

Complexes of hydroxamates IX*: Binary and ternary complexes involved in the systems methioninehydroxamic acid and glycyglycine with Co(II), Zn(II) and Cd(II)

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ABSTRACT

The stability constants of the binary complexes between Co^{2+} , Zn^{2+} or Cd^{2+} (M^{2+}) and methioninehydroxamic acid (MX) were determined by potentiometric pH titration in aqueous solution ($I = 0.15 \text{ M}$, NaCl) at 25°C . The stabilities of the ternary complexes containing glycyglycine (Glygly) in addition were also calculated. The ternary enhancements were determined from K_1 ($\beta_{111k}/\beta_{101i}\beta_{011j}$), K_2 ($\beta_{111k}^2/\beta_{201i}\beta_{021j}$) and K_{22} ($\beta_{2220}/\beta_{1110}$).

Differential pulse polarographic (DPP) techniques were performed to study the reduction properties of these metal ions in the presence of the binary and ternary systems. With the aid of the potentiometric study, differential peaks were assigned to some binary and ternary species. The metal oxidation states (II) were more stable in ternary systems than in binary systems. However, Co(II) systems were not stabilized in the presence of these ligands.

INTRODUCTION

Aminohydroxamic acids and their metal complexes have recently attracted considerable interest due to their involvement in many biological functions (Fishbein *et al.* 1973, Neilands 1973, Munakata 1980, Brown & Chidambaram 1982, Brown *et al.* 1982, Kehl 1982). They have been applied in the treatment of diseases such as urolithiasis (Munakata 1980) and hepatic coma (Fishbein *et al.* 1973). Moreover, they have been examined as tumor inhibitors (Kehl 1982). In addition, their metal chelates were used as suitable oral sources of metals for mammals (Brown & Chidambaram 1982).

Methioninehydroxamic acid, MX, an aminohydroxamic acid, $\text{CH}_3\text{-S-CH}_2\text{CH}_2\text{-CH(NH}_2\text{)CONHOH}$, was found to chelate Fe(III) in solution (El-Ezaby *et al.* 1986). A dimer has been detected in aqueous solution in addition to other monomeric species. In a recent publication (Marafie *et al.* 1992), we have found, from potentiometric study, that MX also has the ability to form mixed metal complexes in solution.

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Table 1. Summary of the experimental conditions of the potentiometric titrations.

System	[ligand] ($\times 10^3$) & (pH range)	[Zn(II)] ($\times 10^3$) & (pH range)	[Cd(II)] ($\times 10^3$) & (pH range)	[Co(II)] ($\times 10^3$) & (pH range)	No. of different runs
MX(binary)	1.0–3.0 M (~4.5–11.0)	1.0–3.0 M (~3.9–11.0)	1.0–3.0 M (~3.2–11.0)	1.0–3.0 M (~4.3–10.5)	8 (Cd=6)*
Glygly (binary)	1.0–3.0 M (~3.0–11.0)	1.0–3.0 M (~2.9–11.0)	1.0–3.0 M (~2.9–9.0)	1.0–3.0 M (~2.8–10.0)	8 (Cd=6, Co=7)*
MX-Glygly (ternary)		1.0–4.0 M (MX) 1.0–4.0 M (Glygly) (~2.9–10.6)	1.0–3.0 M (MX) 1.0–3.0 M (Glygly) (~2.9–11.0)	1.0–3.0 M (MX) 1.0–4.0 M (Glygly) (~2.9–11.0)	6 (Cd=7, Zn=10)*

* Exceptions as indicated.

It has been of interest to investigate whether MX can form polymeric species in the presence of some biological molecules such as glycylglycine. This study can serve as a model for the interaction of metal methioninehydroxamate complexes with proteins such as transferrin.

EXPERIMENTAL

Materials

Solutions of metal salts in the chloride form were prepared in doubly glass distilled water. The concentrations were checked by complexometric EDTA titrations using potentiometric methods as previously described (Moussa *et al.* 1987). Solutions (0.10 M) of the ligands, methioninehydroxamic acid (Sigma; >98%) and glycylglycine (BDH; >99%), were prepared in 0.10 M HCl. The ionic strength of the titrated solutions was adjusted to 0.15 M by the addition of the appropriate amount of 2.0 M NaCl solution.

Measurements

Potentiometric titrations were done using a Metrohm 670 titroprocessor equipped with a Metrohm glass electrode (6.0702.100) and a Metrohm calomel electrode (6.0102.100). The titration cell was thermostatted at $25^\circ \pm 0.10^\circ\text{C}$ by using a Julabo circulator. The electrode system was calibrated by three Schotte-Gerate buffers of pHs 4.01, 6.87 and 9.18. The pH-meter readings were directly used in the calculation of equilibria.

The data were collected by an online IBM personal computer and stored on floppy disks for further processing by the SUPERQUAD program (Gans *et al.* 1985). The pH range used was ~3.0–~11.0. The experimental conditions for the titration sets are given in Table 1.

