IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 10, Issue 9 Ver. I (September. 2017), PP 45-52
www.iosrjournals.org

Computer Simulated Equilibrium Studies of Heterobimetallic Complexes of Pb (II), Cd (II) and Hg (II) with Dipeptide and Pyrimidine

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Abstract**: The stability of mononuclear and mixed-metal complexes of bivalent toxic metal ions (lead,cadmium and mercury) with dipeptide (glycylglycine) / pyrimidine (4,6-dimethyl 2-pyrimidinol) were studied by using pH- metric titration technique in aqueous solution at three different temperatures (20ºC±1, 30ºC±1 and 40ºC±1) and at three ionic strengths (μ=0.05M, 0.10M and 0.15M) , in order to calculate thermodynamic stability constants and other thermodynamic parameters. The complexation model for each system was obtained by processing the potentiometric titration data using the SCOGS program. The stability constant trend of complexes in both systems and the contributions of deprotonated or protonated species formed in a particular equilibrium is discussed. Distribution of various species is presented in the form of speciation curves. The percentage formation of heterobimetallic complexes is appreciably high which is evident from speciation curves. Plausible equilibria for the formation and possible structures of the complex species are also inferred.The two metals are coordinated to the ligand ion simultaneously in a single step. The stability of the mixed-metal complexes relative to their corresponding binary complexes was also investigated by calculating the $\Delta logK$ parameter of each system. In addition, the Gibbs energies of reaction (ΔG°) obtained from the Van't Hoff isotherm. The standard enthalpy change (ΔH°) and entropy change (ΔS°) have been determined by linear least square fit method . The best fit chemical models were selected based on firm statistical grounds employing , $\chi 2$, Skewness and Kurtosis.

***Keywords**: heterobimetallic, potentiometric, SCOGS, Skewness, Van't Hoff isotherm*

Date of Submission: 21-08-2017 Date of acceptance: 08-09-2017

I. Introduction

In the recent time, researchers have developed interest in exploring the formation of mixed metal complexes for the reason that many biological reactions involve the formation of mixed metal species. Also the mixed ionic systems often occur in nature. Heavy metals such as lead, cadmium and mercury are toxic in nature which exert adverse effects on neurological, reproductive, renal and hematological systems in humans and animals.The toxicity effect on organism often involve the formation of complex between metal ion and organic moiety acting as ligand.If more than one type of metal is available in any case, than this may lead to the formation of mixedmetal complex.Hence,it becomes essential to find the stability of mixed metal complexes in comparison to simple species. As a consequence several investigations are made and interesting results are reported on mixed metal systems in recent past [1-10].

Organo- mercury and lead compounds exhibit toxic effect on the central nervous system [11]. Similarly cadmium exhibits various chronic and acute disorders like testicular atrophy hypertension, damage to kidneys and bones, anemia and Itai-Itai [12-16]. The study of metal complexes with pyrimidine and peptides was still lacking , moreover , they are having some remarkable characters. Due to above good characters and complexing agent, the complex study of pyrimidine and peptides with toxic metal ions are also important , these systems also serve as models for metal –protein interactions

The interaction of metal ion with pyrimidine and peptides of aminoacid gained much interest due to their biochemical aspects and their role in the formation of DNA and RNA skeletons.The pyrimidines represent one of the most active classes of compounds possessing wide spectrum of biological activities like significant in vitro activity against unrelated DNA and RNA, viruses including polioherpes viruses, diuretic, antitumour, antiHIV, and cardiovascular[17]. Peptides are amazing diverse and multi-faceted class of compounds constructed from relatively simple building blocks, the amino acids. They are components of tissues exhibiting a remarkable range of biological properties acting as antibiotics, hormones, food additives, poisons or pain-killers [18-19]. Several metal complexes containing peptide groups have displayed diverse pharmacological activities. Peptides are of immense biomedical interest particularly in endocrinology [20-21].

The study of interaction of metal ions with peptides and pyrimidine analogs gained much attention due to their biological role in many living systems[22-28]. Speciation studies of dipeptide and pyrimidine with toxic metal ions in aqueous medium are reported earlier from the investigation carried in our laboratory [29-30] . In continuation of previous work, we present here the formation constants of binary and heterobimetallic complexes of bivalent toxic heavy metal ions with glycylglycine (Glygly) /4,6 dimethyl 2-pyrimidinol (DMP) containing N-O and N-N donor sites.The results can serve as useful tool for understanding the formation of bimetallic species in biological and environmental system [3].

II. Experimental

All the systems were investigated pH metrically in equimolar condition at three different temperatures(20ºC±1, 30ºC±1 and 40ºC±1) and at three ionic strengths (μ=0.05M, 0.10M and 0.15M) in aqueous medium. NaNO3 was used as background electrolyte. For each set of titration moles of alkali required per mole of ligand /metal. 'a' was determined and curves were obtained by plotting pH vs 'a'.

2.1 Solution

All the reagents used were of highest purity Merck/Aldrich products. Solutions of metal and ligand (each 0.01M) were prepared by dissolving accurately weighed amounts in free deionized double distilled water.

