Original Article

http://www.bpasjournals.com/chemistry
DOI: 10.5958/2320-320X.2021.00014.5

Bulletin of Pure and Applied Sciences.
Vol.40 C (Chemistry), No.2
July-December, 2021: P.81-89
Print version ISSN 0970 4620
Online version ISSN 2320 320X

Study of Ternary Complexes of Co(II), Ni(II) and Cu(II) with L-Histidine and 1, 10-Phenanthroline in 1-Propanol-water Mixtures

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Received on 12.09.2021
Accepted on 28.11.2021

ABSTRACT

The ternary systems of Co(II), Ni(II), and Cu(II) complexes containing L-Histidine as primary ligand and 1,10-Phenanthroline as secondary ligand are studied in aqueous medium mixed with different amounts of 1-propanol. Through pH metric technique the stability constants were obtained for the complexes formed at 303K and ionic strength of 0.16 mol / L maintained with NaCl. The predominant species detected are MLXH and ML_2X which were refined by using the computer program MINIQUAD75. The best-fit chemical models were selected Based on statistical parameters. The relative stabilities of the ternary complexes as well as the distributions of all the complexes in solution were explained.

Keywords: Mixed-Ligand complexes, L-Histidine, Phen, Stability Constants, MINIQUAD75.

How to cite this article: Krishnamurthy, P.P., Vandana, A., Pulipaka, S. & Gollapalli, N.R. (2021). Study of Ternary Complexes of Co(II), Ni(II) and Cu(II) with L-Histidine and 1, 10-Phenanthroline in 1-Propanol-water Mixtures. *Bulletin of Pure and Applied Sciences-Chemistry,* 40C (2), 81-89.

INTRODUCTION

L-Histidine is an essential amino acid that also contributes to the citric acid cycle. Neutral histidine is a common coordinating ligand for all transition metals due to its diverse chemistry and pH sensitivity in the physiologically relevant range. It is used as an active site by many enzymes and biomolecules, including superoxide dismutase, ferritin, iron uptake regulation protein-FUR, ceruloplasmin, haemoglobin, metallothionein, and cysteine dioxygenase [1-3]. The imidazole group of histidine is the primary metal ion binding member in all of these proteins. Phenanthroline (1,10-Phenanthroline) is a bidentate ligand that forms strong complexes with a variety of metal ions. The solubility of the neutral species in water is minimal due to the hydrophobicity of aromatic rings in Phen, but it dramatically rises in organic solvents and aqua-organic combinations. Phen has been shown to be physiologically active [4] when used alone or in combination with metal ions.

Trace elements are the small quantities of mineral elements found in both plant and animal tissues. Iron, zinc, manganese, selenium, chromium, copper, cobalt, nickel, molybdenum, and iodine are just a few of the trace elements that meet these requirements. Many of them, known as metalloenzymes [5], work as catalysts in a variety of enzymatic functions. Cobalt is required for the formation of red blood cells. No metal ion antagonism involving cobalt has been reported and no ion other than cobalt has been discovered complexed with the Corrin ring in nature. The effects of cobalt and manganese on rat liver enzymes were investigated [6]. Nickel is abundant in nature, accounting for around 0.008% of the earth's crust. Nickel compounds that are insoluble in water may dissolve in biological fluids [7]. Certain foods, such as meat, eggs, poultry, nuts, seeds, and cereals, contain more copper than others. 2 mg/d [8] is the human adult requirement. Copper is found in the body of an adult at a concentration of 100-150 mg.

1-Propanol, with the chemical formula C_3H_7OH, is a fundamental kind of alcohol. Propan-1-ol, n-propyl alcohol, 1-propyl alcohol, or n-propanol are all other names for this colourless liquid. Catalytic hydrogenation of propionaldehyde is the most common way to prepare it in the industrial world. During fermentation, minor amount of this alcohol is produced naturally. Apart from influencing the development and antibiotic production of an industrial strain of Streptomyces erythreus under varied nutritional conditions [10], n-propanol is mostly employed as a solvent in many industries and in pharma, primarily for resins and cellulose esters [9].

