Synthesis, characterization and antimicrobial studies of some metal complexes with mixed ligands derived from Mannich bases and diamine ligands

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Abstract. The present study deals with the structure and antimicrobial properties of a new series complexes of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) ions with mixed ligands involved Mannich ligand (L) and diamine ligand (L').

L = Mannich ligands involved L₁, L₂, L₃ namely:
L₁ = N-[1-Morpholino-(3-methoxy,4-hydroxy)benzyl]acetamide (MBA)
L₂ = N-[1-Morpholino-(3-methoxy,4-hydroxy)benzyl]Benzamide (MBB)
L₃ = N-[1-Morpholino-(3-methoxy,4-hydroxy)benzyl]Urea (MBU)

L' Ligand is a 1,10-phenanthroline.

These complexes were prepared from the direct reaction of the metal (II) chloride, mannich bases (MBA, MBB, MBU) and diamine ligand namely with mole ration (2:1:1) of L:M:L' categories of complexes were synthesis is mononuclear complexes of formula:

[M(L)₂(L')]nH₂O where

M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II).

L = Mannich base (MBA, MBB, MBU).

L' = 1,10-phenanthroline.

The structure of each complex was characterized by spectroscopic methods (IR, UV-Visible), molar conductivity, elemental analysis (C.H.N) and atomic absorption techniques as well as magnetic data. The completion of the reaction checked by using TLC. The mannich bases (L) and diamine ligands coordinated to the metal ion as bidentated ligands through the oxygen atom of the carbonyl group of amide, nitrogen atom of morpholine and two nitrogen atoms of diamine ligand. The following geometrical with all metal ions showed octahedral geometry. Antibacterial activity of the ligand and its complexes was tested against some select bacterial.

Keywords: Mannich base, metal complexes, antimicrobial activity.
Introduction

Mannich bases with metal complexes containing azomethines have been studied [1-6] extensively in recent years due to the selectivity and sensitivity of the ligands towards various metal ions. Mannich reaction is a three component condensation reaction consisting of active hydrogen containing compound, formaldehyde and secondary amine [7]-[10].

One of the most important classes of biologically active ligands providing potential binding sites through nitrogen and oxygen donor atoms constitute azomethines [11-13]. It is generally accepted that for neutral amide groups, both protonation and metal ion binding will be at the amide oxygen [6]. The compounds containing amide moiety have a strong ability to form metal complexes and exhibit a wide range of biological activity [13]. Upon deprotenation the binding shifts to the amide nitrogen [12]. But for certain reasons like bite size and steric hindrance, the coordination may also take place at amide nitrogen. In continuation of our earlier studies [14-26],

In this paper we describes the synthesis and characterization of transition and non transition metal (II) ions with Mannich base and 1,10-phenanthroline, which have improved by using physicochemical techniques. The ligand (Mannich base) coordinates with metal ion in bidentate manner through oxygen atom of carbonyl group, nitrogen atom of morpholine ring and two nitrogen atoms of 1,10-phenanthrolin. The antibacterial activity of some complexes and ligands described also in this note.

Experimental work:

A. Material and Methods:

All the reagents and solvents were purchased from Fluka and they were used as received. Reactions were monitored by thin layer chromatography. Molar conductance were carried out for 10^{-3} M solution in dimethyl sulfoxide (DMSO) using an electronic conductivity measuring device model LF-42 at 25°C. IR spectra were recorded on Shimadzu UV 1800 spectrophotometer at 25°C using 1 cm quartz cell. Magnetic susceptibility measurements were performed on MSB-MKI (magnetic susceptibility balance) Sherwood scientific using Gouy method. Metal analysis was carried out by using an AA 24 OFS Varian instrument for atomic absorption. Carbon, Hydrogen and Nitrogen contents were determined at the Ibnhiaothem center for research, Baghdad, Iraq.

B. Preparation of N-[1-Morpholin(3-methoxy, 4-hydroxy) Benzyl] acetamide (MBA).

Acetamide (2.9 g, 0.1 mol), vaniline (3-methoxy, 4-hydroxy benzaldehyde), (0.1 mol, 7.69 g) morpholine (0.1 mol, 4.3 ml) were taken in (1:1:1) mole ratio ice cold condition acetamide was dissolved in minimum quantity of ethanol and mixed with morpholine and stirred in ice-bath at 5°C and stirred to get a clear solution. Vaniline was dissolved in ethanol and then added in dropwise with stirring in ice – bath for an hour. The resulting reaction mixture was kept at room temperature for Ca.5d. The solid product formed was filtered, washed with water and ethanol to remove unreacted acetamide and morpholine. The product MBA was then dried and recrystallized in an ethanol purity of the compound was checked by TLC.

