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STUDY OF BINARY AND TERNARY COMPLEXES OF MERCAPTOSUCCINIC ACID AND L-ORNITHINE WITH ESSENTIAL METAL IONS IN ETHYLENE GLYCOL-WATER MEDIA

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ABSTRACT

During this study, the stability constants of the metals with mercaptosuccinic acid (MSA) and L-ornithine (L-Orn), as well as their ternary system have been studied in 0-60% ethylene glycol (EG)-water medium using the Metrohm 877 titrino plus auto-titrator between a pH ranges 0-14 at a temperature of 298 K. The modified Calvin-Wilson titration method was used to figure out the relative compositions of chemical species that were formed with metal ions and ligands. The MINIQUAD75 computer program was used to figure out the stability constants of the complexes. Some statistics have been discussed about the formed binary metal complexes and their ternary system, as well. The structures were proposed based on the observations.

Keywords: Ethylene glycol, Calvin-Wilson, Ternary Complexes.

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INTRODUCTION

"In reaction with ligands, a metal ion can form a range of species dependent on the metal ion and other circumstances".[1,2] Speciation investigations can indicate species formation nature and degree with change in pH.[3,4] Recent work has focused on aqueous and aqueous-organic binary and ternary complexes of important biological ligands. In aqueous-organic solvents, compounds evolve in new ways. Mercaprosuccinic acid (MSA) and L-Ornithine (L-Orn) are potentially important tridentate ligands that can form strong complexes with numerous metal ions with chemotherapeutic applications in a range of solvents.[5-8] Despite extensive literature research[9-12] in this sector, nothing is known about MSA and L-Orn stability constants in ethylene glycol(EG)-water media. In the current study, the stability constants of binary complexes along with their ternary complexes of selected divalent metal ions with MSA and L-Orn have been reported in an aqueous- EG medium. This study gives insight into information about the formation of several species as a role of pH.

EXPERIMENTAL

0.05mol L^{-1} MSA (Himedia, India) and L-Orn (Himedia, India) solutions were prepared with hydrochloric acid to improve the solubility. Ethylene Glycol (Merck, India) was used as received. All metal ion solutions were prepared using G.R. Grade chloride salts and an acidic strength of 0.05 mol L^{-1} was maintained using HCl to inhibit metal salt hydrolysis. Standard approaches were used for the preparation and standardization of all solutions and data were subjected to ANOVA[13] to identify any errors by the Gran plot approach.[14,15]

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Approach

pH metric titrations were conducted in 0-60%v/v EG-Water media by using an auto-titrator Metrohm 877 titrino plus Switzerland in conjunction with a pH-sensitive electrode under the temperature of 298 K as described elsewhere.[16]

RESULTS AND DISCUSSION

Binary Metal-Ligand Complexes

Chemical species formed by metal-ligand interactions were measured using a modified[17] Calvin-Wilson titration approach. On the electrode response, a correction factor was determined using SCPHD.[18] *MINIQUAD75* computer programme[19,20] was used to refine stability constants.

Modeling of Chemical Species

Tables-1 and 2 show the results of the models that suit best the M(II)-MSA and M(II)-L-Orn binary systems, respectively. The possible forms and their distribution of protonated and un-protonated complexes observed that suit best for the metal-ligand hypothesis has been shown in Fig.-1. The $\chi2$, skewness, kurtosis, and crystallographic R-factors were used to assess the rationality and adequacy of the chemical models that reflect the metal-ligand system.

$$M(II) + LH_3 \rightleftharpoons MLH + 2H^+ \quad (1)$$
$$M(II) + 2LH_3 \rightleftharpoons ML_2H + 5H^+ \quad (3)$$
$$M + LH_3 \rightleftharpoons ML + 3H^+ \quad (4)$$
$$ML_2H \rightleftharpoons ML_2 + H^+ \quad (5)$$
$$MLH + LH_2 \rightleftharpoons ML_2H_2 + H^+ \quad (6)$$

Fig.-1: Possible Binary Complex Formation Equilibria for M(II)–L Binary Complexes

