

SYNTHESIS, CHARACTERIZATION AND FUNGICIDAL POTENTIALITIES OF SOME TRANSITION METAL COMPLEXES OF BENZIMIDAZOLE DITHIOCARBAMATE BASED LIGAND

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Abstract

New substituted benzimidazole dithiocarbamate ligand (HL) and a set of its transition metal complexes were synthesized and characterized based on the elemental analyses, IR, MS, solid reflectance, magnetic moment, molar conductance and thermal analyses (TGA and DSC). From the obtained IR data, HL is a neutral tridentate ligand and its complexes were proposed to have the general formulae $[MCl(HL)(H_2O)_2]Cl_2 \cdot 2H_2O$ (M = Cr(III) and Fe(III)) and $[MCl(HL)(H_2O)_2]Cl \cdot yH_2O$ (for y = 2: M = Mn(II), Co(II) and Cu(II) and for y = 1: M = Ni(II), Zn(II) and Cd(II)). The molar conductance data revealed that all the metal chelates were electrolytes. From the magnetic and solid reflectance spectra, it was found that the geometrical structure of the synthesized complexes is octahedral. The thermal behavior of these chelates showed that the hydrated complexes loss water molecules of hydration in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps. Fungicidal activity of the new ligand and its related complexes was evaluated against three soil borne fungi that cause many destructive diseases as damping off, root and stem rots of many plants. The tested fungi are *Fusarium solani*, *Rhizoctonia solani* and *Sclerotium rolfsii*. Data obtained showed that introducing an electron withdrawing nitro group in position (5) of benzimidazole ring enhanced the biological potentialities of the parent ligand and some of its transition metal chelates to show better activity than the standard fungicide *Pencycuron*.

Key Words: Benzimidazole ligand, dithiocarbamate ligand, transition metal complexes, IR, MS, magnetic moment, thermal analysis and soil borne fungi.

INTRODUCTION

Dithiocarbamates, nitrogen containing organic compounds and their transition metal complexes display a wide range of biological activities (Nand 2014; Pedrares *et al.* 2003; Elasmay *et al.* 2004; Ekegren *et al.* 2003; Mevellec *et al.* 2002). Benzimidazole ring system is one of the nitrogen containing organic compounds and known as a very important intermediate for the development of new molecules with pharmaceutical, pesticidal and industrial applications (Nabipour *et al.* 2010; Sen-Lin *et al.* 2015; Hayashi *et al.* 2009; Alasmay *et al.* 2015; Chiba *et al.* 1988; Tuncbilek *et al.*

1997). As a result, many benzimidazoles and/or dithiocarbamates have extensively been used in agriculture as commercial pesticides, especially as fungicides, for more than fifty years (Nand 2014; Chiba *et al.* 1988).

As our interested research area involved designing and evaluation the pesticidal activity of new heterocycles related to benzimidazole nucleus, an efficient approach for the synthesis of many transition metal complexes derived from benzimidazoledithiocarbamate ligand and studying their fungicidal activity were lately reported (Mohamed *et al.* 2009). The reported compounds were found to be promising new molecules as antifungal agent in agriculture field. In this work some modifications for both ligand and its related complexes were carried out hoping to get more efficient molecules against the same tested fungi. The modification involves introducing an electron withdrawing group in position 5 of benzimidazole nucleus and new transition metal chelates.

MATERIALS AND METHODS

1. Reagents

All chemicals used are of the analytical reagent grade (AR), and of highest purity available. They included copper (II) chloride dihydrates (Prolabo); cobalt (II) and nickel (II) chloride hexahydrates (BDH); zinc (II) chloride dihydrate (Ubichem), manganese (II), iron (II) and chromium (III) chlorides (Sigma). Ammonia solution (33 % v/v), ammonium chloride (El-Nasr pharm. Chem. Co.,Egypt), disodium salt of ethylenediaminetetraacetic acid "EDTA" and zinc oxide (Analar) were used. Organic solvents used included absolute ethyl alcohol, diethylether, dimethylformamide (DMF) and dimethylsulphoxide (DMSO). Hydrochloric and nitric acids (MERCK) were used. De-ionized water collected from all glass equipments was usually used in all preparations. Antifungal susceptibility testing was performed in potato-dextrose agar (PDA) media containing drops of 25% lactic acid to prevent the bacterial contamination. A series of concentrations for each investigated compound was carried out using DMSO as a solvent.

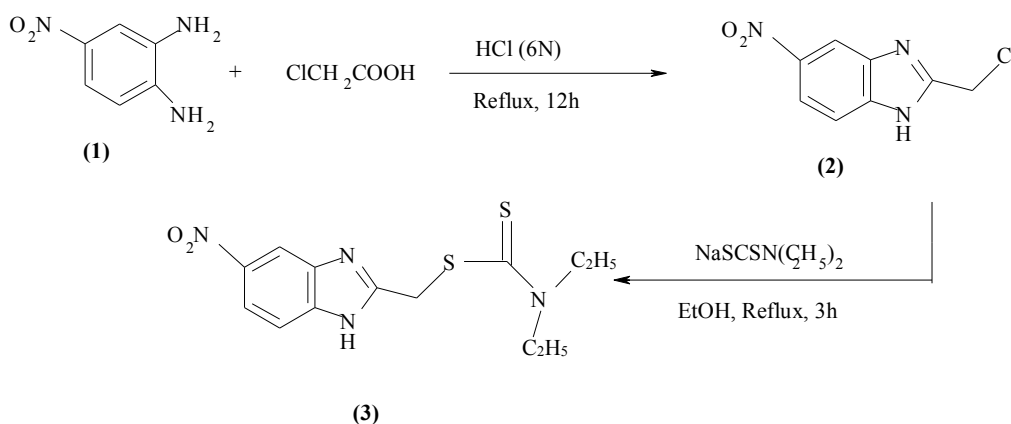
2. Instruments

Elemental microanalyses of the separated solid ligand and chelates for C, H, N and S were performed in the Microanalytical Center, Cairo University. The analyses were repeated twice to check the accuracy of the data. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wave number region 4000 - 200 cm^{-1} . The spectra were recorded as KBr pellets. The mass spectrum of ligand HL was measured on a Shimadzu GCMS- 2010. The molar conductance of solid complexes in DMF was measured using Sybron-Barnstead conductometer

(Meter-PM.6, E = 3406). The solid reflectance spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant. The thermogravimetric analyses (TGA and DrTGA) were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ using Shimadzu TGA-50H thermal analyzers.

