

Speciation of ternary complexes of L-histidine and L-glutamic acid with some toxic metal ions in polar medium

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Abstract : Formation of ternary complexes of Pb^{II} , Cd^{II} and Hg^{II} ions with L-histidine and L-glutamic acid was studied pH metrically in the concentration range of 0–60% v/v DMSO-water mixtures maintaining an ionic strength of 0.16 mol L^{-1} at 303.0 K. Alkalimetric titrations were carried out in different concentrations of metal ($M = Pb^{II}$, Cd^{II} and Hg^{II}) to histidine (L) to glutamic acid (X). Stability constants of ternary complexes were calculated and various models were refined with MINIQUAD75. The best fit chemical models were selected based on statistical parameters and residual analysis. The species detected are $M(LH_2)(XH)$, $M(LH)_2(XH)$ and $M(L)(LH)(XH)$, for Pb^{II} and Cd^{II} , and $M(LH_2)(XH)$ for Hg^{II} . The chemical speciation, metal bioavailability and transportation are explained based on the stability constants.

Keywords : Chemical speciation, mixed-ligand complexes, histidine, glutamic acid, toxic metals, DMSO.

Introduction

Chemical speciation of metals is important for an understanding of their distribution, mobility, bioavailability, toxicity and for setting environmental quality standards¹. Bioavailability of a particular metal depends on its complex chemical reactions of dissolution, binding and complexation with the constituents of the environmental aquatic phase². The activities of bacteria increase the concentration of dissolved organic carbon and decrease the pH of water. This causes an increase in the complexation and mobility of a metal³. Complexation significantly decreases bioavailability⁴.

Lead is a potent environmental pollutant. It has been shown that plants exposed to Pb showed a decline in the photosynthetic rate as a result of distorted chloroplast, restrained synthesis of chlorophyll, obstructed electron transport, inhibited activities of Calvin cycle enzymes, as well as deficiency of CO_2 as a result of stomatal closing⁵. Cadmium is a heavy metal and its harmful effects include a number of chronic and acute disorders such as renal damage, emphysema, hypertension, kidney damage and destruction of red blood cells^{6,7}. Cd induces damage involving free radical generation that alters mitochondrial

integrity and triggers apoptosis^{8,9}. Mercury is one of the most toxic elements and its chemical speciation can affect its availability for microbial methylation¹⁰. The main ligands competing for complexation with Hg^{II} in aquatic environments are sulfide and organic matter^{11–16}.

L-Histidine (His) controls the transmission of metals in biological bases¹⁷ and has been reported to act as a neurotransmitter in mammalian central nervous system (CNS). It is involved in biosynthesis of histamine, secretion of prolactin and antidiuretic hormone and production of red and white blood cells. Due to the high reactivity of its imidazole group, histidine residue is often found at the active site of enzymes and involved directly in catalysis. His is used in the treatment of anemia, allergies, rheumatoid arthritis and other inflammatory reactions^{18–22}. It possesses vasodilating and hypotensive actions. In the animal world, L-glutamic acid (Glu) links the metabolism of carbon and nitrogen and acts as neurotransmitter and precursor of γ -aminobutyric acid^{23,24}.

Dimethyl sulfoxide (DMSO) is a dipolar aprotic solvent with the largest dielectric constant among the common dipolar aprotic solvents. It is miscible in all proportions with water. Protonation equilibria of L-Glu and L-

His²⁵ and their binary complexes with some toxic metal ions^{26,27} in DMSO-water mixtures have been studied in this laboratory.

