

## STRUCTURE–STABILITY RELATIONSHIP OF COPPER(II)–INDOL CARBOXYLIC ACID DERIVATIVE COMPLEXES FROM SPECTROPHOTOMETRIC, THERMOGRAVIMETRIC AND POTENTIOMETRIC STUDIES

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### ABSTRACT

Some copper(II) complexes of *N*-methyl indol carboxylic acid derivatives have been isolated and characterized. These complexes were subjected to elemental and thermogravimetric analyses together with UV, visible and IR spectral studies. Based on these physicochemical studies, the suggested formula for the complexes obtained is  $\text{CuL}_2$  where  $\text{L} = N$ -methyl indol carboxylic acid derivatives  $\text{L}_1$ – $\text{L}_4$ .

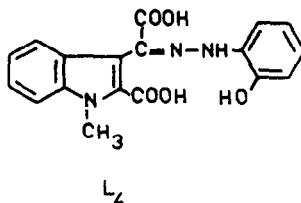
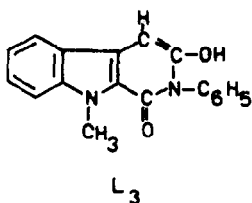
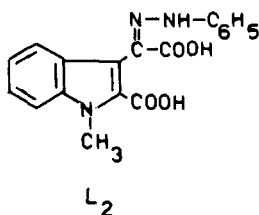
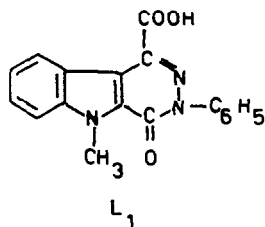
Thermogravimetric analyses of the isolated complexes have already indicated different modes of interaction between the ligands and the central copper(II) metal ions. UV, visible and IR spectral studies have indicated that coordination of the ligands to the central metal ion is via carboxylic-, hydroxyl- and/or nitrogen-containing groups.

The stability constants of some of these metal chelates were determined from potentiometric measurements and found to be in the order  $\text{Cu}(\text{L}_3)_2 < \text{Cu}(\text{L}_2)_2 < \text{Cu}(\text{L}_4)_2$ , which essentially depends on the acid dissociation constants of the ligands, determined under the same conditions.

### INTRODUCTION

The relationship between structure and behaviour of a number of *N*-methyl indol carboxylic acid derivatives ( $\text{L}_1$ – $\text{L}_4$ ) have recently been investigated [1]. Such compounds exhibit distinct changes with pH and form coloured chelates with several cations. Although much interest has been directed towards copper chelates with different ligands [2–7] concerning synthesis, spectral studies and stability, nothing has appeared in the literature concerning the structure–stability relationship of indol carboxylic–copper(II) chelates.

Cupric complexes usually assume the square planar form [8] and under favourable conditions tend towards octahedral structures. In addition to these square merging into tetragonally distorted octahedral complexes, there are some stereofoms, the most important of which is the distorted tetrahedral form. There is also a wide range of pentacoordinated species of



Cu(II): trigonal bipyramidal and, more commonly, square pyramidal configurations [9–11].

The present work aims to investigate the structures of the possible copper(II) chelates formed during interaction with four *N*-methyl indol carboxylic acid derivatives. The preparation and characterization of these copper complexes are presented and discussed, using spectrophotometric studies, chemical analysis and TGA. We also investigated the stability of chelates of these ligands in solution by potentiometry. Due to their limited solubility in aqueous media, measurements were carried out in 50% aqueous dioxane.

## EXPERIMENTAL

*N*-Methyl indol carboxylic acid derivatives ( $L_1$ – $L_4$ ) were prepared as previously described [12]. The derivatives were crystallized from ethanol to a constant melting point and dried in vacuo. The physical constants of the compounds prepared agree with literature data [1].

In order to prepare the copper(II)–indol carboxylic acid complexes, solutions of these ligands (0.5 g/25 ml dioxane) and of copper perchlorate (0.2 g/25 ml water) were mixed, thoroughly stirred and left overnight. Green solids [ $\text{Cu}(L_1)_2$ ,  $\text{Cu}(L_2)_2$ ,  $\text{Cu}(L_3)_2$ ] or a yellow product [ $\text{Cu}(L_4)_2$ ] being formed. These solid complexes were insoluble in water, slightly soluble in solvents, but soluble in dioxane–water mixtures (1 : 1). They were recrystallized from absolute ethanol.