Table-1: Best Fit Models for M(II)-MSA Binary Complexes in Solvent-Water Mixtures

% V/V	log β_{MLXH}(SD)				NP	U_{Corr} x10^{-8}	Skewness	Kurtosis	χ^2	R-Factor
	ML	MLH	ML_2	ML_2H_2						
Co(II)										
0.0	6.51(14)	10.71(19)	11.71(11)	15.16(28)	139	4.4	1.23	14.64	26.1	0.028
20	7.32(16)	11.59(16)	12.84(22)	16.13(23)	123	1.23	-1.49	11.27	11.93	0.014
40	8.32(18)	12.17(14)	13.85(16)	17.04(05)	109	4.5	-1.72	11.05	23.89	0.031
60	9.16(18)	13.05(21)	14.34(22)	17.93(06)	114	4.52	1.31	8.34	11.97	0.012
Ni(II)										
0.0	7.23(21)	11.23(19)	13.41(11)	16.27(14)	121	3.91	1.05	8.23	31.14	0.018
20	8.13(23)	12.14(19)	14.13(31)	17.38(21)	128	6.18	0.85	10.22	23.46	0.036
40	9.05(15)	12.98(27)	15.02(15)	18.31(14)	108	5.66	2.28	16.52	19.25	0.022
60	10.14(17)	13.52(22)	15.92(24)	19.31(13)	129	3.64	0.68	14.70	41.54	0.032
Cu(II)										
0.0	9.54(14)	13.47(22)	16.14(13)	18.51(14)	114	3.41	1.62	2.50	33.14	0.042
20	10.88(15)	14.51(21)	17.28(22)	19.82(25)	114	2.58	-1.53	8.69	29.16	0.056
40	11.76(09)	15.26(08)	18.34(34)	20.68(18)	152	2.63	2.24	8.78	18.52	0.047
60	12.66(24)	16.28(29)	19.21(24)	21.39(25)	139	1.87	1.11	6.95	22.07	0.051
Zn(II)										
0.0	5.82(14)	9.14(17)	10.79(09)	12.21(15)	122	2.34	1.07	8.11	13.52	0.028
20	6.61(08)	10.27(11)	11.92(19)	12.89(14)	126	4.85	1.42	10.11	19.05	0.021
40	7.17(18)	11.04(28)	12.66(25)	13.35(11)	118	2.66	1.55	8.96	26.14	0.022
60	7.96(11)	11.96(19)	13.81(28)	14.05(23)	133	3.64	-2.45	6.52	17.77	0.029

Table-2: Best Fit Models for M(II)-L-Orn Binary Complexes in Solvent-Water Mixtures

% V/V	log β_{MLXH} (SD)				NP	U_{Corr} x10^{-8}	Skewness	Kurtosis	χ^2	R-Factor
	ML	MLH	ML_2	ML_2H_2						
Co(II)										
0.0	6.51(14)	10.71(19)	11.71(11)	15.16(28)	139	4.4	1.23	14.64	26.1	0.028
20	7.32(16)	11.59(16)	12.84(22)	16.13(23)	123	1.23	-1.49	11.27	11.93	0.014

40	8.32(18)	12.17(14)	13.85(16)	17.04(05)	109	4.5	-1.72	11.05	23.89	0.031
60	9.16(18)	13.05(21)	14.34(22)	17.93(06)	114	4.52	1.31	8.34	11.97	0.012
Ni(II)										
0.0	7.23(21)	11.23(19)	13.41(11)	16.27(14)	121	3.91	1.05	8.23	31.14	0.018
20	8.13(23)	12.14(19)	14.13(31)	17.38(21)	128	6.18	0.85	10.22	23.46	0.036
40	9.05(15)	12.98(27)	15.02(15)	18.31(14)	108	5.66	2.28	16.52	19.25	0.022
60	10.14(17)	13.52(22)	15.92(24)	19.31(13)	129	3.64	0.68	14.70	41.54	0.032
Cu(II)										
0.0	9.54(14)	13.47(22)	16.14(13)	18.51(14)	114	3.41	1.62	2.50	33.14	0.042
20	10.88(15)	14.51(21)	17.28(22)	19.82(25)	114	2.58	-1.53	8.69	29.16	0.056
40	11.76(09)	15.26(08)	18.34(34)	20.68(18)	152	2.63	2.24	8.78	18.52	0.047
60	12.66(24)	16.28(29)	19.21(24)	21.39(25)	139	1.87	1.11	6.95	22.07	0.051
Zn(II)										
0.0	5.82(14)	9.14(17)	10.79(09)	12.21(15)	122	2.34	1.07	8.11	13.52	0.028
20	6.61(08)	10.27(11)	11.92(19)	12.89(14)	126	4.85	1.42	10.11	19.05	0.021
40	7.17(18)	11.04(28)	12.66(25)	13.35(11)	118	2.66	1.55	8.96	26.14	0.022
60	7.96(11)	11.96(19)	13.81(28)	14.05(23)	133	3.64	-2.45	6.52	17.77	0.029

