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# Physico-chemical Investigation on Co(II), Ni(II) and Cu(II) Chelates of Ethylene Diamine N,N′-bis-benzoic Acid

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Ethylene diamine N,N′-bis-benzoic acid (EDBBA) leads to the formation with divalent nitrates, quadridentate planar as well as *trans*-polymer complexes. The solution stabilities of these chelates determined pH-metrically are in fair agreement with the Irwing-Williams series of stability—Co(II), Ni(II), Cu(II). The stoichiometry (1 : 1) and the formation stability constants assign the m.f. $C_{16}H_{16}N_2O_4$, thereby defining the arrangement of molecules in the coordination sphere. Conductance, magnetic, electronic and IR techniques indicate the tetradentate coordination through azomethine nitrogen and oxygen of the carboxylic groups.

**Key Words: Co(II), Ni(II) and Cu(II) Chelates of ethylene diamine N,N′-bis-benzoic acid.**

## INTRODUCTION

Owing to the coordinating capability[1], biochemical[2], analytical[3,4] and pharmacological[5] importance of Schiff base complexes, it was thought worth while to undergo equilibrium studies on the formation constants of Co(II), Ni(II) and Cu(II) complexes, as ethylene diamine N,N′-bis-benzoic acid has varied ligational behaviour towards these metal ions and thereby results in the manifestation of novel structural features in the metal complexes[6,7].

## EXPERIMENTAL

All the reagents used were of AR grade. Potentiometric studies were carried out on the complexes using Irwing-Rossotti[8] technique in aqueous medium at ionic strength 0.1 M $KNO_3$ at temperature 25 ± 0.1°C. For the determination of stability constants, a curve was plotted between $\bar{n}$ and log A and at half $\bar{n}$ value, $K_1$ was read directly from the formation curve[9].

The procedures for analysing the metal and the elements were essentially the same as described earlier[10]. Details of the equipments used for various physico-chemical studies were the same as reported earlier[11].

## RESULTS AND DISCUSSION

The potentiometric equilibrium curve of EDBBA reveals the biprotic tetradentate nature of the ligand. Dissociation of the ligand takes place in two stages

indicating that both $H^+$ ions are released simultaneously; hence the two K values are nearly the same [4.18 (4.20) and 5.28 (5.20)], obtained from Bjerrum's and Irwing-Rossotti methods.

The analytical results of the ligand and metal-complexes are presented in Table-1. All the complexes were coloured, insoluble in water, methanol, DMF and $CH_2Cl_2$, largely soluble in pyridine and sparingly soluble in THF. Conductance data in $10^{-3}$ M DMF solution indicate the non-electrolytic nature of the complexes.

TABLE-1
ELEMENTAL ANALYSIS OF METAL-EDBBA COMPLEXES

| Compounds | m.w. found (calcd.) | % Analysis Found (Calcd.) | | | |
|---|---|---|---|---|---|
| | | C | H | N | Metal |
| $C_{16}H_{14}N_2O_4Na_2$ | 343.38 (344.00) | 55.42 (55.80) | 4.01 (4.06) | 8.21 (8.40) | — — |
| Cu-EDBBA | 405.51 (405.71) | 47.46 (47.82) | 3.42 (3.45) | 6.90 (6.90) | 15.71 (15.80) |
| Ni-EDBBA | 400.70 (400.92) | 47.91 (47.97) | 3.99 (4.01) | 6.98 (6.99) | 14.64 (14.95) |
| Co-EDBBA | 400.91 (400.96) | 47.89 (47.94) | 3.99 (3.99) | 6.98 (6.99) | 14.69 (14.66) |
| Ni-EDBBA·$Py_2$ | 558.70 (558.93) | 55.84 (55.89) | 3.41 (3.50) | 7.51 (7.62) | 10.49 (10.61) |
| Co-EDBBA·$Py_2$ | 558.91 (558.98) | 55.32 (55.38) | 3.23 (3.26) | 7.42 (7.48) | 10.49 (10.56) |

In the ligand EDBBA, a carbon-nitrogen double bond, conjugated with the aromatic ring exists preferentially in E-conformation coupled with higher stability associated with E-*trans*-configuration, leads to the conclusion that EDBBA should exist in E-S-*trans*-E-configuration.