TABLE 1

Elemental analysis of copper(II)-indol carboxylic acid derivative complexes I-IV

| Complex <sup>a</sup> | Found (%) |     |      |      |     | Calcd. (%) |      |       |      |        |
|----------------------|-----------|-----|------|------|-----|------------|------|-------|------|--------|
|                      | C         | H   | N    | M    | MW  | C          | H    | N     | M    | MW     |
| I                    | 61.2      | 4.2 | 11.5 | 9.25 | 700 | 61.57      | 3.7  | 11.97 | 9.05 | 701.54 |
| II                   | 59.2      | 4.3 | 11.2 | 8.6  | 710 | 59.87      | 4.7  | 11.64 | 8.8  | 721.54 |
| III                  | 67.8      | 4.2 | 8.9  | 9.3  | 650 | 67.30      | 4.05 | 8.74  | 8.9  | 641.54 |
| IV                   | 55.8      | 4.2 | 10.4 | 8.25 | 760 | 56.13      | 3.89 | 10.90 | 8.25 | 769.54 |

<sup>a</sup> The suggested formulae of copper(II)-indol carboxylic acid complexes from elemental analyses are: **I**,  $\text{Cu}(\text{C}_{18}\text{H}_{13}\text{O}_3\text{N}_3)_2$ ; **II**,  $\text{Cu}(\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_3)_2$ ; **III**,  $\text{Cu}(\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}_2)_2$ ; **IV**,  $\text{Cu}(\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}_3)_2$ .

Partial elemental analyses for C, H and N were performed by microanalysts at Cairo University (Table 1). Analysis of the metal content was made using a Varian Techtron (Model 1100) atomic absorption spectrophotometer. A certain weight of the complex was decomposed by strong acid to give free Cu(II) in solution. The excess acid was evaporated to dryness and the solution made up to 50 ml with distilled water. The percentage of copper in each sample was calculated by comparison with copper standards as a blank under the same conditions applying the equation

$$\text{wt\% metal} = \frac{c \times R_s \times W \times 100}{R_d \times V \times 1000}$$

where  $W$  is the weight of the sample (mg),  $V$  is its volume (50 ml),  $R_s$  and  $R_d$  are absorbances of the sample and the standard, respectively, and  $c$  is the concentration of the standard (ppm). Molecular weights of these complexes were calculated from previously reported percentages of copper [13].

The absorption spectra of ligands  $L_1$ - $L_4$  ( $1.54 \times 10^{-5}$  to  $13.44 \times 10^{-4}$  M) and their copper complexes I-IV ( $0.52$ - $3.08 \times 10^{-5}$  M) were measured in dioxane-water mixtures (1:1) using a Pye Unicam SP 1750 recording spectrophotometer.

Thermogravimetric analysis (TGA) was done on a Shimadzu TG system (Shimadzu 30 series) thermal analyser. The weight losses of 2.28-4.0-mg samples were measured in the temperature range 20-900°C, using a heating rate of 10°C min<sup>-1</sup>.

The IR spectra were recorded as KBr discs on a Pye Unicam SP 3-300 IR spectrophotometer over a wavenumber range of 200-4000 cm<sup>-1</sup>.

Potentiometric determination of the stability constants of these chelates was performed using solutions containing 0.1 M  $\text{KClO}_4$  (in 1:1 dioxane-water) to provide media of constant ionic strength. Solutions (25 ml) containing potassium perchlorate, copper perchlorate ( $10^{-3}$  M) and chelating agent ( $5 \times 10^{-3}$  M) were titrated with 0.1 M KOH in

dioxane–water mixtures (1 : 1). The degree of complex formation,  $\bar{n}$ , and the concentration of free chelating anion,  $[C]$ , were calculated as described previously [14] using the equation

$$\bar{n} = ([ML^+] + 2[ML_2])/C_m$$

where  $C_m$  is the total metal concentration.

Plots of  $\bar{n}$  vs.  $pC (= -\log[C])$  were used to obtain approximate values of  $\log K_1$  and  $\log K_2$  for  $\bar{n} = 0.5$  and  $1.5$ , respectively [15] [ $K_1$  and  $K_2$  are the stability constants for the complexes  $ML^+$  and  $ML_2$ , respectively;  $M = Cu(II)$ ]. Accurate values of stability constants were obtained graphically by plotting  $\bar{n}/(\bar{n} - 1)[C]$  vs.  $(2 - \bar{n})[C]/(\bar{n} - 1)$ , based on the equation [16]

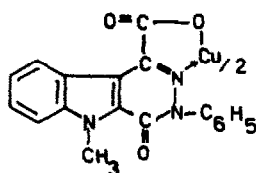
$$\bar{n}/(\bar{n} - 1)[C] = (2 - \bar{n})[C]/(\bar{n} - 1)K_1K_2 - K_1$$

$K_1$  and  $K_2$  were obtained from the slope and intercept. The best straight line for the above plot, which will for convenience be written  $Y = K_1K_2X - K_1$ , was obtained by the method of least squares [17].