Results and discussion

Modeling of chemical speciation :

Protonation constants²⁵ and the stability constants of binary metal complexes^{26,27} of His and Glu were fixed in refining ternary complexes and in testing various chemical models using MINIQUAD75. The ternary complexes detected are M(LH₂)(XH), M(LH)₂(XH) and M(L)(LH)(XH), for Pb^{II} and Cd^{II}, and M(LH₂)(XH) for Hg^{II}. A very low standard deviation (SD) in overall stability constants (log β) indicates the precision of these parameters. The small values of U_{corr} (sum of squares of

deviations in the concentrations of the metal, the ligands and the hydrogen ion at all experimental points corrected for degrees of freedom) indicate that the models represent the experimental data. The Kurtosis values in the present study indicate that the distribution of the residuals shall have sharp peak (platykurtic) pattern in majority of the systems. The values of Skewness recorded in Table 1 evince that the residuals form a part of normal distribution; hence, least squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic R-values.

Effect of dielectric constant on stability of ternary complexes :

The cations and anions have lower solvation energies in DMSO, which is a dipolar aprotic solvent and does not

Table 1. Parameters of best-fit chemical models of ternary complexes of His and Glu with Pb^{II}, Cd^{II} and Hg^{II} in DMSO-water mixtures

% v/v	log β _{mlxh} (SD)			NP	U _{corr} × 10 ⁸	Skewness	Kurtosis	χ ²	R-factor	pH-range
	M(L)(LH)(XH)	M(LH ₂)(XH)	M(LH) ₂ (XH)							
Pb ^{II}										
00.0	30.39(18)	32.14(14)	37.35(37)	16	1.66	0.92	5.18	2.50	0.010	5.5–10.0
10.0	31.53(6)	32.47(6)	38.07(22)	14	0.33	0.68	4.16	7.43	0.004	5.5–10.0
20.0	32.56(23)	33.40(26)	39.27(28)	24	2.76	-0.39	5.60	55.17	0.009	5.5–10.0
30.0	31.96(6)	32.56(10)	38.48(21)	15	0.97	0.63	4.54	10.13	0.008	5.5–10.0
40.0	33.39(6)	33.85(11)	39.87(17)	15	1.36	1.20	6.17	13.33	0.009	5.5–10.0
50.0	32.26(6)	32.40(9)	38.81(11)	11	0.32	0.19	2.45	3.64	0.004	5.5–10.0
60.0	31.93(5)	32.26(9)	38.66(10)	14	0.58	0.43	2.86	11.71	0.006	5.5–10.0
Cd ^{II}										
00.0	30.28(30)	32.19(21)	36.96(43)	74	10.12	2.45	15.13	50.65	0.021	5.5–10.0
10.0	32.68(16)	33.40(25)	39.15(43)	15	8.54	-0.43	4.54	37.60	0.024	5.5–10.0
20.0	32.69(12)	33.16(18)	38.89(31)	56	13.60	-0.06	4.37	50.50	0.023	5.5–10.0
30.0	33.56(10)	34.17(15)	39.85(26)	57	9.65	0.09	4.77	42.04	0.019	5.5–10.0
40.0	34.60(16)	34.50(20)	40.46(37)	53	12.26	0.17	4.35	9.51	0.022	5.5–10.0
50.0	34.31(22)	33.96(31)	40.28(61)	13	12.67	-0.29	4.37	37.54	0.028	5.5–10.0
60.0	33.42(22)	32.06(81)	39.34(61)	16	6.14	0.01	4.20	23.50	0.017	5.0–9.5
Hg ^{II}										
00.0	–	32.94(31)	–	53	3.47	-0.59	5.80	8.68	0.009	4.0–9.0
10.0	–	33.03(70)	–	13	3.01	-0.91	3.97	8.92	0.012	4.0–9.0
20.0	–	33.74(78)	–	26	219.96	-0.85	2.01	86.15	0.097	2.0–9.0
30.0	–	34.47(28)	–	57	8.80	-0.11	3.00	5.68	0.015	4.0–9.0
40.0	–	35.63(39)	–	57	31.59	0.53	7.17	65.47	0.027	4.0–9.0
50.0	–	36.14(40)	–	26	16.57	1.40	5.10	77.85	0.018	4.0–9.0
60.0	–	36.26(34)	–	46	31.00	1.11	5.90	12.96	0.029	5.0–9.0