3. Synthesis of HL Ligand

The used ligand **(3)**, which is formulated as diethyl S-(5-nitro-1H-benzimidazol-2-yl)methylthiocarbamate, was prepared in two stages starting from 4-nitro-1,2-phenyldiamine **(1)** as shown in scheme (1).



Scheme 1. Synthesis of HL ligand.

4. Synthesis of metal complexes

Hot solution ($60 \text{ }^\circ\text{C}$) of the appropriate metal chloride (1 mmol) in an ethanol-water mixture (1:1, 25 mL) was added to the hot solution ($60 \text{ }^\circ\text{C}$) of the HL ligand (0.324 g, 1 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for one hour whereupon the complexes precipitated. They were collected by filtration, washed with a 1:1 ethanol-water mixture and diethyl ether. The analytical data for C, H, N and S were repeated twice.

5. Biological study.

A quantitative assessment of the antifungal activity was determined using the food poisoning technique. Potato-dextrose agar (PDA) was used to evaluate the effect of the selected compounds under investigation on the mycelial linear growth of three tested fungi. Fifty milliliters of the aforementioned medium were poured into 150 ml conical flasks and autoclaved at 121°C for 20 min. Three drops of 25% lactic acid were added to prevent bacterial contamination. Dilutions for each of the tested

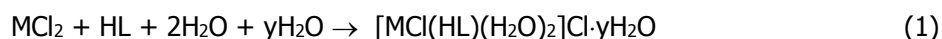
compound were carried out (v/v) by dissolving appropriate amounts of each compound in 10 ml DMSO. Equal volumes of DMSO containing diluted compounds were added to sterile molten (40°C) PDA to get a series of concentrations of 50, 100, 200, 300, 400 and 500 ppm for each compound in PDA (Tremblay *et al.* 2003).

A zero (o) concentration treatment was prepared for each fungus, which contains equivalent volume of solvent only and used as a control. Compounds-amended PDA were dispensed aseptically into 9 cm diameter petridishes. Plugs of mycelium (4 mm diameter) were cut from the margins of actively growing cultures of the *F. Solani*, *R. Solani* and *S. rolfsii* fungi and placed in the center of compound-amended and unamended PDA plates with 3 replicate plates for each fungus. All plates were incubated at $25 \pm 1^\circ\text{C}$. Colony diameter (in millimeters) was measured after 3 days for *R. Solani*, *S. rolfsii* and 7-12 days for *F. Solani* fungi and the percentage of growth inhibition was calculated and corrected using the probit analysis program for each compound. The estimated effective concentration (EC_{50}) which gives 50% inhibition of the fungi radial growth, toxicity index (T.I) and slopes of toxicity lines for each compound under investigation were determined and tabulated in Tables (4-6).

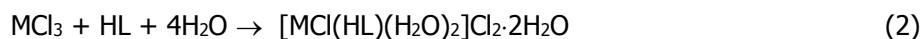
RESULTS AND DISCUSSION

1. Composition and structures of both ligand HL and its binary metal complexes

Free ligand (3) was synthesized from the reaction of substituted 2-chloromethyl-benzimidazole (2) as in scheme (1). Benzimidazole derivative (2) was prepared according to the reported general method (Phillips 1931). The authenticity of the new ligand (3) was confirmed based on the correct elemental analysis and comparable spectral data. IR spectrum displayed well-defined characteristic bands at 3434 cm^{-1} (NH), 3098 cm^{-1} (CH-arom.), $2974, 2932\text{ cm}^{-1}$ (CH-aliph.), 1625 cm^{-1} (C=N), $1519, 1336\text{ cm}^{-1}$ (NO_2) and 1196 cm^{-1} (C=S). The mass spectrum displayed a molecular ion peak at $m/z = 324$ (12.0%), corresponding to the correct molecular weight of the HL ligand (3) under investigation (M.F = $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_2\text{S}_2$ and M.Wt = 324.42). The isolated solid complexes of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Fe(II), Cd(II) and Zn(II) ions with the HL ligand were subjected to elemental analyses (C, H, N, S and metal content), IR, magnetic studies, molar conductance and thermal analyses (TGA and DSC) to identify their tentative formulae in a trial to elucidate their molecular structures. The results of elemental analyses, Table (1), are in good agreement with those required by the proposed formulae. The formation of these complexes may proceed according to the following equations:



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); $\gamma = 1-2$



M = Cr(III) and Fe(III).

1.1- Molar conductivity measurements.

The molar conductance of the chelates in DMF solvent at 25 ± 2 °C were measured and tabulated in Table (1). It was concluded from the results that the chelates were found to have molar conductance values of $62-165 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ indicating that these chelates were electrolytes. It, also, indicated that the chloride anions were outside the coordination spheres.

1.2- Magnetic susceptibility and electronic spectra measurements.