The polarographic measurements were obtained from Metrohm Polarecord E 506 provided with a three electrode arrangement, including a dropping mercury indicator electrode, a saturated calomel reference electrode, and a counter platinum-wire electrode. The settings of the polarograph were as follows: the voltage range varied between 0.0 and –2.0 V depending on the metal ion under consideration, the pulse amplitude was –40 mV, the drop time was one second, the recorder

speed was 0.5 mm/s, and the temperature of the cell was room temperature ($\sim 23^\circ\text{C}$). The pH range was 2.0–11.0 and was obtained using a Radiometer pH meter type 84 provided with a Russell combination electrode. All solutions were deoxygenated by passing through pure humidified nitrogen before taking the differential pulse polarograms (DPP). The surface of the solution was also kept under the same nitrogen flow during experiments.

Calculations

The stoichiometries and formation constants were simultaneously determined by the SUPERQUAD program (Gans *et al.* 1985).

RESULTS AND DISCUSSION

Potentiometric study

Although the formation constants of some of the binary metal complexes encountered in this work have been previously reported, they have been recalculated under the experimental conditions of this work. Some of the reported constants have been confirmed and other new constants have been calculated. The titration data used to obtain the equilibrium models, using the SUPERQUAD program, have been subjected to various estimates of errors in pH, titration volume, and sometimes in ligand and metal concentrations. For the selected equilibrium models, the standard deviation in the formation constants was within the range of experimental error. By means of an accurate statistical analysis (Gans *et al.* 1985), the following parameters were taken into account for each selected model: the standard deviations (σ) of the stability constants, the agreement factor (σ^2), the goodness of fit (χ_i^2) and the chemical significance of the selected species. The protonation constants of the ligands were kept constant in the binary systems, and the computer program SUPERQUAD was used for the refinement of initially-guessed values of the formation constants of the binary complexes. The same approach has been used in treating the titration data of the ternary systems. In this case, the accepted binary constants were also kept constant when the computer program was employed in the refinement of the initially-guessed values of the ternary constants.

The formation constants of the metal hydroxo species were not included in all models. Moreover, the interaction of various ligands in aqueous solutions were ignored in all calculations, either within or out of the inner sphere of metal complexes. Several equilibrium models for the binary and ternary systems were tested. The models that satisfy the above requirements were adopted, as shown in Tables 2 and 3.

The existence of species with negative values of H for Glygly and MX systems (eg. 1:0:1:-1, 2:0:1:-1, 0:1:1:-1 [(MX:Glygly:M:H)], Tables 2 and 3) have been attributed in the case of Glygly, to the deprotonation of the peptide proton (Margerum & Dukes 1974) and probably to the deprotonation of the NH group in case of MX. The acidity of these groupings is only increased in the presence of metal ions (Fig. 1).

The phenomena of polynuclear complex formation exhibited by MX systems is quite interesting. They are shown for Co(II) and Zn(II) in Table 3, and reported for GX-Cu(II) (Shuaib & El-Ezaby 1995) and MX-Fe(III) (El-Ezaby *et al.* 1986)

Table 2. The formation constants of the binary complexes encountered in the systems MX-Co(II) or Cd(II)/Zn(II) and Glygly-Co(II) or Cd(II)/Zn(II). The stoichiometric coefficients p, q, r, and s stand for the MX, Glygly, Co(II) or Cd(II)/Zn(II) and H⁺ free species at 25°C and I = 0.15 M NaCl.

System	p	q	r	s	Log $\beta(\pm\sigma)$	pH range	σ_D	χ_i^2	No. of data points	Remarks	Reported Log β^*
MX-H	1	0	0	1	9.01 (0.00)	6.5-10.2	0.23	9.5	156		
	1	0	0	2	15.93 (0.00)						
Glygly-H	0	1	0	1	8.11 (0.0)	3.0-9.4	1.67	20.7	161		8.15
	0	1	0	2	11.31 (0.01)						11.31
MX-Zn(II)	1	0	1	0	4.90**	4.7-9.1	1.36	9.7	550	White ppt. at pH's >7.2 for 1:1 ratios	
	1	0	1	1	11.78 (0.02)						
	1	0	1	-1	-2.01 (0.01)						
	2	0	1	0	11.10 (estimated value)						
	2	0	1	2	23.58 (0.03)						
	3	0	2	0	17.64 (0.04)						
MX-Co(II)	1	0	1	0	4.67 (0.05)***	5.9-7.3	1.65	10.6	182	Brown ppt. at pH's >7.3 for 1:1 ratios	
	1	0	1	1	11.50 (0.05)						
	1	0	1	-1	-2.67 (0.07)						
	2	0	1	2	23.14 (0.11)						
	2	0	1	0	9.95 (0.02)						
	3	0	2	0	18.04 (0.04)						
MX-Cd(II)	1	0	1	0	3.22 (0.04)	6.1-10.6	1.93	30.4	514	No ppt.	
	1	0	1	1	11.66 (0.08)						
	1	0	1	-1	-3.37 (0.06)						
	1	0	1	-2	-12.12 (0.06)						
	2	0	1	0	9.10 (estimated value)						
Glygly-Zn(II)	0	1	1	0	3.22 (0.09)	2.9-9.3	1.73	25.5	460		3.44
	0	1	1	1	11.05 (0.04)						9.04
	0	1	1	-1	-4.47 (0.03)						
	0	2	1	0	7.04 (0.05)						6.31
	0	2	1	1	14.98 (0.04)						
	0	2	1	-2	-9.76 (0.09)						
Glygly-Co(II)	0	1	1	0	3.27 (0.01)	2.8-9.1	1.32	24.8	536		3.01
	0	1	1	1	9.32 (0.08)						
	0	1	1	-1	-5.83 (0.02)						
	0	2	1	0	5.18 (0.08)						5.35
Glygly-Cd(II)	0	1	1	0	2.75 (estimated value)	3.0-8.6	0.46	35.0	462		2.86
	0	1	1	1	9.84 (0.07)						9.30
	0	1	1	-1	-6.97 (0.08)						
	0	2	1	0	5.86 (0.01)						5.35
	0	2	1	1	13.78 (0.02)						