U_{corr} = U/(NP - m), where, m = number of species; NP = number of experimental points; SD = standard deviation.

form hydrogen bonds with solute species. Hence, it removes water from the coordination sphere of metal ions, making them more reactive towards the ligands. As a result, the stability of the complexes is expected to increase. At the same time, it is a coordinating solvent and it competes with the ligands for coordinating the metals. This decreases the stability of the complexes. Hence, the stability of the complexes is expected to either increase or decrease linearly. The variation of overall stability constants with co-solvent content depends upon electrostatic and non-electrostatic factors. Born's classical treatment²⁸ holds good in accounting for the electrostatic contribution to the free energy change. According to this treatment, the energy of electrostatic interaction is related to dielectric constant. Hence, the $\log \beta$ values should vary linearly as a function of reciprocal of the dielectric constant ($1/D$) of the medium. The non-linear variation observed in the present study (Fig. 1) indicates that non-electrostatic forces are dominating the equilibrium process under the present experimental conditions.

Quantification of change in stability of species :

The change in the stability of the ternary complexes as compared to their binary analogues was quantified based on the disproportionation constant, $\log X$ ^{29,30} given by eq. (1),

$$\log X = 2 \log K_{MLX}^M - \log K_{ML}^M - \log K_{MX}^M \quad (1)$$

corresponding to the equilibrium



Under the equilibrium conditions one can expect the formation of 50% ternary complexes and 25% each of the binary complexes statistically and the value of $\log X$ shall be 0.6. A value greater than this, accounts for the extra stability of MLX.

Another approach to quantify the stability of ternary complexes was based on the difference in stability, $\Delta \log K$ ³¹⁻³⁴ for the reactions ML with X and M(aq) with L and X, where L is the primary ligand (His) and X is the secondary ligand (Glu). It is compared with that calculated purely on statistical grounds as given in eq. (2).