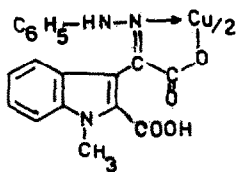
## RESULTS AND DISCUSSION

The anion containing carboxylate groups and basic nitrogen in one skeleton can add to almost all metal ions. Most of these compounds are known to form strong complexes, characterized by the highest log formation constants. In the present work we try to study the structure–stability relationship of such compounds: copper–indol carboxylic acid derivative complexes.

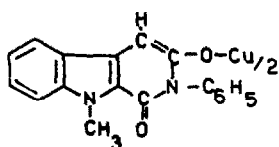
From the microanalytical data presented in Table 1, structures are proposed for the four solid complexes I–IV. The suggested formula is  $CuL_2$ .



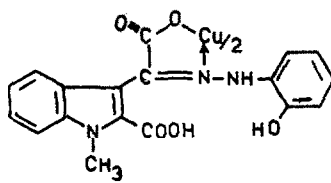
I



II



III



IV

### Absorption spectra

The absorption spectra of ligand  $L_1$  and its possible complex I (Fig. 1a and b) show mainly one broad band centered at 332 nm ( $\epsilon = 0.22 \times 10^5$ ). For  $L_1$ , this is slightly shifted to a longer wavelength (340 nm) of lower intensity ( $\epsilon = 0.75 \times 10^4$ ) in the formation of complex I. It also shows a shoulder starting at 376 nm ( $\epsilon = 0.51 \times 10^5$ ) in the case of  $L_1$ , which became

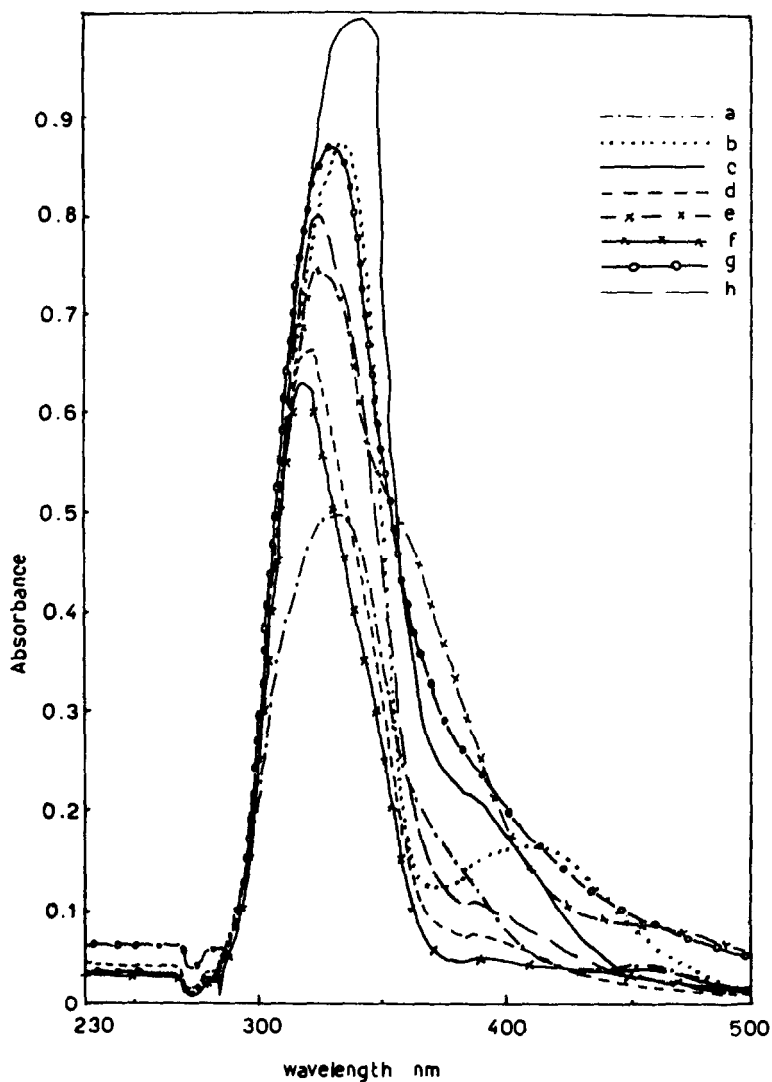


Fig. 1. Absorption spectra of indol carboxylic acid derivatives  $L_1$ - $L_4$  and their complexes I-IV in 1:1 dioxane-water.

