Study in Some Heterochelates. III. Cu(II), Ni(II), Zn(II) or Cd(II)+Histidine or Ethylenediaminetetraacetic Acid+Polyphenols Systems

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An extension of Irving-Rossotti technique has been applied to study the formation constant of mixed ligand complexes as follows:

$$[\mathrm{MA}] + [\mathrm{L}] \rightleftharpoons [\mathrm{MAL}]$$

where M=Cu(II), Ni(II), Zn(II), and Cd(II), A=histidine or ethylenediaminetetraacetic acid and LH_2= catechol, pyrogallol or 2,3-dihydroxynaphthalene. The values obtained for the mixed ligand formation constants K_{MAL} are found to be less than the first formation constant K_{ML}, in the binary systems.

The oxidation of mono and diphenols in biological systems by the enzyme phenol oxidases is considered to proceed through the formation of ternary complex.[1] The enzyme is a Cu-protein complex. In the mixed ligand intermediate, copper gets bound with both protein and the substrate phenol. This leads to oxidation of phenol to quinonoid form and Cu(II) gets reduced to Cu(I). This has led us to study the possibility of the formation of similar mixed ligand complexes MAL where M=Cu(II), Ni(II), Zn(II), and Cd(II), A=histidine or ethylenediaminetetraacetic acid, L=catechol, pyrogallol or 2,3-dihydroxynaphthalene. Systems MAL where A=NTA have been reported by us earlier.[2]

Histidine and EDTA are known to form complexes with several metal ions.[3-6] Histidine exhibits bi- or ter-dentate character,[7] coordination taking place from COO^- and from nitrogen of the imidazole or two nitrogens from both imidazole and amino groups. EDTA mostly exhibits quadridentate character,[8] coordination taking place from two nitrogen atoms and two COO^-.

In case of 1 : 1 histidine or EDTA complexes of metal ions with high coordination numbers, the vacant positions are occupied by water molecules or hydroxyl ions. On addition to this of a bidentate ligand coordinating with metal ion at higher pH, vacant positions around the metal ion are occupied by the secondary ligand, resulting in the formation of the mixed ligand complexes of the type M·histidine·L or M·EDTA·L. The copper complexes retain blue colour and do not indicate reduction to Cu(I). This may be because of the difference between the proteins in the enzymes and the polycarboxylic amino acids used in the present work. The reaction can be represented as follows:

$$[\mathrm{MA}] + [\mathrm{L}] \rightleftharpoons [\mathrm{MAL}]$$

$$K_{\mathrm{MAL}} = \frac{[\mathrm{MAL}]}{[\mathrm{MA}][\mathrm{L}]}$$

A=histidine or EDTA.

The charges have been avoided for the sake of generalisation. The formation constants K_{MAL} corresponding to the association of polyhydroxy phenol, with M·Histidine or M·EDTA have been determined by the modified form of Irving-Rossotti technique.[9,10]

Experimental

Disodium salt of EDTA (Riedel-Haens), histidine, polyhydroxy aromatic ligand (A.R. quality), $NaClO_4$ (A.R. Fluka), perchloric acid (Baker analysed), sodium hydroxide (Chamapol, Czechoslovakia) were used. In order to avoid complexing tendency of anion, metal perchlorates were prepared in solution and their metal contents were determined. All solutions were prepared in doubly distilled water.

Metrohm pH meter type E350A (accuracy ±0.05) was employed for all the pH measurements. Titrations were carried out at 30 °C, using a constant temperature bath (±0.1 °C).

The ionic strength of the solution was raised to 0.2 M. Fifty milliliters of each sample was titrated against 0.2 M NaOH. Nitrogen gas was passed through the solutions to avoid oxidation of the aromatic ligands. The pH titration curves for systems Ni-histidine-catechol and Ni-EDTA-catechol are represented in Figs. 1 and 2. Similar curves are obtained in other systems of Cu^{2+}, Zn^{2+}, and Cd^{2+}.