$$\Delta \log K = \log K_{MLX}^M - \log K_{ML}^M - \log K_{MX}^M \quad (2)$$

The electrostatic theory of binary complex formation and

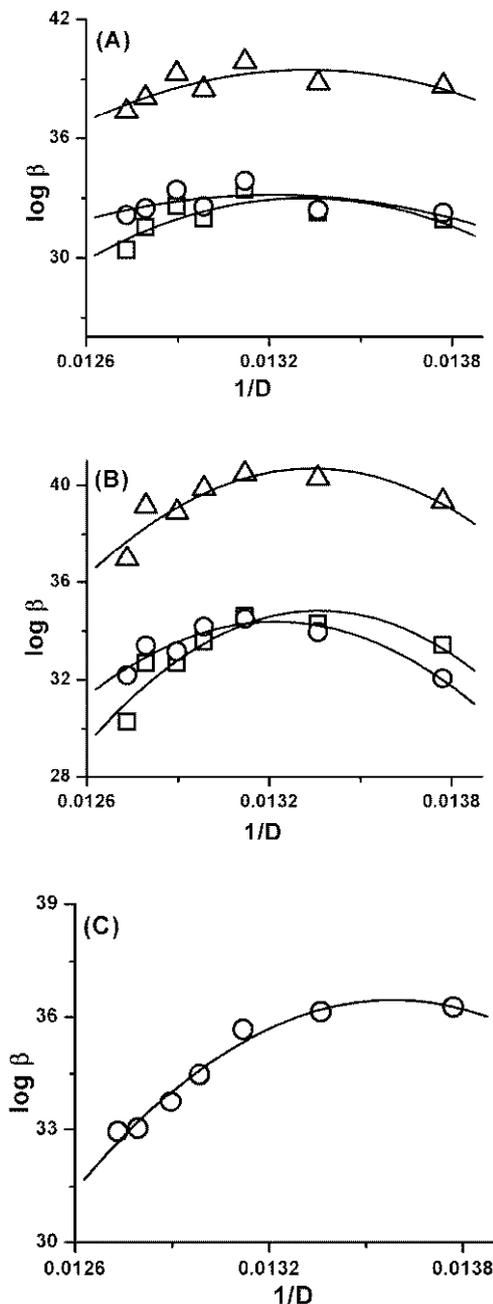


Fig. 1. Variation of stability constants of His-Glu ternary complexes with reciprocal of dielectric constant ($1/D$) of DMSO-water mixtures : (A) Pb^{II} ; (B) Cd^{II} ; (C) Hg^{II} ; (\square) $\log \beta_{M(LH_2)(XH)}$; (\circ) $\log \beta_{M(LH_2)(XH)}$; (Δ) $\log \beta_{M(L)(LH)(XH)}$.

statistical arguments suggest the availability of additional coordination positions of the hydrated metal ion for the first ligand than for the second. Hence, the usual order of stability $K_{ML}^M > K_{ML_2}^M$ applies. This suggests that $\Delta \log K$ should be negative, although several exceptions have

been found³⁵. Negative values of $\Delta \log K$ can be understood as the secondary ligand forms a more stable complex with hydrated metal ion than with ML. Whenever the experimental values of $\Delta \log K$ exceed the statistical values, it can be inferred that the ternary complex is formed as a result of interaction of ML with X or MX with L. The $\log X$ and $\Delta \log K$ values calculated from binary and ternary complexes and the corresponding equations are

Table 2. $\Delta \log K$ and $\log X$ values of mixed ligand complexes of Pb^{II} , Cd^{II} and Hg^{II} -His and Glu in DMSO-water mixtures and the corresponding equations used in the calculations

% v/v	$\Delta \log K$		$\log X$
	M(L)(LH)(XH)	M(LH) ₂ (XH)	
		Pb^{II}	
00.0	3.70	1.51	5.24
10.0	2.80	1.25	4.58
20.0	3.39	2.90	6.66
30.0	4.10	1.87	2.94
40.0	4.00	2.33	4.38
50.0	1.09	2.73	3.46
60.0	1.59	3.44	2.77
		Cd^{II}	
00.0	0.47	1.22	5.54
10.0	1.62	2.33	5.78
20.0	2.10	2.52	7.12
30.0	2.12	3.24	7.37
40.0	2.51	2.92	8.41
50.0	3.14	4.20	6.39
60.0	3.08	4.12	1.23
		Hg^{II}	
00.0	–	–	3.30
10.0	–	–	3.09
20.0	–	–	3.70
30.0	–	–	2.80
40.0	–	–	3.39
50.0	–	–	4.10
60.0	–	–	4.00
$\Delta \log K_{1212}$	= $\log \beta_{1212} - \log \beta_{1202} - \log \beta_{1010}$ = $\log \beta_{1212} - \log \beta_{1201} - \log \beta_{1011}$ = $\log \beta_{1212} - \log \beta_{1200} - \log \beta_{1012}$		
$\Delta \log K_{1213}$	= $\log \beta_{1213} - \log \beta_{1203} - \log \beta_{1010}$ = $\log \beta_{1213} - \log \beta_{1202} - \log \beta_{1011}$ = $\log \beta_{1213} - \log \beta_{1201} - \log \beta_{1012}$ = $\log \beta_{1213} - \log \beta_{1200} - \log \beta_{1013}$		
$\log X_{1113}$	= $2 \log \beta_{1113} - \log \beta_{1203} - \log \beta_{1023}$		