Species Distribution Plots

Selected metal ions interacted with the ligand to produce stable M(II)-L binary complex species. The plausible species with varying pH and their relative distribution have been depicted and plotted using ORIGIN 8.5 as shown in Fig.-2a. The present study found ML, MLH, ML_2, and ML_2H_2 species for M(II) - MSA systems, as well as ML, MLH, ML_2, and ML_2H species for M(II)-Orn.

Inter Comparison of Stabilities of M(II)-L Binary Complexes

The gradual decrease in the free metal (FM) distribution curve compared with the free ligand (FL) signifies the development of binary complexes. Copper(II) has the maximum stability among all M(II)-L binary complexes with MSA and L-Ornithine (Fig.-2b). This is consistent with the "Irving–Williams stabilities order".[21]

Role of Dielectric Constant

The present investigation indicated that the stability constants increased linearly with increasing solvent composition. Because the solvent has a lower dielectric constant than water, the metal-ligand complexes are more stable as illustrated in Fig.-2c.

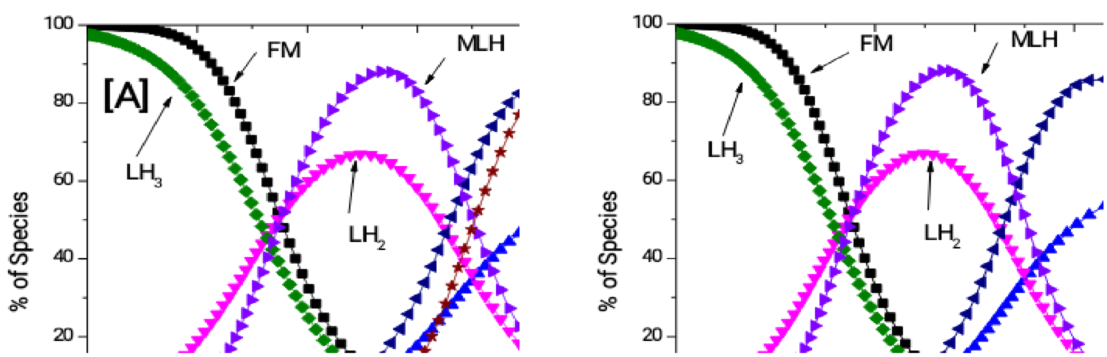


Fig.-2a: Distribution Diagrams of Binary Complexes of MSA in 30 % v/v EG-Water Mixture. [A] Co(II) [B] Ni(II)

Proposed Structure

Several writers have postulated an octahedral structure for Co^{2+} and Ni^{2+} complexes. The Jahn-Teller distortion phenomenon is accounted for in Cu(II) complexes.[22,23] In physiological pH ranges, amino nitrogen electron donor sites seek to connect with potential electron pair acceptors (hydrogen ion). Metal and hydrogen ions compete for these donor sites. Because of this, numerous protonated and un-protonated complex species coexist in metal-ligand acid-base equilibria. MSA has two oxygen and one sulphur atom coordinating locations. These sites could be coordinated with metal ions in complexes. The most plausible structures of observed complexes of M(II)-L (L=MSA or L-Orn) generated from electrical repulsions and Jahn-Teller distortion effect is shown in Fig.-3a and 3b respectively.