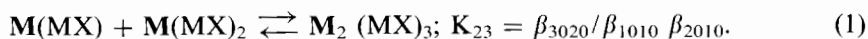
* Munakata *et al.* 1980.**Estimated, Assuming the Coordination Number of Zn²⁺ = 6***Calculated from the 1:1 Composition Ratios of MX : Co²⁺.

systems. These species have been previously reported for other pertinent systems (El-Ezaby *et al.* 1986, Kurzak *et al.* 1986, Leporati 1988, Farkas *et al.* 1989). Since it is believed that the metal ion will select either the nitrogen or oxygen donors of the hydroxamate group to form either a five- or six-membered chelate ring complex, with the amino group, one is left with one or two ligation sites. If the first metal ion coordinate forms a 5-membered chelate, there is a possibility for another metal ion to coordinate with the two other ligating sites to form another 5-membered chelate. This possibility can lead to the formation of the binuclear species 1:0:2:0

Table 3. The formation constants of the ternary complexes encountered in the systems MX-Glygly-Co(II) or Cd(II)/Zn(II). The stoichiometric coefficients p, q, r, and s stand for the MX, Glygly, Co(II) or Cd(II)/Zn(II) and H⁺ free species at 25°C, and I = 0.15 M NaCl.

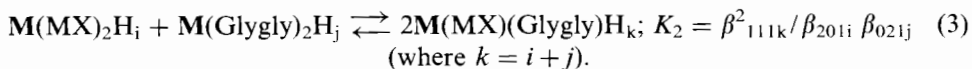
System	p	q	r	s	Log $\beta(\pm\sigma)$	pH range	σ_D	χ_i^2	No. of data points
MX-Glygly-Co(II)	1	1	1	0	8.13 (0.17)	2.9–7.9	1.7	5.8	526
Model I	1	1	1	2	22.05 (0.08)				
	2	2	2	0	20.23 (0.17)				
Model II									
	1	1	1	1	20.71 (0.07)	2.9–7.9	1.6	7.4	526
	1	1	1	2	22.13 (0.06)				
	2	2	2	0	20.14 (0.15)				
MX-Glygly-Zn(II)	1	1	1	0	9.25 (0.07)	5.6–8.2	0.8	15.3	523
	1	1	1	2	23.98 (0.06)				
	2	1	1	2	28.87 (0.07)				
	2	2	2	1	29.75 (0.10)				
MX-Glygly-Cd(II)	1	1	1	0	7.86 (0.04)	3.0–9.1	2.6	30.7	589
	1	1	1	1	15.73 (0.03)				
	2	1	1	0	11.28 (0.15)				
	2	1	1	-1	2.93 (0.12)				

(MX:Glygly:M:H). However, including this species in all equilibrium models of MX systems did not succeed. The formation of polymeric species (3:0:2:0) may arise from the interaction of two binary species in the transition from 1:0:1:0 to 2:0:1:0 such as:



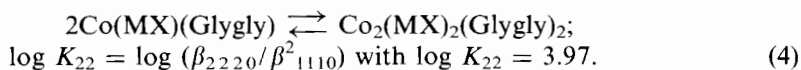
In the above equation, the log *K* value is positive. Other possibilities always lead to negative values.

The ternary enhancement for the 1:1:1:0 species can be appreciated if log *K*'s of the following reactions are calculated:



The values of *K*₁ (1.19, 1.13, and 1.89 for Co(II), Zn(II) and Cd(II)) and log *K*₂ (1.13, 0.36, and 0.76 for Co(II), Zn(II) and Cd(II)) respectively, are always positive and greater than zero when *k* is equal to zero.

The polymerization process encountered in the binary species (Tables 2 and 3) persists in Co(II) and Zn(II) ternary systems. In the case of the Co(II) ternary system, the 2:2:2:0 species could arise from the interactions:



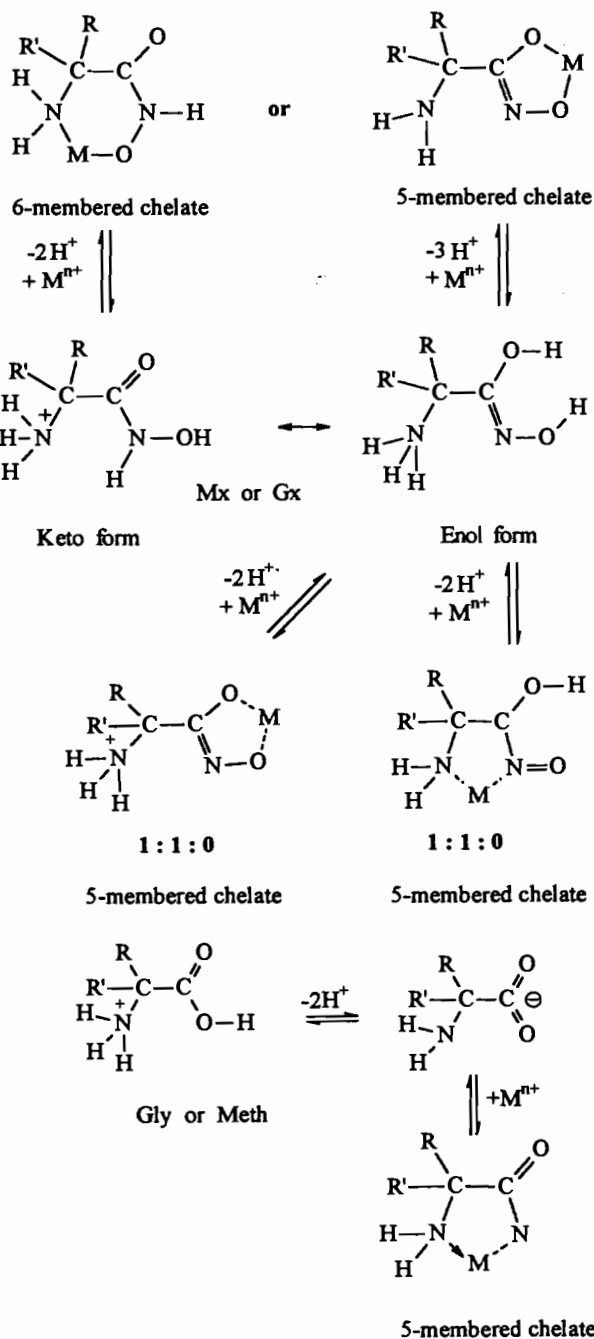
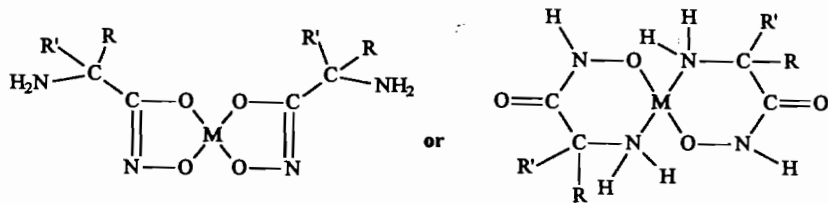


Fig. 1: Schematic diagram of the structural formulae of different ligands and their metal complexes. For glycine, Gly and glycinehydroxamate, GX, R = R' = H and for methionine, Meth methioninehydroxamate, MX, and glycyglycine, Glygly, R = H and R' = -CH₂-CH₂-S-CH₃.



2 : 1 : 0

5-membered chelate

2 : 1 : 0

6-membered chelate

3 : 0 : 2 : 0
(M = Co or Fe)

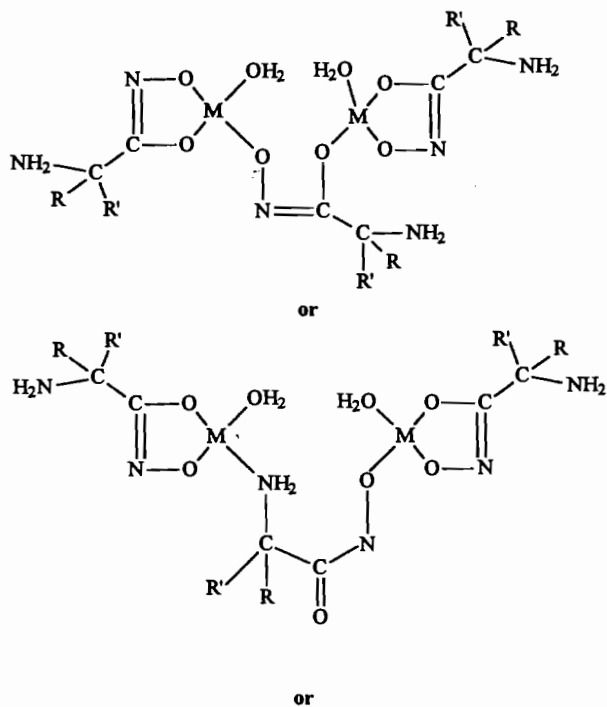
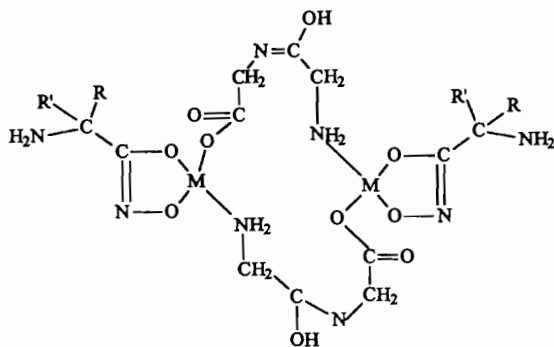
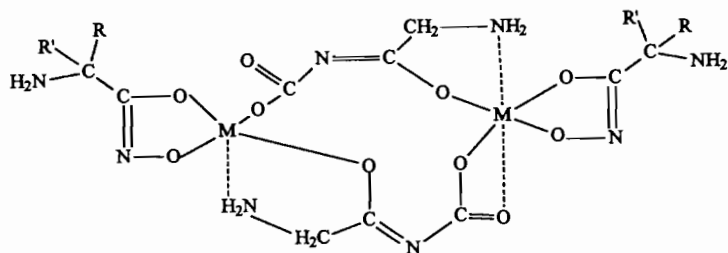


Fig. 1: continued.