2.2 Instrument

pH-measurements were made by using Elico digital pHmeter model LI-127 with ATC probe and combined electrode type (CL-51B- Glass Body; range 0-14pH unit; 0100˚C(Automatic/Manual) with accuracy ±0.01 and standardized by using buffer solution of pH=4.0 and 9.2.

2.3 Measuring Approach

Following sets of titration mixture were prepared by keeping total volume 50mL and titrated with carbonate free 0.10M NaOH solution, ionic strengths (μ=0.05, 0.10, 0.15M) is maintained by adding different concentration of NaNO3 solution to each titration mixture at temperature 20±1°C , 30±1°C and 40±1°C. The composition of each titration mixtures is as follows:-

1. **Acid titration:** HNO3 (2.0×10^{-3}M).
2. **Ligand A titration:** HNO3 (2.0×10^{-3}M) + Ligand A(1.0×10^{-3}M).
3. **Metal (M)-Ligand A (1:1) titration:** HNO3 (2.0×10^{-3}M) + Ligand A (1.0×10^{-3}M) + Metal nitrate (1.0×10^{-3}M).
4. **Metal(M´)-Ligand A (1:1) titration:** HNO3(2.0×10^{-3}M) + Ligand A(1.0×10^{-3}M) + Metal nitrate M´(1.0×10^{-3}M)
5. **Metal (M)- Metal (M´) –Ligand (1:1:1) titration:** HNO3 (2.0×10^{-3}M) + Ligand A(1.0×10^{-3}M) + Metal Nitrate M(1.0×10^{-3}M) + Metal nitrate M´ (1.0×10^{-3}M).

Where,
Ligand A=Glycylglycine abbreviated as (Glygly) / 4,6 Dimethyl, 2- Pyrimidinol abbreviated as (DMP). DMP is used as their diprotonated form by adding one equivalent of acid in the course of titration .
M/M´= Pb(II), Cd(II) and Hg(II) .

Volume of alkali used in each set of titration is converted into moles of alkali per mole of ligand / metal and denoted as 'a'. This is presented in the form of representative titration curves (fig.1-a-b). Results are discussed on the basis of variation in nature of titration curves with respect to 'a'.

III. Results And Discussion

The results of 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 -5 . Very low-standard deviation in overall stability constants (log β) signifies the precision of the results. The small values of mean, median, standard deviation, standard error and variance for the systems are supported by the residual statistical analysis of these constants.

The qualitative analysis of proton-ligand, metal-ligand and metal M-metal M´- ligand equilibria was done by examination of titration curves given in fig -1(a-b). Pattern of experimental curves for the systems M/M´–Glygly/ DMP [M/M´=Pb,Cd,Hg] follow same trend respectively.The ligand titration of Glygly indicates strong basic nature of dissociable proton (fig-1-a) and ligand titration of DMP show that the deprotonation of ligand occurs in two distinct steps (fig-1-b) .The values of dissociation constant of ligands are in close agreement with literature [32].

Representative pH vs. 'a' Titration Curves
Cd^{II}-Hg^{II}-Glygly/Cd^{II}-Hg^{II}-DMP (1:1:1) mixedmetal-ligand (M-M-A´) systems at 30±1°C[μ=0.1M(NaNO3)]

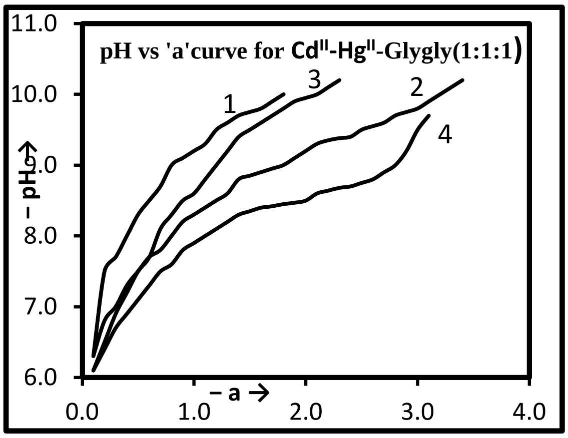


Fig.1(a)

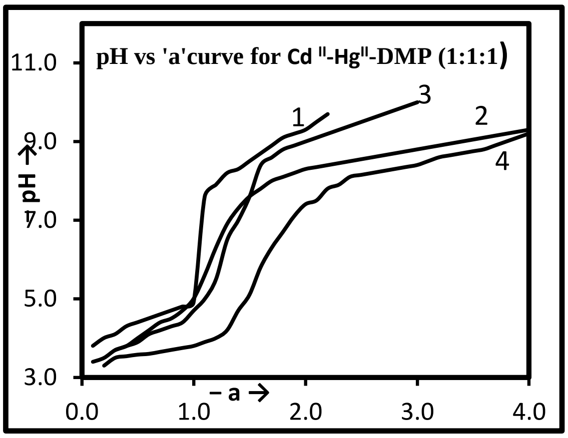


Fig.1(b)

