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# Antifungal Studies of Some Metal Complexes with Schiff Base Ligands

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## Özet

Bu çalışmada HL ligandının nikel(II) ve bakır(II) kompleksleri sentezlendi. HL, 1-naftilamin ve 2-hidroksinaftalin-1-karbaldehitten elde edilen Schiff bazını gösterir. Ayrıca $H_2L'$ ligandının nikel(II), bakır(II), kobalt(II) ve çinko(II) kompleksleri de sentezlendi. $H_2L'$, 1,2-bis-(p-aminofenoksi)etan ve 2-hidroksinaftalin-1-karbaldehitten sentezlenen dier ligandı ifade eder. HL ve $H_2L'$ ligandlarının M. canis, M.gipsium ve C. albicans gelişimi üzerine etkileri incelendi. HL nin 0.6, 1.2, 2.4, 4.8 µg gibi ılımlı değerlerdeki dozları 100 mL sarbose-agar üzerine eklendi. Daha sonra sonuçlar, M. canis ve M. gipsium sporlarının bu dozlarda gelişebileceği şeklinde değerlendirildi. Halbuki doz miktarları arttırıldığında misellerin çaplarının azaldığı tespit edildi. Her iki tür için de spor gelişimi 4.8/100 mL µg dozda inhibe edildi. C. albicans ların koloni sayıları 0.6 and 1.2 µg/100 mL lik doz aralığında belirgin bir şekilde azaldı. HL ve $H_2L'$ ligandlarının çeşitli komplekslerinin kullanılmasında, üç türün gelişimi üzerine birbirinden farklı bir etkileri de yoktu ($P< 0.05$).

**Anahtar Kelimeler:** Schiff bazı, geçiş metal kompleksi, antifungal aktiviteler

## Abstract

In this study, Nickel(II) and Copper(II) complexes of HL were synthesized. HL denotes the Schiff base ligand which derived from 1-naphtylamine and 2-hydroxynaphthalene-1-carbaldehyde while the $H_2L'$ represents the other ligand derived from 1,2-bis-(p-aminophenoxy)ethane and 2-hydroxynaphthalene-1-carbaldehyde with its Copper(II), Nickel(II), Cobalt(II) and Zinc(II) complexes. The effects of metal complexes with HL and $H_2L'$ on the development of M. canis, M.gipsium and C. albicans species were investigated. The mild doses such as 0.6, 1.2, 2.4 µg of HL were added into 100 mL sarbose-agar. Then the results were evaluated that M. canis and M. gipsium spores could be germinated whereas in the case of increasing the dose amounts, the diameters of mycelle were decreased. For the both species; spore germination was inhibited at 4.8/100 mL µg dose. However, it s the point to emphasize that a significant decrease was observed in the number of colonies at 0.6 and 1.2 µg/100 mL doses for C. albicans. There were not any novelties between the effects of different complexes of HL and $H_2L'$ on the development of the three species ($P< 0.05$).

**Key Words:** Schiff base, transition metal complexes, antifungal activities

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## 1. Introduction

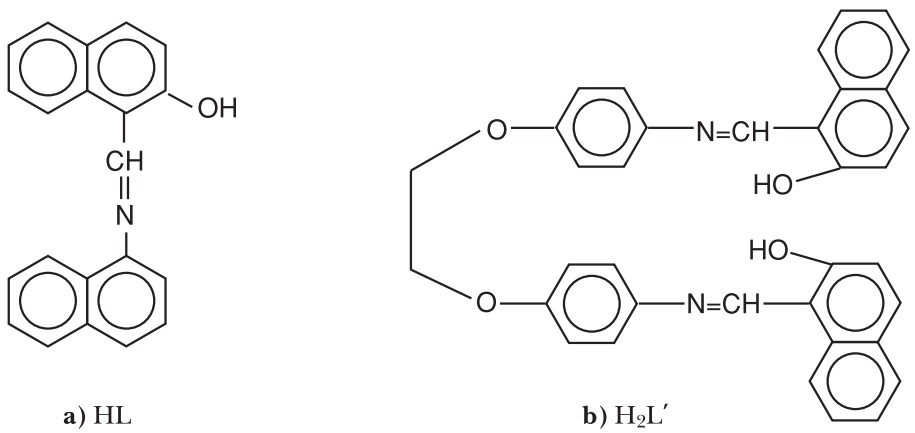
The interest in coordination chemistry of modified bioligands has increased. The focus of extensive investigations has been observed for the potential biological activities of transition metal complexes. Schiff bases have gained an important role due to their physiological and pharmacological activities. Compounds bearing azomethine group (CH = N) in the structure are known as Schiff bases, which are generally synthesized by the condensation of carbonyl groups and primary amines. And also they are well known structures for their pharmacological properties such as antibacterial, anticancer, antifungal and antiviral agents [1].

