

## Synthesis and Characterization of Coordination Polymers of N-(3-hydroxy phenyl) maleamic acid – Formaldehyde Resins with Some Biposvtive Cations

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### الخلاصة

تم تحضير وتشخيص راتنجات N (3-هيدروكسي فنيل) حامض الماليك راتنج الفورمالديهيد، كذلك تم تحضير معقدات تناسقية للأيونات الثنائية لكل من Mn(II) و Co(II) و Ni(II) و Cu(II) للراتنج. أظهرت نتائج تحليل الامتصاص الذري للمعقدات بأن نسبة الفلز في المعقدات هي 1:1 أو 2:1 (فلز:ليكاند) وكذلك بينت قياسات الأشعة تحت الحمراء، فوق البنفسجية والعزوم المغناطيسية للمعقدات بأن لها أشكال فراغية رباعية وثمانية السطوح. وبينت قياسات اللزوجة النسبية في ثنائي فنيل سلفوكسيد عند 30°م بأن المعقدات تمتلك لزوجة أعلى من الليكاندات.

### ABSTRACT

The synthesis and characterization of N(3-hydroxy phenyl) maleamic acid-formaldehyde resin are described. The Mn(II), Co(II), Ni(II) and Cu(II) chelate of the above resin were prepared. Atomic absorption results showed the molar ratio of the metal in the complexes are 1:1 or 2:1, UV-Visible, IR spectra and magnetic measurements of the complexes suggest tetrahedral and octahedral geometry of the complexes. Viscosity measurements in DMSO at 30°C indicate that the complexes are highly viscose.

## INTRODUCTION

Metal chelate polymers are become increasingly important for producing materials of high thermal stability. Various Schiff bases involving aldehydes and aromatic diamines have been extensively studied and critically reviewed (1-4). Bajpai et al reported the synthesis and characterization of polyamide-Schiff base coordination polymers, using amino group terminated poly(methylene-diphenylenetetraphtalamide) and metal complexes of salicyladehyde and 2-hydroxy-1-naphthaldehyde [5].

Many bismaleimides of high thermal stability have been prepared and characterized (6,7) other modified polymaleimides have been synthesized and characterized directly from corresponding maleamic or bismaleamic acids (8).

In continuation of our studies on the synthesis and characterization of polymeric ligands and their metal chelates (9) we present here the synthesis and characterization of N-(3-hydroxy phenol) maleamic acid formaldehyde resin and it's Mn(II), Co(II), Ni(II) and Cu(II) chelates.

## EXPERIMENTAL

All the chemicals used for the synthesis of the resin as well as the metal complexes were of analytical grades.

The N-(3-hydroxyphenyl) maleamic acid used in this study was prepared by the reaction of malic anhydride with corresponding amine according to known method (8). The prepared maleamic acid and 37% formaline solution were mixed in 1:1 molar ratio in reaction tube and 3% (w/w) of oxalic acid was added as a catalyst. The reaction tube was sealed and placed in an oil bath at  $100 \pm 3^\circ\text{C}$  for 24hrs. The tube then was cooled to room temperature, diffused and water were decanted. The remaining solid was dissolved in dimethyl formamide (DMF) and the resulting solution was added dropwise to a large excess of 10% NaCl solution with constant stirring. The resin separated out was filtered, washed several times with distilled water, dried at  $70^\circ\text{C}$ , yield 96%. The intrinsic viscosity in 2% NaOH at  $30^\circ\text{C}$  was  $[\eta]=0.321\text{dL/g}$ .

### General synthesis of metal complexes

In a standard synthetic method for the synthesis of maleamic acid formaldehyde resin complexes (0.01 or 0.02 mol of repeat unit) of N-(3-hydroxyphenyl) maleamic acid formaldehyde resin was dissolved in ( $40\text{ cm}^3$ ) tetrahydrofuran. To this solution (0.01 mol) of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in ( $20\text{ cm}^3$ ) distilled water was added dropwise with constant stirring. The mixture was digested at  $100^\circ\text{C}$  for 3hr. in a sand bath. The separated polymeric

complexes was filtered washed with hot distilled water then methanol and dried at 70°C yield 90% (based on the weight of the resin).