Where,

Curve 1: Ligand A(Glygly/DMP)Titration	Curve 2: Metal-Ligand M-A (1:1) Titration
Curve 3: Metal-Ligand M´-A (1:1) Titration	Curve 4: Mixed-Metal-Ligand M-M´-A (1:1:1)Titration

Curve 2 and 3 depicts the titration curves of M-Glygly/DMP (1:1) and M´-Glygly /DMP(1:1) binary systems respectively. It is observed that curve 2 and 3 are displaced towards right side in (fig1-a) from ligand (Glygly) titration curve 1 showing the formation of non- protonated M/M´-Glygly (MA) binary complexes in higher pH range. Observing fig-1-b it is evidence that curve 2 and 3are displaced towards right followed by an inflection a=1and 2.This suggest the existence of protonated M/M´- DMP (MAH/M´AH type) of complex in the lower range and of non-protonated M/M´-DMP(MA/M´A) type of complex in higher pH range. Displacement of mixed metal titration curve (curve 4) in the fig 1(a)-1(b) towards right hand side from the ligand curve 1, metal/metal´-ligand titration curve 2 and 3, shows formation of Cd^{II}-Hg^{II}-Glygly/Cd^{II}-Hg^{II}-DMP mixed metal complex. A weak inflection in the curve near 'a'=2. indicates formation of non-protonated mixed metal complex. Curve 4 is seen to be diverging from curve 1, 2 and 3 from initial stage of titration thereby suggesting the simultaneous coordination of both the metal ions with ligand. Equilibria involved in above complexation are given here under:

Equilibria involved in above complexation are given in
Scheme 1

[simultaneous complexation equilibria for M-M-´Glygly]

$$M / M' + A \overset{0 \le a \le 1}{\rightleftharpoons} MA/ M'A$$

$$MA + M' \overset{1 \le a \le 2}{\rightleftharpoons} MM'A$$

$$M'A + M \overset{1 \le a \le 2}{\rightleftharpoons} MM'A$$

$$M + A + M' \overset{0 \le a \le 2}{\rightleftharpoons} MM'A$$

Scheme 2

[simultaneous complexation equilibria for M -M´-DMP]

$$M/ M' + HA \overset{0 \le a \le 1}{\rightleftharpoons} MAH/ M'AH$$

$$MAH / M'AH \overset{1 \le a \le 2}{\rightleftharpoons} MA/ M'A + H$$

$$MA + M' \overset{1 \le a \le 2}{\rightleftharpoons} MM'A$$

$$M'A + M \overset{1 \le a \le 2}{\rightleftharpoons} MM'A$$

$$M + A + M' \overset{0 \le a \le 2}{\rightleftharpoons} MM'A$$

All other mixed metal systems involving Glygly /DMP (i.e, Cd^{II}-Pb^{II}-Glygly, Pb^{II}- Hg^{II}-Glygly / Cd^{II}-Pb^{II}-DMP, Pb^{II}- Hg ^{II}- DMP) depict the same trend.

The protonation constants of ligand and formation constants of binary and ternary systems were calculated by method of Chaberek and Martell [33-34], as modified by Dey et.al [35] and values were refined by SCOGS computer program[36-38]. Thermodynamic formation constants are developed by extrapolating the log β vs.$\sqrt{\mu}$ plot to zero ionic strength. The values are given in Tables - 1-2.

The values of the thermodynamic stability constants log $K\mu\rightarrow0$ were used to determine the standard free energy (ΔG°) for the complexation reaction from Van't Hoff isotherm:

$$\Delta G° = -\ 2.303RT \log K\mu\rightarrow0$$

The Gibb's Helmholtz equation (ΔG° = ΔH°-TΔS°) and Van't Hoff equation can be put in the following form:

$$\log K^{\mu\rightarrow0} = \frac{-\Delta H°}{2.303R}\ \frac{1}{T} + \frac{\Delta S°}{2.303R}$$

The standard enthalpy change (ΔH°) and entropy change (ΔS°) have been determined by linear least square fit method by plotting a graph between $\frac{1}{T}$ vs log $K^{\mu\rightarrow0}$ using above equation . In the above equation :

$$\text{Slope} = \frac{-\Delta H°}{2.303R} \quad \text{and} \quad \text{Intercept} = \frac{\Delta S°}{2.303R}$$

The values of ΔG°, ΔH° and ΔS° are presented in Table-3 The stability of ternary complexes over their corresponding binary complexes was evaluated by calculating the parameter ΔlogK and percentage Relative Stabilisation (%R.S) according to the following equation and their values for ternary complexes are given Table-4

$$\Delta \log K_{MM'A} = \log \beta_{MM'A} - (\log \beta_{MA} + \log \beta_{M'A})$$
$$\%\ R.S = \Delta \log K_{MM'A} / \log K_{MA}$$

The qualitative analysis on the basis of the trends of the titration curves are supported by the quantative results obtained by subjecting the experimental data to computational analysis. Speciation curves show the variation of the concentration of different species formed in particular equilibria in the form of percentage distribution against pH. Speciation curves for Cd^{II}-Hg^{II}-Glygly, Cd^{II}-Pb^{II}-Glygly, Pb^{II}-Hg^{II}-Glygly / Cd^{II}-Hg^{II}-DMP, Cd^{II}-Pb^{II}-DMP , Pb^{II}-Hg^{II}-DMP are given in figs. (2.1) – (2.6). All the system bear almost the same trend.

