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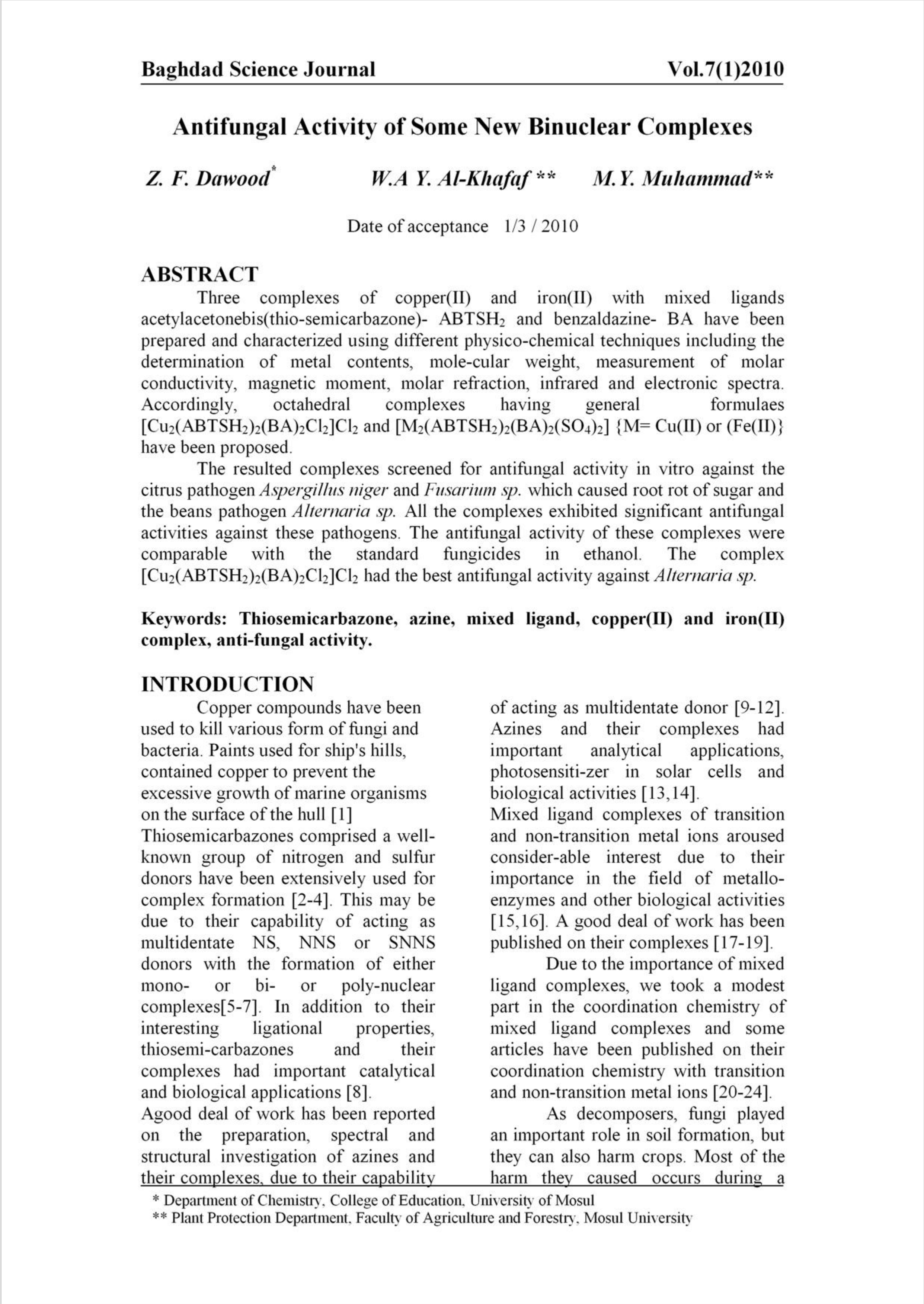

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Antifungal Activity of Some New Binuclear Complexes

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ABSTRACT

Three complexes of copper(II) and iron(II) with mixed ligands acetylacetonebis(thio-semicarbazone)- $ABTSH_2$ and benzaldazine- BA have been prepared and characterized using different physico-chemical techniques including the determination of metal contents, mole-cular weight, measurement of molar conductivity, magnetic moment, molar refraction, infrared and electronic spectra. Accordingly, octahedral complexes having general formulaes $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ and $[M_2(ABTSH_2)_2(BA)_2(SO_4)_2]$ {M= Cu(II) or (Fe(II)} have been proposed.

The resulted complexes screened for antifungal activity in vitro against the citrus pathogen *Aspergillus niger* and *Fusarium sp.* which caused root rot of sugar and the beans pathogen *Alternaria sp.* All the complexes exhibited significant antifungal activities against these pathogens. The antifungal activity of these complexes were comparable with the standard fungicides in ethanol. The complex $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ had the best antifungal activity against *Alternaria sp.*

Keywords: Thiosemicarbazone, azine, mixed ligand, copper(II) and iron(II) complex, anti-fungal activity.