included in Table 2. These values could not be calculated for some systems due to the absence of relevant binary species. In the present study, the $\log X$ values range from 1.23 to 8.41 which are higher than those expected on statistical basis (0.6). These higher values account for the extra stability of the ternary complexes. $\Delta \log K$ values are in the range from 0.47 to 4.20 which indicate that the ternary complexes formed by the Pb^{II} and Cd^{II} are more stable. The reason for the extra stability of these complexes may be due to interactions outside the coordination sphere such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect and stacking interactions^{36,37}. The extra stability of ternary complexes makes them more amenable for metal transport. The less stable binary complexes make the metals bioavailable. The values of $\log X$ and $\Delta \log K$ indicate that the ternary species have enhanced stability compared to their binary species, may be due to the interactions outside the coordination sphere, such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect, stacking interactions and the electrostatic interaction between non-coordinated charge groups of the ligands. The negative values of $\Delta \log K$ suggests the formation of ternary complexes but less stable having destabilized nature of complexes, which has been valid for N and O donors³⁸.

Effect of influential parameters on stability constants :

Any variation in the parameters like concentrations of ingredients affects the magnitudes of equilibrium constants. Such parameters are called influential parameters. In order to rely upon the best fit 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 concentrations of alkali > acid > ligand > $\log F$ > metal > volume. The results of typical samples given in Table 3 emphasise that the errors in the concentrations of alkali and acid affect stability constant more than those of the ligands and metal.

Distribution diagrams :

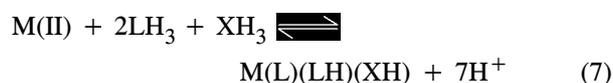
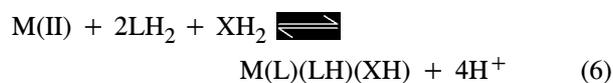
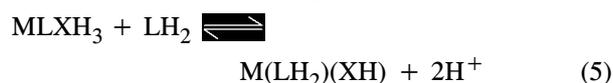
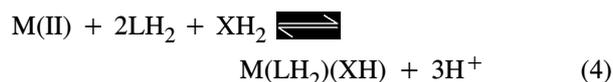
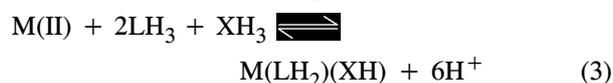
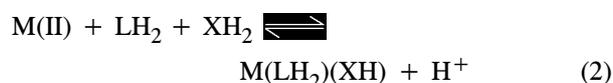
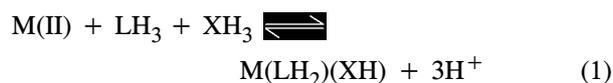
The mixed-ligand complex species of His (L) and Glu

Table 3. Effect of errors in influential parameters on His-Pb^{II}-Glu complex stability constants in 50% v/v DMSO-water mixture

Ingredient	% Error	log β _{mlxh} (SD)		
		M(L)(LH)(XH)	M(LH ₂)(XH)	M(LH) ₂ (XH)
Acid	0	32.26(6)	32.40(9)	38.81(11)
	-5	31.27(94)	Rejected	Rejected
	-2	31.62(11)	Rejected	Rejected
	+2	33.55 ^a	34.47 ^a	40.70 ^a
	+5	Rejected	Rejected	Rejected
Alkali	-5	Rejected	Rejected	Rejected
	-2	Rejected	Rejected	Rejected
	+2	31.50(20)	Rejected	Rejected
	+5	Rejected	Rejected	Rejected
	His (L)	-5	32.09(7)	32.28(9)
	-2	32.19(7)	32.35(9)	38.73(11)
	+2	32.33(7)	32.44(9)	38.90(11)
	+5	32.44(7)	32.52(9)	39.02(10)
Glu (X)	-5	31.89(4)	31.72(6)	38.05(12)
	-2	32.11(5)	32.14(6)	38.55(9)
	+2	32.41(9)	32.67(11)	39.07(14)
	+5	32.68(18)	33.10(20)	39.47(22)
	log F	-5	32.35(10)	32.59(13)
	-2	32.30(10)	32.48(12)	38.79(17)
	+2	32.22(6)	32.32(8)	38.76(11)
	+5	32.16(7)	32.21(9)	38.67(11)
Metal	-5	32.26(6)	32.34(7)	38.73(10)
	-2	32.26(6)	32.38(8)	38.78(10)
	+2	32.26(7)	32.42(9)	38.84(12)
	+5	32.26(7)	32.45(10)	38.88(13)
	Volume	-5	32.24(7)	32.40(9)
	-2	32.25(7)	32.40(9)	38.81(11)
	+2	32.27(7)	32.40(9)	38.82(11)
	+5	32.28(7)	32.40(9)	38.83(11)

^aStandard deviations are very high.