Table-1: Thermodynamic Protonation Constant of Ligand

Parameters	Glycylglycine			Parameters	DMP		
	20°C	30°C	40°C		20°C	30°C	40°C
$\log \beta_1^{HA}$	8.52	8.32	8.20	$\log \beta_1^{HB}$	8.64	8.60	8.52
$\log \beta_2^{H2A}$	-	-	-	$\log \beta_2^{H2B}$	13.94	13.14	13.04

$$\log \beta_1^{HA} = pK_2^H \qquad \log \beta_2^{H2A} = pK_1^H + pK_2^H$$

Table -2: Thermodynamic Formation Constants of M(II) / M′(II) - Ligand 'A'(Glygly/ DMP) in equimolar systems

Parameters	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
	Pb(II)-Glygly			**Cd(II)-Glygly**			**Hg(II)-Glygly**		
$\log \beta_{MA}$	4.46	4.34	4.22	4.10	3.96	3.82	3.60	3.40	3.30
	Pb(II)-DMP			**Cd(II)-DMP**			**Hg(II)-DMP**		
$\log K_{MAH}^{M}$	3.42	3.25	3.12	3.40	3.28	2.98	3.75	3.50	3.32
$\log K_{MAH}^{H}$	-4.32	-4.15	-3.96	-3.55	-3.90	-3.10	-3.92	-3.70	-3.54
$\log K_{MA}^{H}$	-6.38	-6.22	-6.10	-7.33	-7.20	-7.16	-7.54	-7.24	-6.98
$\log \beta_{MAH}$	11.94	11.65	11.52	11.50 1111111 22	11.30	11.23	12.32	12.05	11.84
$\log \beta_{MA}$	6.37	6.18	6.02	5.42	5.20	5.02	7.14	7.18	7.08

$$\log \beta_{MA} = \log K_{MA}^{M} \qquad \log \beta_{MAH} = \log K_{MAH}^{M} + \log \beta_1$$

Table-3: Thermodynamic Formation Constants and Thermodynamic Parametes of M(II) - M′(II) - Ligand ‘A’(Glygly/ DMP) Ternary Complexes in equimolar systems

Parameter	20ºC		30ºC		40ºC		$-\Delta H^o$ kJmol^{-1}	ΔS^o Jk^{-1}mol^{-1}
	log $K_{\mu\to}$	$-\Delta G^o$ kJmol^{-1}	log $K_{\mu\to 0}$	$-\Delta G^o$ kJmol^{-1}	log $K_{\mu\to 0}$	$-\Delta G^o$ kJmol^{-1}		
Cd(II) – Hg(II) - Glygly								
$\log K^{MM'}_{MM'A}$	7.75	43.47	7.53	43.68	7.34	43.98	25.03	62.61
$\log K^{MA}_{MM'A}$	3.98	22.32	3.65	21.17	3.40	20.37	35.14	- 44.42
$\log K^{M'A}_{MM'A}$	4.40	24.68	4.18	24.25	4.02	24.09	22.97	5.36
Cd(II) – Pb(II) – Glygly								
$\log K^{MM'}_{MM'A}$	9.15	51.33	8.92	51.75	8.74	52.37	24.89 89.80	
$\log K^{MA}_{MM'A}$	5.50	30.85	5.30	30.74	5.02	30.08	30.08	2.68
$\log K^{M'A}_{MM'A}$	4.68	26.25	4.32	25.06	4.14	24.81	32.00 20.68	-
Pb(II) – Hg(II) - Glygly								
$\log K^{MM'}_{MM'A}$	8.92	50.04	8.72	50.58	8.64	51.78	16.41 114.12	
$\log K^{MA}_{MM'A}$	4.92	27.60	4.62	26.80	4.45	26.66	28.03	-2.30
$\log K^{M'A}_{MM'A}$	6.34	35.56	6.15	35.67	5.84	34.99	31.59	13.79
Cd(II) – Hg(II) - DMP								
$\log K^{MM'}_{MM'A}$	10.70	60.02	10.42	60.45	10.22	61.24	28.99	105.31
$\log K^{MA}_{MM'A}$	2.72	15.25	2.45	14.21	2.16	12.94	34.60 66.25	-
$\log K^{M'A}_{MM'A}$	3.28	18.40	2.95	17.11	2.84	17.02	25.57	-25.66
Cd (II) – Pb(II) – DMP								
$\log K^{MM'}_{MM'A}$	11.12	62.38	10.92	63.35	10.72	64.24	24.62 128.67	
$\log K^{MA}_{MM'A}$	3.80	21.31	3.56	20.65	3.38	20.25	25.43	-14.55
$\log K^{M'A}_{MM'A}$	3.96	22.21	3.76	21.81	3.42	20.49	34.19	-40.59
Pb(II) – Hg(II) - DMP								
$\log K^{MM'}_{MM'A}$	11.34	63.61	10.98	63.70	10.82	64.84	30.64	111.44
$\log K^{MA}_{MM'A}$	3.30	18.51	2.94	17.05	2.86	17.14	25.16 24.13	-
$\log K^{M'A}_{MM'A}$	3.92	21.99	3.72	21.58	3.40	20.37	32.82 36.76	-