MATERIALS AND METHODS

To improve the solubility of L-Histidine and Phen (Merck, India), solutions (0.05 mol L^{-1}) were prepared in triple-distilled deionised water while maintaining a 0.05 mol L^{-1} hydrochloric acid. 1-Propanol (Merck, India) was utilised exactly as it was received. To maintain the titrand's ionic strength, 2 mol L^{-1} concentration of Sodium Chloride (Merck, India) was prepared. 0.4 mol L^{-1} concentration of sodium hydroxide (Merck, India) and 0.2 mol L^{-1} concentration of hydrochloric acid (Merck, India) was prepared. Co(II), Cu(II), and Ni(II) chlorides of 0.05 mol L^{-1} concentration of solutions were made by dissolving G.R. Grade (Merck, India) salts in triple-distilled water while maintaining acid concentration of 0.05 mol L^{-1}, to prevent metal salt hydrolysis. Standard approaches were used to standardize all of the solutions. The data were subjected to analysis of variance of one way classification [11] to assess any mistakes that may have slipped into the concentration determination. The Gran plot method [12,13] was used to determine the alkali and mineral acid strengths.

Procedure

Using a 905 Titrando Metrohm type-Auto titrator (readability 0.001) and a Teflon stirrer with mechanical stirring, pH measurements of the metal-ligand system were carried out in aqueous media containing varying compositions of organic solvent (1-Propanol) in the range of 0–60% v/v while maintaining an ionic strength of 0.16 mol L^{-1} with sodium chloride at 303.0 ± 0.1 K. For several days, the glass electrode was equilibrated in a well-stirred 1-Propanol-water mixture (0–60% v/v) containing inert electrolyte. The effect of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of the glass electrode was accounted for in the form of correction factor [14-16].

Mixed-Ligand complexes

Titrations were performed with sodium hydroxide in the presence of various ratios of metal ions (M) to primary (His, L) to secondary (Phen, X) ligands (M:L:X = 1:2.5:2.5, 1:2.5:5.0, 1:5.0:2.5). Other conditions are similar to those already mentioned [17]. Table 1, shows the actual concentrations of each of the ingredients. A preliminary investigation of alkalimetric titrations of mixtures of His and Phen, in different mole ratios, in the presence of mineral acid and inert electrolyte confirmed that these two ligands do not form any condensed species.

Table 1: Total initial concentrations of ingredients (in mmol) for mixed ligand titrations in organic solvent-water mixtures. [NaOH] = 0.4 mol L^{-1}; V0 = 50 mL; Temperature = 303 0.1K; Mineral acid = 1.0 mmol; μ = 0.16 mol L^{-1}.

% V/V 1-Propanol	TM_0			TL_0		M:L:X
	Co(II)	Ni(II)	Cu(II)	His	Phen	
0.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5
10.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5
20.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5
30.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5
40.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5
50.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5
60.0	0.099	0.099	0.099	0.25	0.25	1:5:5
				0.25	0.50	1:5:10
				0.50	0.25	1:10:5

RESULTS AND DISCUSSION

The possible primary and secondary ligand forms and resulting ternary complex species are given in Table 2.

Table 2: Some of the possible ternary complex species of M(II)-His-Phen system.

Constraints imposed:

1. Maximum number of primary ligand = 2
2. Maximum number of secondary ligand = 2
3. Primary + Secondary ligands = 3

S. No.	Ligand form		Ligand number		
	Primary	Secondary	2	3	
1	LH_3	XH	$MLXH_2$	ML_2XH_4	MLX_2H_2
2	LH_2	XH	MLXH	ML_2XH_2	MLX_2H
3	LH	XH	MLX	ML_2X	MLX_2

Selection of best fit models

The shift in the precipitation point of mixed ligand systems compared to the binary systems provided qualitative evidence for the development of mixed ligand complexes. The pH for precipitation of mixed ligand systems was found to be higher in all of these systems than in any of the binary systems. In testing several chemical models with the MINIQUAD75 program [18], the formation constants for acido-basic equilibria of both primary and secondary ligands, as well as those for binary metal complexes, were fixed. Different models were created using all of the species listed in Table 2. The models were tested based on the simultaneous existence of various species combinations. The expert system CEES [19] was used to create models with various numbers and combinations of species, which were then refined using MINIQUAD75. An extensive modelling research was used to determine the presence of these species. The models were tested based on the simultaneous existence of various species combinations. The models produced better statistical data indicating the best fit as the number of species rose. This shows that the final model fits the experimental data appropriately. For ternary complexes of His and Phen with Co(II), Ni(II), and Cu(II) in 1-Propanol-water mixtures, such extensive modelling was undertaken, and the final models are listed in Table 3.