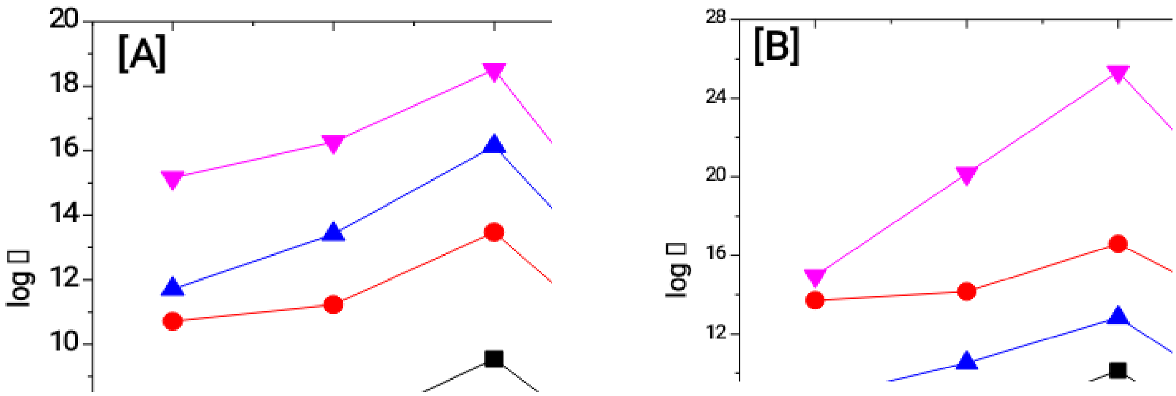


Fig.-2b: Variation of logβ of M(II)-L Binary Complexes with atomic number [A] – MSA and [B]-L-Orn

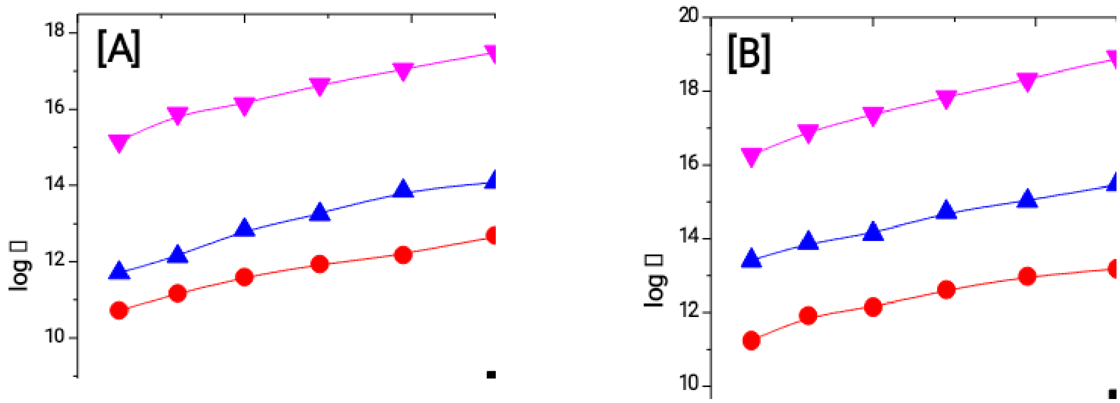
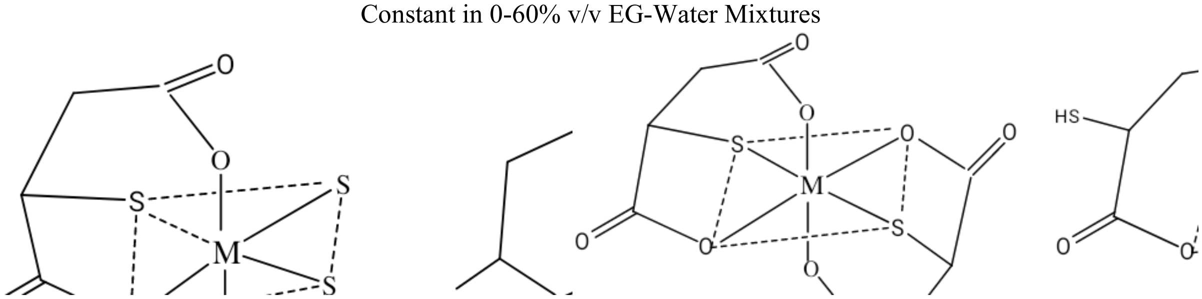
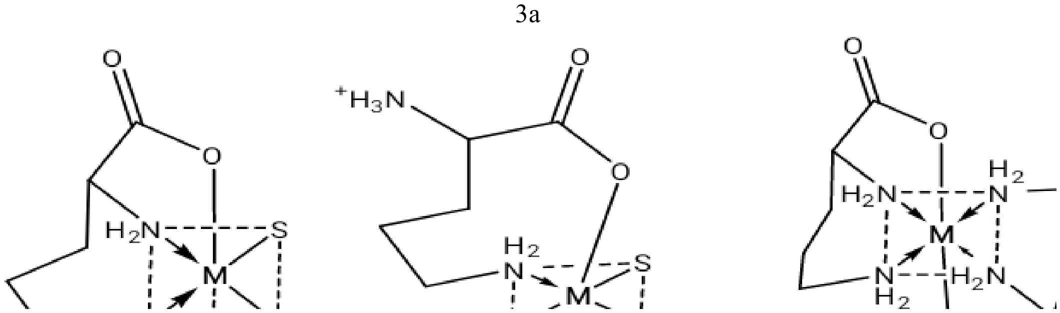