Speciation Curve

It is noted that the formation of 1:1:1 heterobimetallic ternary complexes occur in pH range 4.5 to 8.5 in M-M´Glygly and 3.3 to 7.5 M-M´-DMP systems respectively. The concentration of binary species MA/M´A is very low (below 20%) as compared to ternary species (MM´A) and are formed as dominating species from the preliminary stage .When pH increases upto pH 6.5,concentration of ternary species attain maximum concentrations, vary from 55-75% in these systems . This clearly indicates that in all cases percentage concentration of ternary species (MM´A) are much higher as compared to binary species. Protonated binary species in case of M-M´-DMP system is predominant in lower pH range and its concentration decreases continuously with the increase of pH,whereas concentration of nonprotonated MM´A heterobimetallic complex species increases gradually. Speciation curve also supports the simultaneous co-ordination of both metal ions with ligand. All these curves of M-M´-Glygly and M-M´- DMP system follow the similar pattern respectively. These curves are presented here under in Fig-2.1-2.6.

Representative speciation profiles for various species

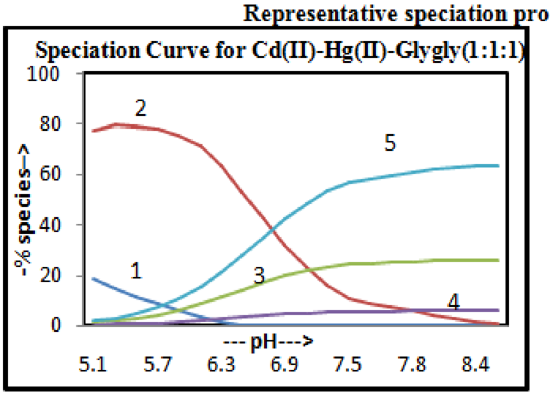


Fig 2.1

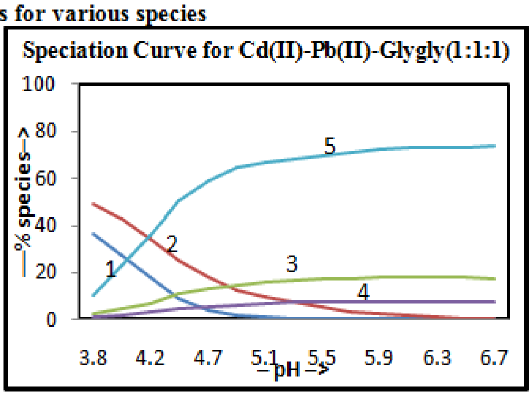


Fig 2.2

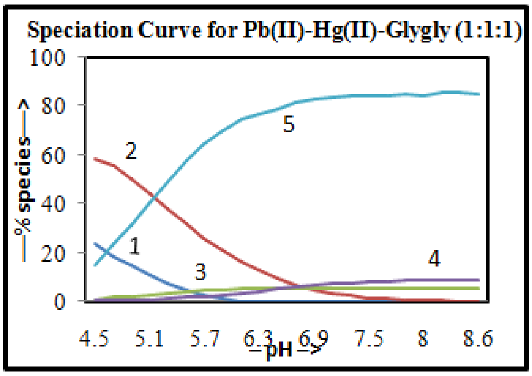


Fig 2.3

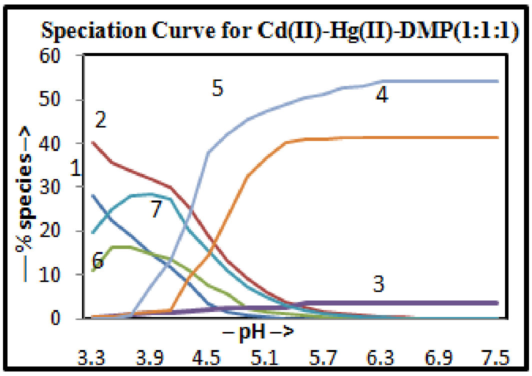
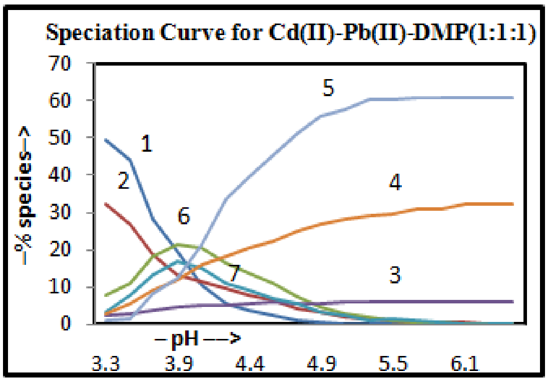