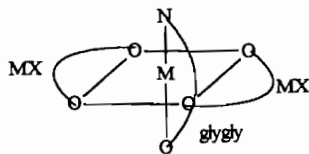
2 : 2 : 2 : r (r = 0 or 1)



or



2 : 1 : 1 : r (r = 0, -1)



or

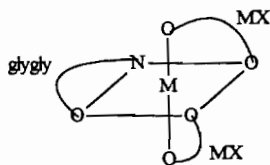


Fig. 1: continued.

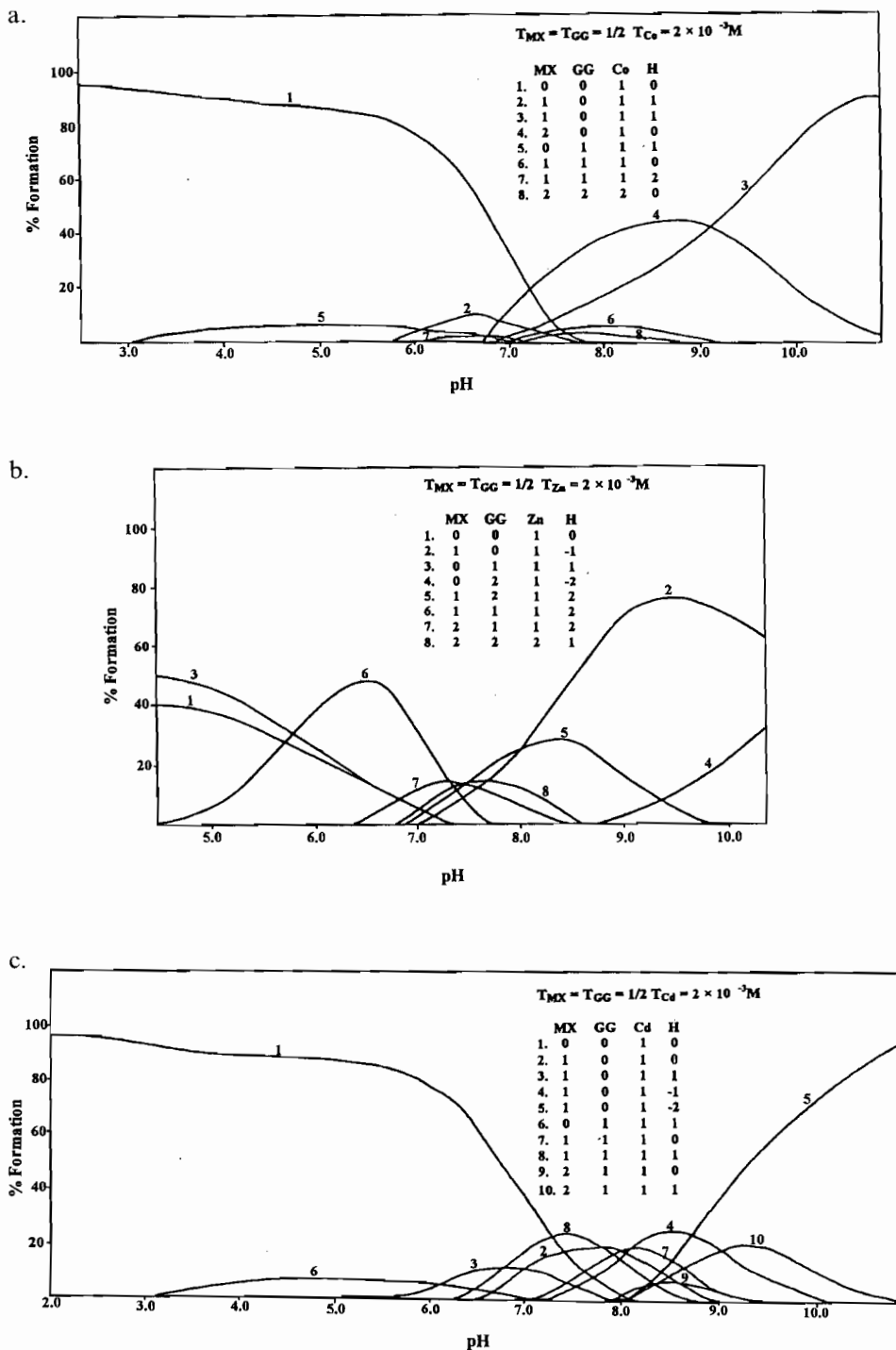


Fig. 2: The distribution curves of the various species in the ternary systems (a) MX-Glygly-Co(II), (b) MX-Glygly-Zn(II), (c) MX-Glygly-Cd(II).

