Metal complexes of 1,6-bis(1-benzimidazolyl) hexane: synthesis, characterization and biological activity against some soil-borne fungi

Abbas Washeel Salman1*, Jawadayn Talib Alkooranee2, Hayder Dawood Arkawazi3, Haitham Kadhim Alsharifi4 and Michaele Hardie5

1Department of Production, College of Agriculture, Wasit University, Kut, Wasit, Iraq.
2Department of Plant Protection, College of Agriculture, Wasit University, Kut, Wasit, Iraq.
3Department of Chemistry, College of Science, Wasit University, Kut, Wasit, Iraq.
4Department of Food Technology, College of Food Science, Al-Qasim Green University, Al-Qasim, Babylon, Iraq.
5School of Chemistry, University of Leeds Woodhouse Lane, Leeds, LS2 9JT (UK).

*E-mail: aws.chem@gmail.com

Abstract. Metal complexes Mn(II), Co(II), Cu(II), Zn(II) and Ag(I) of the ligand 1,6-bis(1-benzimidazolyl)hexane were synthesized by the reaction of the ligand and appropriate metal salts in 1:1 mole ratio. The ligand and its complexes were characterized using IR, Uv-Vis, 1H and 13C NMR, Mass spectroscopy, and elemental analysis CHN. Depending on the abovementioned techniques, a polymeric structure was proposed to the prepared complexes. Further, all the synthesized compounds were tested against some of the soil-borne fungi namely; Rhizoctonia solani, Fusarium oxysporum, Fusarium solani and Pythium aphanidermatum. The results showed that the tested compounds have an effect on the growth of pathogenic fungi. This leads to thinking that these compounds could be used one day as new chemical pesticides as an alternative to chemical compounds that have been shown to be resistant to pathogens.

Keywords. Benzimidazole, NMR, Metal complexes, Rhizoctonia solani, Fusarium oxysporum, Fusarium solani, Pythium aphanidermatum.

1. Introduction

The use of synthetic chemical pesticides is still the most widely used method by farmers in the control of plant diseases. But, unfortunately, over the years and because of the ability of some fungi to develop their resistance, some of these pesticides became inactive and a major problem in agriculture [1]. Despite continuing the research to control the various diseases, many phytopathogens fungi have developed multiple mechanisms of resistance where fungicides are becoming challenged increasingly [2]. At the same time, alternative chemicals pesticides are synthesized, investigated, and then used.
successfully to prevent fungal pathogens from growing and spreading in different environments. The introduction of inorganic fungicides such as copper, sulfur, or mercury compounds, followed by organic fungicides such as phthalimides (e.g., captan) dithiocarbamates (e.g., maneb) was the first milestone in the development of fungicide [3]. Many important chemical fungicides used extensively in the last 50 years in the protection of plants such as dicarboximide, benzimidazoles, strobilurin, phenylpyrrole, anilinopyrimidine, Q. respiration inhibitors, and demethylation inhibitors (DMI) [4]. But, over time some of them lost their importance as a result of the resistance of fungi strains [5]. A new class of fungicides was discovered during the 1960s offered curative of plant disease control, ability to longer-lasting protection, and lower application rates. The benzimidazoles were welcomed enthusiastically by farmers and plant pathologists, but the farmers soon reported great resistance to pesticides and large losses in field crops [3]. Imidazole, benzimidazole and their metal complexes are exhibited different coordination modes [6] with a wide variety of applications, especially the biological [7-13], and catalytical ones [14-16]. Both copper and sulfur elements are used from the 1940s until present in integrated and organic farming. Only a few years after used them, resistance development in the pathogen fungi and the loss of fungicide activity were observed [5]. Excessive spraying programs of fungicides have resulted in appearing of multi-resistant strains of gray mold fungus Botrytis cinerea in several fields, particularly in strawberry ones [5]. Although quinol oxidation inhibitors (QoIs) are the most successful in fungicides, it was proved that they were resistant to fungi through mutations in the cytochrome b gene CYTB in some fungi pathogens [17]. To produce high-quality and quantitatively yield crops, researchers should provide optimal growth conditions for plants and protected from damage caused by pests, including insects, weeds, and fungi pathogens. Also, it is necessary to find new active compounds against the pests, at least at the moment. Therefore, this study aimed to use some synthetic compounds for the first time in the control of plant diseases caused by some soil-borne fungi. It is worth to be mentioned that the tested fungi are causing significant economic losses. In the present study, new transition metal complexes derived from the ligand 1,6-bis(1-benzimidazolyl) hexane were synthesized. The ligand and its complexes are tested against some soil-borne fungi namely *Rhizoctonia solani*, *Fusarium oxysporum*, *Fusarium solani* and *Pythium aphanidermatum*. According to the results obtained, we think that these compounds could be used as alternatives for chemical pesticides after more studies and experiments.