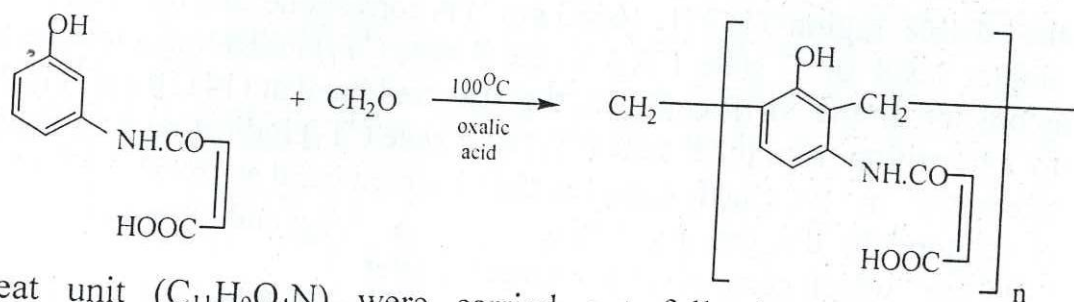
### Physical measurements

IR spectra were recorded on a Perkin-Elmer 580B IR spectrophotometer in the range of 4000-200  $\text{cm}^{-1}$  using Nujol mulls and CsI disc. Elemental microanalyses were carried out on a CHN analyzer type 1106 (Carlo Erba). Conductivity measurements were made on ( $10^{-3}\text{M}$ ) solutions, of the complexes in DMSO at room temperature using conductivity meter model PCM3-Jenway. Electronic spectra were recorded on a Shimadzu UV-16 Spectrophotometer for ( $10^{-3}\text{M}$ ) solutions of the complexes in DMSO at room temperature using 1cm quartz cell. Magnetic measurements were carried out at 25°C by Faraday method on the solid complexes using Bruker B.M6 instrument. Interinsic viscosities of the ligand (repeat unit) and metal complexes were determined at a concentration of 0.05g/10ml of DMSO at 30°C using an Ubbelohde viscometer.

## RESULTS AND DISCUSSION

The maleamic acid formaldehyde resin and its metal complexes have been prepared. The resin is soluble in DMSO and tetrahydrofuran, it is sparingly soluble in methanol and ethanol. It is soluble in aqueous alkali. Resin are formed according to the following equation:

The molecular weight determination of the resin depend on the



repeat unit ( $\text{C}_{11}\text{H}_9\text{O}_4\text{N}$ ) were carried out following the procedure described in earlier work [9]. The analytical data of the complexes (Table 1) agree with the general formula  $[\text{MLCl}_2]_n$  or  $[\text{ML}_2\text{Cl}_2]_n$ , where  $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$  and  $\text{Cu}(\text{II})$ ,  $\text{L} =$  the repeat unit ( $\text{C}_{11}\text{H}_9\text{O}_4\text{N}$ ).

The important IR bands of the ligand and its metal complexes are listed in Table 2. The vibrational absorption bands at 2940, 1475, 748  $\text{cm}^{-1}$  were observed in the spectrum of maleamic acid formaldehyde resin and not in the spectrum of maleamic acid which suggest the presence of methylene bridge in the resin (10). The IR spectrum of the ligand, the band appeared at 3430  $\text{cm}^{-1}$  are due to acidic OH stretching vibration (5). In complex formation this band shifted to lower frequency due to

coordination with metal ion. The band observed at  $3350\text{ cm}^{-1}$  may attributed to NH stretching vibrations of the amide group of the ligand; this band is not affected on coordination. The band due to  $\nu\text{CO}$  which is observed at  $1700\text{ cm}^{-1}$  in the complex formation appears as broad band at lower frequency region  $1650\text{-}1680\text{ cm}^{-1}$ . This may be due to electron withdrawal through connection with the metal ion. Similarly a band in the region  $1650\text{ cm}^{-1}$  due to amide carbonyl is shifted in manganese complex to lower wave number in the region  $1625\text{ cm}^{-1}$ . The lowering frequency of this band by  $25\text{ cm}^{-1}$  on coordination indicate bonding through oxygen atom. Conclusive evidence of these bonding is shown by the observation of  $\nu\text{M-O}$  in the region  $430\text{-}500\text{ cm}^{-1}$  (11, 12).