INTRODUCTION

Copper compounds have been used to kill various form of fungi and bacteria. Paints used for ship's hills, contained copper to prevent the excessive growth of marine organisms on the surface of the hull [1]

Thiosemicarbazones comprised a well-known group of nitrogen and sulfur donors have been extensively used for complex formation [2-4]. This may be due to their capability of acting as multidentate NS, NNS or SNNS donors with the formation of either mono- or bi- or poly-nuclear complexes[5-7]. In addition to their interesting ligational properties, thiosemi-carbazones and their complexes had important catalytical and biological applications [8].

Agood deal of work has been reported on the preparation, spectral and structural investigation of azines and their complexes, due to their capability of acting as multidentate donor [9-12]. Azines and their complexes had important analytical applications, photosensiti-zer in solar cells and biological activities [13,14].

Mixed ligand complexes of transition and non-transition metal ions aroused consider-able interest due to their importance in the field of metallo-enzymes and other biological activities [15,16]. A good deal of work has been published on their complexes [17-19].

Due to the importance of mixed ligand complexes, we took a modest part in the coordination chemistry of mixed ligand complexes and some articles have been published on their coordination chemistry with transition and non-transition metal ions [20-24].

As decomposers, fungi played an important role in soil formation, but they can also harm crops. Most of the harm they caused occurs during a

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plant's early growth stages. Fungi can also spoil stored food and are particularly devastating to the world's fruit harves [25]. Diseases caused in plants by fungi occerred worldwide, caused considerable damage, typically have been unpredictable and difficult to control culturally or chemically, and host resistance to disease has been inadequate. For these reasons, it is imperative that as much basic knowledge as possible be gained about the taxonomy, biology, physiology, ecology, and host-parasite interactions of these important and devastating plant pathogens to enable us to discover and develop new ways to control them [26].

Pathogenesis is a complex, dynamic process involving the Pathogen's inherent capabilities and multiple factors that govern penetration and infection of a host plant. The host plant has an array of defense mechanisms that must be breached, inactivated, or annulled before disease can develop. This interaction between host and Pathogen also is dependent on the surrounding environment and on time. The Pathogen's battery of attacking mechanisms includes cell wall- and middle lamella-degrading enzymes, toxins, enzymes to degrade host tissue and defense substances, and rapidity of infection. The host can resistant attack by the presence of physical barriers, resistant cell wall materials, performed antifungal compounds, infection-stimulated antifungal compounds, and inadequate nutrients for Pathogen growth and development. If the host responds slowly or inadequately with one or more of these defense mechanisms, disease ensures, and death results [26].

We do know that cell wall-degrading enzymes, enzymes capable of destroying cellular components, and production of oxalic acid are associated with disease development. The exact role of these components in pathogenesis is not clearly defined, but the pieces are beginning to fit together [26].

Since, the power of infecting is shown by the power of penetrating the membranes [cuticle] which are evidently dissolved at the point of penetration. Hence it is very probable that this power depends on the presence of a substance which can dissolve the membrane [26].

Pectolytic enzymes associated with diseases caused. These enzymes have been associated with quantitative decrease in the pectic substances contant of diseased tissue and with histochemical and structural changes in host cell middle lamellae. In addition, pectolytic enzyme activity has been localized in infected tissue. Besides cell wall-degrading enzymes, afew other enzymes such as phosphatidase B capable to hydrolyze phosphatide component of cell membranes. Potentially, proteolytic enzyme responsible for degradation of host protoplasm and possibly cell wall constituents may be detected [26].

The effect of pathogens appears to dependent on a complex combination of factors that can overwhelm the host plant by rapidly acting before the host plant can respond. These factors include: production of infection cushions or appressoria to enable mechanical penetration of the host cuticle, formation of specialized, organized infection hyphae that are capable of rapid intercellular development beneath the host cuticle and in the cortex elaboration of appropriate pectolytic enzymes and oxalic acid to degrade the middle lamella of host cells, chelation-inhibitors of enzyme activity, change the pH of host tissue to arrange more favorable for enzymeic action, and toxify host cells, making them less responsive to invasion, and production of degradative enzymes capable of hydrolyzing cell wall and protoplasmic constituents and providing a constant, abundant supply of nutrients for rapid growth and development of infective hyphae [26].

The antifungal activities of coordinated compounds have been studied by many workers. Complexes of Schiff bases [27], copper [28] and mixed ligands [29] showed a good antifungal activities. Moreover, thiosemicarbazone and their complexes showed a very good antifungal activities [30,31].

In the present work, new copper(II) and iron(II) complexes with mixed ligand {acetylacetonebis(thiosemicarbazone) and benzaldazine (Figure 1)} have been prepared and characterized physico-chemically. The complexes were screened for their antifungal activity against *Aspergillus niger, Fusarium sp.* and *Alternaria sp.*, and they have been exhibited significant antifungal activities.