2. Materials and Methods

2.1. Materials and Instrumentations

All the chemicals used in the present work were purchased from commercial sources and used as it is without further purifications processes. 1H and 13C NMR spectra were recorded using Bruker UltraShield TM 500MHz spectrometer, Switzerland in d6-DMSO. Dionex Ultimate 3000 spectrometer, Germany, was used to record the mass spectrum of the ligand. The abovementioned techniques are available at School of Chemistry, University of Leeds, UK. CHN analysis was carried out using Euro EA elemental analyzer CHNS, EA3000 analyzer, Germany. Infra-Red spectra were recorded using a SHIMADZU spectrometer, Japan, on potassium bromide disks in the range 4000-400 cm-1. These techniques are available at the department of chemistry- College of science, Al-Mustansiriya University, Baghdad, Iraq. Furthermore, the spectrophotometer Sp-3000 nano OPTIMA, South Korea, was used to record uv-vis spectra in the range 200-800 nm, which is available in the department of chemistry- college of science- University of Wasit, Iraq.

2.2. Synthesis

2.2.1. Synthesis of the ligand 1,6-bis (1-benzimidazolyl) hexane
The method used in synthesis of the ligand 1,6-bis(1-benzimidazolyl)hexane is described in our previous works [18, 19], except using of 1,6-dibromohexane instead of 1,4-dibromobutane. The resulted light beige precipitate was left standing for 2 hrs, then filtrated, washed with plenty of distilled water and dried at room temperature. The yield percentage was 95 %. Anal. Cal. For C\(_{20}\)H\(_{22}\)N\(_{4}\): C, 75.44; H, 6.96; N, 17.60 %, found: C, 75.12; H, 7.18; N, 17.43 %. IR: ν(C-H\(_{\text{aromatic}}\): 3091-3043 cm\(^{-1}\), δ(C-H\(_{\text{aromatic}}\): 767-634 cm\(^{-1}\), ν(C-H\(_{\text{aliphatic}}\): 2933-2852 cm\(^{-1}\), ν(C=C): 1496-1670 cm\(^{-1}\), ν(C=N): 1506 cm\(^{-1}\). MS: 319.198 [M\(^+\)].

1H NMR (DMSO-d\(_6\), 500MHz): δ 1.242 (t, 4H, 2×CH\(_2\)), 1.738 (m, 4H, 2×CH\(_2\)), 4.181 (t, 4H, 2×CH\(_2\)-N), 7.159-7.235 (m, 4H, 2×Ar-H), 7.534 (d, 2H, 2×Ar-H), 7.627 (d, 2H, 2×Ar-H), 8.179 (s, 2H, NCHN).

13C NMR (DMSO-d\(_6\), 125 MHz): δ 25.54 (CH\(_2\)), 29.15 (CH\(_2\)), 43.91 (CH\(_2\)-N), 110.31, 119.37, 121.35, 122.18, 133.74, 143.37 (Ar-C), 143.93 (NCHN) ppm.

2.2.2. Synthesis of the metal complexes

2.2.2.1. General method

To a solution of the ligand 1,6-bis(1-benzimidazolyl)hexane prepared by dissolving 1 mmol in 10 ml of ethanol, 1 mmol of the appropriate metal salts dissolved in 10 ml of ethanol was added dropwise. The resulting mixture was heated with stirring for 1 hr at ≈ 60 oC. The obtained precipitates were filtered and washed with fresh ethanol and distilled water and left to dry at ambient temperature.

2.2.2.2. Synthesis of Mn (II) Complex

The complex was prepared by the reaction of the ligand with MnCl\(_2\).2H\(_2\)O. The reaction produced the complex as a white precipitate with a yield of 74 %. Anal. Cal. for (C\(_{20}\)H\(_{22}\)Cl\(_2\)MnN\(_4\))\(_n\): C, 51.96; H, 5.23; N, 12.12 %, found: C, 51.32; H, 5.47; N, 11.83 %. IR: ν(C=N): 1492 cm\(^{-1}\).