Thus the maleamic acid formaldehyde resin acts as bidentate chelating agent, coordinating through carbonyl oxygen or amide carbonyl, or hydroxy group and carbonyl groups.

In order to obtain some information about the coordination sphere of the metal ions, the electronic spectra of the complexes have been recorded. The tentative assignments of the absorption bands from the electronic spectra of the complexes are reported in (Table 2). The complexes (1-4) are consistent with tetrahedral coordination geometry.

Mn(II) complexes shows maximum absorption  $23364\text{ cm}^{-1}$  and a charge transfer band at  $29154\text{ cm}^{-1}$  indicating that Mn(II) complex is tetrahedral. In tetrahedral field, the transitions are still spin-forbidden but no longer parity forbidden. That is the reason why tetrahedral compounds are some what more coloured (13).

The electronic spectra of Co(II) complex show bands observed in the visible region ( $14771, 16583\text{ cm}^{-1}$ ) is correspond to a transition from singlet level of F state ( $^4\text{A}_2$ ) to the P state ( $^4\text{T}_1$ ) indicating a tetrahedral geometry. In the Ni(II) complex, the observed band at ( $14150\text{ cm}^{-1}$ ) is due to a transition from the F state ( $^3\text{T}_1$ ) to P state ( $^3\text{T}_1$ ) indicating a tetrahedral geometry. In the Cu(II) complex the observed band at  $16051\text{ cm}^{-1}$  which correspond to the transition  $^2\text{B}_{1g} \longrightarrow ^2\text{A}_{2g}$  and other transition at  $2915\text{ cm}^{-1}$  which correspond to charge transfer.

The electronic spectra of the complexes (5-8) recorded in DMSO are listed in (Table 2). The electronic spectra of Mn(II) complex show an number of bands ( $18700, 19331, 22500, 25433, 30120\text{ cm}^{-1}$ ) of medium intensities. Since Mn(II) has  $d^5$  electronic configuration, the same type of energy level diagram applies whether the metal ion surrounded by tetrahedral or octahedral environment. Generally the four band observed are assigned to the  $^6\text{A}_{1g} \longrightarrow ^4\text{T}_{1g} (^4\text{G}), ^6\text{A}_{1g} \longrightarrow ^4\text{A}_{1g} (^4\text{G}), ^6\text{A}_{1g} \longrightarrow ^4\text{E}_g (^4\text{D})$  and  $^4\text{A}_{1g} \longrightarrow ^4\text{T}_{1g} (^4\text{P})$  transitions respectively. These values suggest octahedral geometry for Mn(II) complex (5). The Co(II) complex show the presence of two bands in the region  $22220$  and  $15150\text{ cm}^{-1}$  which are assigned to  $^4\text{A}_{2g} \longrightarrow ^4\text{T}_{2g} \text{F}(\nu_3)$  and  $^4\text{A}_{2g} \longrightarrow ^4\text{T}_{1g} \text{P}(\nu_2)$

transitions respectively. This shows that the positions of the electronic bands have changed from tetrahedral to octahedral region. The Ni(II) complex show the presence of three bands in the region (28154, 20570, 12500  $\text{cm}^{-1}$ ) which are assigned to  ${}^3A_{2g} \rightarrow {}^3T_{1g} P(\nu_3)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g} F(\nu_2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{2g} F(\nu_1)$  transitions respectively. This shows that these bands belong to an octahedral geometry. Three bands appears as shoulders at 10000, 16590 and 29150  $\text{cm}^{-1}$  which may be assigned to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  or  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions respectively, in a distorted octahedral geometry of Cu(II) ion [14].

The magnetic moment values of the Mn(II) complexes (1,5) are (5.60, 5.4 B.M) (Table 1). These values of magnetic moments reveals the presence of five unpaired electrons thereby showing the complexes are of high spin type.

The Co(II) complexes (2,6) have magnetic moments of (4.1 and 4.4 B.M) which indicates the spin free nature of the complexes. It also shows the presence of three unpaired electrons. The high spin octahedral Co(II) complexes have magnetic moments ranging from (4.0-4.8) and the tetrahedral complexes in the range (4.0-5.2) [15]. So that our Co(II) complexes (2) has tetrahedral while complex No. (6) has an octahedral geometry.