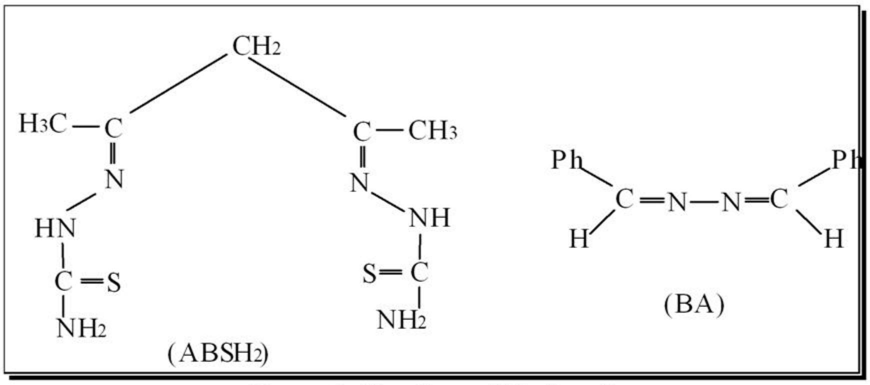


Figure 1: Structures of the ligands

Material and Methods:

1- Starting Materials

All the chemicals used were supplied from BDH or Fluka.

2- Synthetic Methods

Acetylacetonebis(thiosemicarbazone)-$ABTSH_2$ has been prepared according to the standard method [32]. Benzaldazine ligand has been prepared according to previous method [32] .

Complexes of the type $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ has been prepared by the reaction of aqueous solution of copper(II) chloride in 5 ml. distilled water (0.5 g; 0.00186 mole) with hot ethanolic solution of benzaldazine (0.00186 mole) and hot ethanolic solution of 0.00186 mole acetylacetonebis(thiosemicarbazone) in 2:2:2 molar ratio. The mixture has been ref-luxed for three hours followed by evaporation to about half it's volume then cooled. The product was isolated by filteration, washed with diethylether and dried. The other complexes were prepared by applying the same procedure (the amounts in grams were listed in Table 1)

3- Analytical and Physical Measurements :

Copper and iron contents have been determined by applying precipitation method after the decomposition of the complexes with concentrated nitric acid [33]. Molecular weights of the complexes have been determined cryoscopically (decreasing in freezing point) [34]. Refraction measurements have been carried out with Atago Illumination, Atago Co-LTD, Japan using 10^{-3} M dimethylformamide solution. The molar refraction is an additive and constitutive property. It has been used to construct the correct structure of the compound.[34]. The conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 using 10^{-3} M dimethylformamide solution at 25 °C. Magnetic susceptibility of the complexes have been measured by Bruker B.M6 . The infrared spectra of the ligands and their complexes have been recorded on FT-IR Bruker type Tensor 27 in the range 400-4000 cm^{-1} using KBr pellets. Electronic spectra has been recorded by Shimadzu UV-1601 Spectrophotometer for 10^{-4} M solutions of the ligands and their complexes in dimethylformamide at 25 °C , using a 1cm cell .

4- Antifungal Activity:

Three microorganism fungi have been selected to study the antifungal activity of the three complexes in this study *Aspergillus niger, Fusarium sp.,* and *Alternaria sp.* All the fungi have been obtained from Plant Protection Department , Faculty of Agriculture and Forestry, Mosul University.

The fungi were isolated from the affected plants by applying Agnihorti method [35] and purified using classification keys that were put by Barrutt and Hunter [36]. The antifungal activity has been evaluated by applying Al-Khafaf method [37] that depended on Abbott method [38] as follows:

0.1 gm of the complex was dissolved in 100 ml. ethanol (95%) . 1 ml. of this solution was added to sterilized petrydish containing Potato Dextrose Agar (PDA) which was left for one day (24 hr.) until the ethanol was evaporated A part of a side of the colony (4 days age growing) was inoculated in the center of the sterilized dish above. The dish was incubated at 25±3 °C for 5-6 days and the inhibition zone was measured. In all the experiments the mean of each triplicate was measured. Blank dish of ethanol (95%) has been used as control.

RESULTS AND DISCUSSION

The reaction of copper (II) and iron(II) salts with acetylacetonebis (thiosemicarbazone and benzaldazine may be represented by the following reactions :

$$2CuCl_2+2BA+2ABTSH_2 \rightarrow [Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$$

$$2MSO_4.nH_2O+2BA+2ABTSH_2 \rightarrow [M(ABTSH_2)_2(AB)_2(SO_4)_2] + nH_2O$$

(where n = 5 or 7).

The resulted complexes were colored solid. Copper, iron contents and the molecular weights revealed that the complexes had the compositions $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ and $[M(ABTSH_2)_2(AB)_2(SO_4)_2]$ (Table 2). The values of the molar conductivities of the complex-es (Table 2) approached those expected for 1:2 and non-elecotrolytes [39]. The room temperature magnetic moment of Cu(II) complexes lied in the range of 1.82-1.88 which were compared to the expected values for six coordinate high-spin octahedral complexes[22]. The magnetic moment of iron(II) complex has been found to be 5.10 B.M. which is within the range of values corresponding to high spin octahedral complexes of iron(II) ions [20] (Table 2).