Data presented in Table (1) show that three spin-allowed transitions were found in the diffused reflectance spectrum of the hexacoordinated Cr(III) complex at $18,455$, $24,657$ and $33,478 \text{ cm}^{-1}$ that assigned to ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_g({}^4\text{T}_{2g})$, ${}^4\text{B}_{1g} \rightarrow {}^4\text{B}_{2g}({}^4\text{T}_{2g})$ and ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_g({}^4\text{T}_{1g})$ (Cotton *et al.* 1999; Koley *et al.* 2008). The magnetic moment at room temperature was 3.34 BM which corresponds to three unpaired electrons for a d^3 Cr(III) ion and confirmed octahedral geometry for this complex (Cotton *et al.* 1999; Koley *et al.* 2008). The diffused reflectance spectrum of the Mn(II) complex showed three bands at $18,056$, $22,320$ and $26,660 \text{ cm}^{-1}$ assignable to ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$, ${}^4\text{T}_{2g}(\text{G}) \rightarrow {}^6\text{A}_{1g}$ and ${}^4\text{T}_{1g}(\text{D}) \rightarrow {}^6\text{A}_{1g}$ transitions, respectively (Cotton *et al.* 1999). The magnetic moment value was 5.22 BM which indicated the presence of Mn(II) complex in octahedral structure. The diffused reflectance spectrum of the Co(II) complex gave three bands at $15,245$; $18,852$ and $23,652 \text{ cm}^{-1}$ wavenumber regions. The bands observed were assigned to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (1), ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (2) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ (3), respectively, suggesting that there was an octahedral geometry around Co(II) ion (Cotton *et al.* 1999; Mohamed *et al.* 2003; Omar and Mohamed, 2005). The magnetic susceptibility measurements lie at 4.63 BM (normal range for octahedral Co(II) complexes was 4.3–5.2 BM), was an indicative of octahedral geometry (Cotton *et al.* 1999). The Ni(II) complex reported in this article had a room temperature magnetic moment value of 3.32 BM which was in the normal range observed for octahedral Ni(II) complexes ($\mu_{\text{eff}} = 2.9-3.3 \text{ B.M}$) (Cotton *et al.* 1999; El Gamel *et al.* 2001). This indicated that, the complex of Ni(II) was six coordinate (Cotton *et al.* 1999; El Gamel *et al.* 2001). The diffused reflectance spectrum displayed three bands in its solid reflectance spectrum at 1: $16,654 \text{ cm}^{-1}$: ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; 2: $18,432 \text{ cm}^{-1}$: ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and 3: $22,584 \text{ cm}^{-1}$: ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$. The reflectance spectrum of Cu(II) chelate consisted of a broad band at $17,465$ and $20,352 \text{ cm}^{-1}$. The ${}^2\text{E}_g$ and ${}^2\text{T}_{2g}$ states of the octahedral Cu(II) ion (d^9) split under the

influence of the tetragonal distortion and the distortion can be such as the three transitions ${}^2B_{1g} \rightarrow {}^2B_{2g}$; ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ to remain unresolved in the spectrum (Kohout *et al.* 1999). It was concluded that all three transitions lie within the single broad envelope centered at the same range previously mentioned. The magnetic moment of 1.90 BM falls within the range normally observed for octahedral Cu(II) complexes (Cotton *et al.* 1999; Kohout *et al.* 1999). The complex of Zn(II) was diamagnetic. According to the empirical formula, an octahedral is proposed for this complex.

1.3- IR spectra and mode of bonding

The most important characteristic IR absorption bands and their proposed assignments of the dithiocarbamate ligand and its transition metal complexes are given in Table (2). The slight shifts and intensity changes of a few vibration bands caused by different metal ions in the IR spectra of the complexes were taken as an evidence regarding the coordination of the dithiocarbamate ligand. The infrared spectrum of the free ligand was compared with those of its metal complexes in order to have a clear idea about the coordination mode and sites of the ligand bounded to the metal ions.

Table 1. Analytical and physical data of parent HL and its metal complexes.

Compound	Colour (%yield)	M.p (°C)	% Found (Calcd.)					μ_{eff} (B.M)	λ_m $\Omega^{-1} \text{mol}^{-1} \text{cm}^{-2}$
			C	H	N	S	M		
HL	yellowish brown (80)	190	48.45 (48.13)	4.82 (4.97)	17.60 (17.27)	19.32 (19.76)	-----	-----	-----
[CrCl(HL)(H ₂ O) ₂]Cl ₂ .2H ₂ O	Brown (80)	86	28.90 (29.06)	3.78 (4.10)	10.23 (10.43)	11.66 (11.92)	9.29 (9.69)	3.34	136
[MnCl(HL)(H ₂ O) ₂]Cl ₂ .2H ₂ O	Black (83)	234	29.60 (29.86)	4.42 (4.59)	10.44 (10.72)	12.03 (12.25)	10.19 (10.53)	5.22	62
[FeCl(HL)(H ₂ O) ₂]Cl ₂ .2H ₂ O	Green (80)	212	27.72 (27.91)	3.99 (4.29)	9.86 (10.02)	11.10 (11.45)	9.79 (10.02)	5.41	165
[CoCl(HL)(H ₂ O) ₂]Cl ₂ .2H ₂ O	Green (78)	>300	29.41 (29.64)	4.35 (4.56)	10.28 (10.64)	11.89 (12.16)	11.04 (11.21)	4.63	72
[NiCl(HL)(H ₂ O) ₂]Cl.H ₂ O	Black (77)	>300	30.43 (30.68)	4.23 (4.33)	10.84 (11.02)	12.37 (12.59)	11.21 (11.61)	3.32	69
[CuCl(HL)(H ₂ O) ₂]Cl ₂ .2H ₂ O	Deep Brown (86)	193	29.18 (29.38)	4.32 (4.52)	10.25 (10.55)	11.91 (12.06)	11.72 (11.96)	1.90	67
[ZnCl(HL)(H ₂ O) ₂]Cl.H ₂ O	Brown (81)	136	29.98 (30.33)	4.16 (4.28)	10.72 (10.89)	12.12 (12.44)	12.33 (12.64)	Diam.	75
[CdCl(HL)(H ₂ O) ₂]Cl.H ₂ O	Brown (75)	166	27.44 (27.79)	4.06 (3.92)	9.67 (9.98)	11.24 (11.40)	19.66 (19.95)	Diam.	70

The peak at 1625 cm^{-1} attributed to $\nu(\text{C}=\text{N})$ vibration of N-3 imidazole ring, was shifted by $13\text{--}24 \text{ cm}^{-1}$ on complexation, indicating coordination of N-3 atom to

metal ions (Mohamed *et al.* 2001). In addition, IR spectrum of the ligand revealed a sharp band at 1196 cm^{-1} due to (C=S) of side chain, which was slightly shifted to higher frequency at about $11\text{--}19\text{ cm}^{-1}$ after complexation in all complexes, suggesting that sulfur atom of the side chain also contributes to the complexation. The band observed at 1092 cm^{-1} in the dithiocarbamate HL ligand was appeared at relatively lower field ($1076\text{--}1083\text{ cm}^{-1}$) in the complexes which may indicates coordination via the C–S group (Soliman and Mohamed, 2004).