Table 4. The E_{\max} of the metal ions at $\sim 23^\circ\text{C}$ and $I = 0.15\text{ M NaCl}$.

Metal ion	pH range	$-E_{\max}$ (mV)	$W_{1/2}^*$ (mV)
Co^{2+}	$\sim 3.7\text{--}5.0$	1288	136
		1576	160
Zn^{2+}	3.0–5.0	988	60
Cd^{2+}	3.0–7.5	590	56

* Theoretical value of the half-width of the differential wave ($W_{1/2}$) for one electron transfer at -40 mV pulse potential is $\sim 96\text{ mV}$ and for two electrons $\sim 56\text{ mV}$. (Bond 1980).

Ternary complexes involving more than one ligand of the same type are illustrated by the presence of 2:1:1:0 and/or 2:1:1:-1 and 2:1:1:2 species in case of Zn(II) and Cd(II). These species reflect the flexibility of metal ions to adopt coordination numbers in ternary systems higher than in binary systems. This may be interpreted on the basis that ligands in binary systems exercise more steric strain. Fig. 2(a,b,c) shows the distribution of the various species in the ternary systems.

Polarographic study

The differential pulse polagrams (DPP) of the metal ions under consideration are all well defined. Table 4 shows the E_{\max} (the potential at the maximum faradaic current (δ_i)) of these metal ions in 0.15M NaCl. It is clear from the table that only Zn(II) and Cd(II) exhibit reversible waves in the chloride medium. Figure 3 illustrates the effect of pH on E_{\max} . It is commonly accepted that complexing ligands lead to relatively negative shifts in E_{\max} of the metal ions. This has been attributed to the increase in electron density on the metal ion due to delocalization of ligand electrons toward the metal ion in complex formation. In general, this was found to be true for all systems studied except in a few cases in specific pH ranges. These exceptions are encountered in Co(II) systems. This has been rationalised to the delocalization of metal ion electrons toward ligand orbitals in complex formation, leading to an increase in the positive character of the central metal ions. In case of the Co(II) complex systems, the pH at which the positive shift in E_{\max} occurs depends on whether the system is binary or ternary. The affinity of Co(II) for MX is much larger than for Glygly. This is illustrated by the pH at which E_{\max} of the metal ion starts to shift (Fig. 3). This affinity is also reflected in the ternary system; however, the starting pH is different from that of the binary MX-Co(II) system although the concentrations of the ternary species are less than those of the binary species (Fig. 3). DPP is sensitive to environmental changes of the metal ions in solution due to complex formation. Speciation is, however, not feasible in the Co(II) system. As shown in Table 5, the Co(II)-Glygly system exhibits certain reversibilities, especially above pH 7.0.

The DPP of Zn(II) in the presence of Glygly, MX, or both, as a function of pH are shown in Fig. 3. It is clear that Glygly has little effect on the DPP of Zn(II), whereas MX has a significant effect. The DPP of the ternary system is more or less similar to that of the MX-Zn(II) system with the exception that the ternary system has a higher pH of precipitation (Table 5). The DPP of the ternary system is composed of four

