Synthesis, characterization and biological activity of some transition metal complexes of Pyrrolidine derivatives


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ABSTRACT

Two ligands: 4-hydrazinyl-1-(4-methoxyphenyl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (H2L1) and 4-(2-(1H-pyrrol-2-yle)hydrazinyl)-1-(4-methoxyphenyl)-2,5-dihydro-1H-pyrrol-3-carbonitrile (H2L2) have been prepared and characterized. Their copper(II), nickel(II), cobalt(II), manganese(II) and zinc(II) complexes have been also synthesized and characterized by infrared, electronic spectra, magnetic and conductivity measurements in addition to elemental and thermal analyses. Octahedral structures are suggested for the H2L1 complexes of Cu(II) and Mn(II) and the H2L2 complexes of Cu(II), Ni(II) and Mn(II), whereas tetrahedral structures are proposed for the H2L1 complexes of Co(II) and Zn(II) and the H2L2 complex of Co(II). Moreover, the results showed that both ligands are tetradentate in all of their complexes. They also indicated that the complexes exhibit higher antimicrobial activity than their ligands and Mn(II) exhibits a wide range of antimicrobial activity against gram positive, gram negative bacteria and yeast.

Key words: metal complexes, Schiff base, cyano group, biological study.

Introduction

The condensation of an amine with an aldehyde or ketone, forming what is called a Schiff base, is one of the oldest reactions in chemistry. Schiff base ligands coordinate to a metal through the imine nitrogen and another group, usually oxygen, situated on the original carbonyl compound (Prasanta Bhowmik, 2011). Active and well-defined Schiff base ligands are considered as "privileged ligands" because they are easily prepared and are able to stabilize different metals in various oxidation states, (Mohammad Shakir, 2011). Schiff base complexes are extensively studied due to synthetic flexibility, selectivity and sensitivity towards variety of metal ions. Schiff bases are potentially biologically active compounds and have been reported to possess antifungal (Iqbal et al., 2007) antitumor (Singh, 2001) and anticancer activities, (Offiong, 1997). Schiff base metal complexes are more biologically active than their uncoordinated Schiff base molecules (Sau, 2003).

The biological aspects of pyrrolidine derivatives have got attention as they show potential for anti-cancer therapy (Chen et al., 2008; Fiaux et al., 2008), antibacterial agents (Hu et al., 2003), inhibitors of the P-substance (Wu et al., 2000), anti-amebic agents, affecting the nervous system (Thamotharan et al., 2003), antiepileptic substances (Kenda et al., 2004), selective inhibition activity against matrix metalloproteinase-2 (Cheng et al., 2008), inhibitors of the reverse transcriptase enzyme of the HIV (Tamazyan et al., 2004), and characteristics of potent anti-tumor agents (Li et al., 2006).

Cyanide is an efficient ligand for the stabilization of the transition metals in either low or high oxidation states. This high electronic and coordinate versatility prompts its terminal coordination to almost all transition metals, and permits a wide number of binding modes in cyanide bridged complexes (Potočnák et al., 2006). In addition, some of N-(p-substituted phenyl)4-cyanopyrrolidin-3-ones derivatives were prepared and screened for their serotonin antagonistic and antianxiety activities, and they showed high activities compared to buspirone and diazepam as controls. (Abdalla et al., 2009)

In view of these observations and in continuation of our previous work on Schiff base transition metal complexes, we report herein the synthesis and characterization of some Schiff bases complexes of 4-hydrazinyl-1-(4-methoxyphenyl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (H2L1) and 4-(2-(1H-pyrrol-2-yle)hydrazinyl)-1-(4-methoxy phenyl)-2,5-dihydro-1H-pyrrol-3-carbonitrile (H2L2) for their pharmacological screening.
Materials:

All the reagents employed for the preparation of the ligands and their complexes were of the best grade available and used without further purification. They include copper(II) acetate (Cu(CH₃COO)₂), Nickel(II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O), Cobalt(II) acetatetetrahydrate(Co(CH₃COO)₂·4H₂O), Zinc acetate dihydrate(Zn(CH₃COO)₂·4H₂O), Manganese(II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O).