The IR bands at $913\text{--}954$ and $843\text{--}875\text{ cm}^{-1}$, $\nu(\text{H}_2\text{O})$ of coordinated water, is an indication of the binding of the water molecules to the metal ions. New bands were found in the spectra of the complexes in the regions $542\text{--}560$, $491\text{--}520$, $420\text{--}436$ and $444\text{--}470\text{ cm}^{-1}$, which were assigned to $\nu(\text{M--O})$ of coordinated water, $\nu(\text{M--N})$, $\nu(\text{M--S})$ and $\nu(\text{M--S})$ stretching vibrations, respectively (Soliman and Mohamed, 2004; Zayed *et al.* 2007).. Therefore, from the IR spectra, it is concluded that HL ligand behaves as a neutral tridentate ligand coordinated to the metal ions via the imidazole N-3, C=S and C–S groups.

Table 2. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) of HL and its binary metal complexes.

Assignment	HL	[CrCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	[MnCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	[FeCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	[CoCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	[NiCl(HL)(H ₂ O) ₂] Cl ₂ .H ₂ O	[CuCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	[ZnCl(HL)(H ₂ O) ₂] Cl ₂ .H ₂ O	[CdCl(HL)(H ₂ O) ₂] Cl ₂ .H ₂ O
$\nu(\text{C=N})$	1625sh	1610m	1602m	1608s	1600m	1612m	1603m	1601m	1603m
$\nu(\text{C=S})$	1196m	1209s	1188s	1185m	1203m	1179m	1186sh	1182m	1184m
$\nu(\text{C-S})$	1092sh	1082m	1080m	1078s	1077m	1083m	1076s	1080m	1079m
$\nu(\text{M-N})$	----	496s	491s	500s	499w	520w	502w	505w	500w
$\nu(\text{M-S})$	----	420w	425w	432w	428s	429w	433s	436w	430w
H ₂ O stretching of coordinated water	----	920m, 865w	933s, 872s	954w, 871w	913s, 843s	942w, 855w	936w, 875s	933w, 861s	927w, 860s
M-O stretching of coordinated water	----	547s	564w	546w	550s	560w	552w	546w	542w
$\nu(\text{M-S})$	----	444w	449w	464w	457w	446w	456w	470w	456w

sh = sharp, m = medium, br = broad, s = small, w = weak

1.4- Thermal analyses (TGA and D_rTG).

The thermal analysis data are shown in Table (3). The weight losses for each chelate are calculated within the corresponding temperature ranges where the heating rates were suitably controlled at $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere and the weight loss was measured from the ambient temperature up to $\sim 1000\text{ }^{\circ}\text{C}$. The TGA curve of the $[\text{CrCl}(\text{HL})(\text{H}_2\text{O})_2]\text{Cl}_2.2\text{H}_2\text{O}$ chelate showed four steps of decomposition within the temperature range of $40\text{--}850\text{ }^{\circ}\text{C}$. The first stage within the temperature

range from 40 to 100 °C correspond to the loss of two water molecules of hydration (mass loss = 6.49%; calcd. = 6.30%). While the subsequent (2nd, 3rd and 4th) steps involved the loss of 2H₂O, Cl₂ and ligand molecules with a mass loss of 81.38% (calcd. 79.75%). The overall weight loss amounts to 87.68% (calcd. 86.24%).

The TGA curve of the [CuCl(HL)(H₂O)₂]Cl·2H₂O chelate represents three decomposition steps as shown in Table (3). The first one was found to be within the temperature range 40–170 °C, corresponds to the loss of two hydrated water molecules with a mass loss of 5.90% (calcd. 6.78%). The remaining steps of decomposition, within the temperature range 170–800 °C, correspond to the removal of Cl₂, 2H₂O and HL ligand as gases with an estimated mass loss of 79.37% (calcd. 78.17%). The overall weight losses amount to 85.27% (calcd. 84.95%).

The thermogram of [MnCl(HL)(H₂O)₂]Cl·2H₂O complex showed four decomposition steps within the temperature range 30–760 °C. The first step of decomposition, within the temperature range 30–110 °C, corresponds to the loss of two water molecules of hydration and ½Cl₂ molecule with a mass loss of 14.48% (calcd. 13.69%). The subsequent steps occurred within the temperature range 110–670 °C and correspond to the removal of the organic part of the ligand, ½Cl₂ and 2H₂O molecules (mass loss = 72.65%; calcd. = 72.72%) leaving MnO as a residue. The overall weight loss amounts to 87.20% (calcd. 86.34%).

On the other hand, [CoCl(HL)(H₂O)₂]Cl·2H₂O and [NiCl(HL)(H₂O)₂]Cl·H₂O complexes exhibited five decomposition steps. The first step within the temperature range 30–120 and 30–115 °C (mass loss = 12.82% and 10.19%; calcd. 13.58% and 10.52% for Co(II) and Ni(II) complexes, respectively) that may accounted for the loss of water molecule of hydration and ½Cl₂. As shown in Table (3), the mass losses of the remaining decomposition steps amount to 74.80% (calcd. 75.13%) and 76.12% (calcd. 74.64%) for Co(II) and Ni(II) complexes, respectively. They correspond to the removal of 2H₂O, ½Cl₂ and HL molecules leaving CoO and NiO as residues. [FeCl(HL)(H₂O)₂]Cl·2H₂O complex was thermally decomposed in four decomposition steps within the temperature range of 40–850 °C. The first two steps with an estimated mass loss of 32.40% (calcd. mass loss = 31.94%) within the temperature range 40–320 °C, may be attributed to the loss of hydrated and coordinated water molecules and 3/2Cl₂. The remaining decomposition steps (two steps) found within the temperature range 320–850 °C with an estimated mass loss of 54.14% (calcd. mass loss = 53.68%) which were reasonably accounted for the removal of HL ligand as gases leaving iron oxide as a residue.