In IR spectra, a strong band appears at 3220 $cm^{-1}$ for $\nu_{asym}$(N—H) stretch and a medium sharp band at 1580 $cm^{-1}$ of $\nu_{sym}$(N—H). 1610 $cm^{-1}$ and 1400 $cm^{-1}$ are assigned for antisymmetric and symmetric —COO vibrational modes respectively. Weak bands around 1250 $cm^{-1}$ and 1150 $cm^{-1}$ identify aromatic primary ν(CN) and aliphatic ν(CN) stretches respectively. A medium sharp band at 750 $cm^{-1}$ explains the adjacent four hydrogen atoms on the aromatic ring.

**Cu(II)-Complexes:** Its magnetic moment is found to be 1.79 B.M. Electronic spectra show a band at 638 nm (ε = 112) and the IR reveals the magnitude of several bands which on chelation are lowered (Table-2).

**Co(II)-Complexes:** The magnetic moment of this compound is found to be 2.25 B.M. Its electronic spectrum show a shoulder at 425 nm and bands at 478 (ε = 6.8) and 520 nm (ε = 8.2). IR spectral data is given in Table-2.

**Ni(II)-Complexes:** It is diamagnetic in nature and its electronic data reveal a band at 560 nm ($\varepsilon = 15$) and IR bands are given in Table-2.

**Ligation at axial positions by pyridine, imidazole, tryptophan and histidine:** Metal complexes of EDBBA are mostly insoluble but on long standing in THF with constant stirring gets dissolved. The solubility is low. To the THF solution when bases like imidazole, tryptophan and histidine are added, new complexes are formed. The electronic spectra of these compounds indicate that in case of copper and cobalt, the ligation at the fifth and sixth position does take place but no such evidence is observed in case of nickel. Ni-complex is quite inert to these base ligands except pyridine as shown in Table-3 Magnetic moments and spectral data (Table-3) reveal the stereochemistry of the complexes and the adducts.

For the Cu-EDBBA complexes a square-planar[11] polymeric structure is proposed, but when suitable amino acids like histidine, imidazole and tryptophan are added to the Cu-EDBBA solution, it is presumed that these ligands get attached to the axial positions at the copper centre changing the geometry from square-planar to octahedral.

Pyridine-cobalt adduct shows an octahedral arrangement, a change from square-planar as in Co-EDBBA. Thus on the basis of low molar extinction coefficient of the principal absorption band it is assumed that it has a *trans*-octahedral[12] configuration in imidazole adduct. More or less similar results were observed in tryptophan and histidine adducts.

Ni(II)-complex being diamagnetic showed only one band at 560 nm which is a characteristic transition for low spin square-planar complexes. Besides, its low solubility suggests the complex may be polymeric in nature. With pyridine it shows 1 : 2 stoichiometry and moment 3.2 B.M. which suggests a high spin octahedral adduct.

TABLE-2
KEY IR BANDS ($cm^{-1}$) FOR THE LIGAND AND THE METAL COMPLEXES

| Ligand | Cu-EDBBA | Ni-EDBBA | Co-EDBBA | Assignments |
|---|---|---|---|---|
| 3220 | 3095 | 3100 | 3100 | $\nu_{asym}$(NH) |
| 1610 | 1590 | 1595 | 1595 | $\nu_{asym}$(COO) |
| 1580 | 1560 | 1570 | 1570 | $\nu_{sym}$(NH) |
| 1400 | 1385 | 1390 | 1390 | $\nu_{sym}$(COO) |
| 1520 | 1535 | 1540 | 1540 | Aromatic mode |
| 1250 | 1235 | 1240 | 1240 | ν(NH) arom. |
| 1150 | 1135 | 1140 | 1140 | ν(CN) alip. |
| 750 | 735 | 740 | 740 | 4H adjacent |
| — | 410 | 420 | 380 | ν(M—O) |
| — | 320 | 330 | 310 | ν(M—N) |

TABLE-3
ELECTRONIC SPECTRAL DATA FOR THE METAL–BASE COMPLEXES

| Complex | Band position $\lambda_{max}$ (nm) | $\varepsilon$ (moles$^{-1}$ cm$^2$) |
|---|---|---|
| $CuLIm_2$ | 560 | 240 |
| $CuLTr_2$ | 590 | 175 |
| $Cu\ LHis_2$ | 580 | 200 |
| $CoLIm_2$ | 480, 530, 565, 590 | — |
| $CoLTr_2$ | 518 | — |
| $CoLPy_2$ | 530, 642 | — |
| $NiLPy_2$ | 580 | — |

where Im = Imidazole, His = Histidine, Tr = Tryptophan, Py = Pyridine

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