Experimental:

The ligands and their metal complexes were analyzed for C, H, N, and metal contents at the Micro analytical Laboratory, Faculty of Science, Cairo University, Egypt. IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400-4000 cm⁻¹ and in the 500-100 cm⁻¹ region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. Electronic spectra of the ligands and their complexes were obtained in Nujol mulls using a Shimadzu UV–240 UV–Vis recording spectrophotometer. Magnetic susceptibilities were measured at 25°C by the Gouy method using mercuric tetra thiocyanato cobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal’s constant. (Salama et al., 2006) The magnetic moments were calculated from the equation:

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi \text{ M} \text{T}} \]

Molar conductances were measured on a Tacussel type CD₆SONG conductivity bridge using 10⁻¹M DMF solutions. ¹H NMR spectrum was obtained on Brucker Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. ESR measurements of solid complexes at room temperature were made using a Varian E-109 spectrophotometer, with DPPH as a standard material.

Synthesis of ligands:

A mixture of 4-hydrazinyl-1-(4-methoxyphenyl)-2,5-dihydro-1H-pyrrole-3-carbonitrile (0.46 g, 2 mmol) and methyl ketone, namely o-hydroxyacetophenone in case of H₂L₁ or 2-acetylpyrrole in case of H₂L₂ (2 mmol) in 20 cm³ absolute ethanol containing a few drops of acetic acid was heated under reflux for 1 h. (Abdalla et al., 2009). The formed solid was filtered off, dried and recrystallized to afford the target ligands, (Fig 1).

![Fig. 1: Structure of the H₂L₁ and H₂L₂ ligands.](image)

Synthesis of metal complexes:

All complexes were prepared by refluxing hot ethanolic solution of the ligand H₂L₁ or H₂L₂ with a hot ethanolic solution of the corresponding metal salt in a ratio L:M (1:2). The reaction mixtures were refluxed with constant stirring for a time depending on the transition metal salt used. The resulting precipitates were filtered off, washed with hot ethanol (40°C) and dried in a vacuum desiccator over P₂O₅.

In-vitro Antibacterial and Antifungal Activities:

Antimicrobial activity of the synthesized compounds (1-10) in comparison with that of control drugs Chloramphenicol (Chemical Industries Development Company (CID), Cairo, Egypt) was evaluated against
Gram positive (Bacillus subtilis NRRL-B-4219 and Staphylococcus aureus ATCC 29213), Gram-negative bacteria (Escherichia coli ATCC 25922, Alcaligenes faecalis B-170) and fungi (Candida albicans ATCC 10321 and Aspergillus niger NRRL-363) by the agar diffusion technique (Domig et al., 2007). All microorganisms used were obtained from the culture collection of the Department of Chemistry of Natural and Microbial Products, National Research Center, Cairo, Egypt. The microorganisms were passaged at least twice to ensure purity and viability. The compounds were mounted on a concentration of 500 μg/disc. The bacteria were maintained on nutrient agar medium while yeast and fungi were maintained on potato dextrose agar medium. DMSO showed no inhibition zone. The agar media were incubated with different microorganism cultures tested. After 24 h of incubation at 30 °C for bacteria and yeast and 72 h of incubation at 28 °C for fungi, the diameter of inhibition zone in mm was measured (Table 3). Chloramphenicol was used as a positive control for antimicrobial activity in a concentration of 100 μg/disc.

Preparation of the discs:

Compounds 1-10 together with the positive control Chloramphenicol were mounted on a paper disc prepared from blotting paper (5 mm diameter) with the help of a micropipette on a concentration of 500 μg/10μL DMSO/disc. The discs were applied on the microorganism-grown agar plates.

Preparation of agar plates:

Minimal agar was used for the growth of specific microbial species. The preparation of agar plates for Bacillus subtilis, Staphylococcus aureus and Escherichia coli (bacteria) utilized nutrient agar (2.30 g; obtained from PanreacQuimica SA, Spain) suspended in freshly distilled water (100 ml), and potato dextrose agar medium (3.9 g/100 ml; obtained from Merck) for Candida albicans and Aspergillus niger (fungi). This was allowed to soak for 15 min and then boiled on a water bath until the agar was completely dissolved. The mixture was autoclaved for 15 min at 120 °C and then poured into previously sterilized Petri dishes and stored at 30 °C for inoculation.

Procedure of inoculation:

Spore suspension was prepared with the help of a platinum wire loop to reach a microbial concentration equivalent 0.5 Mac-Farland.