(X) in DMSO-water mixtures are M(LH₂)(XH), M(LH)₂(XH) and M(L)(LH)(XH). The active forms of these ligands²⁵ are LH₃²⁺, LH₂⁺, LH and L⁻ and XH₃⁺, XH₂, XH⁻ and L²⁻. The binary complex species of His are ML₂H₄, ML₂H₃, ML₂H₂, ML₂H and ML₂ for Pb^{II} and Cd^{II} and ML₂H₄, ML₂H₃, ML₂ and ML for Hg^{II}^{26,27}. In the case of Glu the binary species detected are MX₂H₄, MX₂H₃, MX₂H₂, MX₂ and MX for Pb^{II} and Cd^{II} and MX₂H₄, MX₂H₃, MX₂H₂ and MX for Hg^{II}. The plausible formation of species is given in the following equilibria.



Some typical distribution diagrams drawn using the formation constants of the best fit model are shown in Fig. 2. Mixed ligand complexes of Pb^{II}, Cd^{II} and Hg^{II} are detected in the pH range 4.0–10.0. M(LH₂)(XH) is the predominant species formed in the pH range 2.0–5.0 by the interaction of free metal ion (FM) with protonated ligands [Equilibria 1 and 2]. In the case of Cd^{II} and Hg^{II}, the species is formed at the pH below 4.0. M(LH)₂(XH) species may be formed from the Equilibria 3–5. The species M(L)(LH)(XH) is formed through Equilibria 6–8 or by the deprotonation of M(LH)₂(XH) with increasing pH [Equilibrium 9].

Structures :

Depending upon the nature of the ligands and metal ions, and based on the chemical knowledge, the structures of ternary complexes are proposed as shown in Fig. 3. These structures indicate that His and Glu act as bidentate or tridentate ligands depending upon the pH conditions³⁹.