2.2.2.3. Synthesis of Co (II) Complex

The complex was prepared by the reaction of the ligand with CoCl\(_2\). The reaction produced the complex as a blue precipitate with a yield of 69 %. Anal. Cal. for (C\(_{20}\)H\(_{22}\)Cl\(_2\)CoN\(_4\))\(_n\): C, 53.59; H, 4.95; N, 12.50 %, found: C, 53.41; H, 5.11; N, 12.39 %. IR: ν(C=N): 1494 cm\(^{-1}\).

2.2.2.4. Synthesis of Cu(II) Complex

The complex was prepared by the reaction of the ligand with CuCl\(_2\). The reaction produced the complex as a light-green precipitate with a yield of 66 %. Anal. Cal. for (C\(_{20}\)H\(_{22}\)Cl\(_2\)CuN\(_4\))\(_n\): C, 53.04; H, 4.90; N, 12.37 %, found: C, 53.22; H, 5.08; N, 12.15 %. IR: ν(C=N): 1468 cm\(^{-1}\). IR: ν(C=N): 1494 cm\(^{-1}\).

2.2.2.5. Synthesis of Zn(II) Complex

The complex was prepared by the reaction of the ligand with ZnCl\(_2\). The reaction produced the complex as a white precipitate with a yield of 76 %. Anal. Cal. for (C\(_{20}\)H\(_{22}\)Cl\(_2\)ZnN\(_4\))\(_n\): C, 52.83; H, 4.88; N, 12.32 %, found: C, 52.52; H, 4.94; N, 11.96 % IR: ν(C=N): 1494 cm\(^{-1}\). 1H NMR (DMSO-d\(_6\), 500MHz): δ 1.217 (t, 4H, 2×CH\(_2\)), 1.749 (m, 4H, 2×CH\(_2\)), 4.281 (t, 4H, 2×CH\(_2\)-N), 7.271-7.333 (m, 4H, 2×Ar-H), 7.646 (d, 2H, 2×Ar-H), 7.824 (d, 2H, 2×Ar-H), 8.455 (s, 2H, NCHN). 13C NMR (DMSO-d\(_6\), 125 MHz): δ 25.35 (CH\(_2\)), 28.89 (CH\(_2\)), 44.41 (CH\(_2\)-N), 111.06, 118.71, 122.52, 123.15, 133.15, 141.14 (Ar-C), 144.45 (NCHN) ppm.

2.2.2.6. Synthesis of Ag(I) Complex
The complex was prepared by the reaction of the ligand with AgNO₃. The reaction produced the complex as a light-grey precipitate with a yield of 72%. Anal. Cal. for (C₃₀H₃₃AgN₆)(NO₃)ₙ: C, 55.65; H, 5.14%; N, 15.14%. Found: C, 55.37; H, 5.31; N, 15.02%. IR: ν(C=N): 1495 cm⁻¹. ¹H NMR (DMSO-d⁶, 500MHz): δ 1.203 (t, 4H, 2×CH₂), 1.734 (m, 4H, 2×CH₂), 4.261 (t, 4H, 2×CH₂-N), 7.293-7.303 (m, 4H, 2×Ar-H), 7.625 (d, 2H, 2×Ar-H), 7.80 (d, 2H, 2×Ar-H), 8.426 (s, 2H, NCHN). ¹³C NMR (DMSO-d⁶, 125MHz): δ 25.33 (CH₂), 28.69 (CH₂), 44.38 (CH₂-N), 110.86, 118.59, 122.50, 123.19, 133.11, 141.15 (Ar-C), 144.47 (NCHN) ppm.

2.3. Pathogen fungi materials

The pathogens soil-borne fungi R. solani, F. oxysporum, F. solani, P. aphanidermatum isolates were obtained from the field crops department, College of Agriculture, Wasit University, Iraq and maintained and cultured on autoclaved potato dextrose agar (P.D.A) medium (200 g peeled potato, 20 g dextrose, 15 g agar to 1 liter distilled water) in the dark at 25±2°C. The laboratory experiments were conducted in the microbiology laboratory of field crops department in the winter season of 2019.