Application of the discs:

Sterilized forceps were used for the application of the paper disc on previously inoculated agar plates. When the discs were applied, they were incubated at 37 °C for 24 h for bacteria and yeast, and at 28 °C for 48 h for fungi. The zone of inhibition around the disc was then measured in millimetres.

Results and Discussion

The analytical and physical data of the ligands and their metal complexes reported in (Table 1) and spectral data shown in (Tables 2-3, Fig 2), are compatible with the suggested structures (Fig. 3). The complexes are colored, stable in air and insoluble in H2O, ethanol and non-polar solvents such as benzene. However, they dissolve in polar solvents such as DMF and DMSO. All the complexes are non-electrolytes as shown in (Table 1).

Infrared spectra:

The most characteristic vibrational frequencies and their tentative assignments for the ligands H3L1, H2L2 and their transition metal complexes are listed in Table 2. The assignments were made by comparison with the vibrational frequencies of the free ligand (Fig. 2).

The IR data obtained for the ligand (H2L1) showed that the ligand behaves as a neutral tetra dentate coordinating through C–OH, C=N, NHbd and C≡N groups in its complexes, and the mode of coordination was suggested by the following pieces of evidence:i) The weakness and shift of υOH band to lower wave number which is further supported by the shift in the stretching frequency of phenolic oxygen υ(C–O) in the complexes (Naresh Kumar et al., 2005).ii) The imines bands are shifted to lower wave number by 23-33 cm⁻¹ (Pal et al., 2002; Ramesh et al., 2003).iii) The υ(C=N) shifts to higher frequencies and the range for terminal cyan ligands extends from 9-29 cm⁻¹ (Vavra et al., 2009). iv) The shift of υN–N to higher wave number (Chandra et al., 2005).
The IR data obtained for the H$_2$L$^2$ ligand suggested that this ligand can behave as a neutral tetra dentate coordinating through NH$_{hyd}$, C=N, NH$_{pyr}$ and C=N groups. In these complexes, the mode of coordination was suggested by the following pieces of evidence: i) In the spectra of all the compounds the $\nu$(NH) band due to the pyrrolic ring is influenced on complexation. ii) The imines bands are negative shifted by 10-40 cm$^{-1}$ (Youssef et al., 2012). iii) The positive $\nu$(C=N) shift in the range forterminal cyano ligands extends from 35-37 cm$^{-1}$ (Vavra et al., 2009). iv) The positive $\nu$N–N shift by 8-18 cm$^{-1}$ (Chandra et al., 2005).