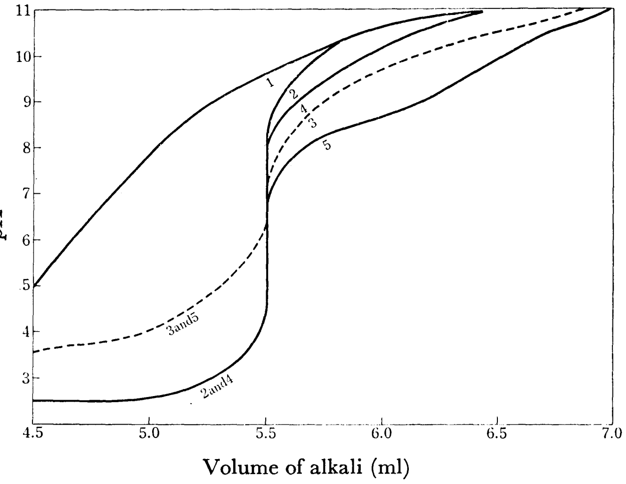

Fig. 1. Ni·histidine·catechol.

1: 0.02 M perchloric acid, 0.002 M histidine, 0.178 M sodium perchlorate.
2: 0.022 M perchloric acid, 0.178 M sodium perchlorate.
3: 0.02 M perchloric acid, 0.002 M histidine, 0.002 M metal perchlorate, 0.176 M sodium perchlorate.
4: 0.022 M perchloric acid, 0.002 M secondary ligand, 0.176 M sodium perchlorate.
5: 0.02 M perchloric acid, 0.002 M histidine, 0.002 M metal perchlorate, 0.002 M secondary ligand, 0.174 M sodium perchlorate.

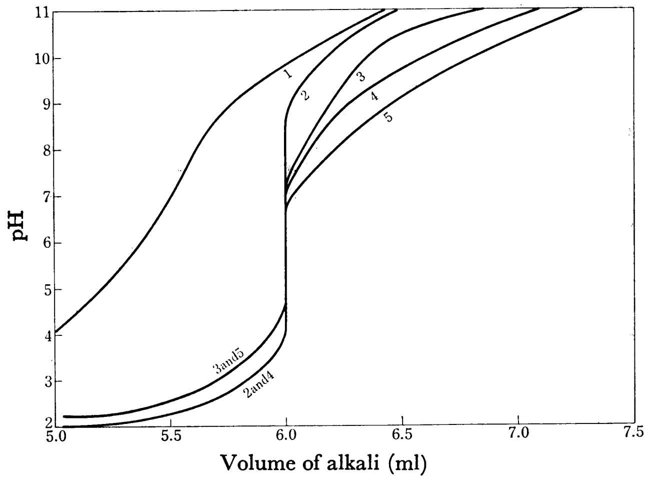

Fig. 2. Ni·EDTA·catechol.
1: 0.02 M perchloric acid, 0.002 M EDTA, 0.178 M sodium perchlorate.
2: 0.024 M perchloric acid, 0.176 M sodium perchlorate.
3: 0.02 M perchloric acid, 0.002 M EDTA, 0.002 M metal perchlorate, 0.176 M sodium perchlorate.
4: 0.024 M perchloric acid, 0.002 M secondary ligand, 0.174 M sodium perchlorate.
5: 0.02 M perchloric acid, 0.002 M EDTA, 0.002 M metal perchlorate, 0.002 M secondary ligand, 0.174 M sodium perchlorate.

Discussion

It is evident from curves (1) and (3) that 1: 1 complex of histidine and EDTA with Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} are formed at lower pH and are stable at higher pH. The separation between two curves starts at low pH and reaches maximum at pH ~5 in histidine and at pH ~4.2 in EDTA. This shows that 1: 1 complex formation is complete at lower pH. At higher pH, the curves converge showing absence of hydrolysis or hydroxy complex formation. M+histidine or EDTA+secondary ligand (catechol, pyrogallol, 2,3-dihydroxynaphthalene) curve (5) is not below the M+histidine or EDTA curve (3), in the lower pH range. This is an evidence that in this range where M^{2+} and histidine or EDTA 1: 1 complexation takes place, the polyhydroxy phenols do not combine with metal ion. In the polyhydroxy phenols curve (4) one and two equivalents of extra perchloric acid (where primary ligand is histidine or disodium salt of EDTA respectively) have been added to compensate for hydrogen ions liberated by the combination of M^{2+} with histidine or EDTA, in the M+primary ligand+secondary ligand solutions. Below pH 5.5 in histidine and 4.5 in EDTA, the curve (5) is not overlapping curve (4) but it is slightly above it. This is due to the fact that in the lower pH range amino acids take up hydrogen ion from the solution and exist as a mixture of species $CH_2NH_3^+\cdot COOH$ and $CH_2NH_3^+\cdot COO^-$. After pH 6 curve (5) goes below the curve (4). This confirms that in this range coordination of secondary ligand with M·histidine or M·EDTA takes place resulting in the liberation of extra hydrogen ions. Reactions can be represented as follows:

Table 1. Stability constants of mixed ligand chelates (30 °C)

Ligand	$\log K^{Ni\cdot Hist}_{Ni\cdot Hist\cdot L}$	$\log K^{Zn\cdot His}_{Zn\cdot His\cdot L}$	$\log K^{Cd\cdot Hist}_{Cd\cdot Hist\cdot L}$
Catechol	6.82	7.24	5.76
Pyrogallol	5.69	6.84	—
2,3-Dihydroxy-naphthalene	8.53	—	7.74

$$M^{2+} + \text{Histidine} \rightleftharpoons [\text{M Hist}]^+ + H^+$$

$$[\text{M Hist}]^+ + C_6H_4(OH)_2 \rightleftharpoons [\text{M Hist}(C_6H_4O_2)]^- + 2H^+$$

and in case of EDTA, (disodium salt),

$$M^{2+} + Na_2H_2\ \text{EDTA} \rightleftharpoons [\text{MEDTA}]^{2-} + 2Na^+ + 2H^+$$

$$[\text{MEDTA}]^{2-} + C_6H_4(OH)_2 \rightleftharpoons [\text{MEDTA}(C_6H_4O_2)]^{4-} + 2H^+$$

From the horizontal distance between curve (4) and curve (5), $\bar{n}$ values have been calculated. pL has been calculated using known equation.[9] The precise values of mixed complex formation constants have been worked out as done in earlier communication.[10] The values have been reported below:

Table 2. Stabliity constants of mixed ligand chelates (30°C)

Ligand	$\log K^{Cu\cdot EDTA}_{Cu\cdot EDTA\cdot L}$	$\log K^{Zn\cdot EDTA}_{Zn\cdot EDTA\cdot L}$	$\log K^{Ni\cdot EDTA}_{Ni\cdot EDTA\cdot L}$	$\log K^{Cd\cdot EDTA}_{Cd\cdot EDTA\cdot L}$
Catechol	7.01	3.73	4.44	3.53
Pyrogallol	6.13	—	—	—
2,3-Dihydroxy-naphthalene	7.73	5.25	5.38	4.96

In case of Cu·Hist·L system and also Zn·Hist·2,3-dihydroxynaphthalene the method could not be applied because the coordination of secondary ligand starts before the formation of M·histidine 1: 1 complex is complete. In the system M·EDTA·pyrogallol, where (M=Zn, Ni, or Cd) calculations could not be possible because the separation between curves (4) and curve (5) is very small. In the system Cd·Hist·Pyrogallol, there is a precipitation after pH 6 onwards and hence calculation was not carried out.

It is observed that in all cases K_{MAL} has lower value than K_{ML}. The value of $K^{M\cdot EDTA}_{M\cdot EDTAL}$ is less than K^{M}_{ML} (where L=polyhydroxy aromatic ligands) by about 3 to 4.5 log unit, and $K^{M\cdot Hist}_{M\cdot HistL}$ is less than K^{M}_{ML} by about 1 to 1.2 log unit. This can be explained to be due to electrostatic repulsion between the incoming charged ligand and already existing charged ion histidine or EDTA. The values of K_{MAL} are higher where A=histidine. This is because histidine has one negative charge and hence exerts lesser repulsion on the incoming ligand than EDTA with four negative charges.

The order of the stability constants of the complexes with different metal ion is as follows:

2,3-dihydroxynaphthalene > catechol > pyrogallol

This is in accordance with their basicities. It is also observed that the difference $K^{Cu.EDTA}_{Cu.EDTA.L}-K^{Cu}_{CuL_1}$ is more than $K^{Ni.EDTA}_{Ni.EDTA.L}-K^{Ni}_{Ni.L_2}$. This can be explained by the consideration of Jahn-Teller effect in case of copper complexes as done earlier.[11,12]

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