The infrared spectra of $ABTSH_2$ ligand (Table 3) showed a strong band at 1635.58 cm^{-1} assigned to C=N group shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation [40]. The next strong band at 1200.25 cm^{-1} and 1169.12 cm^{-1} attributed to the stretching and bending frequencies of C=S group. The first value splitted into two peaks one remained at the same position and the other shifted towards a lower frequency on coordination, indicating the formation of chelation between the sulfur of one C=S group and the metal ion [40]. The other strong bands at 3399.04 cm^{-1} and 1450.00 cm^{-1} attributed to υ_{NH2} and ∂_{NH2} remained unaltered in all the complexes indicating that there is no coordination through this group [21,29,30] .

The spectra benzaldazine showed a strong band in the region 1624.00 cm^{-1} due to C=N stretching vibration group [40]. This band was shifted towards a lower frequency (Table 3) which demonstrated that the two azine nitrogen was coordinated to the metal ion[40]. Moreover, the positive shift in the N-N vibration band on complexation can be added as further support to the coordination of the azine nitrogen to the metal ion.

The spectra of complex 1 showed a new band at 525.50 cm^{-1} attributed to ionic M-Cl [40], whereas the $\upsilon_{M\text{-}Cl(coord.)}$ was not observed due to instrumental limitation. The spectra of the complexes 2 and 3 showed three bands around 1010.00, 1073.00 and 1125.00 cm^{-1} due to SO group [40] indicating that the sulphato group acted as monodentate ligand bonding to the metal ion through the oxygen atom [40].

On the other hand the spectra of all the complexes showed new bands around 450.82-456.45 cm^{-1} and 556.62-558.27 cm^{-1} due to $\upsilon_{M\text{-}N}$ and $\upsilon_{M\text{-}S}$, respectively [17,21,31]. The presence of these bands supported the formation of the complexes under investigation.

The electronic spectra of the complexes in DMF solution have been recorded giving ultraviolet spectra, d-d spectra and charge transfer spectra (Table 4).The ultraviolet spectra for $ABTSH_2$ showed bands at 39550 cm^{-1} and 26178 cm^{-1} attributed to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic transitions, respectively. The ultraviolet spectra for BA ligand showed bands at 38750 cm^{-1} and 27941 cm^{-1} attributed to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electronic transitions, respectively. All these transitions were also found in the spectra of the complexes but they were shifted to lower frequencies ($\Delta\upsilon$=1700-2000 cm^{-1}) confirming the coordination of the ligands to the metal ions[41]. The electronic spectra of Cu(II) complex showed a band at 13835 and 13850 cm^{-1} which may be assigned to $^2Eg\rightarrow {}^2T_2g$ transition in an octahedral environment. The eg group state is highly susceptible to John-Teller configurational stability due to which copper (II) ion in the complexes had distorted octahedral geometry. The electronic spectra of copper(II) complexes also showed a band at 31200 and 31215 cm^{-1} due to charge transfer spectra[42]. The electronic spectra of Fe(II) complex is a characteristic of an octahedral geometry having high spin electronic configuration. According to this electronic distribution, only one well-defined $^5T_2g\rightarrow {}^5Eg$ transition .However, due to the Jahn Teller effect, the ^5Eg term is split in two terms which are responsible for the occurrence of a band and a shoulder in the spectrum. Hence Fe(II) complex showed a pair of low intensity bands at 12500 and 10210 cm^{-1}, arising from $^5T_2g\rightarrow {}^5A_1g$ and $^5T_2g\rightarrow {}^5B_1g$, transitions similar to those found for distorted octahedral complexes. The doublet is attributed to a Jahn Teller distortion in the excited state [42]. The electronic spectra of iron(II) complex also showed a band at 35200 cm^{-1} due to charge transfer spectra [42].

It is well known that in order to the antifungal activity to be effective the antifungal compounds must have ability to penetrate inside the fungi cell (some times the antifungal compounds caused changes in the medium in which the fungi was grown and made it unsuitable for the growth of the fungi).

After the antifungal compound was penetrated through the protoplasmic membrane of the fungi, the compound started to did it's toxic effect inside the fungi cell. Some antifungal compounds may increase the resistance of the host plant in a way that can made changes in the cell wall tissue of the plant and made it very difficult to be penetrated by the fungi that caused the diseases. There are numbers of explanations that can allow the antifungal compound to does it's toxic effects including the following points:

1- Reaction of antifungal compound with the vital enzymes and inhibited them.

2- Influence the oxidation-reduction reaction which affect the production of energy.

3- Influence the vital processes through the similar composition of some antifungal compound with the compound exist in fungi cell, therefore it can enter wrongly in a numer of vital reactions and sometimes can led to the death of fungi.