### Table 1: Analytical and physical data of the ligand H$_2$L$^1$, H$_2$L$^2$ and their metal complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ligands/Complexes</th>
<th>Color</th>
<th>FW (g/mol)</th>
<th>Yield (%)</th>
<th>Anal./found (calc.) (%)</th>
<th>Molar conductance (10$^3$ Ω$^{-1}$ cm$^2$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>H$<em>2$L$^1$ C$</em>{10}$H$_{12}$N$_5$O$_2$</td>
<td></td>
<td>334.37</td>
<td>80</td>
<td>67.60 (68.25)</td>
<td>4.95 (5.43)</td>
</tr>
<tr>
<td>2</td>
<td>[Cu$_3$H$_2$L$^2$(OC(O)CH$_3$)$_3$.4H$<em>2$O]$<em>2$C$</em>{27}$H$</em>{30}$Co$_2$N$<em>4$O$</em>{10}$</td>
<td></td>
<td>805.73</td>
<td>75</td>
<td>41.11 (40.25)</td>
<td>5.85 (5.25)</td>
</tr>
<tr>
<td>3</td>
<td>Co$_3$H$_2$L$^1$(OC(O)CH$<em>3$)$<em>3$ C$</em>{27}$H$</em>{30}$N$<em>5$O$</em>{15}$</td>
<td></td>
<td>688.41</td>
<td>72</td>
<td>46.55 (47.11)</td>
<td>3.85 (4.39)</td>
</tr>
<tr>
<td>4</td>
<td>[Mn$_3$H$_2$L$^2$(OC(O)CH$_3$)$_3$.4H$<em>2$O]$<em>2$C$</em>{27}$H$</em>{30}$Mn$_2$N$<em>5$O$</em>{15}$</td>
<td></td>
<td>806.53</td>
<td>66</td>
<td>40.70 (40.21)</td>
<td>6.20 (5.50)</td>
</tr>
<tr>
<td>5</td>
<td>[Zn$_3$H$_2$L$^2$(OC(O)CH$_3$)$<em>3$.5H$<em>2$O] C$</em>{27}$H$</em>{30}$N$<em>5$O$</em>{15}Zn$_2$</td>
<td></td>
<td>791.44</td>
<td>70</td>
<td>40.15 (40.97)</td>
<td>4.55 (5.09)</td>
</tr>
<tr>
<td>6</td>
<td>H$<em>2$L$^1$ C$</em>{10}$H$_{12}$N$_5$O$_2$</td>
<td></td>
<td>321.38</td>
<td>75</td>
<td>64.55 (67.27)</td>
<td>5.62 (5.96)</td>
</tr>
<tr>
<td>7</td>
<td>Cu$_3$H$_2$L$^1$(OC(O)CH$_3$)$<em>3$.4H$<em>2$O C$</em>{27}$H$</em>{30}$Cu$_2$N$<em>5$O$</em>{15}$</td>
<td></td>
<td>756.71</td>
<td>72</td>
<td>41.80 (41.27)</td>
<td>4.40 (5.19)</td>
</tr>
<tr>
<td>8</td>
<td>[Co$_3$H$_2$L$^2$(OC(O)CH$_3$)$<em>3$.3H$<em>2$O] C$</em>{27}$H$</em>{30}$Co$_2$N$<em>5$O$</em>{15}$</td>
<td></td>
<td>729.46</td>
<td>76</td>
<td>41.55 (42.81)</td>
<td>6.50 (5.11)</td>
</tr>
<tr>
<td>9</td>
<td>[Ni$_3$H$_2$L$^2$(OC(O)CH$_3$)$<em>3$.4H$<em>2$O] C$</em>{27}$H$</em>{30}$Ni$_2$N$<em>5$O$</em>{15}$</td>
<td></td>
<td>747.00</td>
<td>66</td>
<td>40.16 (41.80)</td>
<td>5.70 (5.26)</td>
</tr>
<tr>
<td>10</td>
<td>[Mn$_3$H$_2$L$^2$(OC(O)CH$_3$)$_3$.4H$<em>2$O]$<em>2$C$</em>{27}$H$</em>{30}$Mn$_2$N$<em>5$O$</em>{15}$</td>
<td></td>
<td>775.52</td>
<td>80</td>
<td>41.15 (40.27)</td>
<td>6.36 (5.59)</td>
</tr>
</tbody>
</table>

Table 2: IR frequencies of the bands (cm$^{-1}$) of ligands H$_2$L$^1$, H$_2$L$^2$, their metal complexes and their assignments.

### Table 3: The electronic absorption spectral bands (nm) and magnetic moment (B.M) for the ligands H$_2$L$^1$, H$_2$L$^2$ and its complexes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ligand/Complexes</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\mu_{eff}$ (B.M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$L$^1$</td>
<td>366, 302, 270</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[Cu$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.4H$_2$O]</td>
<td>650, 398, 366, 330, 296</td>
<td>1.55</td>
</tr>
<tr>
<td>3</td>
<td>Co$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$</td>
<td>621, 366, 328, 300</td>
<td>4.00</td>
</tr>
<tr>
<td>4</td>
<td>Mn$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.4H$_2$O</td>
<td>650, 390, 320, 299</td>
<td>4.87</td>
</tr>
<tr>
<td>5</td>
<td>[Zn$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.5H$_2$O]</td>
<td>412, 366, 328, 296</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>H$_2$L$^2$</td>
<td>346, 262</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Cu$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.4H$_2$O</td>
<td>645, 388, 352, 296</td>
<td>1.65</td>
</tr>
<tr>
<td>8</td>
<td>Co$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.4H$_2$O</td>
<td>615, 348, 328, 288</td>
<td>3.90</td>
</tr>
<tr>
<td>9</td>
<td>Ni$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.3H$_2$O</td>
<td>630, 450, 354, 286</td>
<td>2.45</td>
</tr>
<tr>
<td>10</td>
<td>Mn$_3$H$_2$L$^1$(OC(O)CH$_3$)$_3$.4H$_2$O</td>
<td>625, 373, 328, 290</td>
<td>4.98</td>
</tr>
</tbody>
</table>
The acetato group in all complexes acted as a monodentate ligand, which is supported by the appearance of two new bands in the ranges 1558-1532 cm\(^{-1}\) and 1342-1314 cm\(^{-1}\), which may be attributed to \(\nu_{\text{asym.}}(\text{COO}^-)\) and \(\nu_{\text{sym.}}(\text{COO}^-)\), respectively (Karbasanagouda et al., 2008), where the difference between them is more than 200 cm\(^{-1}\). The broad bands in the 3400-3466 cm\(^{-1}\) region in all complexes are due to anti symmetric and symmetric OH stretching of water molecules.