a broad band centered at 412 nm of lower intensity ( $\epsilon = 0.94 \times 10^4$ ) in the spectra of complex I. The band and the shoulder in the spectra of  $L_1$  are assigned as  $\pi-\pi^*$  transitions within the indol rings [1]. The red shift of these bands and hypochromic effects during the interaction of this ligand with copper ions may be attributed to the excitation of the  $\pi$ -electrons of the ligand during the formation of complex I.

The spectra of  $L_2$  (Fig. 1c) refer to the presence of a sharp band at 340 nm ( $\epsilon = 0.74 \times 10^3$ ) which is mainly assigned to  $\pi-\pi^*$  transitions of the delocalized  $\pi$ -electrons of the indol rings and/or of the hydrazone group of this ligand. This band was shifted to a shorter wavelength (320 nm) in the spectra of complex II (Fig. 1d) and increased in intensity ( $\epsilon = 0.93 \times 10^5$ ). This blue shift and increase in intensity may be attributed to the stabilization of the  $\pi$ -electrons of the ligand during the formation of five-membered chelate rings involving the substituted acetic acid carboxylic groups of the indol rings and the nitrogen of the hydrazone group as indicated by structure II. The spectra of  $L_2$  also show a shoulder starting at 388 nm ( $\epsilon \approx 74$ ) which is attributed to  $n-\pi^*$  transitions due to non-bonding electrons of N and O atoms in this compound. This shoulder became a more intense band at a longer wavelength (414 nm;  $\epsilon = 0.23 \times 10^4$ ) in the spectra of complex II. This red shift and increase in intensity may be due to excitation of the  $\pi$ -electrons of the ligand molecules during interaction with Cu(II) to form complex II.

The spectra of ligand  $L_3$  (Fig. 1e) show a sharp band at 328 nm ( $\epsilon = 0.11 \times 10^5$ ) and a shoulder starting at 432 nm ( $\epsilon \approx 0.15 \times 10^4$ ), which may be attributed to  $\pi-\pi^*$  transitions of the delocalized  $\pi$ -electrons in the three cyclic rings of this ligand. The spectra of complex III (Fig. 1f) show a slight blue shift of the first band of the ligand to 320 nm and an increase in intensity ( $\epsilon = 0.93 \times 10^5$ ). The shoulder changes into a small band at 388 nm ( $\epsilon = 0.74 \times 10^4$ ). This blue shift and increase in intensity are mainly attributed to the perturbation of the  $\pi$ -electron configuration of the three rings in enol form of ligand  $L_3$  as a result of bonding of the OH group to Cu(II) by an  $M \cdots O$  bond in which  $L_3$  acts as a monodentate ligand.

The spectra of ligand  $L_4$  (Fig. 1g) show a sharp band at 332 nm ( $\epsilon = 0.52 \times 10^5$ ) together with a small shoulder starting at 392 nm ( $\epsilon = 0.16 \times 10^5$ ) which may be assigned to  $\pi-\pi^*$  transitions in the cyclic rings and hydroxyphenylazo group of this ligand. The spectra of complex IV (Fig. 1h) show a slight blue shift of the first band to 324 nm and an increase in intensity ( $\epsilon = 0.15 \times 10^6$ ), whereas the small shoulder became more pronounced at a shorter wavelength (388 nm;  $\epsilon = 0.21 \times 10^5$ ). This blue shift and increase in intensity of bands during the formation of complex IV are essentially due to stabilization of the ring systems of the ligand molecules and to the formation of new, stable five-membered chelate rings involving the nitrogen of the hydrazone group and the substituted acetic acid carboxylic groups of the indol rings.

The appearance of small bands around 284 nm ( $\epsilon \approx 115\text{--}600$ ) in the spectra of all ligands and their complexes may be attributed to  $n\text{--}\pi^*$  transitions of the non-bonding electrons of N and O atoms of groups which are unshared in complex formation.

### Thermogravimetric analysis

Thermogravimetric analysis is very useful for studying the thermal decomposition of solid substances involving both simple compounds [18] and complexes [19,20].