2.3.1. In vitro inhibition of mycelia length growth

To determine the effects of the tested compounds on mycelial length growth of pathogens fungi in dual-culture techniques, 0, 10, and 20 ppm of each compound were added as 1-20 ml to Petri dish contain molten P.D.A media (40°C ± 2°C) (autoclaved at 121°C 15 psi for 30 min) separately, and mixed properly prior to plating. One mycelium of 5-mm of each pathogen was inoculated at the center of each Petri dish, separately. For the control, a set of plates was inoculated similarly, but with the pathogen only. Three replicate dishes per fungus strain with each concentration combination were set up and incubated at 25°C ± 3°C for 6 days. The radial mycelial growth of the pathogens (measured in centimeters) was assessed after 6 days, and the percent mycelial growth inhibition of each pathogen was calculated using the following growth inhibition equation:

Percent inhibition = (R - r) / R x 100

Where R (a control value) represents the radial growth of fungus pathogen in control sets, and r is the radial growth of the fungus in sets with tested compounds.

2.4. Statistical analysis

GenStat software was used to analyze the significant differences between different treatments using least significant difference (LSD) tests and the means (P < 0.05).

3. Results and Discussion

3.1. Synthesis and Characterization

In the synthesis of the ligand 1,6-bis(1-benzimidazolyl)hexane, an equimolar of benzimidazole and NaOH were reacted in DMSO at 80-90 °C for 2 hr. After cooling the mixture to about 40 °C, a half equivalent of 1,6-dibromohexane was added with constant stirring for more 2 hr. Then, the resultant mixture was poured into cooled distilled water to give instantly the product as an off-white precipitate which was filtered and washed with plenty of distilled water and left to dry at ambient temperature. For the complexes, an equimolar of ethanolic solution of the ligand and appropriate metal salt was heated with stirring between 50-60 °C for about 1 hr. The resultant precipitates were filtered, washed with fresh ethanol and water and left to dry (Scheme 1).
Scheme 1. Synthesis of the ligand and its metal complexes.

FT-IR spectrum of the ligand showed different bands at the range 3091-3043 cm\(^{-1}\). These bands can be assigned to the stretching of aromatic C-H bond and to the vibration of benzimidazole ring. The bending of same groups appeared at the range 767-634 cm\(^{-1}\). The stretching of aliphatic groups appeared at the range 2933-2852 cm\(^{-1}\), while the stretching of C=C bond appeared at the range 1670-1496 cm\(^{-1}\). Last but not least, a characteristic band of \(\nu(C=\text{N})\) of benzimidazole is appeared at 1506 cm\(^{-1}\). It is worth to be mentioned that most of the abovementioned bands are appeared too in complexes spectra, but in different positions or shapes or intensities. Particularly, the stretching vibration of benzimidazole \(\nu(C=\text{N})\) which shifted to lower frequency in all complexes (Figures 1 and 2). These changes assigned to the coordination of tertiary nitrogen in azoles with the metal ions [20-22].
In UV-vis spectra, the free ligand showed a broad band with two shoulders in the range 250-300 nm. These peaks are belongs to the transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, respectively. In complexes spectra, the mentioned peaks are slightly shifted to higher wavelength, which is another evidence for complexation with metal ions [19]. $^1$H and $^{13}$C NMR spectra for the ligand and their Zn(II) and Ag(I) are recorded in DMSO-$d_6$. In the $^1$H NMR spectrum, the ligand showed the characteristic signals which consistent with its proposed structure. The signals at $\delta$ 1.242, 1.738 and 4.181 are belongs to ($-$CH$_2$), ($-$CH$_2$) and ($-$CH$_2$-N), respectively (Figure 3). The signals of the benzimidazole appeared in the range $\delta$ 7.159-7.627. Further, the signal of the proton (NCHN) is appeared as singlet at $\delta$ 8.179. In the $^{13}$C NMR spectrum (Figure 4), the signals appeared at $\delta$ 25.54, 29.15 and 43.91 are assigned to the carbon of (CH$_2$), (CH$_2$) and (CH$_2$-N), respectively. The signals of fused benzene ring appeared at $\delta$ 110.31, 119.37, 121.35, 122.18, 133.74, and 143.37. Last but not least, the signal appeared at $\delta$ 143.93 is belongs to the carbon of (NCN) group.