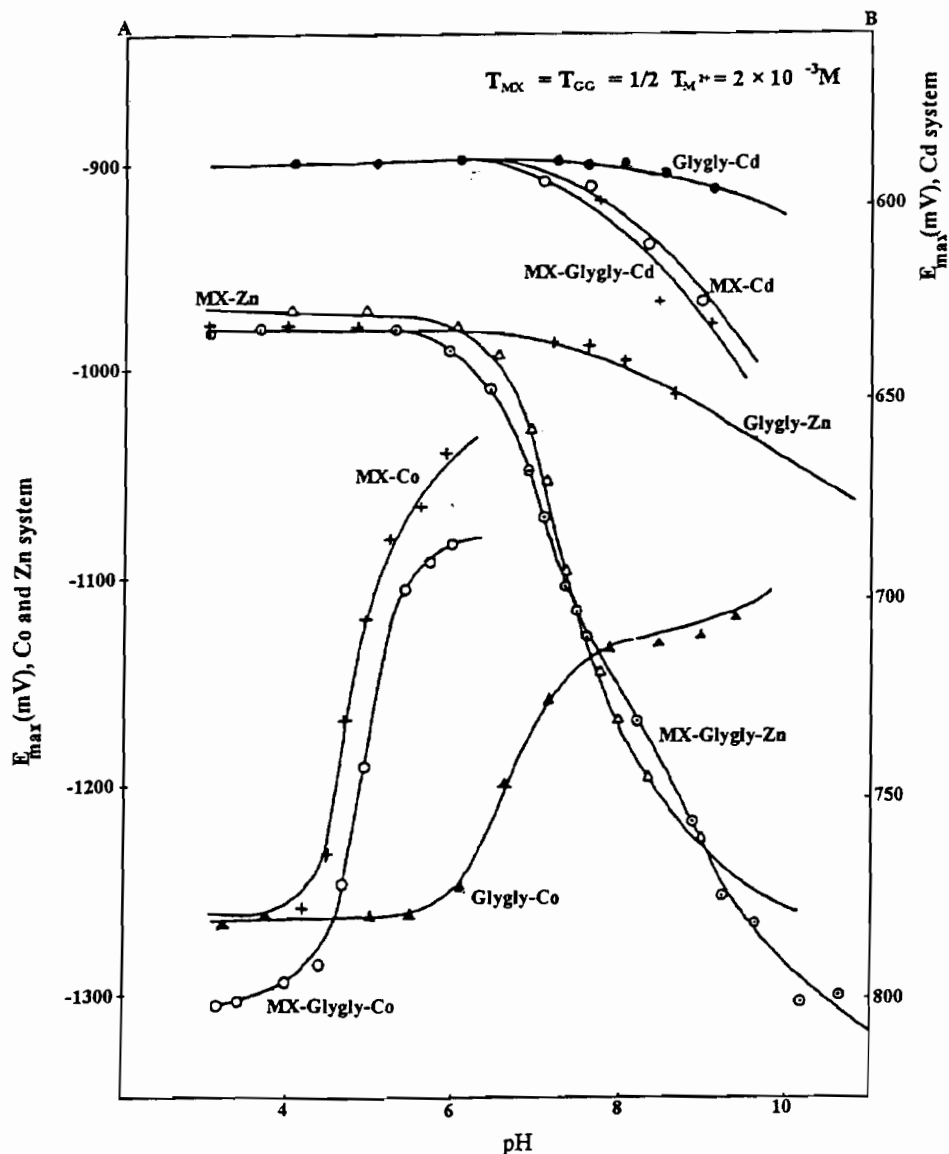


Fig. 3: The effect of pH on E_{max} for Co(II), Zn(II) and Cd(II) systems.

segments. The first is at pH's <5.0 and has a constant E_{max} value, primarily due to the reduction property of free Zn ions. The second is in the pH range 5.0–7.5 and may be assigned to the species 0:1:1:1, 1:1:1:2 and 2:1:1:2. The third segment, which is in the pH range 7.5–9.0, may be due to the reduction of several overlapping species, namely, 1:1:1:0, 2:1:1:2 and 1:0:1:1. However, the fourth segment, which is at pH's above ~9.0, may correspond to the binary species 1:0:1:1 and the ternary species 1:1:1:0.

Table 5. Representative values of E_{\max} and $W_{1/2}^*$ for Co (II), Zn (II) and Cd (II) in presence of MX, Glygly or both at $\sim 23^\circ\text{C}$ and $I = 0.15\text{ M NaCl}$.

Metal Ion	Free Metal Ion (pH range) $-E_{\max}$, $W_{1/2}$	Binary Complexes of Glygly pH, $-E_{\max}$, $W_{1/2}$	Binary Complexes of MX pH, $-E_{\max}$, $W_{1/2}$	Ternary Complexes pH, $-E_{\max}$, $W_{1/2}$
Co(II)	($\sim 3.7-5.0$) 136,160 1288,1576	6.10, 1256, ~ 76 7.11, 1160, ~ 60	Overlapped peaks at pH's > 4.9 4.61, 1192, 216	Overlapped peaks at pH's > 4.6 4.54, 1272, 180
Zn(II)	(3.0-5.0) 988, 60	8.04, 996,74 precipitation at pH's > 9.0	7.91, 1176, ** precipitation at pH's > 9.0	7.70, 1124, ** 10.06, 1480, **
Cd(II)	3.0-7.5 590, 56	8.02, 592, 56	8.32, 610, 70	8.45, 624, 52

*Half-peak width (mV).

** Ill-defined peaks.

The DPP of Cd(II) in the presence of Glygly, MX, or both, as a function of pH are quite similar to those of the Zn(II) systems (Fig. 3). However, the $W_{1/2}$ values of DPP peaks for all systems, except MX-Cd(II), are close to the value obtained for the two-electron reduction process. However, there is no definite peak for each species (Table 5).

One pertinent fact concerning the DPP of these metal ions in the presence of Glygly, MX, or both, needs to be discussed. Most of these systems show peaks with negative δ_i (they should all be positive since the pulse amplitude was -40 mV). Of course this situation mainly depends on the pH and system under consideration. Only Cd(II) systems do not exhibit this behavior. One should add that these peaks are highly reproducible through scanning either to more negative or positive potentials, or from low to high pH, or vice versa. There is, however, no report about this phenomenon and more investigation needs to be carried out to decipher the origin of such peaks. They may be due to an adsorption process of the reduced, oxidized or both forms of the species contents of the solution, either electroactive or non-electroactive, or they may be due to non-faradaic processes, although in principle this kind of process should be totally negligible in DPP except in a few Co(II) complexes.

Conclusion

Although Glygly complexes of Co(II), Zn(II) and Cd(II) are less stable than their MX complexes, the ternary complexes of both ligands are more stable than both binary species in neutral and alkaline media. This fact indicates that hydroxamate complexes can interact with protein as intermediate species in many biological processes involving hydroxamates. In general, most of these intermediate species are stable to reduction in biological media as confirmed by DPP.