Table 3: Parameters of best-fit chemical models of ternary complexes of His and Phen with Co(II), Ni(II) and Cu(II) in 1-Propanol-water mixtures. Temperature =303K, Ionic strength =0.16 mol dm^{-3}

%v/v OL	Log β_{mlxh} 1111	1210	NP	U_{corr}	χ^2	Skewness	Kurtosis	R-Factor	pH range
Co(II)									
0	21.047 (370)	-	30	2.2225	10.53	-0.33	2.64	0.265	2.8-4.0
10	21.684 (552)	24.251 (516)	26	1.8529	20.00	0.45	5.30	0.098	2.9-8.0
20	21.784 (427)	24.440 (436)	28	2.0429	28.86	0.87	6.56	0.102	2.8-8.0
30	21.854 (533)	25.048 (702)	32	4.6961	45.13	1.62	9.42	0.158	2.8-8.0
40	21.776 (482)	24.976 (619)	31	4.1093	35.61	0.97	7.13	0.148	2.8-8.0
50	21.887 (512)	24.486 (505)	28	1.9880	29.86	0.89	6.78	0.101	2.8-8.0
60	21.966 (541)	25.242 (721)	32	4.8316	46.75	1.71	9.88	0.160	2.8-8.0
Ni(II)									
0	20.957 (828)	-	21	3.9258	29.71	-0.61	5.86	0.117	2.5-5.0
10	21.457 (451)	23.899 (223)	25	5.9745	58.56	-0.81	7.59	0.151	2.5-5.0
20	21.755 (456)	24.180 (507)	25	2.1998	16.16	0.32	4.57	0.107	2.9-6.0
30	21.613 (399)	24.077 (487)	30	3.0429	27.73	0.86	6.38	0.123	2.8-6.0
40	21.780 (450)	24.434 (456)	28	2.0467	28.86	0.87	6.55	0.103	2.8-8.0
50	21.851 (546)	25.046 (731)	32	4.6976	45.13	1.62	9.42	0.158	2.8-8.0
60	21.964 (617)	25.334 (926)	32	3.8996	36.75	0.99	7.41	0.144	2.8-8.0
Cu(II)									
0	21.369 (716)	-	30	3.5679	42.00	-0.52	5.87	0.131	2.8-6.0
10	21.612 (222)	24.929 (671)	30	5.8871	76.00	1.20	6.98	0.183	2.8-6.0
20	21.683 (392)	24.512 (506)	32	2.8370	29.50	0.56	4.76	0.122	2.8-6.0
30	22.038 (354)	24.775 (447)	30	1.8459	43.47	0.19	4.84	0.098	2.8-6.0

40	22.075 (421)	25.182 (493)	31	2.4974	28.13	1.06	6.03	0.116	2.8-8.0
50	22.199 (395)	24.393 (480)	30	1.8948	38.67	0.39	4.87	0.100	2.8-8.0
60	22.156 (390)	25.300 (482)	32	3.2627	32.13	1.08	6.09	0.133	2.8-6.0

Effect of systematic errors

By minimizing random errors in the data, the computer programs refine the stability constants. However, if there are significant systematic errors, not just β's in error, but even some species may be rejected. MINIQUAD75 has no provision to vary the dangerous parameters. Pessimistic errors are introduced in influential parameters such as alkali, mineral acid, ligands and metal ion concentrations in order to rely on the best-fit chemical model for critical evaluation and compilation. This study is beneficial because the data are collected under a variety of experimental circumstances with varying accuracies. The effect of errors in the concentrations of ingredients (Table 4) is as follows.