The Ni(II) complexes (3,7) have magnetic moments of (3.98 and 3.30 B.M) at room temperature this suggest the presence of two unpaired electrons which reveal the spin nature of the complexes. The tetrahedral Ni(II) complexes have magnetic moments in the range (3.2-4.0 B.M) while the octahedral Ni(II) complexes have magnetic moments in the range (2.9-3.4 B.M) (15). The value of Ni(II) complex (3) is well in the range (3.2-4.0 B.M) so the complex have tetrahedral geometry and depending on electronic spectra the Ni(II) complex (7) may have an octahedral stereochemistry .

The magnetic moment of Cu(II) complex (4) has been found to be 2.00 B.M this corresponding to the presence of one unpaired electron in the complex. This value indicate tetrahedral geometry for the complex. While complex No. (8) have magnetic moment of (1.91 B.M) this value is slightly higher than the spin only value of respective metal ions indicating the spin free octahedral environment around the Cu(II) ion (16).

The molar conductivities for  $10^{-3}\text{M}$  solutions of the complexes (Table 1) indicate that they are non electrolytes in DMSO (17).

Results of intrinsic measurements are listed in Table 1. The interinsic viscosities of metal complexes are higher than that of the ligand (repeat unit) that is due higher molecular weight of the complexes (18).

## Synthesis & Characterization of Coordination...

On the basis of the above discussions we propose the following structures for the metal (II) complexes.

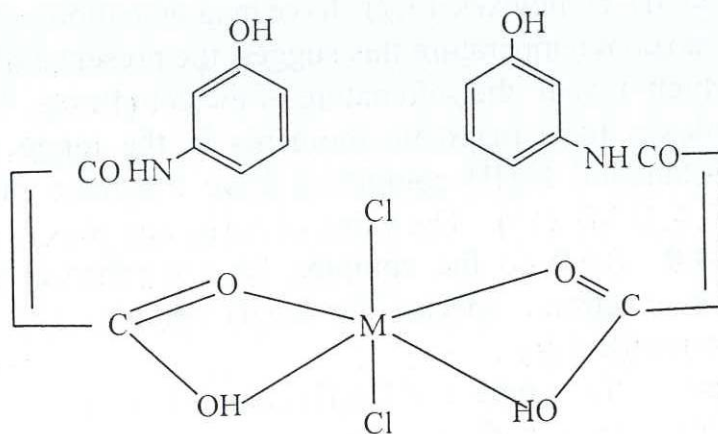
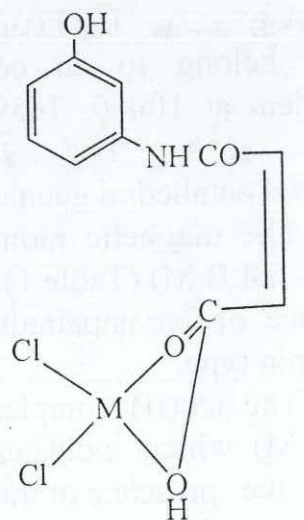
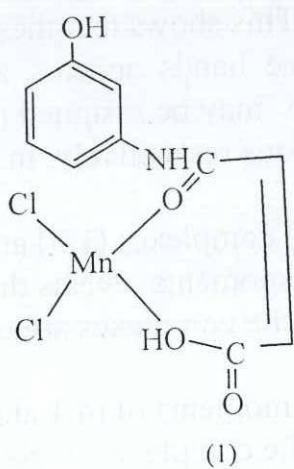


Fig 1: Suggested structures for the metal (II) complexes

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Table 1. Physical properties of the resin and its metal complexes