In Zn(II) and Ag(I) complexes, the signal of (NCHN) proton in benzimidazole is appeared at $\delta$ 8.455 and $\delta$ 8.426, respectively (Figure 5). While, the carbon signal of (NCN) is appeared at $\delta$ 144.45 and $\delta$ 144.47, respectively. Depending on the references, the observed shifting is a good signal for the coordination with metal ions [20, 22]. Unfortunately, no NMR spectra have been recorded for other
complexes due to their paramagnetism. Mass spectroscopy also confirmed the molecular weight of the synthesized ligand [M+] = 319.198 which is in fully agreement with the calculated theoretically (Figure 6).

![Figure 4. $^{13}$C NMR spectrum of the ligand.](image)

![Figure 5. $^1$H NMR spectrum of the Zn(II) complex.](image)

![Figure 6. Mass spectrum of the ligand.](image)
3.2. Antifungal activity

To maintain the increase of agricultural production, new possible fungicides should be diagnosed and deeply studied to know their antifungal activity. So, this study aimed to evaluate the efficiency of some new compounds towards some pathogenic fungi. The results obtained in the present study are shown in Tables (1-4). It is clear that the radial growth of all fungi was adversely affected by the tested compounds. Also, it was shown that the inhibitory effect on the growth of mycelium fungi was increased with increasing of concentrations from 10 ppm to 20 ppm of all compounds. Amongst the tested compounds, Cu$^{2+}$ complex proved to be the most effective against all pathogens fungi with 100% inhibition in radial growth at 20 ppm.

Table 1: reveals that the R. solani fungus was affected with all tested compounds, with highest reduction in fungal growth at 20 ppm which was 100%, while, it was 64.44% at 10 ppm. On the other hand, for the tested compounds, Co$^{2+}$ complex caused the highest reduction in growth 46.33 and 90.0% at 10 and 20 ppm, respectively.

| Compounds  | Growth of R. solani |
|------------|---------------------|
|            | 0 ppm               | 10 ppm              | 20 ppm              |
|            | % inhibition        | % inhibition        | % inhibition        |
| Ligand     | *9.00  0.00         | 9.00  0.00          | 6.34  29.56         |
| Mn$^{2+}$ complex | 9.00  0.00 | 7.56  16.00         | 3.88  56.89         |
| Co$^{2+}$ complex | 9.00  0.00 | 4.83  46.33         | 0.90  90.00         |
| Cu$^{2+}$ complex | 9.00  0.00 | 3.20  64.44         | 0  100             |
| Zn$^{2+}$ complex | 9.00  0.00 | 7.75  13.89         | 2.35  73.89         |
| Ag$^{+}$ complex | 9.00  0.00 | 6.00  33.33         | 4.48  50.22         |
| L.S.D      | NS NS               | 1.33  4.79          | 0.65  6.25          |

*Each number represents three replicates

In case of F. oxysporum (Table 2), Cu$^{2+}$ complex again showed the highest inhibition of mycelial growth with 76.67% at 10 ppm and 100% at 20 ppm. While, the ligand showed the lowest inhibition with 9.5% and 31.10% at 10 ppm and 20 ppm, respectively. Co$^{2+}$ and Zn$^{2+}$ complexes showed inhibition of 36.11 and 48.89% at 10 ppm, whereas at 20 ppm, they showed 87.75 and 85.0%, respectively.

Table 2. Effect of different concentrations of the compounds on the growth of Fusarium oxysporum

| Compounds  | Growth of F. oxysporum |
|------------|------------------------|
|            | 0 ppm                  | 10 ppm                | 20 ppm                |
|            | % inhibition           | % inhibition         | % inhibition         |
| Ligand     | *9.00  0               | 8.14  9.56           | 6.20  31.10          |
| Mn$^{2+}$ complex | 9.00  0   | 5.74  36.22         | 2.12  76.44         |
| Co$^{2+}$ complex | 9.00  0  | 3.32  63.11         | 1.10  87.75         |
| Cu$^{2+}$ complex | 9.00  0  | 2.10  76.67         | 0  100             |
| Zn$^{2+}$ complex | 9.00  0  | 4.60  48.89         | 1.35  85.00         |
| Ag$^{+}$ complex | 9.00  0  | 7.34  18.44         | 4.58  49.11         |
| L.S.D      | NS NS                 | 2.11  6.13          | 0.78  9.65          |