In the present investigation, copper(II) complexes (I–IV) of *N*-methyl indol carboxylic acid derivatives were subjected to this technique (Fig. 2). The stage of decomposition, temperature range, thermal decomposition products and estimated and calculated mass losses are listed in Table 2. Estimated mass losses were based on thermogravimetric analysis (found) and the calculated mass losses were obtained using microanalysis results for these solid complexes (Table 1).

For complex I (Fig. 2a) the first stage of decomposition ( $170\text{--}450^\circ\text{C}$ ) indicates the loss of one molecule of each of  $L_1$ , CO,  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{C}_6\text{H}_6$  as a

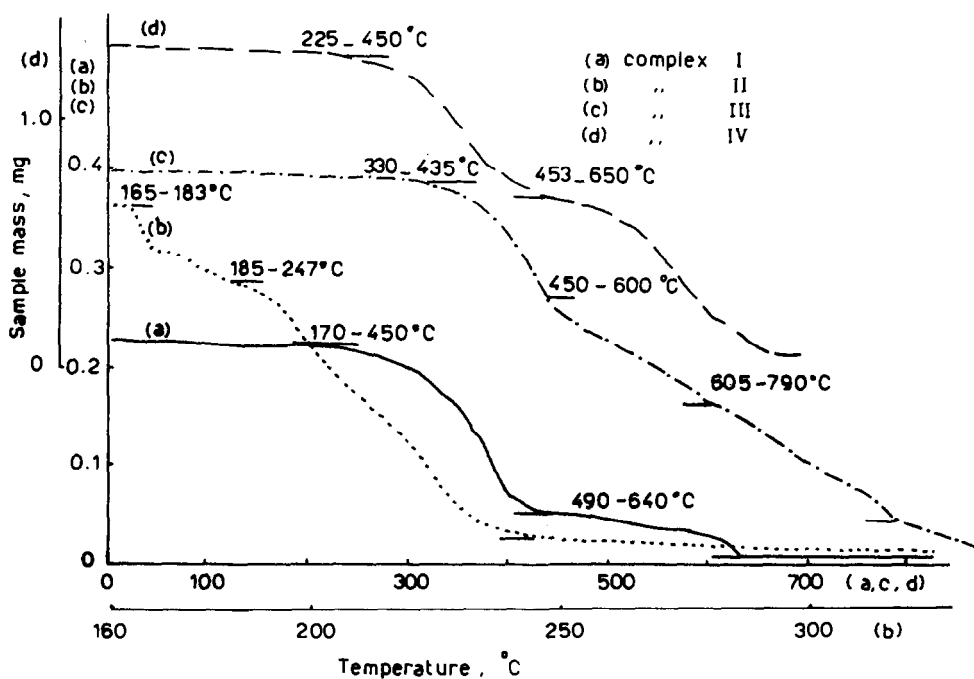


Fig. 2. Thermogravimetric analysis of copper(II)–indol carboxylic acid derivative complexes: (a) complex I, (b) complex II, (c) complex III, (d) complex IV.

TABLE 2

Mass loss of indol carboxylic acid derivative (L<sub>1</sub>-L<sub>4</sub>)<sup>a</sup> complexes of copper(II)

| Complex | Temp. range<br>(°C) | Decomposition<br>products lost   | Wt. loss (%) |        |
|---------|---------------------|--|--------------|--------|
|         |                     |  | Found        | Calcd. |
| I       | 170-450             | L <sub>1</sub> + CO + CO <sub>2</sub> + N <sub>2</sub> + C <sub>6</sub> H <sub>6</sub> | 71.20        | 70.84  |
|         | 490-645             | C <sub>10</sub> H <sub>7</sub> N   | 19.70        | 20.09  |
| II      | 165-183             | C <sub>10</sub> H <sub>9</sub> N   | 19.17        | 19.54  |
|         | 185-247             | 2 CO <sub>2</sub> + N <sub>2</sub> + C <sub>6</sub> H <sub>6</sub> + L <sub>2</sub>    | 72.23        | 72.48  |
| III     | 330-435             | 2 CO + C <sub>9</sub> H <sub>7</sub> N   | 26.00        | 26.65  |
|         | 450-600             | C <sub>10</sub> H <sub>9</sub> N   | 22.50        | 22.30  |
|         | 605-790             | 2 CO + N <sub>2</sub> + 2 C <sub>6</sub> H <sub>6</sub>                                | 37.00        | 37.09  |
| IV      | 225-450             | L <sub>4</sub>   | 45.00        | 45.87  |
|         | 453-650             | L <sub>4</sub>   | 45.15        | 45.87  |

