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A study of the formation constants of ternary and quaternary complexes of some bivalent transition metals

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Abstract: The formation of hetero-ligand 1:1:1, M(II)-Opda-Sal/Gly ternary and 1:1:1:1, M(II)-Opda-Sal-Gly quaternary complexes, where M(II) = Ni, Cu, Zn and Cd; Opda = *o*-phenylenediamine, Sal = salicylic acid, Gly = glycine, was studied pH-metrically in aqueous medium. The formation constants for the resulting ternary and quaternary complexes were evaluated at a constant ionic strength, $\mu = 0.20 \text{ mol dm}^{-3}$ and temperature, $30 \pm 0.1^\circ \text{C}$. The order of the formation constants in terms of the metal ion for both type of complexes was found to be $\text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Cd(II)}$. This order was explained based on the increasing number of fused rings, the coordination number of the metal ions, the Irving – William order and the stability of various species. The expected species formed in solution were pruned with the Fortran IV program SPEPLOT and the stability of the ternary and quaternary complexes is explained.

Keywords: formation constants; transition metals; salicylic acid; quaternary complexes.

INTRODUCTION

Solution studies on binary and ternary complexes using divalent and trivalent metal ions has been extensively studied.^{1–4} Although the formation of ternary complexes has been very well studied,^{5–7} the formation of quaternary species with transition and inner transition metal ions has been limited to a few papers.^{8–12} Only a few references have reported on quaternary complexes in which the metal ions not only form stable complexes, but also expand their coordination number. The increasing importance of ternary complexes, especially those involving ligands containing functional groups identical to those present in enzymes, viz. $-\text{COOH}$, $-\text{NH}_2$, etc., is obvious from the application of such complexes in many analytical and biological reactions.^{13–14} Diamines, hydroxy acids and amino acids as complexing agent have been widely studied in binary systems^{15–17}

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but hitherto the literature does not corroborate where these ligands are used in combination for either ternary and quaternary systems. In addition, there is no comparative study which was performed on the formation constants of binary (monoligated), ternary (biligated) and quaternary (triligated) complexes of transition metals.

Herein, a comparative solution state electrometric study is reported on ternary (MLL', ML'L'', MLL'') and triligated (quaternary) (MLL'L'') complexes, where M = Cu(II), Ni(II), Zn(II) and Cd(II) metal ions, and L = *o*-phenylenediamine, L' = salicylic acid and L'' = glycine as ligands using the pH-metric technique in aqueous medium at a constant ionic strength $\mu = 0.20 \text{ mol dm}^{-3}$ and temperature $30 \pm 0.1^\circ \text{C}$. The aim was to compare the stabilities of the various species in the solution state. The active forms of the species found in a computer-augmented modeling study were ML, ML₂, ML', ML'', ML₂, ML''₂, ML₂H, MLL', MLL'', ML'L'' and MLL'L''.

EXPERIMENTAL

Employed chemicals

All the chemicals used were of analytical reagent grade. *o*-Phenylenediamine, salicylic acid, glycine and the metal chlorides (Aldrich-USA) were used without further purification. The metal chloride solutions were acidified with accurately known amounts of HClO₄ to prevent hydrolysis. The exact concentrations of the solutions of the lanthanide nitrates were determined by complexometric titration with the disodium salt of EDTA.¹⁸ All solutions were prepared in doubly distilled CO₂-free water. The carbonate-free NaOH solution was standardized by a reported method.¹⁹ Perchloric acid was standardized with a standard NaOH solution and the constant ionic strength was maintained with the inert electrolyte sodium perchlorate (NaClO₄) (Reidel).

Apparatus

Potentiometric titrations were performed using a Systronics μ pH meter 361, having a combined glass electrode and a temperature probe with a readability $\pm 0.1^\circ \text{C}$. The temperature was maintained using a High Precision Water Bath Cat. No. MSW-274 with a readability $\pm 0.1^\circ \text{C}$. The titrations were realized in a specially designed glass cell with a magnetic stirrer under a nitrogen atmosphere to avoid any side reactions. The experimental procedure involved the potentiometric titration of the following sets of solutions:

1. acid titration: perchloric acid (0.20 M, 5.0 ml);
2. first ligand titration (L): perchloric acid (0.20 M, 5.0 ml) + Opda (0.020 M, 5.0 ml);
3. second ligand titration (L'): perchloric acid (0.20 M, 5.0 ml) + Sal (0.020 M, 5.0 ml);
4. third ligand titration (L''): perchloric acid (0.20 M, 5.0 ml) + Gly (0.020 M, 5.0 ml);
5. metal + first ligand titration (ML): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Opda (0.020 M, 5.0 ml);
6. metal + second ligand titration (ML'): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Sal (0.020 M, 5.0 ml);
7. metal + third ligand titration (ML''): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Gly (0.020 M, 5.0 ml);
8. metal + first + second ligand titration (MLL'): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Opda (0.020 M, 5.0 ml) + Sal (0.020 M, 5.0 ml);