4- The antifungal compound may interacts with some vital compounds, this can influence the vital immunity of the compound which the fungi cell needed. The reaction with some amino acids may influence the process of protein synthesis [43].

The activity of the prepared compounds were compared with other known antifungal compounds(dodine and rovral used as antifungal for *Alternaria sp.*, and benlate used as antifungal for *Aspergillus niger* and *Fusarium sp.*).

The complex $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ showed a good antifungal activity against *Aspergillus niger* and *Alternaria sp.*, but very low activity against *Fusarium sp.* While the complex $Cu_2(ABTSH_2)_2(BA)_2(SO_4)_2]$ showed a good antifungal activity against only *Aspergillus niger* but no activity against the other two fungi (*Fusarium sp.* and *Alternaria sp.*). Whereas the complex $[Fe_2(ABTSH_2)_2(BA)_2(SO_4)_2]$ showed a good antifungal activity against only *Aspergillus niger* and *Alternaria sp.,* but very low activity against *Fusarium sp.*

CONCLUSSION

According to the analytical , physical and spectral studies, the following observations have been achieved that lead to establish the following points:

1- The ligand $ABTSH_2$ acted as tridentate chelating bridging ligand joint to the metal ion through the two azomethine nitrogen and one thiosulfur.

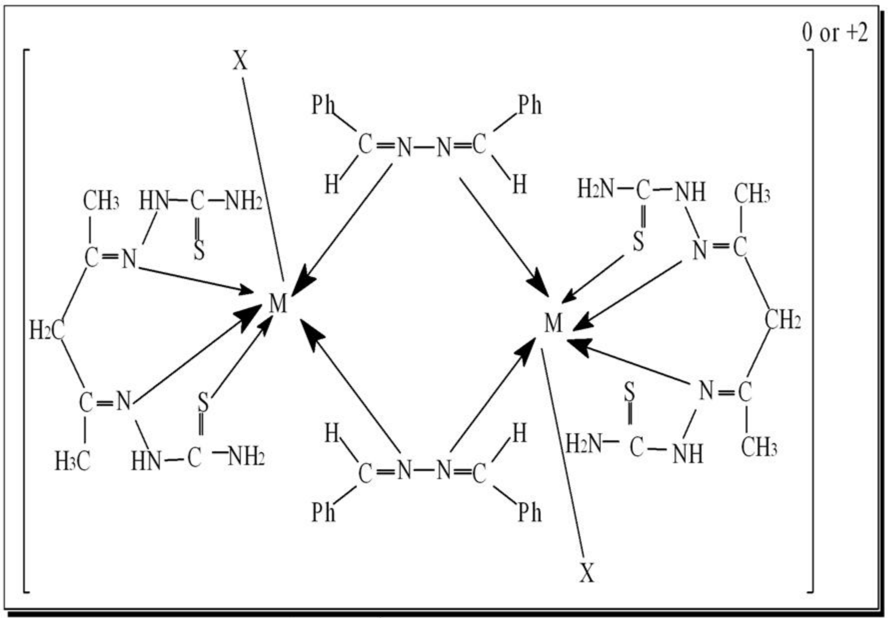
2- The ligand BA acted as bridging ligand joint through the two nitrogen atoms.

3- The chloride ion acted as monodentate ligand and also as countert ion in complex 1.

4- Sulfate ion acted as monodentate ligand joint through oxygen atom

5- Copper(II) and iron(II) ions had hexacoordinated resulting in a high spin distorted octahedral geometry. From the present study we can concluded that the complexes had the following proposed geometries(Figure 2).

6- The complexes showed good antifungal activity against *Aspergillus niger* and *Alternaria sp.*, whereas no or very low activity against *Fusarium sp.* The complex $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ showed best antifungal activity against *Alternaria sp.*



M = Cu(II) or Fe(II) ; X = Cl^- or SO_4^{-2}

Figure 2 : Proposed structures of the complexes

Table 1 : Amounts of ligands, %yield of the complexes

No.	Complexes	Wt of $ABTSH_2$ (gm)	Wt of BA (gm)	%Yield
1	$[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$	0.9145	0.7732	90.2
2	$[Cu_2(ABTSH_2)_2(BA)_2(SO_4)_2]$	0.4930	0.4168	89.9
3	$[Fe_2(ABTSH_2)_2(BA)_2(SO_4)_2]$	0.4424	0.3741	87.5

Table 2: Analytical and physical properties of the complexes

No.	Color	M.P °c	$*\wedge_M$	$**M_{eff.}$	Ref. $x10^{-4}$	M% Calc. Obs.)	M. Wt. Calc. (Obs.)
1	Green	204d	135.5	1.82	1.435574	10.79 (10.72)	1177 (1190)
2	Dark green	166d	11.4	1.88	1.435571	10.35 (10.38)	1227 (1233)
3	Dark Green	220	6.5	5.10	1.435577	9.24 (9,20)	1212 (1202)