Experimental

0.1 mol L⁻¹ aqueous solutions of Pb^{II} and Cd^{II} and

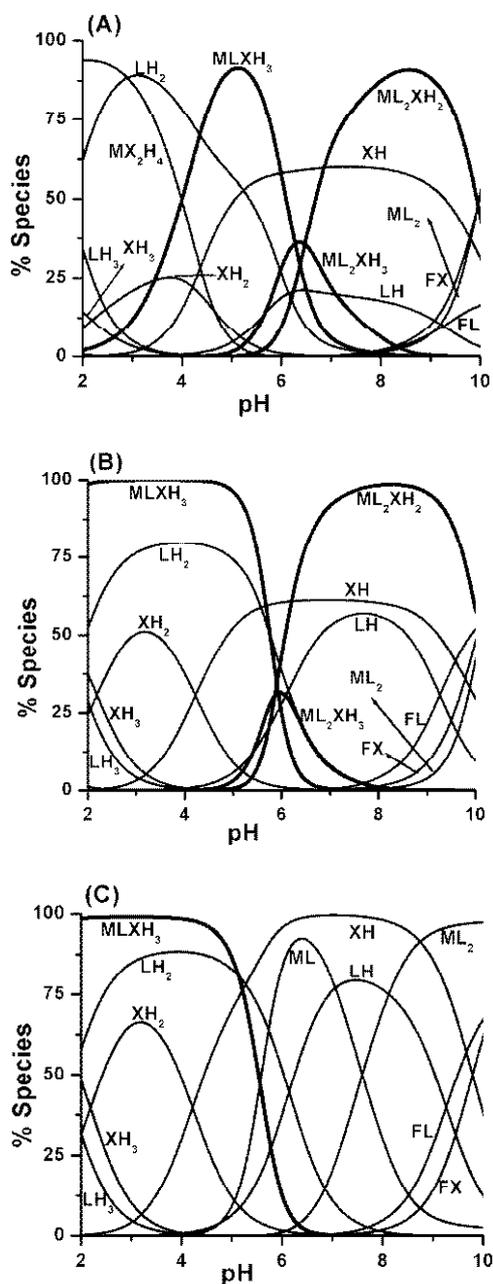


Fig. 2. Distribution diagrams of mixed-ligand complexes of His and Glu in 40% v/v DMSO-water mixture : (A) Pb^{II} , (B) Cd^{II} and (C) Hg^{II} .

$0.05 \text{ mol L}^{-1} \text{ Hg}^{\text{II}}$ nitrates G.R. grade (E. Merck, Germany) were prepared by dissolving them in triple distilled water. 0.05 mol L^{-1} aqueous solutions of L-histidine and L-glutamic acid (E. Merck, Germany) were also prepared. To increase the solubility of the ligands and metal salts, 0.05 mol L^{-1} nitric acid (Qualigens, India)

was maintained in the solutions. DMSO (Qualigens, India) was used as received. The strength of alkali was determined using the Gran plot method^{40,41}. Errors in the concentrations of the ligands, metal ions and alkali were subjected to analysis of variance of one way classification⁴².

Procedure :

The alkalimetric titrations were carried out in the medium containing varying concentrations of DMSO maintaining an ionic strength of 0.16 mol L^{-1} with sodium nitrate (Merck, India) at 303.0 K , using ELICO (Model LI-120) pH meter of 0.01 readability in conjunction with a glass and calomel electrode. The pH meter was calibrated with 0.05 mol L^{-1} potassium hydrogen phthalate in acidic region and 0.01 mol L^{-1} borax solution in basic region. The glass electrode was equilibrated in a well stirred DMSO-water mixtures containing inert electrolyte. The effect of variations in asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of correction factor ($\log F$) which was computed from the experimental and simulated acid-base titration data calculated by SCPHD program⁴³. A correction was applied to the pH meter dial readings to account for the solvent effect on pH. Titration of strong acid with alkali was carried out at regular intervals to check whether complete equilibration was achieved. The calomel electrode was refilled with DMSO-water mixtures of equivalent composition as that of the titrand. In each of the titrations, the titrand consisted of 1 mmol of nitric acid in a total volume of 50 mL . Titrations were carried out in the presence of different relative concentrations of the metal (M) to His (L) to Glu (X) ($\text{M} : \text{L} : \text{X} = 1.0 : 2.5 : 2.5, 1.0 : 2.5 : 5.0, 1.0 : 5.0 : 2.5$ in the case of Pb^{II} and Cd^{II} and $1.0 : 5.0 : 5.0, 1.0 : 5.0 : 10.0$ and $1.0 : 10.0 : 5.0$ in the case of Hg^{II} with $0.4 \text{ mol L}^{-1} \text{ NaOH}$. The best-fit chemical model for each system investigated was arrived at using a non-linear least squares analysis program MINIQUAD75⁴⁴.

Conclusions

- (1) The mixed ligand complex species detected are $\text{M}(\text{LH}_2)(\text{XH})$, $\text{M}(\text{LH})_2(\text{XH})$ and $\text{M}(\text{L})(\text{LH})(\text{XH})$,