9. metal + first + third ligand titration (MLL'"): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Opda (0.020 M, 5.0 ml) + Gly (0.020 M, 5.0 ml);

10. metal + second + third ligand titration (ML'L'"): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Sal (0.020 M, 5.0 ml) + Gly (0.020 M, 5.0 ml);

11. metal + first + second + third ligand titration (MLL'L'"): perchloric acid (0.20 M, 5.0 ml) + metal (0.020 M, 5.0 ml) + Opda (0.020 M, 5.0 ml) + Sal (0.020 M, 5.0 ml) + Gly (0.020 M, 5.0 ml).

The total volume used in each cell was 50 ml and the ionic strength was maintained at 0.20 M (NaClO₄) at the temperature 30±0.1 °C in all sets. The titrations performed with carbonate-free standardized 0.20 M NaOH solution. The carbonate content was checked with a Gran Plot²⁰ and the required correction was made in the input file before using the computer programs.

Calculations

Ligand formation constants. The dissociation constants of o-phenylenediamine ($pK_1' = 4.61$, $pK_2' = 2.81$), salicylic acid ($pK_1' = 9.32$, $pK_2' = 2.31$) and glycine ($pK_1'' = 12.03$, $pK_2'' = 2.93$) were calculated by the method of Irving and Rossotti.²¹ The formation constants were calculated using the BEST computer program; the results were comparable with literature values.²²

Binary formation constants. The binary formation constant were calculated using the BEST program and results were comparable with literature values.²³

Ternary formation constants. The ternary formation constants were calculated using a modified form of the Irving and Rossotti titration technique and equations reported earlier.²⁴

Quaternary formation constants. The formation constants ($\log K_{MLLL''}$) of the quaternary complexes formed by the simultaneous coordination of all the ligands to the metal ion were calculated by the method of Ramamoorthy and Santappa²⁵ from the following expression:

$$K_{MLLL''} = \frac{T_M - (1/3)AX}{(1/3)^4 A^4 X}$$

$$A = \frac{5T_M - T_{OH^-} [H^+]}{3a + 6b}$$

where $a = [H^+]/(K_2 + K_2' + K_2'')$; $b = [H^+]/(K_1K_2 + K_1'K_2' + K_1''K_2'')$; $X = 1 + 3a + 3b$, and K_1 , K_1' and K_1'' are the first dissociation constants and K_2 , K_2' and K_2'' are the second dissociation constants of the selected ligands L, L' and L'', respectively.

RESULTS AND DISCUSSION

The diamine has two protonable -NH₂ groups, salicylic acid two dissociable groups -OH and -COOH, while glycine has one protonable and one dissociable group. Using the Irving and Rossotti method, the pK_a values for diamine, glycine and salicylic acid were calculated and compared with literature values.^{21,22} The nature of the curves was similar for all four metal ions selected in the present study. For the sake of brevity and comparison, only the curves for the binary, ternary and triligated (quaternary) complexes of Cu(II) with the Opda, Sal and Gly systems are discussed in detail and the titration results are presented in graphical form in Fig. 1.

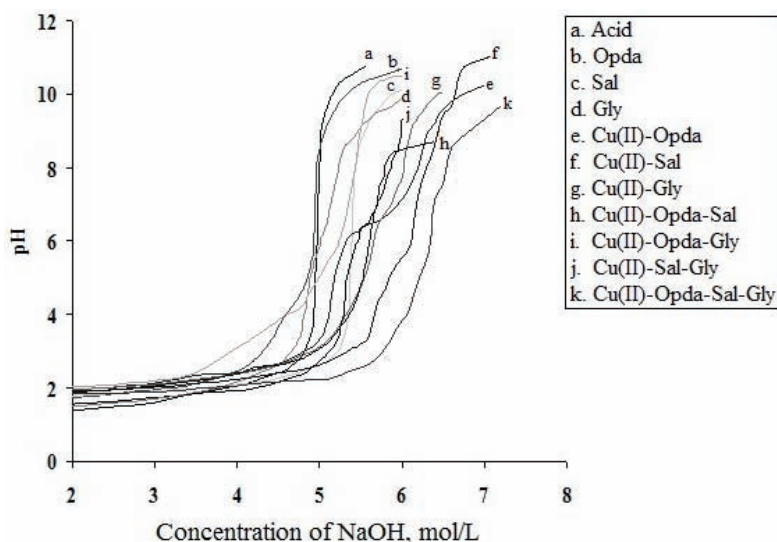
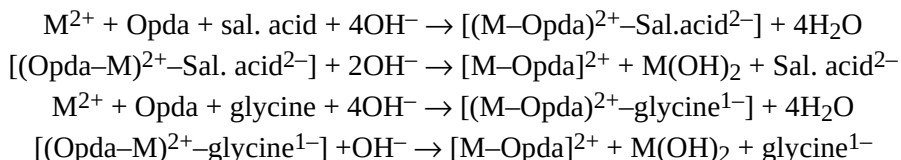


Fig. 1. Representative titration curves for triligated Cu(II)-Opda-Sal-Gly complexes at 30 ± 0.1 °C, $\mu = 0.20$ M (NaClO_4).