Fig.-2c: Variation of logβ of M(II)-L Complexes of [A] Co(II)-MSA, [B] Ni(II)-MSA, with Reciprocal of Dielectric Constant in 0-60% v/v EG-Water Mixtures



3a



3b

Fig.-3: Proposed plausible structures of M(II)-L binary complexes [S is either solvent or water molecule, 3a: L-MSA, 3b:L-L-Orn]

Ternary Complexes of MSA and L-Orn Modelling of Chemical Species

The best fit model for ternary complexes with MSA and L-Orn has been chosen by considering all statistical parameters given in Table-3. MLX, MLX_2, and ML_2X species were detected. Overall stability constants (log β) with minimal standard deviation (SD) in specifies the exactness of these constraints.

Table-3: Best Fit Model of M(II)-MSA-L-Orn Ternary Complexes in 0-60% v/v EG-Water Mixtures

% V/V	log β_{MLXH}(SD)			NP	U_{Corr} x10^{-8}	Skewness	Kurtosis	χ^2	R-Factor
	MLX	MLX_2	ML_2X						
Co(II)									
0.0	10.61(12)	18.13(29)	20.61(07)	111	1.21	1.61	3.72	12.61	0.020
20	11.81(11)	19.88(23)	22.28(25)	168	7.19	0.85	1.17	37.12	0.017
40	12.92(18)	20.80(21)	22.82(08)	148	1.14	-1.24	6.84	38.27	0.018
60	13.69(09)	22.91(08)	23.86(17)	149	2.94	-1.14	7.21	69.89	0.011
Ni(II)									
0.0	11.34(19)	20.15(09)	22.64(28)	131	3.91	-1.49	4.22	29.38	0.024
20	13.02(14)	21.09(14)	23.89(24)	147	2.50	2.07	1.93	53.16	0.016
40	14.12(25)	22.59(19)	24.22(21)	128	1.84	0.69	3.01	39.25	0.015
60	15.64(14)	23.44(25)	25.64(21)	161	2.08	1.19	5.27	36.58	0.019
Cu(II)									
0.0	15.75(25)	28.23(21)	30.97(14)	108	2.81	1.02	3.80	29.56	0.032
20	16.38(09)	30.22(09)	31.39(11)	153	1.56	-0.63	2.68	10.41	0.011
40	18.32(26)	31.14(28)	32.19(16)	171	2.96	2.08	3.29	66.14	0.015
60	18.45(24)	31.84(21)	33.11(14)	125	2.44	-0.75	7.92	49.16	0.025
Zn(II)									
0.0	10.23(12)	17.11(11)	18.61(21)	112	1.91	1.08	3.01	21.65	0.021
20	11.01(20)	17.69(09)	19.53(18)	133	11.09	1.03	3.22	11.62	0.03
40	11.92(17)	18.80(11)	20.14(13)	129	5.31	-1.63	4.41	32.53	0.011
60	12.29(19)	19.91(18)	21.01(26)	136	5.18	0.09	1.63	29.56	0.023