In addition, [ZnCl(HL)(H₂O)₂]Cl·H₂O and [CdCl(HL)(H₂O)₂]Cl·H₂O complexes exhibited four and three decomposition steps, respectively. The first two and the first

steps occurred within the temperature range 35–260 and 40–280 °C (mass loss = 24.86% and 16.45%; calcd. 24.30% and 15.94%) for Zn(II) and Cd(II) complexes, respectively that may accounted for the loss of water molecules of hydration and coordination in addition to Cl₂ molecule. As shown in Table (3), the mass losses of the remaining decomposition steps amount to 60.08% (calcd. 59.88%) and 61.67% (calcd. 61.19%) for Zn(II) and Cd(II) complexes, respectively. They correspond to the removal of HL molecules leaving ZnO and CdO as residues.

Table 3. Thermo-analyses results (TG and DrTG) of the synthesized transition metal complexes.

Complex	TG range (°C)	DTG _{max} (°C)	n*	Mass loss Estim (Calcd) %	Total mass loss (Calcd) %	Assignment	Residue
[CrCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	40-100 100-300 350-350 850	90 300 498, 740	1 1 2	6.30 (6.71) 32.75 (32.41) 50.63 (50.01)	89.68 (89.13)	-Loss of 2H ₂ O. -Loss of Cl ₂ , 2H ₂ O and C ₄ H ₅ N. -Loss of C ₉ H ₁₁ N ₃ O _{1.5} S ₂ Cl.	1/2Cr ₂ O ₃
[MnCl(HL)(H ₂ O) ₂]Cl.2H ₂ O	30-110 110-280 280-280 760	102 235 490	1 1 2	14.48 (13.69) 13.58 (13.69) 59.14 (58.96)	87.20 (86.34)	-Loss of 2H ₂ O and 1/2Cl ₂ . -Loss of 1/2Cl ₂ and 2H ₂ O. -Loss of C ₁₃ H ₁₆ N ₄ OS ₂ .	MnO
[FeCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	40-320 320-320 850	90, 260 345, 710	2 2	32.40 (31.94) 54.14 (53.68)	86.54 (86.62)	-Loss of 2H ₂ O, 3/2Cl ₂ and 2H ₂ O. -Loss of C ₁₃ H ₁₆ N ₄ O _{1.5} S ₂ .	1/2Fe ₂ O ₃
[CoCl(HL)(H ₂ O) ₂]Cl.2H ₂ O	30-120 120-490 490-490 820	70 220, 390 575, 715	1 2 2	12.82 (13.58) 32.91 (32.20) 41.89 (42.93)	87.62 (88.71)	-Loss of 1/2Cl ₂ and 2H ₂ O. -Loss of 1/2Cl ₂ , 2H ₂ O and C ₃ H ₅ NO. -Loss of C ₉ H ₈ N ₃ OS ₂ .	CoO
[NiCl(HL)(H ₂ O) ₂] Cl.H ₂ O	30-115 115-310 310-310 800	82 165, 267 452, 630	1 2 2	10.19 (10.52) 15.09 (14.06) 61.03 (60.58)	86.31 (85.16)	-Loss of 1/2Cl ₂ and H ₂ O. -Loss of 1/2Cl ₂ and 2H ₂ O. -Loss of C ₁₃ H ₁₆ N ₄ OS ₂ .	NiO
[CuCl(HL)(H ₂ O) ₂]Cl.2H ₂ O	40-170 170-310 310-310 800	135 246 387, 690	1 1 2	5.90 (6.78) 21.22 (20.15) 58.15 (58.02)	85.27 (84.95)	-Loss of 2H ₂ O. -Loss of Cl ₂ and 2H ₂ O. -Loss of C ₁₃ H ₁₆ N ₄ OS ₂ .	CuO
[ZnCl(HL)(H ₂ O) ₂] Cl.H ₂ O	35-160 160-260 260-260 935	125 229 330, 765	1 1 2	10.72 (10.40) 21.14 (20.80) 60.08 (59.88)	91.94 (91.08)	-Loss of 1/2 Cl ₂ and H ₂ O. -Loss of Cl ₂ and 2H ₂ O -Loss of C ₁₃ H ₁₆ N ₄ OS ₂ .	ZnO
[CdCl(HL)(H ₂ O) ₂]Cl.H ₂ O	40-280 280-280 840	165 360, 645	1 2	16.45 (15.94) 61.67 (61.19)	78.12 (77.13)	-Loss of 1/2Cl ₂ , H ₂ O and 2H ₂ O. -Loss of 1/2Cl ₂ and C ₁₃ H ₁₆ N ₄ OS ₂ .	CdO

n* = number of decomposition step.

1.5- Structural interpretation.

The structures of the substituted benzimidazole ligand HL and its related complexes with Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Cd(II), Fe(II) and Zn(II) ions were confirmed by the elemental analyses, IR, MS, molar conductance, magnetic and solid reflectance spectra as well as thermal analysis data. Therefore, from the IR

spectra, it was concluded that HL behaves as a neutral tridentate ligand coordinated to the metal ions via the imidazole N-3 and two side chain S atoms. The molar conductance data revealed that the complexes are electrolytes. On the basis of the above observations and from the magnetic and solid reflectance measurements, octahedral geometries were suggested for the investigated complexes. As a general conclusion, the investigated metal complex structures can be given as shown in Figure (1).