<sup>a</sup> The formulae of the ligands are: L<sub>1</sub>, C<sub>18</sub>H<sub>13</sub>O<sub>3</sub>N<sub>3</sub>; L<sub>2</sub>, C<sub>18</sub>H<sub>17</sub>O<sub>4</sub>N<sub>3</sub>; L<sub>3</sub>, C<sub>18</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>; L<sub>4</sub>, C<sub>18</sub>H<sub>15</sub>O<sub>5</sub>N<sub>3</sub>.

gradual mass loss. Both estimated (71.2%) and calculated (70.84%) mass losses were in reasonable agreement. In the temperature range 490-640°C (second decomposition stage) about 20% mass loss occurs, which is interpreted as the loss of the remaining part of the decomposed second ligand molecule (C<sub>10</sub>H<sub>7</sub>N) corresponding to a calculated mass loss of 20.09%.

For complex II (Fig. 2b) the initial loss in the temperature range 165-183°C is attributed to the main part of the first molecule of ligand L<sub>2</sub> decomposed (C<sub>10</sub>H<sub>9</sub>N). The mass loss found (19.82%) agrees satisfactorily with the calculated mass loss (19.82%). The second decomposition stage (185-247°C) comprises breaking of the second metal-ligand bond with the consequent release of one molecule of L<sub>2</sub> together with 2 CO<sub>2</sub>, N<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> molecules remaining from the first decomposition stage. The mass losses found (72.23%) and calculated (72.48%) are in good agreement.

The thermogram of complex III (Fig. 2c) shows a mass loss (~26%) in the temperature range 330-435°C, due to the decomposition of the first molecule of monodentate ligand L<sub>3</sub> to give the fragment C<sub>9</sub>H<sub>7</sub>N together with two carbonyl groups (calculated mass loss 26.65%). The second decomposition stage (450-600°C) is responsible for a mass loss of 22.5%, which is due to the loss of the main part (C<sub>10</sub>H<sub>9</sub>N) of the dissociated second ligand molecule from complex III (calculated mass loss 22.3%). The third mass loss (found 37.0%) immediately following the second (605-790°C) is attributed to the loss of 2 CO, N<sub>2</sub> and 2 C<sub>6</sub>H<sub>6</sub> molecules (calculated 37.09%) as residual parts of the first and second decomposition stages of complex III.

Figure 2d refers to the two main stages of decomposition of complex IV. The first stage occurs in the temperature range 225-450°C (mass loss 45.0%) which corresponds reasonably well with the loss of the loosely bound ligand



molecule from complex **IV** (calculated mass loss 45.87%). This step is directly followed by a second identical mass loss (45.15%) in the temperature range 453–650°C due to the loss of the remaining more tightly bound ligand molecule (calculated mass loss 45.87%).

### *IR spectra*

To understand the nature of bonding in these complexes, assignment of IR bands is necessary [21] (Table 3). In the spectra of ligand  $L_1$  the bands at 3400–3600 and 1530  $\text{cm}^{-1}$  are assigned as  $\nu_{\text{OH}}$  of the carboxylic group and  $\nu_{\text{C=N}}$ , respectively. On formation of complex **I**, the first band disappears and the second band shifts to 1510  $\text{cm}^{-1}$  (lower energy) indicating bonding of  $L_1$  molecules to the central copper(II) ions via O and N atoms of the COOH and C=N groups by ionic and coordinate bonds, respectively (see structure **I**). Indeed, the formation of  $\text{O} \cdots \text{M}$  bonds makes the broad band at 1580–1680  $\text{cm}^{-1}$  for ligand  $L_1$ , which is assigned as  $\nu_{\text{COOH}}$ , become sharp and appear at 1620  $\text{cm}^{-1}$ . The sharp band at 1710  $\text{cm}^{-1}$ , assigned to  $\nu_{\text{CO}}$ , is still unchanged during interaction of  $L_1$  with Cu(II), which means that CO groups in the cyclic rings of the ligand are unchanged in the formation of complex **I**.