* Λ_M : Molar conductivities in $\Omega^{-1} cm^2 mol^{-1}$; $**\mu_{eff}$: Magnetic moment in Bohr Magneton; d=decomposition points; Ref.= refraction

Table 3 : IR spectra of complexes (values in cm-1)

No.	$\upsilon_{C=N}$	$\upsilon_{C=S}$ (thio)	υ_{NH}	δNH_2	$\upsilon_{C=N}$ (azine)	υ_{N-N}	υ_{M-N}	υ_{M-S}
$ABTSH_2$	1635.00	1200.25	3399.04	1450.00	-	-	-	-
BA	-	-	-	1455.00	1624.00	950.00	-	-
1	1600.54	1200.25,1145.54	3400.20	1455.00	1556.21	980.20	450.82	558.27
2	1601.59	1200.25, 1142.50	3399.05	1455.00	1558.05	982.50	451.00	556.62
3	1602.24	1200.25,1150.35	3399.45	1455.00	1556.25	983.50	456.45	557.35

Table 4 : Electronic spectral data of the ligands and their complexes

No.	UV region		d-d transition		C.T
	π→π* cm^{-1}	n→π* cm^{-1}	$υ_1$ cm^{-1}	$υ_2$ cm^{-1}	cm^{-1}
$ABTSH_2$	39550	26178			
BA	38750	27941			
1	37800, 37050	24378, 25191	13835		31200
2	37550, 36750	244750, 26241	13850		31215
3	37750, 36750	24175, 25940	12500	10210 (shoulder)	35200

Table 5: Antifungal activity of the complexes

	Aspergillus niger				*Fusarium sp.*				*Alternaria sp.*			
Comp. No.	Trip.	Dia.	Inh.%	mean %	Trip.	Dia.	Inh.%	mean %	Trip.	Dia.	Inh.%	mean %
1	1	0.00	100.00	85.83	1	1.75	-20.69	5.75	1	0.00	100.00	100.00
	2	1.70	73.23		2	1.15	20.69		2	0.00	100.00	
	3	1.00	84.25		3	1.20	17.25		3	0.00	100.00	
2	1	0.95	85.04	87.14	1	1.40	3.45	-8.05	1	0.50	43.18	-7.95
	2	0.00	100.00		2	1.50	-3.45		2	0.95	-7.95	
	3	1.50	76.38		3	1.80	-24.14		3	1.40	-59.09	
3	1	1.20	81.10	78.74	1	1.45	0.00	5.75	1	0.70	20.45	73.48
	2	1.30	79.53		2	1.55	-6.90		2	0.00	100.00	
	3	1.55	75.59		3	1.10	24.14		3	0.00	100.00	
St. Exp.		6.35										

Dia. = Average of two perpendicular diameter of the fungi colony; Inh. = inhibition zone

REFERENCES

1- A. Stwertka, A guide to the elements; Oxford Univ., Press, Inc., Perlin, Rev. ed., 93 (1998).

2- B. Singh and H. Misra; Complexes of cobalt(II), copper(II), zinc(II), cadmium(II) and dioxouranium(II) with thiophene-2-aldehydethiosemicarbazone; J. Indian Chem. Soc.; 63: 692-694 (1986).

3- W. Kaminsky, J.P. Jasinski, R. Noudenberg, K.I. Goldberg and D.X. West; Structural study of two N(4)-substituted thiosemicarbazones prepared from 1-phenyl-1,2-propanedione-2-oxime and their binuclear nickel(II) complexes; J. Mol. Struct.; 135-141.5-H(2002).

4- F.A. El-Saied, A.A. El-Asmy, W. Kaminsky and D.X. West; Spectral and structural studies of cobalt(II,III), nickel(II) and copper(II) complexes of de hydroaceticacid N_4-dialkyl and 3-azacyclothiosemicarbazones; Trans. Met. Chem.; 28:954-960 (2003).

5- Z.H. Chohan, H. Pervez, K.M. Khan, C.T. Supuran; Organometallic-based antibacterial and antifungal compounds: transition metal complexes of 1,1-diacetylferrocene derived thiocarbo-hydrazone, carbohydrazone, thiosemicarbazone and semicarbazone; J.Enzym Inhib. Med. Chem.; 20(1): 81-88 (2005).

6- M.C. Aguirre, J. Borrãs, A. Castifieiras, J.M. Gurcia-Monteagudo, I. Garcia-Santos, J. Niclõs and D.X. West; Synthesis, characterization, and properties of some copper complexes of 2-pyridineformamidethiosemicarbazone (Ham_4DH); European J. Inorg. Chem.; 1231-1244 (2006).

7- V.M. Leovac, L.S. Jovanovic, V. Divjakovic, A. Pervec, I. Lebnan and Tr. Armbruster; Transition metal complexes with thiosemicarbazide-based ligand-part LIV-nickel(II) complex-es with pyridoxalsemicarbazone (PLSC) and thiosemicarbazone (PLTSC) crystal and molecular structure of $[Ni(PLSC)(H_2O)_3](NO_3)_2$ and $[Ni(PLTSC-H)Py]NO_3$; Polyhedron; 26(1): 49-58 (2007).