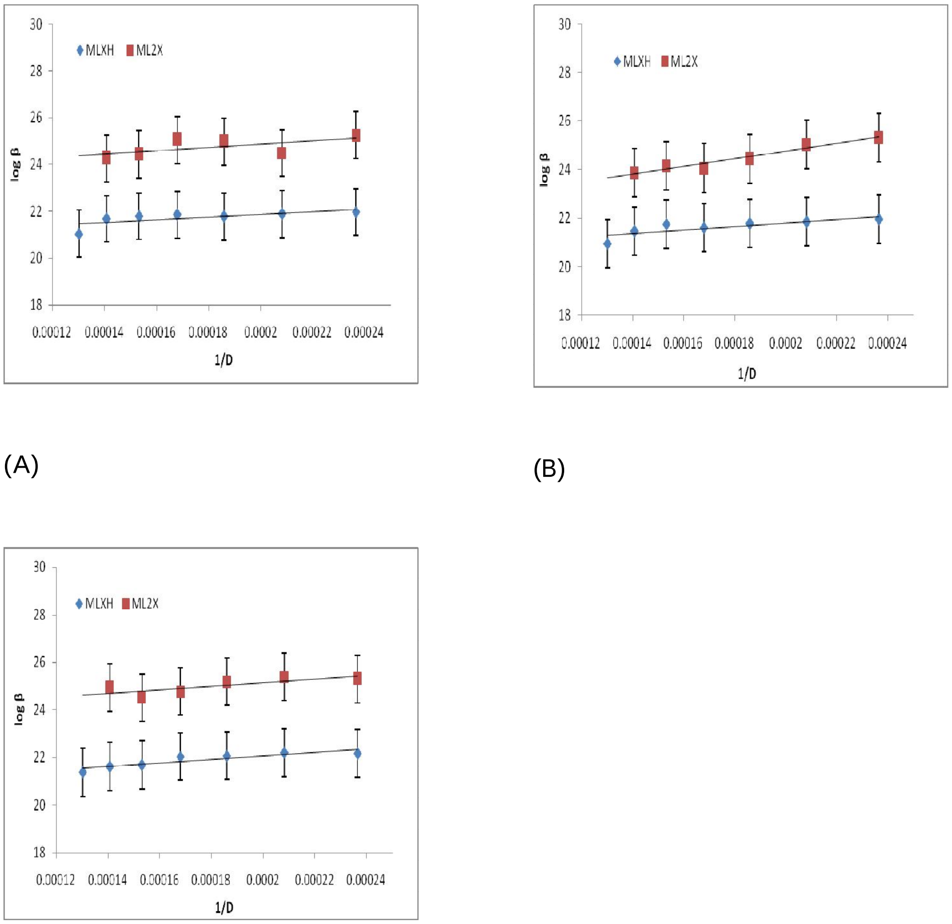
alkali > acid > metal > Phen > His

Table 4: Effect of errors in influential parameters on the stability constants of ternary complexes of Co(II) with L-Histidine and Phen in 30.0% v/v 1-Propanol-water mixture

Ingredient	% Error	MLXH	ML_2X
Acid	-5	Rejected	Rejected
	-2	Rejected	Rejected
	0	21.854 (533)	25.048 (702)
	2	21.697 (516)	24.602 (685)
	5	20.935 (559)	Rejected
Alkali	-5	21.082 (675)	Rejected
	-2	21.695 (460)	24.432 (610)
	2	Rejected	Rejected
	5	Rejected	Rejected
Ligand (L)	-5	22.214 (795)	25.824 (340)
	-2	21.905 (794)	25.180 (441)
	2	21.704 (680)	24.741 (968)
	5	21.630 (605)	24.583 (761)
Ligand (X)	-5	21.698 (559)	24.802 (699)
	-2	21.719 (620)	24.826 (832)
	2	21.889 (534)	25.087 (723)
	5	21.937 (595)	25.145 (893)
Metal	-5	21.705 (662)	24.768 (911)
	-2	21.739 (623)	24.830 (855)
	2	21.863 (621)	25.065 (917)
	5	21.890 (553)	25.118 (767)