Fig 2.4



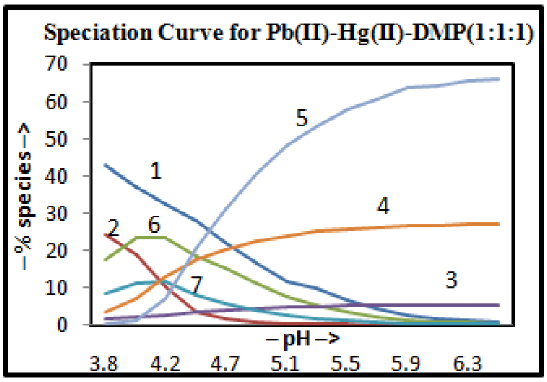


Fig 2.5 **Fig 2.6**

Where, Curve 1: [M]; 2: [M']; 3:[MA]; 4 :[M´A]; 5 :[MM'A]; 6 :[MAH]; 7: [M'AH]

IV. Structure Of Complex

The binding mode of Glygly /DMP ligand (A) in mixed metal ligand[M-M´-A] species is similar to its bidentate binding mode in the corresponding binary systems. Thus, the two coordinating positions in [M–M´-A] systems would be occupied by the bidentate bonding of A and the remaining positions would be occupied by solvent water molecules(Figure 3 a-b) to form a stable four coordinated environment. The binding of dipeptide(Glygly) / pyrimidine (DMP) ligands in [M-M´-A] species involves a stable five-four membered chelate ring. It is also supported by principle of Hard and Soft Acid and Bases (HSAB), the soft character of M/M´ shows the preference for the amine nitrogen site over the harder carboxylate or amide oxygen atom[29]. However, this needs further support of spectral studies. Possible structure so proposed for the species as shown in fig -3(a-b)

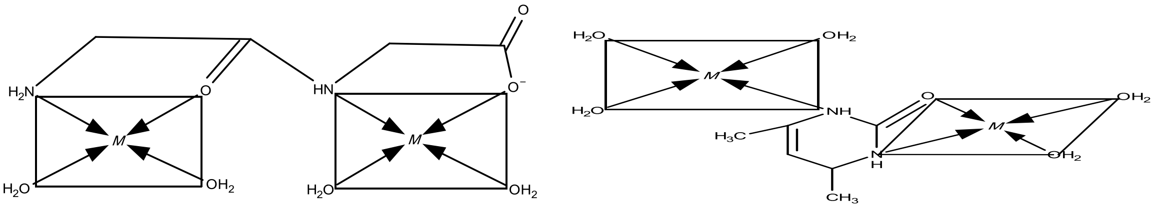


Fig.3(a) **Fig-3(b)**

Figure 3: Proposed structure (a) M-M′-Glygly (b) M-M′-DMP complexes

Table -4: Value of Δ log K for M(II) / M′(II) - Ligand ‘A ’ (Glygly/ DMP) Ternary Complex

Parameters	20°C			30°C			40°C		
M(II) - M′(II) - Glygly									
	Cd^{II}-Hg^{II}	**Cd^{II}-Pb^{II}**	**Pb^{II}-Hg^{II}**	**Cd^{II}-Hg^{II}**	**Cd^{II}-Pb^{II}**	**Pb^{II}-Hg^{II}**	**Cd^{II}-Hg^{II}**	**Cd^{II}-Pb^{II}**	**Pb^{II}-Hg^{II}**
log $\beta_{MM'A}$	7.75	9.15	8.92	7.53	8.92	8.72	7.34	8.74	8.64
log β_{MA}	4.10	4.10	4.46	3.96	3.96	4.34	3.82	3.82	4.22
log $\beta_{M'A}$	3.60	4.46	3.60	3.40	4.34	3.40	3.30	4.22	3.30
Δlog $_{MM'A}$	0.05	0.59	0.86	0.17	0.62	0.98	0.22	0.72	1.12
% R.S	1.21	14.3	19.2	4.29	15.6	22.5	5.75	18.8	26.5
M(II) - M′(II) - DMP									
	Hg^{II}-Cd^{II}	**Hg^{II}-Pb^{II}**	**Pb^{II}-Cd^{II}**	**Hg^{II}-Cd^{II}**	**Hg^{II}-Pb^{II}**	**Pb^{II}-Cd^{II}**	**Hg^{II}-Cd^{II}**	**Hg^{II}-Pb^{II}**	**Pb^{II}-Cd^{II}**
log $\beta_{MM'A}$	10.70	11.12	11.34	10.42	10.92	10.98	10.22	10.72	10.82
log β_{MA}	7.52	6.37	7.52	7.18	6.18	7.18	7.08	6.02	7.08
log $\beta_{M'A}$	5.42	5.42	6.37	5.20	5.20	6.20	5.02	5.02	6.02
Δlog $_{MM'A}$	-2.24	-2.55	-0.67	-1.96	-2.38	-0.46	-1.88	-2.28	-0.32
% R.S	-29.7	-33.9	-10.5	-27.2	-33.1	-7.4	-26.5	-32.2	-5.3

log $\beta_{MM'A} = \log K^{MM'}_{MM'A}$; log β MA $= \log K^{M}_{MA}$; log β M′$= \log K^{M'}_{M'A}$