8- B.K. Rai, K. Kumer and Y.P. Srivastava; Spectroscopic investigation and antifungal studies of some mixed ligand complexes of Co(II), Ni(II) and Cu(II) with 6-methyl-2-pyridylformamidesemicarbazone and thiosemicarbazone; Asian J. Chem.; 17(3): 1773-1779 **(**2005**).**

9- S. Satapathy and Sahoo.; Salicylaldazinate metalchelates and their IR. Spectra; *J. Inorg. Nucl. Chem;.* 23: 2223-2227 (1970).

10- R.C. Aggarwal, N. K. Singh and R.P. Singh; Synthesis and structural studies of salicylaldazine complexes of oxovanadium(IV), manganese(II), Iron(II), Cobalt(II), nickel(II), copper (II) and zinc(II); *J. Indian Chem. Soc.*; LXIII: 466-468 (1986).

11- W. Dinkn, N. Megersa, V.J.T. Raju, J.A. Jonsson and N. Retla; Studies of transition metal complexes of herbicidal compounds 1: Transition metal complexes of 2-methylthio-4-azido-6-isopropylamino-S-triazine (aziprotryn); *Bull. Chem. Soc. Ethiopia*; 15: (1), 29-38 (2003).

12- B. Singh and U.R. Singh; Synthesis and structural characterization of 2-aminoacetophe-nones salicyldazine complexes of some bivalent transition metal ions; *Cryst. Res. Tech.*; 26: (8), 1039-1045 (2006).

13- S.D. Perera, B.L. Shaw and M. Thornton-Pett.; Agerieral strategy for inducing C-H bond fission (cycloiridation) in some aryl heterocyclic, alkenyl or alkyl groups in azine derived from aldehydes or methyl ketone; *J. Chem. Soc. Dalton Trans,*; 1689 (1995).

14- Kalyanasundaram K.; Use of azine dye as a photosensitizer in solar cell: Different reductants-safranine; *Int. J. Enorgy Res.*; 21: (14), 1345-1350 (1997).

15- M.M. Ajaily, A.A. Maihub, S.F. Ben-Gweirif, A.M. Belazi and R.S. El-Zweay; Chara-cterization and antibacterial activity of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes; *Orient. J. Chem.;* 23: 1 (2007).

16- B.K. Rai, K. Kumar and Y.P. Srivastava; Spectroscopic investigation and antifungal studies of some mixed ligand complexes of Co(II), Ni(II) and Cu(II) with 6-methyl-2-pyridyl-formamide semicabazone and thiosemicarbazone; *Asian J. Chem.;* 17: (3), 1773-1779 (2005).

17- P. Bindu, M.R.P. Kurup and T.R. Satyakeerty; EPR, cyclic voltametric and biological studies of copper(II) complexes of salicylaldehyde N(4) substituted thiosemicarbazone and heterocyclic bases; Polyhedron, 18, 321(1998).

18- R. Ramesh and M. Sivamasundari; Synthesis, spectral and antifungal activity of mixed ligand complexes; Synth. React. Inorg. Met-Org. Chem.; 33(5), 899-910 (2003).

19- B.K. Choudhary, P. Sahi and S. Rana; Structural characterization and antifungal studies of some mixed ligand Schiff base complexes with 6-bromo-2-thio-3-phenylquinazoline4(3H)-onethiosemicarbazone; Oriental J. Chem.; 23, 1 (2006).

20- Z. F. Dawood & A.A. Mohamad; Preparation and characterization of Fe(II) complexes containing mixed ligands; Al-Taqani; 19(2),100-108(2006)

21- Z. F. Dawood & A. Y. Ritha; Preparation of binuclear complexes; R. J. of Aleppo Univ. Basic Sciences Series; 54 (2007)

22- Z. F. Dawood and Y. T. Mahmood, Preparation and radiolysis of new mixed ligand copper(II) complexes; J. Of Col. Of B. Ed.; 51, 13-28 (2007).

23- Z. F. Dawood and M.W. Ibrahim, Preparation of some nickel(II) complexes containing mixed ligands (salicylaldehydesemicarbazone) and carboxylic acids; Nat. J. Chem.; 30, 330-337(2008).

24- Z. F. Dawood, T.J. Mohammed and M.R. Sharif; New nickel(II) complexes with benzil-bis(semicarbazone) & dithiocarbamate ligands; Iraqi J. Veterinary Sci.; 23(II), 135-141 (2009).

25- J. Suchocki; Conceptual chemistry: Understanding our world of atoms and molecules; Fungicides kill funge; Addison Wesley, United States, 506-507 (2001).

26- R.D. Lumsdcn; Histology and physiology of pathogenesis in plant diseases caused by Sclerotinia Species; Phytopathoogy;; 69(8), 890-896 (1979).