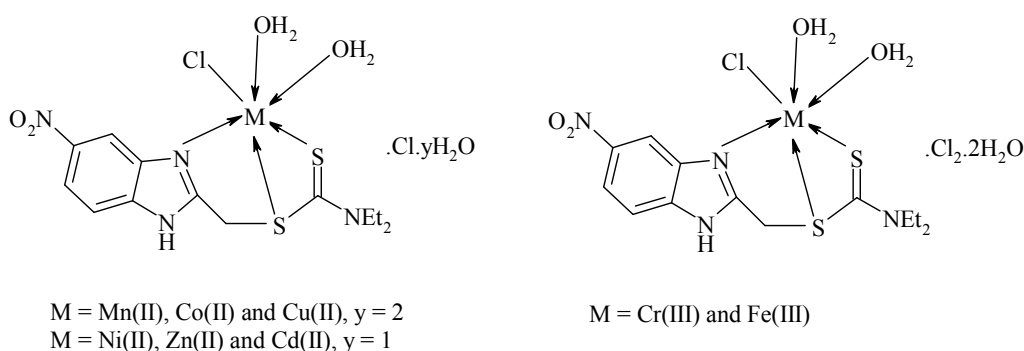


Figure 1. Structure of metal complexes.

II- Fungicidal activity.

Data in Tables (4-6) represented the fungicidal activities of the synthesized free ligand (HL) and its transition metal chelates against three tested soil borne fungi. The activity was measured in term of the efficiency of such compounds to inhibit the radial linear growth of the tested fungi. Both EC_{50} values and toxicity indexes (T.I) were calculated to measure the activities and discuss the effect of variation of the metal ions on the activities of such compounds. To study the biological impacts due to adding the nitro group in position 5 of benzimidazole ring for both ligand and chelates, both EC_{50} values of the current new compounds ($R = \text{NO}_2$; $M = \text{Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cr(III), Fe(III)}$ and Cd(II)) and that of the last reported ones ($R = \text{H}$; $M = \text{Mn(II), Co(II), Ni(II), Cu(II), Zn(II)}$ and Cr(III)) [13] were discussed and illustrated in Tables (4-6) and Figure (2).

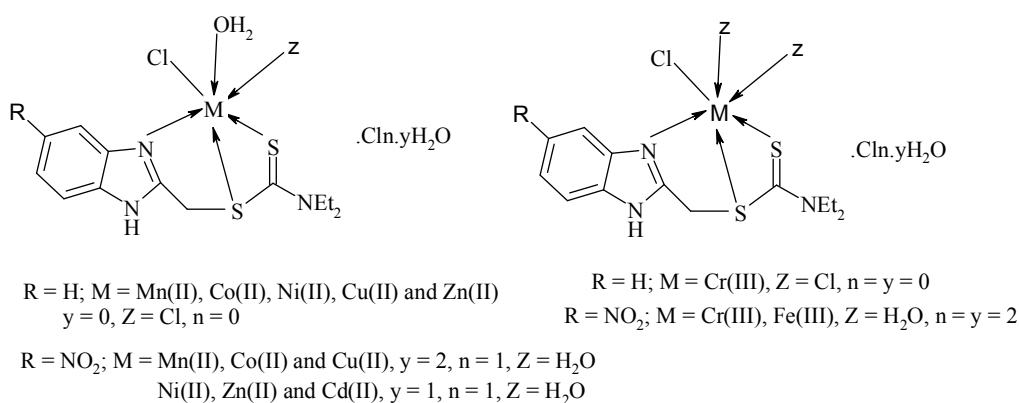


Figure 2. General structures of the synthesized complexes.

Data in Table (4) show the activity of both ligand and its chelates on the *F. Solani* fungus. It is clear that fungicidal activity of the tested compounds increases linearly with increasing the concentrations. Toxicity index of the free ligand is the highest (100.0), means it is the most active ones against this fungus. Its EC_{50} value is 333.5 ppm which is the least one, but chromium complex was found to be the least activity as its EC_{50} value is the highest (943.1 ppm) and toxicity index is the lowest percentage (35.4) when compared with the free ligand. Opposite to most of the synthesized chelates, introducing the nitro group on benzimidazole nucleus enhances the activity of the free ligand dramatically against the *F. Solani* fungus. The EC_{50} value of the ligand decreased from 526.1 to 333.5 ppm that means increasing in activity by about 37%. In case of the copper(II) complex the fungicidal activity slightly increased. The EC_{50} value of the nitro derivative is 568.2 ppm but that of hydrogen derivative is 662.6 ppm.

Table 4. Rate of inhibition of the synthesized compounds against *F. Solani* fungus.

Compound Conc. (ppm)	% of inhibitions						EC_{50} (ppm)	T.I.*	Slope	EC_{50}^* (ppm)
	50	100	200	300	400	500				
Ligand (HL)	4.7	14.5	32.6	46.3	56.4	63.9	333.5	100.0	2.03	526.1
$[\text{CrCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	4.0	9.0	17.8	24.7	30.8	35.3	943.1	35.4	1.37	525.6
$[\text{MnCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	0.0	0.4	5.8	17.8	32.3	45.8	534.1	62.4	3.68	535.8
$[\text{FeCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	0.0	0.8	6.5	16.4	27.4	37.9	632.4	52.7	3.03	***
$[\text{CoCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	0.0	0.1	3.4	14.1	29.3	44.7	537.2	62.1	4.25	353.5
$[\text{NiCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	0.0	0.2	3.8	13.6	26.6	39.9	584.3	57.1	3.80	469.1
$[\text{CuCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	0.0	0.0	1.0	7.7	21.6	38.7	568.2	58.7	5.15	662.6
$[\text{ZnCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	0.1	1.1	8.1	19.1	30.9	41.7	587.1	56.8	2.99	555.2
$[\text{CdCl}(\text{HL})(\text{H}_2\text{O})_2]$ $]\text{Cl}_2.2\text{H}_2\text{O}$	1.1	5.5	18.3	30.9	41.7	50.6	493.0	67.6	2.31	***

* Toxicity index is the % of activity of the tested compounds to the most potent one whose T.I is 100.