Table-5 : Parameters of best fit chemical model of Mixed metal complex species(1:1:1) in aqueous media

S.No	Type of complex species	log β	NP	SE	SD	Variance	χ^2	Skewness	kurtosis	pH range
1.	Pb-Cd-DMP	10.76	30	0.225	1.23	1.530	4.12	0.676	0.013	3.3-6.4
2.	Hg-Pb-DMP	10.81	27	0.263	1.36	1.875	4.51	1.150	0.731	3.7-6.5
3.	Hg-Cd-DMP	10.28	40	0.143	0.91	0.826	3.13	2.457	7.304	3.3-7.4
4.	Pb-Hg-Glygly	10.24	27	0.248	1.29	1.666	4.23	1.304	1.374	3.7-6.7
5.	Cd-Hg-Glygly	7.34	25	0.192	0.96	0.925	4.23	0.353	0.973	5.9-8.5
6.	Cd-Pb-Glygly	8.62	19	0.199	0.87	0.758	1.58	1.523	2.319	4.7-6.6

log β= overall stability constant ; NP= number of points ; SE=standard error ; SD= standard deviation

V. Conclusion

The analysis of pH vs ‘a’ and species-distribution plots indicates the marked stabilization of the heterobimetallic complexes relative to the binary complexes through simultaneous coordination i.e., the ternary complexes occur in larger concentrations than the binary complexes at higher pH in each of the systems studied.The metals used in present investigation are bivalent usually having coordination number four. The ligands (Glygly/DMP) are tetra/ tridentate in nature respectively.The binding mode of Glygly /DMP ligand (A) in mixed metal ligand [M^{II}-M'^{II}-A] species is similar to its bidentate binding mode in the corresponding binary systems so the metal ion get coordinated to the ligand by two coordination sites, still leaving a vacant coordination site available for interaction with another metal, thus making the formation of mixed metal complex possible and the remaining positions would be occupied by solvent water molecules. The percentage formation of ternary species and values of log $\beta_{MM'A}$ are highest as shown in fig (2.1-2.6) and table- 3 in comparison to the binary species. However, no absolute relation could be established between percentage formation and relative thermodynamic stabilites. It is observed from the table-4 that the values of ΔlogK are positive for M-M′-Glygly [39-40] and negative for M-M′-DMP[8-9] systems which indicates the higher stability of dipeptide ternary complex and less stability for pyrimidine ternary species over binary species.Percent relative stabilization(% R.S)are found to be positive for dipeptide and negative for pyrimidine ternary species indicating that the dipeptide binds stronger in mixed metal (M-M′) system than pyrimidine . The negative value of Δ log K and %R.S attributes to the fact that there are fewer coordination position available on the pyrimidine complex and also less flexibility of pyrimidine than dipeptide ligand.

The metal-ligand stability constant log K decrease with an increase in temperature and ionic strengths.The negative ΔG° in each case indicates that both the dissociation of the ligand and complexation process are spontaneous. The negative value of enthalpy changes (ΔH°) suggest that all the reactions are exothermic. The negative change in entropy (ΔS°) values indicate a highly solvated metal complex while positive values for ΔS° indicate that complexation reactions are entropically favoured under the experimental conditions[41-42].

The ligands selected for the present studies are very good chelating agents which interacted with metal ions to form various metal chelates,thereby,indicating that these can serve as effective antidote in case of mixed metal poisoning. However, invitro studies need to be conducted to confirm the prediction.

Acknowledgement

The authors are highly thankful to Retd.Prof. K.Dwivedi, and Prof. Sanjay Srivastava,HOD,Department of Chemistry, Jiwaji University (M.P.), for providing necessary facilities to complete the paper.