27- G.I. Devi, G. Parameswaran and S.S. Veena; Antifungal studies of complexes of Schiff base derived from anthracene carboxaldehyde-L-tyrosin; Asian J. Chem.; 16(2), 884-890 (2004).

28- B. Dudová, D. Hudecová, R. Pokorný, M. Micková, M. Palicová, P. Segla and M. Melnik; Copper complexes with bioactive ligands. Part II; Antifungal activity; Folia Microbiol.; 47, 225-229 (2002).

29- R. Ramesh and M. Sivagamasundari; Synthesis, spectral and antifungal activity of mixed ligand complexes; Synth. React. Inorg. Met.-Org. Chem.; 33(5), 899-910 (2003).

30- E. Bermejo, R. Carballo, A. Castineiras, R. Domnguez, C. Maichle-Mossmer, J. Strahle and D.X. West; Synthesis, characterization and antifungal activity of group 12 metal complexes of 2-acetylpyridine-^4N-ethylthiosemicarbazone (H4EL) and 2-acetylpyridine-N-oxide-^4N-ethylthiosemicarbazone (H4ELO); Polyhedron; 18(27), 3695-3702 (1999).

31- M.A. Ali, M.H. Kabir, M.N. Uddin, S.M.M. Majumder, M.T.H. Tarafder and M.A. Khair; Synthesis, characterization and antifungal properties of some four-coordinate nickel(II) and four and five coordinate copper(II) complexes containing tridentatethiosemicarba-zone and heterocyclic bases; Indian J. Chem.; 27A, 1064 (1988).

32- A.I. Vogel; Textbook of Practical Organic Chemistry; Longman Green, London, 3rd ed., 344 (1964).

33- A. I. Vogel; Textbook of Quantitative Inorganic Analysis; Longman Green, London, 3rd ed., (1978).

34- J. W. Danials; Experimental Physical Chemistry; McGraw-Hill, 6th ed., 81 (1962).

35- V.P. Agnihorti; Effects of certain fungi toxicants on the viability and pathogenicity of sclerotia of waitea circinata phytopath; 70, 71-80 (1971).

36- H.L. Barnett and B.B. Hunter; Illustrated genera of imperfect fungi. American Phyto-pathological Society 3340 Pilot knob road st Paul Minnesota 55121-2097.USA, 217P (2003).

37- W,A.Y. Al-Khafaf; Ecological and biological studies on the poplar clearwing moth *Eusphecia pimplaeformis* Ob.(Aegeriidae Lepidoptera) and it's control; Ph,D., Mosul University, College of Agriculture and Forestry (1999).

38- W.S. Abbott; A method of computing the effectiveness of an insecticides; J. Econom. Entomol.; 18, 265-267(1925)

39- W. J. Geary; Use of conductivity measurements in organic solvents for the characteriza-tion of coordination compounds; Coord. Chem. Rev. , 7, 81-87(1971).

40- K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compound'', John Wily and Sons, New York, 3rd ed., (1976).

41- A.I. Scott; Interpretation of the ultraviolet spectra of natural products; Pergamon Student ed., (1964)

42- D. Sutton; "Electronic Spectra of transition metal complexes'', McGraw-Hill publishing Co., London; (1968).

43- عواد شعبان و نزار مصطفى الملاح، المبيدات. دار الكتب للطباعة والنشر- جامعة الموصل، 188-189، 206 211، (1993)

الفعالية مضادة الفطريات لبعض المعقدات ثنائية النواة الجديدة

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الخلاصة

حضرت ثلاث معقدات للنحاس(II) والحديد(II) مع خليط من ليكندي الاسيتيل اسيتون بس(ثايوسميكاربازون) - $ABTSH_2$ والبنزالدازاين- BA في الوسط المتعادل وشخصت المعقدات الناتجة باستخدام تقنيات فيزيائية-كيميائية مختلفة تتضمن التقدير الكمي للعنصر الفلزي وحساب الوزن الجزيئي والتوصيل الكهربائي والعزم المغناطيسي والانكسار المولاري وقياس أطياف الأشعة تحت الحمراء والالكترونية، واستنادا الى ذلك إقترحت أشكال ثمانية السطوح ذات صيغ عامة $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ و $[M_2(ABTSH_2)_2(BA)_2(SO_4)_2]$ (حيث M= Cu(II) أو Fe(II)) للمعقدات الناتجة.

درست الفعالية مضادة الفطريات مختبريا ضد الفطر المسبب لمرض العفن على البرتقال *Aspergillus niger* والفطر المسبب لمرض تعفن جذور وسيقان البنجر *Fusarium sp.* والفطر المسبب لتبقع الفاصوليا *Alternaria sp.* أعطت جميع المعقدات فعالية ملحوظة ضد هذه الفطريات المسببة للأمراض. قورنت الفعالية المضادة للفطريات لهذه المعقدات مع المادة الضابطة بالايثانول . اتضح ان المعقد $[Cu_2(ABTSH_2)_2(BA)_2Cl_2]Cl_2$ يمتلك أفضل فعالية ضد الفطر *Alternaria sp.* .