The purpose of the Schiff bases have become a frequently used ligand to get a chelating compounds in coordination chemistry [2-4], in catalysis, antioxidative activity, medicine as antibiotics, anti-inflammatory agents and industry for anticorrosion properties [5-8]. Amino acid-based Schiff bases are very effective metal chelators and their metal complexes are models for a number of important biological systems [9-10]. They are key intermediates in a diversity of metabolic reactions containing amino acids such as: decarboxylation, recemization, transamination, and C-C bond cleavage, which are catalyzed by enzymes [11].

Schiff bases continue to occupy an important position as ligands in coordination chemistry even after almost a century since their discovery. Schiff bases and their metal complexes are becoming increasingly important as biochemical, analytical, industrial and antimicrobial agents [12-21].

Candida albicans is known to cause infections in nail and vagina. When Candida albicans are reproduced through budding, the cells divided do not separate from each other and constitute pseudohyphe. The antibiotics such as Nystum Amphus are used against fungus infections. The antibiotics manifest their effects by combining with sterols within the cell membrane (microbiologist). Sihlehermurds, however, affect 80 S ribosome in fungus (micalegy). The elements such as Mn, Ni, Co, Zn and Cu have been reported to influence pigmentation in microorganisms [22-27]

Continuing our work [15-16] on Schiff base compounds of transition metals, we report here the antifungal activities of the some metal complexes with two Schiff base ligands derived from condensation of 1-naphtylamine and 2-hydroxynaphthalene-1-carbaldehyde (HL), or 1,2-bis-(p-aminophenoxy)ethane with 2- hydroxynaphthalene-1-carbaldehyde ($H_2L'$) (Fig. 1.).




**a)** HL **b)** $H_2L'$

**Figure 1.** Schiff Base Ligands a) HL: 2-hydroxynaphthalene-1-carbaldehydene1-naphtylamine b) $H_2L'$: N,N 2-bis(-2-hydroxynaphthalene-1-carbaldehydene)-1,2-bis-(p-aminophenoxy) ethane.

## 2. Experimental

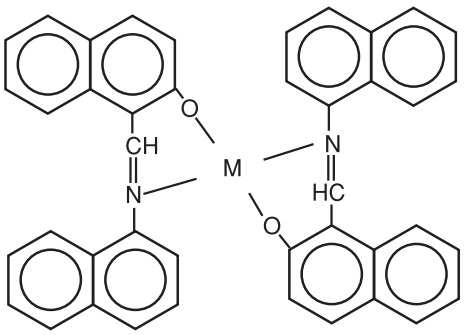
All the chemicals were obtained from Aldrich and used without further purification.

### 2.1. Synthesis of Ligands (HL and $H_2L'$)

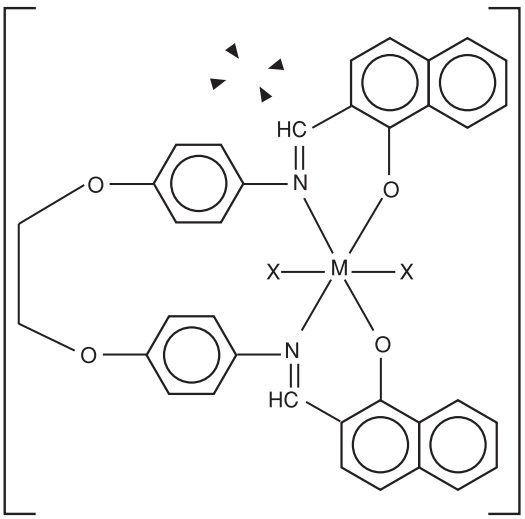
Schiff bases were derived from condensation of stoichiometric amounts of analytically pure 1-naphtylamine and 2-hydroxynaphthalene-1-carbaldehyde (HL), or 1,2-bis-(p-aminophenoxy)ethane with 2-hydroxynaphthalene-1-carbaldehyde ($H_2L'$) in absolute ethanol, in the usual way. The mixtures were heated under reflux on a water bath until the appearance of shining yellow crystals. The crude products were recrystallized from ethanol [17-18].

### 2.2. Preparation of Complexes

The following general procedure was used to prepare all the complexes. A solution of metal salt in 95 % ethanol (10 mmol) was mixed with the Schiff base ligands 95 % ethanol (10 mmole or 20 mmole) 1:2 or 1:1 (M:L) ratios and contents were refluxed in 50 mL ethanol on a water bath for 2-3 h. The refluxed solution was then poured into ice cold water when a colored solid separated out which was isolated by filtration and washed with ether, recrystallized from absolute ethanol and dried in vacuum at room-temperature [13-16] (Fig. 2).




a) $CuL_2$ and $NiL_2$ (Cu, Ni)




b) CuL', NiL', ZnL' and CoL'$2H_2O$

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

| X= $H_2O$ | - | - | - |
|---|---|---|---|
| n= | - | 1 | 1 | 1 |

Figure 2. Suggested structure of square-planar $NiL_2$, $CuL_2$, CuL' and NiL' and the tetrahedral ZnL' and octahedral CoL'$2H_2O$ complexes.