Species Distribution Plots

Fig.-4 depicts the plausible forms and their distribution of protonated and un-protonated complexes observed that suit best the ternary complex hypothesis. The present study found MLX, ML_2X, and MLX_2 species in the pH range 3.0-9.5 for M(II)-MSA-L-Orn ternary complexes. The relative distribution plots of several species were plotted shown in Fig.-5a.

$$MLH + XH_3 \quad\quad MLX + 4H^+ \quad (7)$$

$$M(II) + 2LH_3 + XH_3 \quad\quad ML_2X + 6H^+ \quad (8)$$

$$MLH + 2XH_3 \quad\quad MLX_2 + 7H^+ \quad (9)$$

$$MXH + LH_3 + XH_3 \quad\quad MLX_2 + 7H^+ \quad (10)$$

$$ML_2XH \quad\quad ML_2X + H^+ \quad (11)$$

Fig.-4: Possible Binary Complex Formation Equilibria for M(II) – L Binary Complexes

Inter Comparison of Stability Constants

As illustrated in Fig.-5b, the lower size of Cu(II) causes the stability constants to be higher than those of Co(II), Ni(II), and Zn(II) ternary complexes.

Role of Dielectric Constant

Being a protophilic and structural forming nature of EG, eliminates water from the metal ions coordination sphere and creates them highly reactive to ligands resulting in the complexes being more stable. Thus, log values should be directly related to the reciprocal of the medium's dielectric constant (1/D), as shown in the present study (Fig.-5c).

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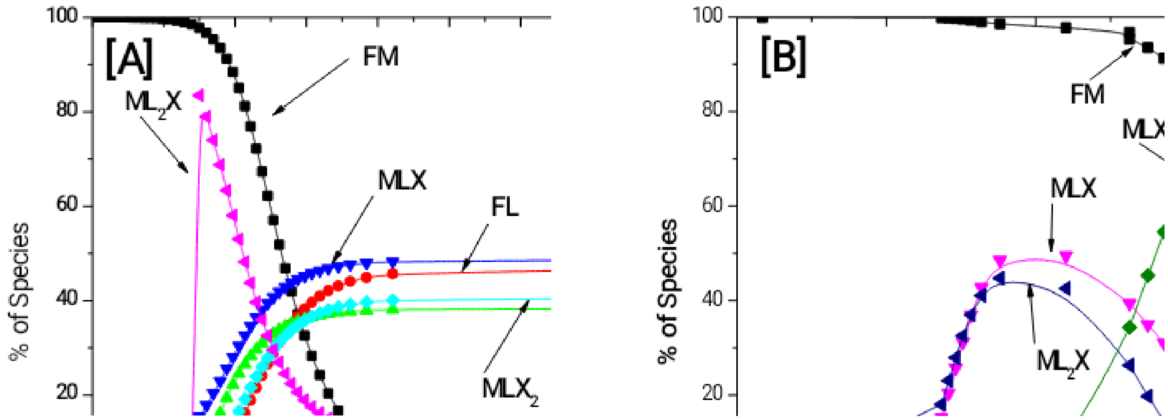

Fig.-5a: Distribution Plot of Ternary Complexes of M(II)-MSA-L-Orn in 40% EG-Water Mixture. [a] M = Co(II), [b] M = Ni(II)