** The EC_{50} value of published non nitrated derivative.

*** Compound did not evaluated.

Data in Table (5) display the inhibition potentialities of the tested compounds to the radial growth of the *S. Rolfesii* fungus. Data clearly show that *S. Rolfesii* fungus is more sensitive to the investigated compounds than *F. Solani* fungus. The range of EC₅₀ values was 144.0 – 292.3 ppm and 333.5 – 943.1 ppm for *S. Rolfesii* and *F. Solani* fungi respectively, a thing that reflect the sensitivity of *S. Rolfesii* fungus towards these compounds. Data also show that parent ligand (HL) is the most active one against this fungus. Free ligand have the lowest EC₅₀ value (144.0 ppm) and the highest toxicity index (100.0). In addition, zinc(II) complex possessed the second order in activity after the free ligand. Its EC₅₀ value is 155.8 ppm and T.I is 92.4 as compared with the ligand (HL). Cadmium(II) chelate also possessed an activity close to that of zinc(II) chelate. Introducing the nitro group increases the activity of the free ligand, Cr(III), Mn(II), Ni(II) and Zn(II) chelates which is clearly shown by comparing the EC₅₀ values of the nitrated and non-nitrated compounds.

Table 5. Rate of inhibition of the synthesized compounds against *S. Rolfesii* fungus.

Compound	% of inhibitions						EC ₅₀ (ppm)	T.I*	Slope	EC ₅₀ ** (ppm)
	50	100	200	300	400	500				
Ligand (HL)	6.5	30.0	68.1	85.4	92.9	96.3	144.0	100.0	2.30	800.1
[CrCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	1.9	12.0	39.1	59.8	73.2	81.8	247.8	58.1	2.97	389.0
[MnCl(HL)(H ₂ O) ₂] Cl.2H ₂ O	2.3	16.7	52.5	74.7	86.3	92.3	191.6	75.2	3.42	294.3
[FeCl(HL)(H ₂ O) ₂] Cl ₂ .2H ₂ O	4.1	17.5	44.6	63.0	74.7	82.2	224.9	64.0	2.66	***
[CoCl(HL)(H ₂ O) ₂] Cl.2H ₂ O	1.0	9.1	36.5	59.4	74.0	83.2	254.7	56.5	3.27	196.1
[NiCl(HL)(H ₂ O) ₂] Cl.H ₂ O	9.4	22.4	43.0	56.3	65.4	71.9	247.7	58.1	1.89	277.6
[CuCl(HL)(H ₂ O) ₂] Cl.2H ₂ O	0.8	7.3	30.3	51.4	66.5	76.7	292.3	49.2	3.13	261.0
[ZnCl(HL)(H ₂ O) ₂] Cl.H ₂ O	16.0	34.9	58.6	71.6	79.5	84.6	155.8	92.4	2.01	393.6
[CdCl(HL)(H ₂ O) ₂] Cl.H ₂ O	16.1	34.9	58.6	71.6	79.4	84.5	156.0	92.3	2.00	***

* Toxicity index is the % of activity of the tested compounds to the most potent one whose T.I is 100.

** The EC₅₀ value of published non nitrated derivative.

*** Compound did not evaluated.

Data in Table (6) show that *R. solani* fungus possessed a higher sensitivity to the synthesized compounds than the other two ones under investigation. Cadmium(II) complex was found to be the most potent compound on. It has the lowest EC₅₀ value (52.0 ppm) and the highest toxicity index (100.0). Beside the free ligand, iron(III) and cobalt(II) complexes were found to be very active towards the *R. solani* fungus as they have EC₅₀ values less than 100 ppm. The same fashion as the previous two cases, introduction of a nitro group in benzimidazole nucleus remarkably enhances the activity of the benzimidazole ligand and its transition metal chelates towards the *R. solani* fungus. Fungicidal activity of the standard fungicide (pencycuron) used to control diseases caused by these fungi was carried out and provided in Table (7). The EC₅₀ values of this positive control and of the more active benzimidazole derivatives prepared were calculated and provided in the same Table. From data, new compounds showed a higher activity than that of the standard fungicide against all tested fungi.

Table 6. Rate of inhibition of the synthesized complexes against *R. Solani* f fungus.

Compound	% of inhibitions						EC ₅₀ (ppm)	T.I*	Slope	EC ₅₀ ** (ppm)
	Conc. (ppm)	50	100	200	300	400				
Ligand (HL)	29.9	52.7	75.0	84.3	89.6	92.7	92.8	56.0	1.99	521.0
[CrCl(HL)(H ₂ O) ₂]Cl ₂ . 2H ₂ O	9.6	26.9	52.9	68.3	77.7	83.8	185.7	28.0	2.29	220.7
[MnCl(HL)(H ₂ O) ₂]Cl. 2H ₂ O	15.9	33.9	56.6	69.4	77.3	82.5	163.9	31.7	1.93	***
[FeCl(HL)(H ₂ O) ₂]Cl ₂ . 2H ₂ O	30.1	53.0	74.9	84.7	89.9	92.9	91.6	56.8	1.97	282.3
[CoCl(HL)(H ₂ O) ₂]Cl.2 H ₂ O	32.2	50.9	69.5	78.6	84.0	87.5	96.7	53.8	1.62	205.5
[NiCl(HL)(H ₂ O) ₂]Cl.H 2O	21.9	41.6	63.8	75.2	82.0	86.4	129.7	40.1	1.87	227.2
[CuCl(HL)(H ₂ O) ₂]Cl.2 H ₂ O	18.8	37.2	59.3	71.3	78.7	83.6	149.7	34.7	1.86	232.5
[ZnCl(HL)(H ₂ O) ₂]Cl.H 2O	19.2	40.6	65.3	77.7	84.7	89.0	129.9	40.0	2.10	305.1
[CdCl(HL)(H ₂ O) ₂]Cl. H ₂ O	49.1	65.2	78.9	85.2	88.8	91.1	52.0	100.0	1.37	***

* Toxicity index is the % of activity of the tested compounds to the most potent one whose T.I is 100.