**Mass Spectra of the ligand (H\(_2\)L\(^1\))**:

The mass spectra of the Schiff base ligand (H\(_2\)L\(^1\)) exhibit the molecular ion peak at \(m/e\) 334 which is coincident with the formula weight of this ligand. Its proposed pathway fragmentation pattern is described (Scheme1), which supports the identity of its structure.
The proposed structures of H$_2$L$^1$ and H$_2$L$^2$ complexes.

**$^1$H NMR Spectra:**

The $^1$H NMR spectrum of the free ligand (H$_2$L$^1$) in DMSO solution showed proton signals appearing at 8.9, 9.95 and 11.09 ppm for the azomethine (CH=N), N-H, phenolic OH protons, respectively (Bacchi et al., 1998), whereas in case of ligand H$_2$L$^2$ the $^1$H NMR and mass spectra have been characterized before (Abralla et al., 2009).

**Molar conductivity:**

The molar-conductance of the metal complexes (Table 1) are in the 8-18 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ range, indicating their non-electrolytic nature (Golcu et al., 2005).

**Electronic spectra and magnetic moments:**

The UV–Vis spectra of H$_2$L$^1$ and H$_2$L$^2$ exhibits an intense absorption peak at 270-366 and 262-346 nm, respectively (Table 3) assigned to overlap of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectra of the copper complexes 2 and 7 showed one broad absorption band due to the $^5$T$_2g$(G)$\rightarrow$$^3$E$_g$ transition. This band lie at 650 and 645 nm in complexes 2 and 7, respectively, suggesting octahedral geometry (Emara et al., 2006; Swamy et al., 2008). The magnetic moments of copper complexes 2 and 7 are 1.55 and 1.65 BM, respectively, which indicate the presence of an unpaired electron on Cu(II) ion in an octahedral geometry environment (Emam et al., 2009; Rosu et al., 2010). The lower magnetic moment values of these complexes may be attributed to the exchange existing between the metal ions (Youssef et al., 2009).
Scheme 1: The pathway fragmentation pattern of the mass spectrum of the ligand H$_2$L$^1$
In the tetrahedral environment, cobalt(II) complexes are reported to consist of only one transition, due to $^4A_2(F) \rightarrow ^4T_1(F)$ (Lever, 1984). The spectrum of cobalt(II) complexes 3 and 8, showed only one band in the visible region at 621 and 615 nm, respectively. This indicates the tetrahedral geometry for these cobalt(II) complexes (Josephus et al., 2006). The lower magnetic moment values of these complexes (4.00 and 3.90 B.M), respectively, may be attributed to the antiferromagnetic exchange existing between the metal ions (Youssef et al., 2009)

The spectrum of the Zn(II) complex 5 exhibited bands assigned to of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (Al-Jeboori et al., 2010). This complex is diamagnetic as expected. The zinc metal ion normally prefers tetrahedral coordination.

The electronic spectra of the nickel complex showed a band at 630 nm arising from the transition $^3T_1(F) \rightarrow ^3T_1(P)$ which is consistent with a tetrahedral geometry around the nickel(II) ion. The observed magnetic moment of 2.45 B.M lies lower than the normal range found for a tetrahedral environment ($\mu_{eff} 3.02$ B.M) which may be due to the antiferromagnetic exchange contribution (Zaky et al., 2011).

Mn complexes 4 and 10 showed $\mu_{eff}$ of 4.87 and 4.98 B.M, respectively, indicating the presence of five unpaired electrons in these complexes. Their electronic spectra showed absorption bands at 625-650, 375-390 and 320-328 nm, respectively. The first band shown at 625-650 nm is assigned to the $^6A_{1g} \rightarrow ^4T_{1g}$ transition for a high spin octahedral geometry around Mn (II) (Singh et al., 2009). The high energy bands at 375-390 and 320-328 nm may be assigned to the intraligand/charge transfer transition. The lower magnetic moment values of these complexes may be due to the antiferromagnetic exchange between Mn (II) ions (Youssef et al., 2009).