C. Preparation of N-[1-Morpholin(3-methoxy, 4-hydroxy) Benzyl] benzamide (MBB).

The ligand MBA was prepared by the same procedure in B using 0.1 mol, 6.1 ml benzamide to obtain orange crystals.

D. Preparation of N-[1-Morpholin(3-methoxy, 4-hydroxy) Benzyl] Urea (MBU).

MBU was prepared by the same procedure in (B) by using (0.1 mol, 3g) of urea.
The preparation of Mannich base (L) may be represented as below (scheme 1).

\[
\text{H}_3\text{CO}-\text{C} = \text{H} + \text{O}-\text{NH} + \text{R}-\text{C} = \text{NH}_2 \xrightarrow{-\text{H}_2\text{O}} \text{HO}-\text{H}_3\text{CO}-\text{H} = \text{N} = \text{C} = \text{R} \\
\text{N-[(1-Morpholino(3-methoxy, 4-hydroxy)benzyl)actemide, } \text{R} = \text{CH}_3 \text{ (MBA)}
\]

\[
\text{N-[(1-Morpholino(3-methoxy, 4-hydroxy)benzyl)benzamidine, } \text{R} = \text{C}_6\text{H}_5 \text{ (MBB)}
\]

\[
\text{N-[(1-Morpholino(3-methoxy, 4-hydroxy)benzyl)urea, } \text{R} = \text{NH}_2 \text{ (MBU)}
\]

**Scheme (1): Preparation of ligand L (MBA, MBB, MBU)**

**E. Preparation of metal complexes:**

All complexes were prepared in non-aqueous medium. A solution of 0.1M of MCl$_2$.nH$_2$O (M=Fe, Co, Ni, Cu, Zn) in ethanol, 0.2 M of ligand (L) (MBA, MBB, MBU) dissolved in chloroform and 0.1M of 1,10-phenanthroline (L') in ethanol were added to around bottomed flask, gently warmed on water bath, stirred well for an hour. The complex formed was filtered, washed with distilled water, ethanol and dried. The preparation of the metal complexes may be represented as below scheme (2).

\[
2 \text{N} = \text{H} + \text{C} = \text{N} = \text{C} = \text{R} + \text{MCl}_2 \cdot n\text{H}_2\text{O} + 1,10\text{-phenanthroline} \\
\xrightarrow{} \text{HO} - \text{OCH}_3
\]

**Scheme (2): Synthesis of transition metal complexes**
R = CH₃, C₆H₅, NH₂
M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II)
N = 1,10-phenanthroline

Iii. Results and discussion

The physical properties, elemental analysis of ligands were given in table (1). The complexes were air stable at room temperature and coloured solid. The physical properties elemental analysis, molar conductance of complexes are listed in table (1).

The molar conductivity in DMSO of complexes were between (16-24) ohm-1.cm2.mol⁻¹, indicates as non-electrolyte nature [27-31]. The ligands (L, L') and their complexes were analysed for elemental analysis show 2:1:1 (L:M:L') table (1).

Table (1): Physical characterization analyticals molar conductance data of Ligands and their complexes