** The EC₅₀ value of published non nitrated derivative.

*** Compound did not evaluated.

Table 7. Fungicidal activity of the standard fungicide against the three tested fungi.

Conc. (ppm)	<i>F. Solani</i>		<i>R. Solani</i>		<i>S. Rolfsii</i>	
	Growth zone (mm)	% of inhibitions	Growth zone (mm)	% of inhibitions	Growth zone (mm)	% of inhibitions
0.00	90.0	0.0	90.0	0.0	90.0	0.0
100.0	86.0	4.4	79.0	12.2	73.0	18.9
200.0	64.0	28.9	48.3	46.3	43.0	52.2
400.0	51.7	32.0	35.7	60.3	29.0	67.8
600.0	44.0	51.1	23.0	74.4	25.0	72.2
EC ₅₀ *	593.2 (ppm)		282.4 (ppm)		237.1 (ppm)	
Slope	1.79 ± 0.26		2.15 ± 0,24		1.88 ± 0.25	
EC ₅₀ **	333.5 (ppm)		52.0 (ppm)		144.0 (ppm)	

* The EC₅₀ value of the standard fungicide Pencycuron.

** EC₅₀ value of the most active derivative (Cd complex in case of *R. Solani* fungus but ligand HL in case of *F. Solani* and *S. Rolfsii* fungi).

Generally, the synthesized benzimidazole ligand and its related transition metal chelates possessed different fungicidal activities towards the tested fungi. Introducing the nitro group remarkably increased the competencies. Data obtained clearly show that fungicidal activities of both ligand and all of its binary chelates having nitro substituent are better than that before such modification. The improvement in activity due to introducing the nitro group in position 5 of benzimidazole ring is compatible with the literature. Some recently published works proved that introducing some electron withdrawing groups, as nitro or halogen, in position 5 of benzimidazole ring enhances the antimicrobial activity of its related compounds (Alasmary *et al.* 2015; Ulkuseven *et al.* 2002). Chelation of benzimidazole ligand with new transition metal ions as Cd(II) and Fe(III) affected remarkably only in case of *R. solani* fungus where cadmium complex was found to be the most potent one.

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تخليق و توصيف و دراسة الكفاءة الإبادية لبعض متراكبات العناصر الإنتقالية و المتضمنة لليجاندا بينزايميدازول دايثيوكراميت

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٢. المعمل المركزى للمبيدات - مركز البحوث الزراعية - الدقى - الجيزة - مصر.

في هذه الدراسة تم تخليق ليجاندا جديد مشتق من مركبات البنزايميدازول دايثيوكراميت و مجموعة من متراكباته الجديدة مع بعض العناصر الإنتقالية. تم أثبات التراكيب البنائية لكلا من الليجاندا و متراكباته بأستخدام العديد من طرق التحليل الدقيقة المعروفة في هذا المجال كالتحليل الكمي للعناصر المكونة لهذه المركبات ، و دراسة اطيافها لجهاز الأشعة تحت الحمراء (IR) ، و جهاز تحديد الكتل الجزيئية للمركبات (MS) ، و كذلك دراسة الأنعكاسات الصلبة و العزم المغناطيسى و التوصيل المولارى و التحلل الحرارى لهذه المركبات. من خلال النتائج المتحصل عليها تبين أن الليجاندا المُستخدم في هذه الدراسة ثلاثى الشُعَب ، و أن الصيغة البنائية العامة لمتراكباته مع العناصر الأنتقالية هي $[MCl(HL)(H_2O)_2]Cl_2 \cdot 2H_2O$ (M = Cr(III) Fe(III)) ، و كذلك دراسة الأنعكاسات الصلبة و العزم المغناطيسى و التوصيل المولارى و التحلل الحرارى لهذه المركبات. من خلال النتائج المتحصل عليها تبين أن الليجاندا المُستخدم في هذه الدراسة ثلاثى الشُعَب ، و أن الصيغة البنائية العامة لمتراكباته مع العناصر الأنتقالية هي $[MCl(HL)(H_2O)_2]Cl \cdot yH_2O$ (y = 2: M = Mn(II), Co(II), Cu(II) / y = 1: M = Ni(II), Zn(II), Cd(II)) و قد أوضحت نتائج التوصيل المولارى لهذه المركبات أنها مركبات ألكتروليتية ، كما أوضحت نتائج قياس الأنعكاسات الصلبة و العزم المغناطيسى لهذه المركبات بأن ذراتها تأخذ ترتيب الشكل الثماني في الفراغ ، كما أوضحت نتائج التحلل الحرارى لهذه المركبات أنها تحتوى على جزيئات لماء التبلر و التي تفقدها أولاً قبل تحللها حرارياً.

و في هذه الدراسة تم أيضاً دراسة الكفاءة الأبادية لهذه المركبات كمبيدات فطرية جديده على ثلاث أنواع من فطريات التربة و هم *Fusarium solani*, *Rhizoctonia solani*, *Sclerotium rolfesii*. و قد أظهرت نتائج التقييم البيولوجى المتحصل عليها لهذه المركبات تباين في كفاءتها و قدرتها على تثبيط نمو هذه الفطريات. كما أوضحت النتائج أيضاً أن الليجاندا الأسمى قد أعطى أعلى كفاءة أبادية على الفطرين *F. Solani*, *S. Rolfesii* ، بينما أعطى متراكب الكادميوم أعلى كفاءة تجاه الفطر *R. Solani*. كما أوضحت النتائج أيضاً أن أستبدال ذرة الهيدروجين المتصلة بذرة الكربون رقم (٥) من حلقة البنزايميدازول بمجموعة ساحبة للإلكترونات قد زاد من الكفاءة البيولوجية للمركبات بشكل كبير جداً. كما أوضحت النتائج أيضاً أن بعض المركبات الجديدة و المُخلقة في هذه الدراسة قد أظهرت كفاءة أبادية تفوق المبيد القياسى (Pencycuron) على الفطريات محل الدراسة.