References

[1] P.Rajathirumoni, P.T. Arasu and M.S.Nair, Indian .J.Chem., .31-A,1992, 760.
[2] M.S.Nair, P.T. Arasu and T.L.Fernando, Indian J. Chem., .32-A, 1993,807.
[3] G.K.Mishra, K.P. Dubey and V.Krishna, J. Indian Chem. Soc., 76,1999, 151.
[4] R.N.Patel, R.P.Shrivastava, N. Singh and S.Kumar, Indian J. Chem., 40-A,2001, 361
[5] G.K.Mishra, K.P. Singh and V.Krishna, J. Indian, Chem. Soc., 79,2002, 753.
[6] N.Singh, R.N.Patel, K.K. Shukla and P.K.Singh, Indian J. Chem., 42-A,2003, 1883.
[7] G.K.Mishra, B.K.Shrivastava, I. Dey and V.Krishna, J. Indian Chem. Soc., 82,2005, 421.
[8] Meena Devi, R.Nair, K.Seema Yadav anK.Dwivedi J. Chem. Bio. Phy. Sci. Sec.A. 4(3), 2014 , 1972.
[9] Seema Yadav (Kumari), Pratibha Paliwal (Bhatele),IJSR, . 5 (2),2016,.935-939.
[10] Gurveer Singh Dhaliwal,IJSR 5(5), 2016, 1930- 1933.
[11] L.W. Chang, Toxicol. Sci., 15, 1990,125
[12] H. Nakagowa, M. Tabata, Y. Morikawa, M. Senma, Y. Kitagawa, S. Kawano, T. Kido, Arch. Environ. Health, 45,1990, 283.
[13] R.M. Jacobs, M.R. Spiveryfo, M.H. Aldridge, J. Nutr., 99,1969, 119.
[14] H.A. Schroede, J. Chronic Dis., 18, 1965,647.
[15] T.H. Bui, J. Lindsten, G.F. Nordberg, Environ. Res., 9,1975, 187.
[16] G.A. Drash, Sci. Total Environ., 67,1993, 75.
[17] C. O. Kappe, Tetrahedron, 49, 32,1993, 6937– 6963.
[18] Dogan, A., Ozel, A. D. and Kilic¸ E. Amino Acids,36,2009, 373-379.
[19] Kiani, F., Rostami, A. A., Sharifi, S. and Bahad ,J. Mol. Struct., 956,2010, 20-25.
[20] Udobanes, Bryan, J. Fgner and Marke Berguhutt, J. Tetrahedron Letters, Pergamon, 41, 2713.
[21] Murray, R.K., Granver, P.A., Myes, P.A. and Rodweel, V.W., Honper's Biochemistry (24th E) 1996.
[22] Seema Kumari Yadav, Renu Nair (Ahuja), J.Indian Chem.Soc.,88(10),2011,1599-1603.
[23] Nimmagadda Padmaja & Gollapalli Nageswara Rao, Chemical Speciation and Bioavailability,24(4),2014,234-240.
[24] M.S. Nair & M. Santappa, Indian J. Chem.,20(A),1981,990; J. Chem. Soc., Dalton Trans, 991,981.
[25] D. Chdraborty & P.K. Bhattacharya, J. Chem. Soc., Dalton Trans, 3225, 1990.
[26] T. R. Barman and G.N. Mukherjee ,J. Indian Chem. Soc., 87,2010, 1291-1297.
[27] Divya et.al ,Chem. Sci Rev Lett , vol.1(4),pp201- 208,2013.
[28] More Ashok et.al, Int. J .Chem.Tech Res., Vol. 6 (7),pp.3509-3516 ,2014.
[29] Anjali Sinha, Renu Nair (Ahuja) ,Int.l J. of Innovative Res. in Sci., Engg. & Tech. ,5 (9),2016,16297-16309.
[30] AnjaliSinha,RenuNair(Ahuja) ,IJSR, 5 (10),2016,1067- 1072,2016
[31] S. Ramamoorthy, P.G. Manning, J. Inorg. Nucl.Chem., 34, 1972,1997.
[32] A.E.Martell and R.J.Motekaitis, “The Determination and Use of Stability Constants",VCH,Weinheim,1988
[33] S. Chaberek and A.E. Martell, J. Am. Chem. Soc.,74,1952,5052 .
[34] Chaberek and A.E. Martell, J. Am. Chem. Soc. 77, 1955,1477.
[35] R. Nayan and A.K. Dey, Indian J. Chem. ,14(A), 1976,892.
[36] I.G. Sayce, Talanta, 15, 1968,1397.
[37] I .G. Sayce, Talanta, 18,1971, 653.
[38] I.G. Sayce, and V.S. Sharma, Talanta, 19,1972,831 .
[39] A.M.D.S. Chandrathilaka, O.A. Ileperuma and C.V,. Hettiarachchi, J. Natn. Sci. Foundation Srilanka 41(4),2013,337-344.
[40] JyotsnaGupta,RenuNair(Ahuja)andK.Dwivedi, Int.J.Theoretical&AppliedSciences,7(1),2015,22- 34.
[41] H. Sigel, Cordination Chemistry, Pergamon Press, Oxford, UK,1980.
[42] R Thanavalen G.Manikandan G Ramalingamand ,V.Thanikachalan, Pelagia Res. Library, 2(4) ,2011,9098.

IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Anjali Sinha. “Computer Simulated Equilibrium Studies of Heterobimetallic Complexes of Pb (II), Cd (II) and Hg (II) with Dipeptide and Pyrimidine.” IOSR Journal of Applied Chemistry (IOSR-JAC), vol. 10, no. 9, 2017, pp. 45–52.