| Compound No. | Compound | Color | Yield (%) | Melting point (°C) | Molar conductivity (Ω⁻¹.cm².mol⁻¹) | % C, H, N (found)calc |
|--------------|----------|-------|-----------|-------------------|-----------------------------------|----------------------|
| 1 | L₁MBA | C₃H₆N₂O₄ | Orange | 75 | 198 | ---- | ---- | 9.931 | 7.191 | 59.984 |
| 2 | L₂MBB | C₃H₆N₂O₄ | Orange | 64 | 192 | ---- | ---- | 8.181 | 6.476 | 66.650 |
| 3 | L₃MBU | C₃H₆N₂O₄ | Orange | 69 | 167 | ---- | ---- | 14.937 | 6.807 | 54.363 |
| 4 | [FeC₆H₅NO₂]₂H₂O | Brownish orange | 74 | 202 | 18 | 6.706 | (6.776) | (9.487) | (5.977) | (57.213) |
| 5 | [CoC₆H₅NO₂]₂H₂O | Pale brown | 90 | 206 | 16 | 7.050 | (6.782) | (10.098) | (5.362) | (56.654) |
| 6 | [NiC₆H₅NO₂]₂H₂O | Orange | 62 | 228 | 19 | 7.024 | (7.635) | (9.643) | (6.011) | (56.635) |
| 7 | [ZnC₆H₅NO₂]₂H₂O | Orange | 63 | 212 | 19 | 6.222 | (56.898) | (7.021) | (10.221) |
| 8 | [FeC₆H₅NO₂]₂H₂O | Red | 73 | 208 | 20 | 5.698 | (6.276) | (5.836) | (8.782) |
| 9 | [CoC₆H₅NO₂]₂H₂O | Pale orange | 82 | 224 | 22 | 5.879 | (6.887) | (6.139) | (8.545) |
| 10 | [NiC₆H₅NO₂]₂H₂O | Orange | 76 | 226 | 21 | 5.881 | (6.988) | (6.476) | (6.992) | (8.238) |
| 11 | [CoC₆H₅NO₂]₂H₂O | Pale brown | 68 | 250 | 23 | 5.851 | (6.259) | (6.588) | (8.712) |
| 12 | [NiC₆H₅NO₂]₂H₂O | Brownish red | 50 | 218 | 19 | 5.840 | (6.142) | (7.312) | (8.723) |
| 13 | [FeC₆H₅NO₂]₂H₂O | Brown | 73 | 220 | 21 | 6.140 | (5.843) | (5.981) | (6.102) | (10.034) |
| 14 | [CoC₆H₅NO₂]₂H₂O | Pale brown | 63 | 216 | 20 | 7.126 | (6.876) | (10.986) | (6.089) | (56.975) |
| 15 | [NiC₆H₅NO₂]₂H₂O | Green | 81 | 200 | 19 | 11.835 | (10.967) | 6.083 | 55.095 | (6.684) | (54.652) |

Table 1: Physical characterization analyticals molar conductance data of Ligands and their complexes.
A. Infrared spectral studies

The IR spectrum of the free ligand was compared with the spectra of the complexes by using KBr disc in order to study the binding mode of the mannich base to the metal in the complexes. Table (2).

The ligand L (MBA), (MBB), (MBU) shows bands between (3330-3361 cm\(^{-1}\)), (1637-1658 cm\(^{-1}\)) and (1035-1116 cm\(^{-1}\)) which have been assigned to \(\nu(\text{NH})\) amide, \(\nu(\text{C}=\text{O})\) and \(\nu(\text{C}-\text{N}-\text{C})\) of morpholine group[32,33].

In the infrared spectra of all complexes the \(\nu(\text{NH})\) band observed in the ligands is absent in the complexes, suggesting deprotonation of NH of the ligand prior to the coordination to the metal [34].

The C-N-C morpholine which undergo negative shifts with fairly low intensity on complex ion [34,35]. This is further supported by the appearance of new bands at (412-462 cm\(^{-1}\)) due to M-N bands[37,38,39]. The \(\nu(\text{C}=\text{O})\) mode of the free ligand is not observed indicating the enolisation of C=O followed by deprotonation and complexation with metal ions and show a new bands in the region (1224-1236 cm\(^{-1}\)) due to the \(\nu(\text{C}=\text{O})\). Appearance of new bands at (486-521 cm\(^{-1}\)) support the formation of M-O bond via-de-protonation, indicating coordination through the oxygen atom of amide moiety [35,36].

The stretching vibration of C=N in diamine ligand L’ (phen) observed in the region 1557 cm\(^{-1}\) but it shifted to low frequency (65-134 cm\(^{-1}\)) in all complexes indicate the coordination to metal ion [39,40].

The presence of phenolic –OH group in all complexes in between (3400-3461 cm\(^{-1}\)) indicates that which was not involved in coordination [36].

The rocking vibration of water is not observed in the IR spectra of complexes. This is confirmed that the water molecule is not coordinated [37,41].

The band in the region (1290-1292 cm\(^{-1}\)) are observed in the IR spectra of ligands and complexes belonged to the methoxy group [42].