The bands at 1550  $\text{cm}^{-1}$  for  $\nu_{\text{C=N}}$ , 2900–3200  $\text{cm}^{-1}$  for  $\nu_{\text{NH}}$ , 1720–1730  $\text{cm}^{-1}$  for  $\nu_{\text{CO}}$  and 1670  $\text{cm}^{-1}$  for  $\nu_{\text{COOH}}$  in the spectra of ligand  $L_2$  are slightly shifted to a lower energy (1520, 2810–2980, 1700 and 1630  $\text{cm}^{-1}$ , respectively) during the formation of the resultant complex **II**. This shift is attributed to the bonding of the phenylhydrazone group and one of the carboxylic groups to the central metal ion. It is also attributed to the electron-withdrawing ability of both C=N and  $\text{COO}^-$  groups during coordination to copper ions as in the proposed structure **II**. The bands in the range 700–800  $\text{cm}^{-1}$ , assigned to  $\nu_{\text{C-H}}$  modes in the spectra of  $L_2$ , are shifted to 740–900  $\text{cm}^{-1}$  on complex formation. This shift is attributed to the decrease in electron density on the indol rings of the two ligand molecules attached to the central metal ion as a consequence of the formation of  $\text{C=N} \rightarrow \text{M}$  and  $\text{COO-M}$  bonds.

The weak broad band at 3500–3600  $\text{cm}^{-1}$  in the spectra of  $L_3$ , assigned as  $\nu_{\text{OH}}$  of its enol form, was shifted to 3300–3490  $\text{cm}^{-1}$  as a result of coordination of this monodentate ligand via the O atom of this OH group in the formation of complex **II**. The change in the broad band at 1410–1480  $\text{cm}^{-1}$ , assigned as ring vibrations in the spectra of  $L_3$ , into two sharp bands at 1430 and 1460  $\text{cm}^{-1}$  in the spectra of complex **II** is attributed to the changes occurring in the electron clouds of the ring systems during formation of this complex.

In the spectra of ligand  $L_4$  the strong broad band at 2920–3100  $\text{cm}^{-1}$  and the sharp band at 1540  $\text{cm}^{-1}$  which are assigned as  $\nu_{\text{NH}}$  and  $\nu_{\text{C=N}}$ , respectively, were shifted to 2910 and 1550–1580  $\text{cm}^{-1}$  and became weak.

TABLE 3  
Assignment of the fundamental group vibrations of indol carboxylic acid derivatives L<sub>1</sub>-L<sub>4</sub> and their copper(II) complexes I-IV (cm<sup>-1</sup>)

| Com-<br>pound  | Mode | $\nu_{OH}$     | $\nu_{>N-}$    | $\nu_{C=N}$ | $\nu_{NH}$      | $\nu_{CO}$          | $\nu_{C-H}$   | $\nu_{rings}$  | $\nu_{COOH}$ | $\nu_{M-O}$ |
|----------------|------|----------------|----------------|-------------|-----------------|---------------------|---------------|----------------|--------------|-------------|
| L <sub>1</sub> |      | 3400-3500 b    | 1310-1360 w, b | 1530 sh     | -               | 1710 sh             | 710-900 sh    | 1400-1500 sh   | 1580-1680 b  | -           |
| I              |      | -              | 1300-1330 b    | 1510 sh     | -               | 1710 sh             | 710-800 sh    | 1400-1500 sh   | 1620 sh      | 430 sh      |
| L <sub>2</sub> |      | 3300-3600 b    | 1330 w, sh     | 1550 sh     | 2900-3200 b     | 1720 sh             | 700-800 sh    | 1400-1500 sh   | 1670 sh, b   | -           |
| II             |      | 3300-3600 b    | 1300 w, sh     | 1520 sh     | 2810-2980 sh, b | 1700                | 740-800 sh    | 1400-1500 sh   | 1630 w       | 450 sh      |
| L <sub>3</sub> |      | 3500-3600 w, b | 1320 w, m      | -           | 2910 sh         | 1710 sh, b          | 720-750 sh, b | 1410-1480 b    | -            | -           |
| III            |      | 3330-3490 b    | 1370 w, m      | -           | 3200 sh         | -                   | -             | -              | -            | 430 sh      |
|                |      |                | 1320 sh        | -           | 2910 sh         | 1710 w, b           | 740-750 sh, b | 1430 sh        | -            | -           |
|                |      |                | 1370 sh        | -           | 3200 sh         | -                   | -             | 1460 sh        | -            | -           |
| L <sub>4</sub> |      | 3400-3500 s, b | 1330 w, sh     | 1540 sh     | 2920-3100 s, b  | 1710, 1750, 1780 sh | 730 sh        | 1400-1510 sh   | 1580-1630 sh | -           |
| IV             |      | 3300-3600 b    | 1330 w, sh     | 1550-1580 b | 2910 w, sh      | 1710 w, sh          | 710-750 sh    | 1440-1500 w, b | 1580 w, sh   | 430 s, sh   |

b, broad; m, medium; s, strong; sh, sharp; w, weak.