*Each number represents three replicates
The inhibitory effect of the compounds on the mycelial growth of *F. solani* isolate are shown in Table 3. In general, all the tested compounds showed more than 50% mycelial growth inhibition at a concentration of 20 ppm. Significantly, Cu$^{2+}$ and Co$^{2+}$ complexes were the most effective than others, showing 100% growth inhibition. While, Ag$^+$ and Mn$^{2+}$ complexes showed 86.22 and 82.22% growth inhibition at the same concentration. At 10 ppm, the inhibitory effect of the compounds was ranging from 23.71% to 65.00%.

**Table 3.** Effect of different concentrations of the compounds on the growth of *Fusarium solani*.

| Compounds       | Growth of *F. solani* |
|-----------------|-----------------------|
|                 | 0 ppm | 10 ppm | 20 ppm |
|                 | Growth rate cm | % inhibition | Growth rate cm | % inhibition | Growth rate cm | % inhibition |
| Ligand          | *9.00* | 0       | 7.10   | 23.71       | 4.29       | 52.33         |
| Mn$^{2+}$ complex | 9.00  | 0       | 5.38   | 40.22       | 1.60       | 82.22         |
| Co$^{2+}$ complex | 9.00  | 0       | 3.90   | 56.67       | 0          | 100           |
| Cu$^{2+}$ complex | 9.00  | 0       | 3.15   | 65.00       | 0          | 100           |
| Zn$^{2+}$ complex | 9.00  | 0       | 6.65   | 26.11       | 2.85       | 68.33         |
| Ag$^+$ complex  | 9.00  | 0       | 5.78   | 35.78       | 1.24       | 86.22         |
| L.S.D           | NS    | NS      | 1.56   | 7.78        | 1.02       | 6.81          |

*Each number represents three replicates.

Presented data in Table 4 reveals that tested *P. aphanidermatum* fungus was also affected with all compounds. Again, Cu$^{2+}$ and Co$^{2+}$ complexes were the most effective compounds, showing 100% growth inhibition, followed by Mn+2 where growth inhibition of pathogen reached 93.67% at 20 ppm. The ligand was the least effective one, showing 30.33 and 63.56% growth inhibition at 10 ppm and 20 ppm, respectively. Generally, the inhibitory effect of compounds increased as the concentration increased from 10 ppm to 20 ppm, showing more than 50% growth inhibition for the fungus pathogen.

**Table 4.** Effect of different concentrations of the compounds on the growth of *Pythium aphanidermatum*.

| Compounds       | Growth of *P. aphanidermatum* |
|-----------------|-------------------------------|
|                 | 0 ppm | 10 ppm | 20 ppm |
|                 | Growth rate cm | % inhibition | Growth rate cm | % inhibition | Growth rate cm | % inhibition |
| Ligand          | *9.00* | 0       | 6.27   | 30.33       | 3.28       | 63.56         |
| Mn$^{2+}$ complex | 9.00  | 0       | 3.62   | 59.78       | 0.57       | 93.67         |
| Co$^{2+}$ complex | 9.00  | 0       | 1.45   | 83.89       | 0          | 100           |
| Cu$^{2+}$ complex | 9.00  | 0       | 1.11   | 87.67       | 0          | 100           |
| Zn$^{2+}$ complex | 9.00  | 0       | 5.83   | 35.22       | 3.37       | 68.30         |
| Ag$^+$ complex  | 9.00  | 0       | 2.84   | 68.44       | 0          | 100           |
| L.S.D           | NS    | NS      | 1.17   | 13.81       | 0.64       | 5.06          |

*Each number represents three replicates.