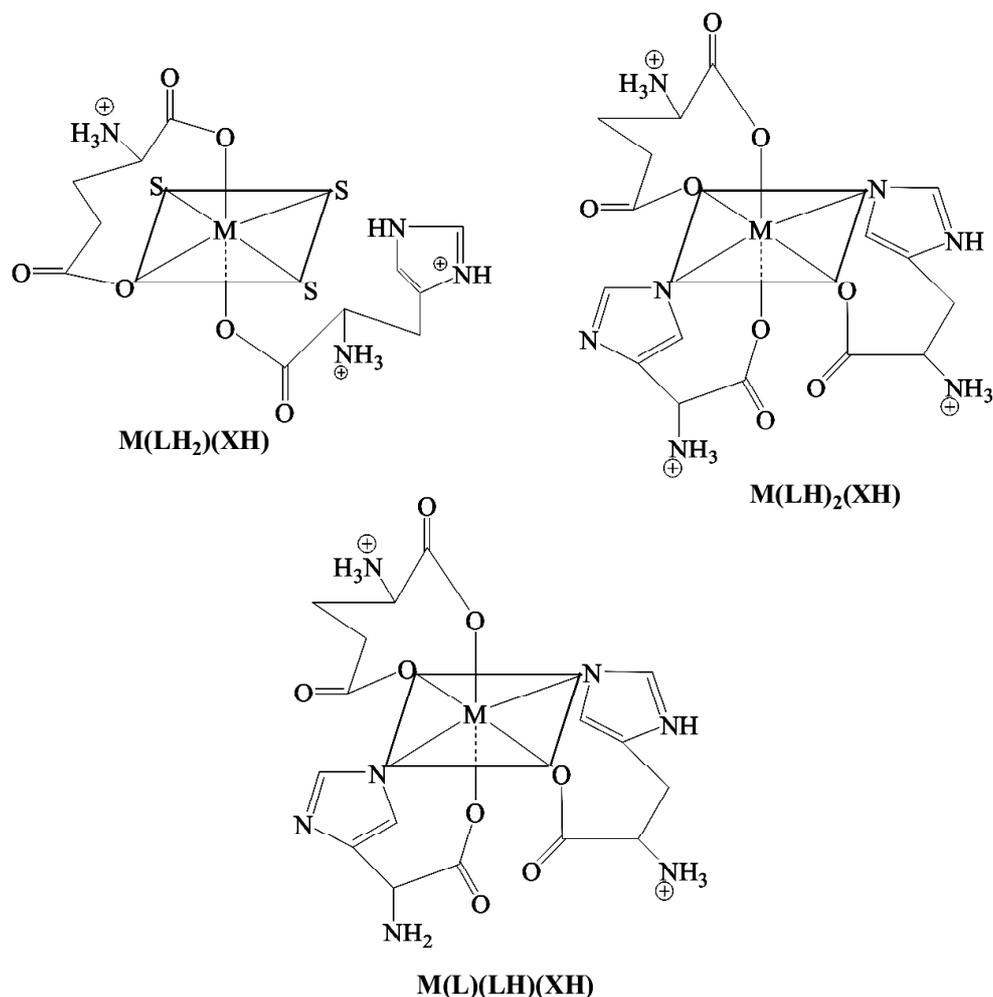


Fig. 3. Structures of His-Metal-Glu complexes, where S is either solvent or water molecule.

for Pb^{II} and Cd^{II} and $\text{M}(\text{LH}_2)(\text{XH})$ for Hg^{II} where $\text{L} = \text{His}$ and $\text{X} = \text{Glu}$.

- (2) The values of $\Delta \log K$ and $\log X$ indicate that the ternary species have extra stability compared to their binary species, may be due to the interactions outside the coordination sphere, such as the formation of hydrogen bonds between the coordinated ligands, charge neutralization, chelate effect, stacking interactions and the electrostatic interaction between non-coordinated charge groups of the ligands.
- (3) The non-linearity in the stabilities of mixed-ligand complexes is due to the dominance of non-electrostatic forces over electrostatic forces.
- (4) The magnitudes of the stability constants for

mixed-ligand complexes are affected by the errors in the concentrations of the ingredients. The order of influence is alkali > acid > ligands > $\log F$ > metal > volume.

- (5) The ternary complexes are more amenable for "metal transport" in biofluids because of their extra stability.

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