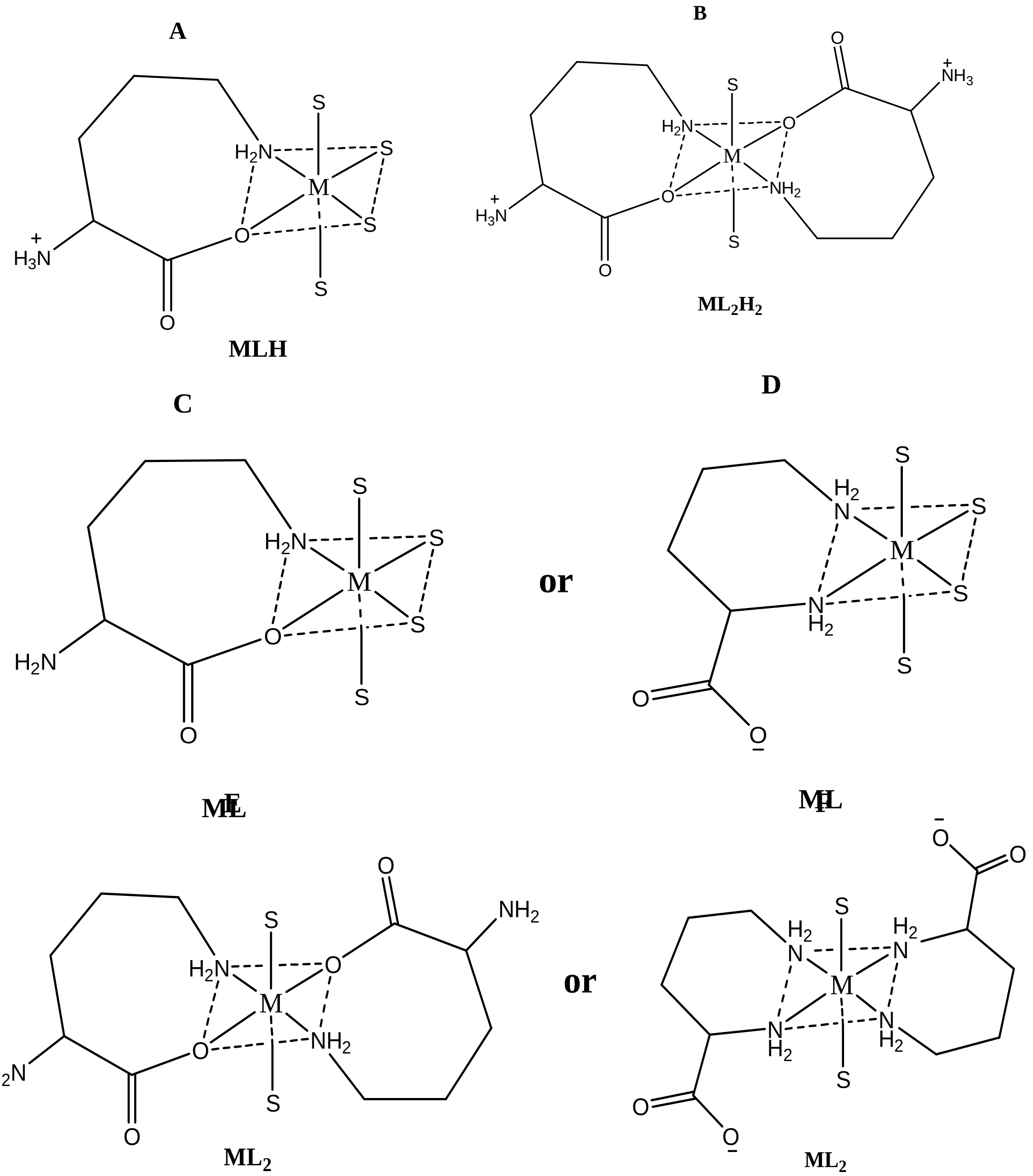


Fig. 3: Suggested structures of Orn complexes, where S is either solvent or water molecule and M is Co(II), Ni(II) or Cu(II)

CONCLUSION

The present biomimetic studies of metal ion complexes with L-ornithine in DMSO-water mixtures indicate the formation of protonated complexes at low pH (up to pH 8). Under these pH conditions, the ά-amino nitrogen atom of L-ornithine is protonated, carboxyl and ω-amino groups are bonded to the metal ion. As the pH increases, the ά-amino is deprotonated. The species formed due to the interaction of L-ornithine with the metals are CoL, CoL_2, CoLH, CoL_2H_2, NiL, NiL_2, NiLH, NiL_2H_2, CuL, CuL_2, CuLH, and CuL_2H_2. The linear variation of stability constants as a function of dielectric constant of the medium indicates the dominance of electrostatic forces over non-electrostatic forces. The influence of errors in the concentrations of ingredients on the magnitude of stability constants is alkali>acid>ligand>metal. Proximity of the protonation constants determined from proton ligand titration data to those retrieved from metal ligand titration data confirms the sufficiency of the models. High concentrations of the complex chemical species indicate that metals are more amenable for transportation at biological pH.

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