The shift and the weakening of these bands indicate coordination of hydroxyphenyl hydrazone groups to the central metal ion via the N atom of the C=N group to form complex **IV**. The change in the strong broad band at 1580–1630  $\text{cm}^{-1}$  in the spectra of the ligand, assigned as  $\nu_{\text{COOH}}$  of carboxylic acid groups, into a weak sharp band at 1580  $\text{cm}^{-1}$  in the spectra of complex **IV** indicates that one of the two carboxylic groups of each ligand is chelated to copper ions with the other one still free. The most probable carboxylic group is that of the substituted acetic acid of the indol ring which forms a strong five-membered ring (see structure **IV**). This is also confirmed by the disappearance of two bands at 1750 and 1780  $\text{cm}^{-1}$  of the ligand in the spectra of complex **IV**, assigned as  $\nu_{\text{CO}}$  modes of the COOH group, and the band at 1710  $\text{cm}^{-1}$  remaining during the formation of complex **IV**.

#### *Stability of complexes in solution*

The method involves determining the hydrogen ion concentration of a solution containing known quantities of copper(II) perchlorate, chelating substance, potassium perchlorate and base in a medium of constant ionic strength. From the known acid dissociation constant of the chelating substance [1], together with the concentration of each of the materials used, it should be possible to calculate all the quantities required to determine the stability constant of the given copper chelates, as described in the experimental using computer programs. We assumed stepwise reactions and that the copper was present as Cu(II),  $\text{CuL}^+$  and  $\text{CuL}_2$ . For the calculations we turned to methods reported elsewhere [14–16]. We calculated the successive constants  $K_1$  and  $K_2$  of (CuL) 1:1 and 1:2 complexes from  $n$ , the average number of L bound to a copper ion. These results are given in Table 4, indicating the order of stability of complexes to be **III** < **II** < **IV**.

Values of  $\log K_1/K_2$  are normal for complexes **II** and **III** in that they are not very high; this implies a lack of steric hindrance to the addition of the

TABLE 4

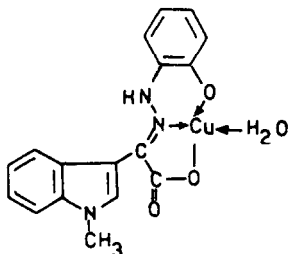
Calculated stability constants  $K_1$  and  $K_2$  for copper(II)–indol carboxylic acid derivative complexes **II–IV**. (Due to the low solubility of complex **I** and its precipitation at high pH, its stability constant cannot be determined by this method.)

|                          | <b>II</b>              | <b>III</b>         | <b>IV</b>              |
|--------------------------|------------------------|--------------------|------------------------|
| Slope ( $Y/X = K_1K_2$ ) | $6.27 \times 10^{31}$  | $2.19 \times 10^5$ | $2.68 \times 10^{24}$  |
| Log $K_1K_2$             | 31.79                  | 5.33               | 24.43                  |
| Intercept ( $= -K_1$ )   | $-2.52 \times 10^{16}$ | $-3.5 \times 10^3$ | $-2.19 \times 10^{14}$ |
| Log $K_1$                | 16.40                  | 3.54               | 14.34                  |
| Log $K_2$                | 15.39                  | 1.79               | 10.09                  |
| Log $K_1/K_2$            | 1.00                   | 1.75               | 4.25                   |
| CC <sup>a</sup>          | 0.99                   | 0.84               | 0.82                   |

<sup>a</sup> CC is the correlation coefficient for the given calculations.

second chelate group. In the case of chelating agent  $L_4$ , containing bulky substituents near the donor atoms, the steric hindrance to the addition of the second group causes  $\log K_1/K_2 = 4.25$  to be unusually high [22].

The exceptional behaviour of  $L_4$  towards Cu(II) ions in solution may be explained by the formation of a complex of stoichiometric ratio 1 : 1 (M/L) of the proposed structure:



which may finally be changed into the 1 : 2 ratio, by competition of COOH and C=N groups of the second ligand molecule to displace OH and  $H_2O$  (1 : 2) to form two stable, five-membered chelate rings (see structure IV). This competition may also explain the unusual value of  $\log K_1/K_2$  obtained in the determination of the stability constants for  $L_4$  complexes.

The correlation coefficients of such calculations ranged from 0.82 to 0.99, indicating the accuracy of the calculations.

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