| (Main Unit)  | Analysis found (calc.) |                |                |                  | M.P<br>(°C) | Colour      | $\mu_{\text{eff}}$<br>(B.M) | Viscosity<br>( $\eta$ ) | $\Delta \epsilon$<br>$\text{cm}^2 \text{mol}^{-1}$ |
|--|------------------------|----------------|----------------|------------------|-------------|-------------|-----------------------------|-------------------------|--|
|  | C%                     | H%             | N%             | M%               |             |             |                             |                         |  |
| $\text{C}_{11}\text{H}_6\text{O}_4\text{N}$ (Resin)                      | 60.16<br>(60.27)       | 4.08<br>(4.11) | 6.34<br>(6.39) | -                | 210         | Yellow      | -                           | 0.321                   | 10   |
| 1. $[\text{Mn}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})\text{Cl}_2]$   | (38.37)                | (2.62)         | (4.07)         | -                | 350         | Black       | 5.6                         | 0.412                   | 20   |
| 2. $[\text{Co}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})\text{Cl}_2]$   | (37.93)                | (2.58)         | (4.02)         | 16.89<br>(16.95) | 360         | Olive       | 4.1                         | 0.493                   | 24   |
| 3. $[\text{Ni}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})\text{Cl}_2]$   | (37.91)                | (2.68)         | (4.02)         | 16.80<br>(16.94) | 340         | Brown       | 3.98                        | 0.354                   | 22   |
| 4. $[\text{Cu}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})\text{Cl}_2]$   | (37.5)                 | (2.56)         | (3.98)         | 18.00<br>(18.04) | 310         | Olive       | 2.00                        | 0.342                   | 28   |
| 5. $[\text{Mn}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})_2\text{Cl}_2]$ | (46.69)                | (3.19)         | (4.97)         | -                | 330         | Black       | 5.4                         | 0.573                   | 15   |
| 6. $[\text{Co}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})_2\text{Cl}_2]$ | (46.56)                | (3.17)         | (4.94)         | 10.39<br>(10.41) | 360         | Dark gray   | 4.4                         | 0.598                   | 20   |
| 7. $[\text{Ni}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})_2\text{Cl}_2]$ | (46.51)                | (3.17)         | (4.91)         | 10.31<br>(10.35) | 350         | Brown       | 3.3                         | 0.480                   | 18   |
| 8. $[\text{Cu}(\text{C}_{11}\text{H}_6\text{O}_4\text{N})_2\text{Cl}_2]$ | (46.23)                | (3.15)         | (4.90)         | 11.10<br>(11.12) | 360         | Olive-black | 1.91                        | 0.469                   | 23   |



Table 2. Electronic and infrared data of the resin and its metal complexes

| Complex<br>(Main unit)   | Band position (cm <sup>-1</sup> )    | Selected IR band (cm <sup>-1</sup> ) |                   |                     |                   |                   |                    |
|--|--------------------------------------|--------------------------------------|-------------------|---------------------|-------------------|-------------------|--------------------|
|  |                                      | $\nu(\text{OH})$                     | $\nu(\text{C=O})$ | $\nu(\text{C=O})^a$ | $\nu(\text{C-O})$ | $\nu(\text{M-O})$ | $\nu(\text{M-Cl})$ |
| Resin  | 31211, 38330                         | 3430 m<br>3200 m                     | 1700 s            | 1650 s              | 1280              | -                 | -                  |
| 1. [Mn(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 23364, 29154                         | 3420 m<br>3200 m                     | 1695 s            | 1625 s              | 1295 w            | 490 w             | 290 w              |
| 2. [Co(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 14771, 16583                         | 3250 m                               | 1675 s            | 1650 s              | 1300 w            | 430 w             | 300 w              |
| 3. [Ni(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 14150                                | 3200 w                               | 1680 s            | 1650 s              | 1290 m            | 500 w             | 305 w              |
| 4. [Cu(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 16051, 29150                         | 3225 w                               | 1660 s            | 1640 s              | 1305 m            | 480 w             | 300 w              |
| 5. [Mn(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 18700, 19331, 22500,<br>25433, 30120 | 3200 m                               | 1700              | 1610                | 1300              | 460 w             | 305 w              |
| 6. [Co(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 15150, 22220                         | 3220 m                               | 1660              | 1650                | 1290              | 500 w             | 300 w              |
| 7. [Ni(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 12500, 20570, 28154                  | 3260 m                               | 1650              | 1640                | 1310              | 480               | 290 w              |
| 8. [Cu(C <sub>11</sub> H <sub>9</sub> O <sub>4</sub> N) <sub>2</sub> Cl <sub>2</sub> ] | 10000, 16540, 29150                  | 3210 m                               | 1655              | 1650                | 1305              | 500 w             | 300 w              |

a = amide carbonyl s = strong, m=medium, w=weak