Effect of Dielectric Constant of Medium

1-Propanol is a versatile polar protic and a combination of protic and protic solvents with a wide range of dielectric constants and observing good solubility of both polar and non-polar solvents. The trends of the stability constant ($\log \beta$) values of the mixed ligand complexes with 1/D (D is the dielectric constant of the medium) of 1-Propanol-water media is given in Fig. 1. The linear trend indicates that either the dielectric constant or the long range interactions are responsible for the trend in stability. This linear increase in log β values indicates the dominance of the structure-forming nature of 1-Propanol over the complexing ability. The minor divergence of the linear relationship is due to the cation stabilising character of co-solvents, specific solvent-water interactions, charge dispersion, and specific interactions of co-solvent with solute (shown by differences in the solubility of various species in aqua-organic mixtures).



(A)

(B)

(C)

Figure 1: **Variation of magnitude of stability constant (log β) of ternary complexes of L-Histidine-Phen with 1/D of 1-Propanol-water mixtures: (A) Co(II), (B) Ni(II) and (C) Cu(II): (■) logβML2X, (◆) logβMLXH.**

The distribution diagrams (Fig. 2) were drawn using the formation constants of the best fit model. They reveal the dominance of ternary species over binary complexes due to the extra stability of the ternary complexes. Distribution of MLXH is high at lower pH and as pH increases ML_2X species is more predominant and stable. MLXH must have formed through equilibria represented in Eqs. 1-4. ML_2X species might have been formed by the interaction of M(II) with various forms of L and X (Eqs. 5-7), by the interaction of $MLXH^{2+}$ with LH_2^+species (Eq. 8) or by the interaction of protonated binary complexes with XH^+(Eqs. 9, 10).

$$M(II) + LH_3^{2+} + XH^+ \rightleftharpoons MLXH^{2+} + 3H^+ \qquad \text{-------(1)}$$

$$M(II) + LH_2^{+} + XH^+ \rightleftharpoons MLXH^{2+} + 2H^+ \qquad \text{-------(2)}$$

$$M(II) + LH + XH^+ \rightleftharpoons MLXH^{2+} + H^+ \qquad \text{-------(3)}$$

$$MLH^{2+} + XH^+ \rightleftharpoons MLXH^{2+} + H^+ \qquad \text{-------(4)}$$

$$M(II) + 2LH_3^{2+} + XH^+ \rightleftharpoons ML_2X + 7H^+ \qquad \text{-------(5)}$$

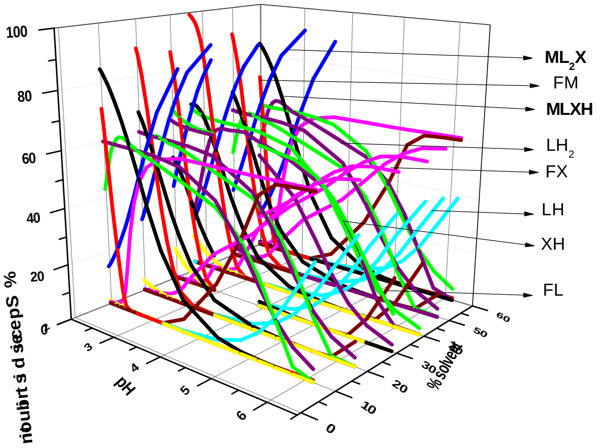
$$M(II) + 2LH_2^{+} + XH^+ \rightleftharpoons ML_2X + 5H^+ \qquad \text{-------(6)}$$

$$M(II) + 2LH + XH^+ \rightleftharpoons ML_2X + 3H^+ \qquad \text{-------(7)}$$

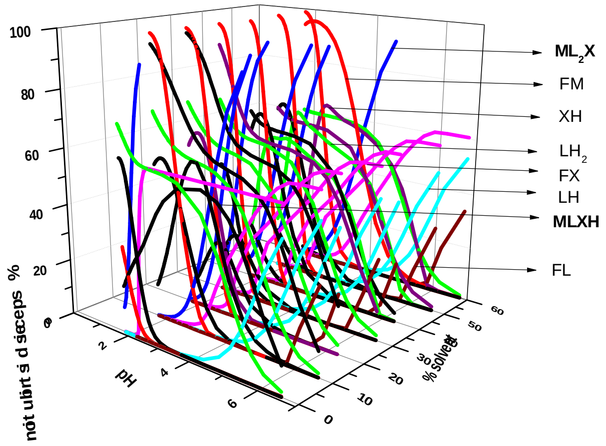
$$MLXH^{2+} + LH_2^{+} \rightleftharpoons ML_2X + 2H^+ \qquad \text{-------(8)}$$