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References

- Bond, A. M. 1980.** Modern polarographic methods in analytical chemistry, Marcel Dekker, New York, NY, USA, p.251.
- Brown, D.A., Chidambaram, M.V. & Glennon, J.D. 1980.** Design of metal chelates with biological activity. 2. Solution properties of iron(III) glycine hydroxamate. *Inorganic Chemistry* **19**: 3260–3264.
- Brown, D.A. & Chidambaram M. V. 1982.** Metal Ions in Biological Systems. **Sigel, H., (Ed.)** Marcel Dekker, New York, NY, USA, **Vol. 14.**
- El-Ezaby, M.S., Marafie, H.M., Hassan, M.M. & Abu Soud, H.M. 1986.** Complexes of hydroxamates. Part I. Interaction of methioninehydroxamic acid with iron (III) in aqueous solution. *Inorganica Chimica Acta* **123**: 53–59.
- Farkas, E., Szoke, J., Kiss, T., Kozlowski, H. & Bal, W. 1989.** Complex-forming properties of L- α -alaninehydroxamic acid (2-amino-N-hydroxy propanamide). *Journal of the Chemical Society, Dalton Transactions*: 2247–2251.
- Fishbein, W.N., Streeter, C.L. & Daly, J.E. 1973.** Physiologic disposition of short chain aliphatic hydroxamates in the mouse. II. Absorption, distribution, metabolism, and excretion of acetohydroxamic-1-C-14 acid. *Journal of Pharmacology and Experimental Therapeutics* **186**: 173–182.
- Gans, P., Sabatini, A. & Vacca, A. 1985.** SUPERQUAD: an improved general program for computation of formation constants from potentiometric data. *Journal of the Chemical Society, Dalton Transactions*: 1195–1200.
- Kehl, H. (Ed.), 1982.** Chemistry and Biology of Hydroxamic Acids. Karger, New York, NY, USA.
- Kurzak, B., Kurzak, K. & Jesurska, J. 1986.** Solution properties of Cu(II)- L- α -alaninehydroxamic acid. *Inorganica Chimica Acta* **125**: 77–82.
- Leporati, E. 1988a.** Potentiometric study on complex-formation equilibria between 2-amino-N-hydroxyhexanamide and α -amino-1H-indole-3-N-hydroxypropanamide and Co(II), Ni(II), Cu(II), and hydrogen ions in aqueous solution. *Journal of the Chemical Society, Dalton Transactions*: 421–426.
- Leporati, E. 1988b.** Possible biological activity in proton, metal, and aminohydroxamic acid equilibria. Protonation and complex formation reactions between N-hydroxy-D-asparagine and Co(II), Ni(II), Cu(II), and hydrogen ions in aqueous solution. *Journal of the Chemical Society, Dalton Transactions*: 953–959.
- Marafie, H.M., Makhyoun, M., Al-Salem, N. & El-Ezaby, M.S. 1992.** Complexes of hydroxamates VIII. The affinity of methioninehydroxamic acid for mixed metal complexation potentiometric and polarographic studies. *Electroanalysis* **4**: 611–667.
- Margerum, D.W. & Dukes, G.R. 1974.** Metal Ions in Biological Systems. **Sigel, H. (Ed.)** Marcel Dekker, New York, NY, USA. **Vol. 1.**
- Moussa, N.M., Marafie, H.M., El-Ezaby, M.S. & Rashad, M. 1987.** Complexes of vitamin B₆. XVIII. Ternary and quaternary complexes involving pyridoxamine, glycylglycine and imidazole and some bivalent metal ions. *Polyhedron* **6**: 1477–1482.
- Munakata, K., Kobashi, K.K., Takebe, S. & Hase, J. 1980.** Quantitative structure-activity relationships between hydroxamic acids and their urease inhibitory potency. *Journal of Pharmacobio-Dynamics* **3(9)**: 457–462.
- Neilands, J.B. 1973.** *Inorganic Biochemistry.* **Eichorn, G. (Ed.)** Elsevier Amsterdam, The Netherlands, p. 167.
- Shuaib, N. & El-Ezaby, M.S. 1995.** Complexes of vitamin B₆ – Part XXII. The interaction of vitamin B₆ compounds with Cu(II)-glycinehydroxamic acid binary system. *Polyhedron* **14**: 1965–1979.

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متراكبات الهيدروكساميت

المتراكبات الثنائية والثلاثية للأنظمة ميثايونين حمض الهيدروكساميك و جلايسايل جلايسين
مع أيونات الكوبالت ، الزنك والكادميوم الثنائية

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خلاصة

على الرغم من أن متراكبات الجلايسايل جلايسين الثنائية لأيونات الكوبالت ، الزنك و الكادميوم الثنائية أقل ثباتية من متراكبات ميثايونين حمض الهيدروكساميك فإن المتراكبات الثلاثية لكليهما أكثر ثباتية من الأصناف الثنائية لهما في الوسط المتعادل والقلوي . هذه الحقيقة تثبت إمكانية تفاعل متراكبات الهيدروكساميت مع البروتين كأصناف وسيطة في العمليات البيولوجية التي تشمل على الهيدروكساميت . وبصفة عامة معظم هذه الأصناف الوسيطة ثابتة لعملية الاختزال في الوسط البيولوجي ، كما أثبتت بواسطة طريقة قياس تباين القمم.