These results are consistent with [23] reported that the tested concentrations of 12.5, 25, 50 and 75 ppm of six fungicides of Techigaren 30%, Monceren 25%, Hymexate 30.0%, Moncut 25%, Topsin M70% and Aracur 72.7% led to significantly inhibition of mycelial growth of *R. solani* and *F. solani* isolates in Potato dextrose agar (PDA) medium. Godswill and co-workers [24] were determined the antifungal of two synthetic fungicides (SF1) and (SF2), at different doses against *F. oxysporum* and *P. microspora*. One of the tested compounds (SF1) showed 100% inhibition against both fungi, while
SF2 was less effective at all doses. Three pesticides Benomyl (fungicide) and Karate (insecticide) Galex (herbicide) were lead to significant inhibition, and reduction of mycelial weights of growth of some fungi, Aspergillus flavus, Fusarium oxysporum and Fusarium moniliforme at 0, 100, 200, 400 and 500 mg L\(^{-1}\) rate [25]. [26] studied several fungicides including carbindazim (BCM) for inhibiting the growth of S. sclerotiorum fungus, where the percentage of inhibition reached 100% when adding different concentrations of the fungicide from 50, 100, 200, 500 and 1000 ppm. Youssef et al [27] reported ability of some chemical to reduce the mycelial growth of S. sclerotiorum, the colony diameter of fungus inhibited by 100% at 8 days after being treated with 0.1 % SA and prevented formation of new sclerotia until 21.

4. Conclusion

The ligand 1,6-bis(1-benzimidazolyl) hexane and its respective metal complexes Mn(II), Co(II), Cu(II), Zn(II) and Ag(I) are synthesized and characterized. Depending on the results obtained in this work and the literature, a polymeric structure was proposed for the synthesized complexes. Furthermore, the ligand and its complexes are tested against some soil-borne fungi namely; Rhizoctonia solani, Fusarium oxysporum, Fusarium solani and Pythium aphanidermatum. In general, all the tested compounds showed an activity against the studied pathogens. Significantly, Cu\(^{+2}\), Co\(^{+2}\) and Mn\(^{+2}\) complexes were the most effective on mycelial growth of soil born fungi pathogen isolates. The effective compounds acts as anti-fungal agents and inhibits their growth possibly because they negatively affect the metabolic process of these pathogenic fungi.

5. References

[1] Wilson C and Tisdell C 2001 Why farmers continue to use pesticides despite environmental, health and sustainability costs Ecol. Economics 39 449.
[2] Brown TM 1996 ACS Symposium Series American Chemical Society Washington 1.
[3] Köllner, W and Scheinpflug H 1987 Fungal resistance to sterol biosynthesis inhibitors: A new challenge Plant Dis. 71 1066.
[4] Yang L, Xie JT, Jiang DH, Fu YP, Li GQ 2008 Antifungal substances produced by Penicillium oxalicum strain PY-1-potential antibiotics against plant pathogenic fungi World J. Microb. Biot. 24 909.
[5] Hahn M 2014 The rising threat of fungicide resistance in plant pathogenic fungi: Botrytis as a case study J Chem Biol, 7 133.
[6] Sundberg RJ and Martin RB 1974 Interactions of histidine and other imidazole derivatives with transition metal ions in chemical and biological systems Chem. Rev. 74 471.
[7] Mansour AM, El Bakry EM and Abdel-Ghani NT 2016 Co (II), Ni (II) and Cu (II) complexes of methyl-5-(Phenylthio) benzimidazole-2-carbamate: Molecular structures, spectral and DFT calculations J. Mol. Struct. 1111 100.
[8] Haque RA, Salman AW, Budagumpi S, Abdullah AAA and Abdul Majid AMS 2013 Sterically tuned Ag(I)- and Pd(II)-N-heterocyclic carbene complexes of imidazol-2-ylidenes: synthesis, crystal structures, and in vitro antibacterial and anticancer studies Metallomics 5 760.
[9] Sarı Y, Akkoç S, Gök Y, Sifniotis V, Özdemir I, Günal S and Kayser V 2016 Benzimidazolium-based novel silver N-heterocyclic carbene complexes: synthesis, characterisation and in vitro antimicrobial activity J. Enzyme Inhib. Med. Chem. 31 1527.
[10] Haque RA, Ghhdhayeb MZ, Budagumpi S, Salman AW, Ahmed MBK and Abdul Majid AMS 2013 AMSA: Non-symmetrically substituted N-heterocyclic carbene-Ag(I) complexes of benzimidazol-2-ylidenes: Synthesis, crystal structures, anticancer activity and transmetallation studies Inorg. Chim. Acta 394 519.
[11] McCann M, Curran R, Ben-Shoshan M, McKee V, Devereux M, Kavanagh K and Kellett A 2013 Silver(i) complexes of 9-anthracencarboxylic acid and imidazoles: synthesis, structure and antimicrobial activity Polyhedron 56 180.