A well-defined inflection on curve b at $\text{pH} \approx 2.6$ is due to protonation of ligand L, similarly types of inflection points at $\text{pH} \approx 3.4$ and 5.7 are seen for curves c and d, which are the first dissociation constants for ligand L' and L'', respectively.

Binary systems. Curve e shows an inflection at $\text{pH} \approx 3$, which may be attributed to the 1:1 Cu(II)-Opda binary complex. Another inflection at $\text{pH} \approx 7$ can be attributed to 1:2 Cu(II)-Opda binary complexes. Similar types of inflection curves were obtained for Cu(II)-Gly at $\text{pH} \approx 2.7$ and ≈ 6.5 , and for Cu(II)-Sal at $\text{pH} \approx 2.5$ and ≈ 6.8 , respectively.

Ternary systems. Curve h, representing the titration of 1:1:1 Cu(II)-Opda-Sal species, gives an inflection at $\text{pH} \approx 3.0$, showing the formation of the 1:1:1 ternary complex in the lower pH range. Curve i depicts the titration of Cu(II)-Opda-Gly system. The inflection at $\text{pH} \approx 3.5$ indicates complexation of the metal ion with both ligands and the formation of ternary complexes. A precipitate appeared at $\text{pH} \approx 7.0$. The reactions for the formation of 1:1:1 ternary complexes are presented below:



A well-defined separation of curve j from curve f indicates the formation of 1:1:1 Cu(II)–Gly–Sal. Another inflection at pH 5.5 on curve (j) indicates disproportionation of the initially formed ternary complex at higher pH values.

Quaternary systems. Curve k represents the titration of the 1:1:1:1 Cu(II)–Opda–Sal–Gly quaternary system. An initial lowering of the pH value as compared to the binary and ternary systems and the separation at pH ≈ 2.2 represents the simultaneous addition of three ligands to the metal ion whereby 1:1:1:1 mixed ligand complexes are formed. The calculated values of the formation constants for the ternary and quaternary complexes and the corresponding free energies of formation are presented in Table I. The relative stabilities of the resulting quaternary species $\log K_{LL'L''}$ in terms of the metal ions have the following order: Cu(II) > Ni(II) > Zn(II) > Cd(II), which is the same as in earlier observations.²⁶ This order can be explained based on the decreasing size and increasing ionic potential (charge/ratio) of the transition metals. The higher stabilities of the quaternary complexes compared to the ternary ones can be attributed to the increased number of fused rings and extra-stabilization caused by ligand–ligand interactions in the quaternary complexes.

TABLE I. Formation constants and free energies of formation of ternary (1:1:1) and triligated (1:1:1:1) complexes of M(II) ions at 30 ± 0.1 °C and ionic strength, $\mu = 0.20$ M (NaClO₄)

Metal ions	1:1:1, M(II)-Opda-Sal/Gly				1:1:1:1 M(II)-Opda-Sal-Gly	
	Sal		Gly			
	log $K_{MLL'}$	ΔG / kcal mol ⁻¹	ΔG / kcal mol ⁻¹	log $K_{MLL'}$	log $K_{MLL'}$	ΔG / kcal mol ⁻¹
Cu(II)	9.27	-1.34	-1.15	6.75	10.07	-1.39
Ni(II)	8.34	-1.26	-1.05	5.68	8.94	-1.32
Zn(II)	8.20	-1.27	-1.06	5.81	8.93	-1.31
Cd(II)	7.224	-1.19	-1.04	5.66	8.92	-1.32

The constancy of the calculated values of the stability constants observed in the region of the formation of the quaternary complex supports the formation of mixed ligand complexes. The almost negligible values of the percentage dissociation of the second proton of salicylic acid (0.99 %) and glycine (0.20 %) in the lower pH range (2.5–3.2), evaluated by the method of Serjent,²⁷ indicate that salicylic acid and glycine behave as monobasic acids and their second proton is liberated at pH > 5.