IR data concludes that the mannich base ligand L (L1, L2, L3) in all complexes studied behaves as a chelating bidentate one and the binding sites are one carbonyl oxygen atom and the morpholine ring.
Table 2: Infrared dates (cm⁻¹) of ligands and their complexes

| o. | Compound                 | -H | -H | =O | -N-C | -CH3 | O | =N | -O | -N |
|----|-------------------------|----|----|----|------|------|---|----|----|----|
| 1  | (MBA)                   | 361| 462| 640| 118  | 290  | - | -  | -  | -  |
|    | [Fe (MBA)₂(phen)]       | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 461| 041  | 292  | 236| 431| 18 | 14 |
|    | [Co (MBA)(phen)]        | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 459| 041  | 292  | 223| 436| 11 | 24 |
|    | [Ni (MBA)(phen)]        | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 460| 068  | 292  | 224| 440| 86 | 18 |
|    | [Cu (MBA)(phen)]        | -  | -  | 462| 070  | 292  | 228| 444| 13 | 14 |
|    | 2H₂O                    | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | [Zn (MBA)₂(phen)]       | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 460| 043  | 292  | 228| 492| 20 | 18 |
| 2  | (MBU)                   | 348| 400| 640| 120  | 290  | - | -  | -  | -  |
|    | [Fe (MBU)(phen)]        | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 398| 039  | 290  | 222| 440| 14 | 24 |
|    | [Co (MBU)(phen)]        | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 404| 039  | 290  | 230| 444| 13 | 14 |
|    | [Ni (MBU)(phen)]        | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 400| 041  | 290  | 226| 444| 91 | 18 |
| 3  | [Cu (MBU)(phen)]        | -  | 3  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | 3  | -  | 1    | 1    | - | -  | -  | -  |
|    | [Zn (MBU)]              | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 400| 041  | 290  | 224| 438| 11 | 12 |
| 4  | (MUB)                   | 330| 461| 658| 118  | 292  | - | -  | -  | -  |
|    | [Fe (MUB)]              | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 458| 033  | 292  | 236| 423| 01 | 30 |
|    | [Co (MUB)]              | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 454| 068  | 292  | 225| 438| 21 | 14 |
|    | [Ni (MUB)]              | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 461| 039  | 292  | 226| 446| 10 | 24 |
| 5  | [Cu (MUB)]              | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
|    | 2H₂O                    | -  | -  | 462| 035  | 292  | 232| 427| 11 | 22 |
|    | [Zn (MUB)]              | -  | -  | -  | 1    | 1    | - | -  | -  | -  |
B. Electronic spectra and magnetic moment.

The electronic spectra and magnetic moment of metal complexes are listed in table (3). The uv-visible spectrum in DMSO registers two intense bands at (34.965, 41.322 cm\(^{-1}\)) due to the \(\pi^*\) transition of the carbonyl group and \(\pi\) \(\pi^*\) transition of the carbonyl group and benzene ring of ligands (MBA, MBB, MBU). The electronic absorption spectra of the ligand and its iron (II), cobalt (II), nickel (II), copper (II), and zinc(II) recorded in DMSO solution.

The electronic spectra of Fe(II) complexes (26) Table (3) show bands at (11214 cm\(^{-1}\)) due to \(^5T_{2g}\) \(^3E_g\) and at (24161 cm\(^{-1}\)) due to the charge transfer [44, 45, 46,47]. The other complexes of iron (II) [16,21] Table (3) show bands in the region (19157-20325) cm\(^{-1}\) due to \(^5T_{2g}\) \(^3E_g\) and at (26455-34965 cm\(^{-1}\)) due to charge transfer[48, 49,50]. The position of these bands is in agreement with hexa coordinated iron(II) complexes with octahedral geometry. The magnetic moment of Fe(II) complexes Table (3) indicates as reported for octahedral high spin [51].

The electronic spectra of Co(II) complexes Table (3) shows absorption at 10204-11412 cm\(^{-1}\), 14468-15841 and 20491-21186 cm\(^{-1}\) assignable to \(^4T_{1g}(F)\) \(^4T_{2g}(F)\), \(^4T_{1g}(F)\) \(^4A_{2g}(F)\) and \(^4T_{1g}(F)\) \(^4A_{1g}(F)\) transition respectively [18,49,52]. The magnetic moment values of Co(II) complexes are (4.43-4.94 B.M), suggesting an octahedral geometry [19,53,54].

The electronic spectra of Ni(II) complexes exhibits three bands at (10231-11714), (19250-20408), (23094-25385 cm\(^{-1}\)), which may reasonably be assignable to \(^3A_{2g}(F)\) \(^3T_{2g}(F)\), \(^3A_{2g}(F)\) \(^3T_{1g}(F)\), and \(^3A_{2g}(F)\) \(^3T_{1g}(p)\) transitions, respectively. The magnetic moments for Ni(II) complexes (2.82-3.01 B.M) are within range of an octahedral geometry[52,55,56,57,58,59,60].