$$ML_2H_2^{2+} + XH^+ \rightleftharpoons ML_2X + 3H^+ \qquad \text{-------(9)}$$

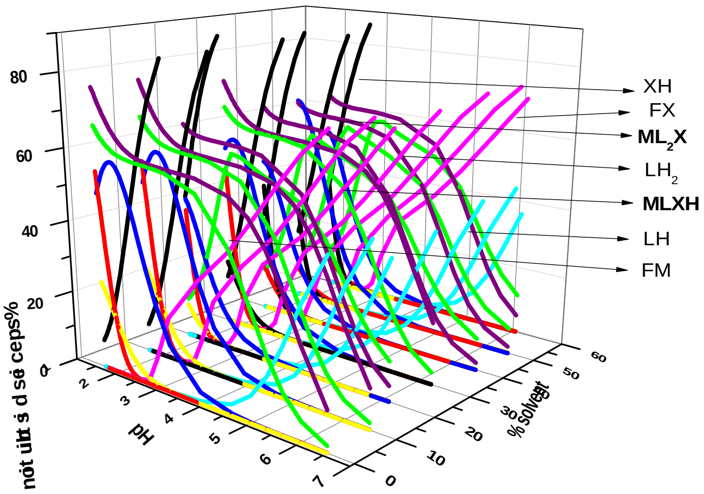
$$ML_2H^{+} + XH^+ \rightleftharpoons ML_2X + 2H^+ \qquad \text{-------(10)}$$



(A)



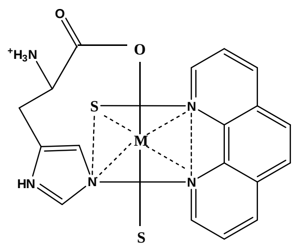
(B)



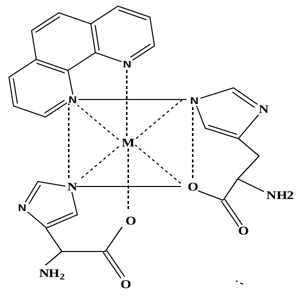
(C)

Figure 2: **Species distribution diagrams of ternary complexes of M(II)-His-Phen in 1-Propanol-water mixture. (A) Co(II), (B) Ni(II) and (C) Cu(II).**

Structures of ternary complexes: The possible structures (Fig. 3) of the complexes proposed are based on the nature of the metal ions and the active sites of ligands (His and Phen).



MLXH



ML₂X

Figure 3: Suggested structures of M(II)-His-Phen complexes, where S is either solvent or water molecule and M= Co(II), Ni(II) or Cu(II).

CONCLUSIONS

The following conclusions have been drawn from the modeling studies of the ternary complexes of Co(II), Ni(II) and Cu(II) with L-Histidine and Phen in 1-Propanol–water mixtures.

1. The mixed-ligand complex species detected are ML_2X, MLXH for all the three metals Co(II), Ni(II) and Cu(II) Where L = L-Histidine and X = Phen.
2. The linear increase in the stabilities of the ternary complexes with a decrease in the dielectric constants is due to the dominance of the electrostatic forces.
3. The linear variation of stability constants as a function of 1/D of the medium indicates the dominance of electrostatic forces over non-electrostatic forces. The linear increasing trend with 1-Propanol content supports the predominance of the structure forming nature of 1-Propanol over its complexing ability.

Highlights

1. To find the most stable species of Ternary complexes of L-Histidine and

1,10Phenanthroline with Co(II), Ni(II) and Cu(II) in 1-Propanol containing media.

2. Distribution of ternary Species with varying pH.
3. Influence of dielectric constant on the pattern of speciation.
4. Exploring the significance of L-Histidine and 1,10 Phenanthroline in chelationtherapy.

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