Species distribution diagrams

The various expected species of stoichiometric triligated systems are: LH, LH₂, L'H, L'H₂, L''H, L''H₂, MLH, ML, ML₂, ML'H, ML', ML'₂, ML''H, ML'', ML''₂, MLL', MLL'', ML'L'', MLL'L'' and these were assumed in different chemical models. The species distribution diagrams for all the systems under investigation were obtained for different metal to ligand ratios in solutions using the va-

lues of the calculated formation constants in the BEST fit chemical model, which supports the formation and stability of 1:1:1:1 MLL'L'' quaternary complexes.

In order to demonstrate these quantitative trends, the species distribution diagram obtained in a 1:1:1:1 solution of M(II), diamine (L), salicylic acid (L') and glycine (L'') is shown in Fig. 2. The possibility of hydroxo and polynuclear species was also tested and detected by use of the SPEPLOT computer program.²⁸ The concentration of MLL'L'' species was 70 % for M(II)-Opda-Sal-Gly triligated systems. The negative values of the free energies of formation also supported the spontaneity of the reactions in the formation of the complexes.

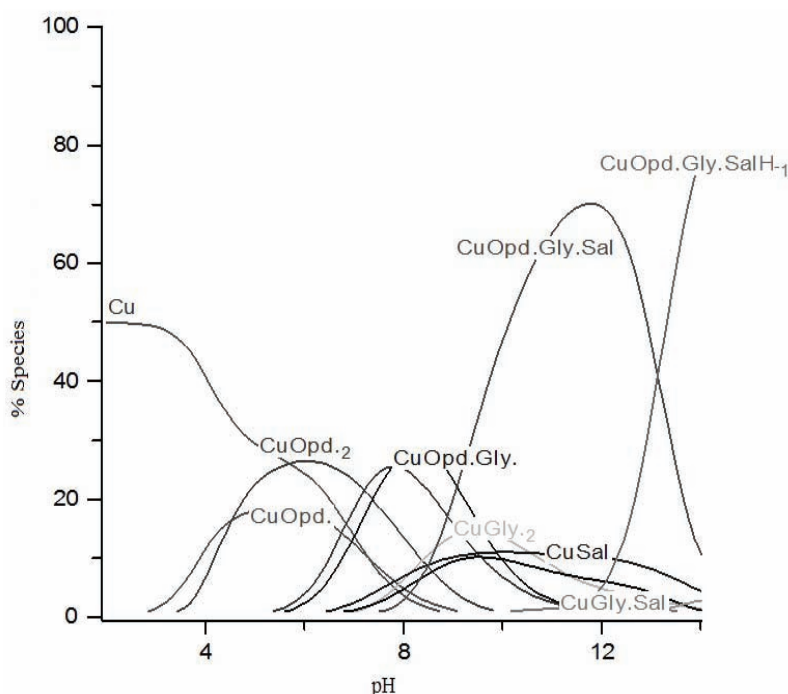


Fig. 2. Species distribution diagram for triligated Cu(II) Opda-Sal-Gly complexes at 30 ± 0.1 °C, $\mu = 0.20$ M (NaClO_4).

CONCLUSIONS

The stability of all the analogous complexes was in the order of $\text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Cd(II)}$ as anticipated from the increasing charge density along the transition metal series. In term of complex species, the order was quaternary $>$ ternary, which can be explained based on the increased number of fused rings and the extra stabilisation caused by ligand-ligand interactions.

ИЗВОД

ПРОУЧАВАЊЕ КОНСТАНТИ НАСТАЈАЊА ТЕРНЕРНИХ И КВАТЕРНЕРНИХ КОМПЛЕКСА НЕКИХ ДВОВАЛЕНТНИХ ПРЕЛАЗНИХ МЕТАЛА

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Пехаматријски је изучавано настајање хетеролиганд 1:1:1 M(II)-Opda-Sal-Gly тернерних, односно 1:1:1:1 M(II)-Opda-Sal-Gly кватернерних комплекса у воденој средини, где је M(II) = Ni, Cu, Zn и Cd, а Opda = *o*-фенилендиамин, Sal = салицилна киселина, Gly = глицин. Константе настајања за добијене тернерне и кватернерне комплексе процењене су на константној јонској јачини $\mu = 0,20 \text{ mol dm}^{-3}$ и температури од $30 \pm 0,1 \text{ }^\circ\text{C}$. Редослед константи настајања у односу на металне јоне за оба комплекса је био Cu(II) > Ni(II) > Zn(II) > Cd(II). Он је објашњен на основу Irving-William-овог редоследа заснованог на повећању броја кондензованих прстенова, координационог броја металних јона, редоследа и стабилности разних врста. Очекиване врсте настале у раствору су обрађене програмом SPEPLOT Fortran-a IV и објашњена је стабилност тернерних и кватернерних комплекса.

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