[12] McGinley J, McCann M, Ni K, Tallon T, Kavanagh K, Devereux M, Ma X and McKee V 2013 Imidazole Schiff base ligands: Synthesis, coordination complexes and biological activities Polyhedron 55 169.

[13] Haque RA, Salman AW, Budagumpi S, Abdullah AAA, Al-Mudaris ZAH and Abdul Majid AMS (2013 Silver(I)-N-heterocyclic carbene complexes of bis-imidazol-2-ylidenes having different aromatic-spacers: synthesis, crystal structure, and in vitro antimicrobial and anticancer studies App. Organomet. Chem. 27 465.

[14] Salman AW, Rehman GU, Abdullah N, Budagumpi S, Endud S, Abdullah HH, Wong WY 2014 Sterically modulated palladium(II)-N-heterocyclic carbene complexes for the catalytic oxidation of olefins: Synthesis, crystal structure, characterization and DFT studies Polyhedron 81 499.

[15] Yılmaz U, Küçükbay H, Deniz S and Şireci N 2013 Synthesis, characterization and microwave-promoted catalytic activity of novel N-phenylbenzimidazolium salts in Heck-Mizoroki and Suzuki-Miyaura cross-coupling reactions under mild conditions Molecules 18 2501.

[16] Salman AW, Rehman GU, Abdullah N, Budagumpi S, Endud S and Abdullah HH (2015 Synthesis, characterization, density function theory studies and catalytic performances of palladium(II)-N-heterocyclic carbine complexes derived from benzimidazol-2-ylidenes Inorg. Chim. Acta 438 14.

[17] Fernández-Ortuño D and Torés JA, Vicente A. and Pérez-García A. 2010 The Qol Fungicides, the Rise and Fall of a Successful Class of Agricultural Fungicides 203.

[18] Al-Saadi ZN, Salman AW, Arkawazi HD and Hardie, MJ 2019 Synthesis, characterization and antibacterial activity of some transition metal complexes derived from the ligand N-Benzylimidazole against methicillin-resistant Int. J. Drug Delivery Technol. 9 666.

[19] Salman, AW, Al-Mayahie SM, Shallal ZS, Arkawazi HD, Al-Obaidi ZHK and Hardie MJ 2018 J. Glob. Pharm Tech. 10 305.

[20] Küçükbay H, Mumcu A, Tekin S and Sandal S 2016 Synthesis and evaluation of novel N,N′,N,N′,N′′-disubstituted benzimidazolium bromides salts as antitumor agents Turk. J. Chem. 40 393.

[21] Küçükbay H, Yılmaz Ü, Akkurt M and Büyükgünöör Ö 2015 Synthesis and characterization of substituted benzimidazole Co(II), Fe(II), and Zn(II) complexes and structural characterization of dichlorobis{1-[2-(1-piperidinyl)ethyl]-1H-benzimidazole-KN3} zinc(II) Turk. J. Chem. 39 108.

[22] Apohan E, Yılmaz U, Yılmaz O, Serindag A, Küçükbay H, Yesilada O and Baran Y 2016 Synthesis, cytotoxic and antimicrobial activities of novel cobalt and zinc complexes of benzimidazole derivatives J Organomet. Chem. 828 52.

[23] Haggag, KHE and El-Gamal NG 2012 Isolation and identification of fungi associated with tomato root at Misurata region and testing their pathogenicity Nat. Sci. 10 16.

[24] Godswill NN, Bernadette-Sorele NT, Ulrich DDC and Aoudou Y 2020 J. Agric. Studies 8 111.

[25] Dare M D and Fawole O 2009 In vitro effects of some pesticides on pathogenic fungi associated with legumes Austr. J. Crop Sci. 3 137.

[26] Rakesh, Rathi AS and Kumar A 2016 Singh Evaluation of fungicides for the control of Sclerotinia stem rot of Indian mustard caused by Sclerotinia sclerotiorum (Lib.) de Bary J. Appl. Nat. Sci. JANS 8 441.

[27] Youssef SAM, Ezzat SM and El-Ghareeb NR 2015 Ecofriendly Strategy for Inhibition of Sclerotia formation of Sclerotinia sclerotiorum (Lib.) De Bary in vitro. Int. J. Sci. Res. Agric. Sci. 2 100.