**Thermal analyses (DTA and TGA):**

Complex 2 : TGA % found (% Calc., temp.): H$_2$O 4.59 (4.47, 82 °C), H$_2$O 8.81 (8.95, 128 °C), acetate 30.01 (29.29, 264 °C), CuO 19.64 (19.75, 510 °C).
Complex 3 : TGA % found (%Calc., temp.): acetate 35.03 (34.28, 285 °C), Co$_2$O$_3$ 24.17 (24.09, 601 °C).
Complex 4: TGA % found (%Calc., temp.): H$_2$O 6.99 (6.70, 77 °C), H$_2$O 8.97 (8.93, 125 °C), acetate 30.57 (29.26, 281 °C), Mn$_2$O$_3$ 19.86 (19.57, 585 °C).
Complex 5 : TGA % found (%Calc., temp.): H$_2$O 11.52 (11.37, 87 °C), acetate 30.56 % (29.82 %, 292 °C), ZnO 20.41 % (20.57 %, 510 °C).
Complex 7 : TGA % found (%Calc., temp.): H$_2$O 9.68 (9.53, 137 °C), acetate 31.59 (31.19 , 295 °C), CuO 21.18 (21.03, 515 °C).
Complex 8 : TGA % found (%Calc., temp.): H$_2$O 7.58 (7.41, 73°C), acetate 32.77 (32.35, 287°C), Co$_2$O$_3$ 22.86 (22.74, 585°C).
Complex 9 : TGA % found (%Calc., temp.): H$_2$O 9.83 (9.65, 78°C), acetate 32.77(31.59, 315 °C), NiO 20.16 (20.06, 522°C).
Complex 10 : TGA % found (%Calc., temp.): H$_2$O 4.6 (4.64, 84 °C), H$_2$O 9.39 (9.29, 126°C), acetate 31.09 (30.43, 325 °C), Mn$_2$O$_4$ 40.90 (40.71, 608°C).

The thermogravimetric analysis (TG) was measured in the temperature range of 20-800 °C. The results were in good agreement with the proposed structures. Dehydration of lattice water in lie in the range of 67-78 °C, while removal of coordinated water lie at higher values in the range of 125-137°C. The removal of acetate lie in the range of 264-325 °C. The last stage in all complexes comprises the decomposition of the organic constituents of the complexes leaving the metal oxides at 510-608 °C.

**Suggested Structural Formulae of the Complexes:**

From the spectral data and the elemental analyses, the structure of the prepared complexes may be formulated as shown in (Fig. 3).

**Antibacterial and Antifungal Screening:**

A comparative study of the antimicrobial activity values for ligands and their complexes indicates that the complexes exhibit higher antimicrobial activity than the ligand. The results shown in Table 4 revealed that compound 10 exhibited a wide range of antimicrobial activity against gram positive, gram negative bacteria and yeast. Moreover, compounds 2 and 3 exhibited a moderate antimicrobial activity against A. niger and C. albicans. Such an increased activity of the complexes can be explained on the basis of Overtone’s concept (Knopp et al., 1990) and Tweedy’s chelation theory (Dharmaraj et al., 2001). This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane and chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring. Such chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane.
Table 4: Antimicrobial activity of compounds 1-10.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Inhibition zone (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E. coli</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
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<tr>
<td>2</td>
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<td>9</td>
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<tr>
<td>10</td>
<td>++</td>
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</table>

Chloramphenico 1

Inhibition zone diameter (% inhibition): +, 6–9 mm (33–50%); ++, 10–12 mm (55–67%); ++++, 13–15 mm (72–83%); ++++, 16–18 mm (89–100%). Percentage inhibition values were relative to inhibition zone (18 mm) with 100% inhibition.

Conclusion:

We report here the syntheses and characterization of two Schiff bases ligands, H₂L¹ and H₂L² and their Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) metal complexes. All their data collected are in agreement with their proposed structures. The results indicated that the complexes showed higher antimicrobial activity than their parents ligands whereas Mn (II) exhibited a wide range of antimicrobial activity against gram positive, gram negative bacteria and yeast.

References