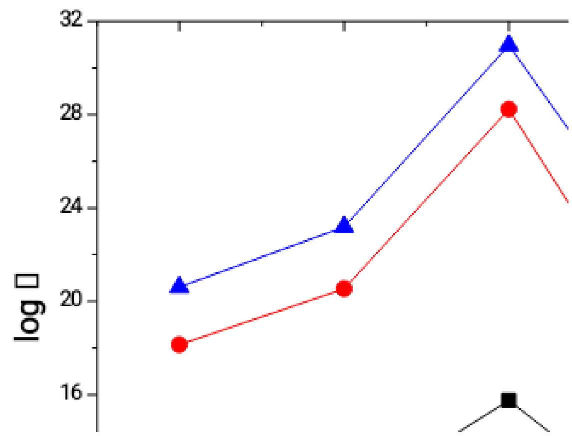

Fig.-5b: Variation of Stability Constants of M(II)-MSA-L-Orn Ternary Complexes with Atomic Number

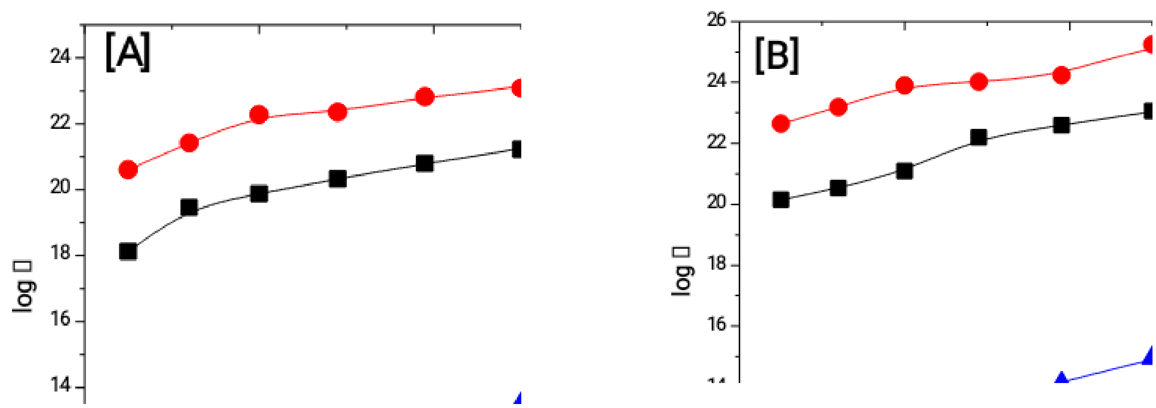

Fig.-5c**:** Variation of log β of M(II)-MSA-L-Orn with reciprocal of dielectric constant (1/D) of EG: [a] M = Co(II), [b] M = Ni(II).

Proposed Structure

The structures of the ternary complexes are hypothesized and sketched using Chem Draw 18.1 as shown in Fig.-6.

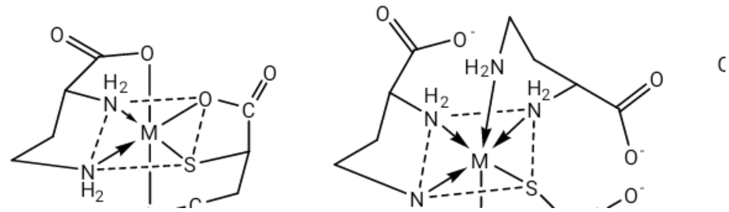

Fig.-6: Proposed Structures of Ternary Complexes, where M= Co(II), Ni(II), Cu(II), or Zn(II) Structure of Complexes

CONCLUSION

According to the current biomimetic research ML, MLH, ML_2, MLH_2, and ML_2H_2 were identified. Statistical data validated the species detected. Protonated species changes to un-protonated species when the pH of the titration mixture increased. MLH and ML_2H are protonated at low pH while ML is non-protonated. Statistical data validated the species detected. Among all the M(II)- binary complexes with MSA as well as L-Ornithine, copper exhibits the highest stability and adheres to the Irving–Williams order of stabilities. Ternary complex species MLX, MLX_2 and ML_2X were found (L = MSA, X = L-Orn). The linear increase in ternary complex stabilities with the percentage of solvent is due to electrostatic forces. The study also examines metal obtainability/transportation in biofluids and metal toxicity. Because Cu(II) is smaller than other studied metal ions, its stability constants are larger.

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