The observed magnetic moments for Cu(II) complexes are (1.02-1.12 B.M) Table (3) respectively, an octahedral geometry of the legand around the central metal ion which much less than the spin only value indicating the interaction between unpaired spins in the solid state [43,52]. The bands observed at (13477-14925 cm\(^{-1}\)), (1607-19920 cm\(^{-1}\)) due to \(^2B_{1g}\) \(^2B_{2g}\), \(^2B_{1g}\) \(^2E_g\), and observed bands at in the region 11477 cm\(^{-1}\) for complex (29) only due to \(^2B_{1g}\) \(^2A_{1g}\)[39,52,61,62]. The position of these bands suggest on octahedral geometry. The Zn(II) complexes are diamagnetic as expected for d10 system[52,58].
Table (3): Electronic spectra and magnetic moment of complexes

| o.  | Compound                   | eff (B.M) | C.T. cm\(^{-1}\) | d\(\rightarrow\)d transition cm\(^{-1}\) |
|-----|----------------------------|-----------|-------------------|---------------------------------|
| 0   | [Fe MBA\(_2\)](phen)\(2\)H\(_2\)O | 4.7       | 26455,            | 19157                           |
| 1   | [Co (MBA\(_2\))](phen)\(2\)H\(_2\)O | 4.9       | 27027,            | 10204, 14468,                   |
| 2   | [Ni (MBA\(_2\))] (phen)\(2\)H\(_2\)O | 2.8       | 30674,            | 20491                           |
| 3   | [Cu (MBA\(_2\))] (phen)\(2\)H\(_2\)O | 1.1       | 30112,            | 11454, 19230,                   |
|     | [Zn (MBA\(_2\))] (phen)\(2\)H\(_2\)O | --        | 28901,            | 24154                           |
| 4   | [Fe (MBB\(_2\))] (phen)\(2\)H\(_2\)O | 4.0       | 29628,            | 20325                           |
| 5   | [Co (MBB\(_2\))] (phen)\(2\)H\(_2\)O | 4.8       | 32722,            | 11124, 15841,                   |
| 6   | [Ni (MBB\(_2\))] (phen)\(2\)H\(_2\)O | 2.8       | 32679,            | 11714, 20408,                   |
| 7   | [Cu (MBB\(_2\))] (phen)\(2\)H\(_2\)O | 1.0       | 31055,            | 13477, 19920,                   |
| 8   | [Zn (MBB\(_2\))] (phen)\(2\)H\(_2\)O | --        | 38314,            | 43859                           |
| 9   | [Fe (MBU\(_2\))] (phen)\(2\)H\(_2\)O | 4.5       | 24161,            | 11214                           |
| 10  | [Co (MBU\(_2\))] (phen)\(2\)H\(_2\)O | 4.4       | 32722,            | 11412, 14845,                   |
| 11  | [Ni (MBU\(_2\))] (phen)\(2\)H\(_2\)O | 3.0       | 32679,            | 10231, 20408, 5385              |
| 12  | [Cu (MBU\(_2\))] (phen)\(2\)H\(_2\)O | 1.0       | 31055,            | 11477, 14925, 19920             |

C.

Analytical activity:

The in vitro biological screening effects of the investigated compounds were tested against bacteria staphylococcousaureus. The zone of inhibition values of the compounds against the growth of microorganic are summarized in Table (4). A comparative study of the ligand and its complexes indicates that the metal chlates exhibit higher activity than the free ligand. The increase in antibacterial activity is due to faster diffusion of metal complexes as whole through the cell membrane or due to the combined activity effect of the metal and ligand [63].

Table (4): Antibacterial activity of the ligands and their complexes

| Compound No. | Compound               | Staphylococcus | Pseudomonousaeruginose |
|--------------|------------------------|----------------|------------------------|
| 2            | [Co (MBA\(_2\))](phen)\(2\)H\(_2\)O | 6.5            |                        |
| 6            | [Fe (MBA\(_2\))](phen)\(2\)H\(_2\)O | 6.5            |                        |
| 7            | [Co (MBB\(_2\))](phen)\(2\)H\(_2\)O | 12             |                        |
| 12           | [Co (MBU\(_2\))](phen)\(2\)H\(_2\)O | 7              |                        |
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