### 2.3. Preparation of Microbial Culture

In this study, Microsporum gypseum, Microsporuna canis and Candida albicans were used as the test organisms in an antifungal study. Yeast and fungus strains were inoculated into Sabouraud Dextrose Agar (Oxoid). The Schiff base complexes were added in this base medium at concentrations of 1.2 μg/100 mL, 2.4 μg/100 mL, and 4.8 μg/100 mL. Schiff base complexes were not added to the control media. The yeast strain was incubated for 24 hours, at 37 °C and fungus strains were incubated five days at 25 ± 2 °C. The inoculated fungus colonies were evaluated five days later. The diameters of fungus colonies were measured. The experiments were made three times and the results sense as statistics ($P<0.05$).

### 3. Antifungal Activity

The antifungal activity of some of the complexes and that of the free Schiff bases have been screened by the Agar Plate Technique [28]. Ligand $H_2L'$ and its metal complexes (Co, Zn, Cu and Ni) as well as ligand HL and its metal complexes (Ni and Cu) were determined to have an antifungal effect an M. canis (Table 1), M. gipsium (Table 2) and C. albicans (Table 3).

The effect of ligand $H_2L'$ and its complexes such as Co, Zn, Cu, Ni on M. canis and M. gipsium was observed as spore germination at the dosen of 0.6, 1.2 and 2.4 μg/100 mL. However, a decrease was noticed in diameter of mycelle parallel to the increasing dose, with respect to control, but spore germination was not observed at 4.8 μg/100 mL. In M. canis, the lowest mycelle diameter was obtained in HL with Cu complex at 1.2 and 2.4 μg/100 mL doses (Table 4), in $H_2L'$ at 1.2 μg/100 mL and with Zn at 2.4 μg/100 mL. The lowest mycelle diameter in M. gipsium was determined in $H_2L'$ with Co complex at 1.2 and 2.4 μg/100 mL as 1.5 and 0.7 cm, respectively, in HL as 2.0 cm at 1.2 μg/100 mL and with Cu complexes in HL at 2.4 μg/100 mL. There was not a remarkable difference between the effects of HL and $H_2L'$ complexes on C. albicans. While the decrease at 0.6 and 1.2 μg/100 mL for the two ligands and metal complexes diminished, incubation was not observed at 2.4 μg/100 mL. According to the results of the study, C. albicans were found to have an inhibiting effect at lower doses with respect to M. gipsium and M. canis.

In literature, it is maintained that ligands and their metal complexes are considerably active against Bacillus megaterium and Candide tropicals, but that the effect of metal complexes is stronger than that of ligands [29-30]. It was also reported that ligands and their metal complexes are active against Euherica coli, Barilum sp and Pseudomanan acurtuginan, while that Cu are more effective[26-28]. Moreover, Cu complexes of ligands were reported to be inhibiting active agents against bacteria and fungus [24]. It was also determined that ligands could produce an inhibiting effect on the development of Aupergillus, nager, penisilium rubium and Augergillus ferreus [32]. Furthermore, it was also established that ligands had an antibacterial effect at 100 ppm concentration and that they had an antifungacide effect [33-34].

The effect of different metal complexes (Co, Zn, Cu and Ni) of $H_2L'$ and HL on Spore germination and colonies diameter is seen in Tables 1,2,3 and 4. Spore germination was not observed at 0.6, 1.2 and 2.4 μg/100 mL doses of $H_2L'$ and HL but a decrease occurred in the diameter of mycelle parallel to the increasing dose, with respect to control.

In C. albicans species, however, spore germination was not noticed at 0.6 and 1.2 μg/100 mL doses of $H_2L'$ and HL as well as in both Schiff bases. The reason why M. gipsium and M. conis have been affected from these Schiff bases nearly at the same proportions may have resulted from the fact that these two species are biologically of the same origin. In addition, we could not identify any difference between the effects of metal complexes of $H_2L'$ and HL in three species. It was reported that free ligands and their complexes are considerably active against Candida. Nevertheless in view of the antimicrobial activity of the molecule, metal complexes were found to be more active with respect to ligands.

In our study, it was determined that $H_2L'$ and HL were effective against M. canis and C. albicans and that the complexes such as Cu, Ni, Co and Zn increased this efficiency, but that this effect statistically was not significant.

## 4. Results and Discussion

In our study, ligand $H_2L'$ and its complexes such as Co, Zn, Cu and Ni are seen to show antifungistic effect on M.canis (Table 1), M. gipsium (Table 2), C. albicans (Table 3) and ligand HL and complexes such an Ni and Cu on M. canis (Table 4), M. gipsium (Table 5) and C. albicans (Table 6). The effect of $H_2L'$ and HL on their complexes was determined as the decrease in mycelle diameter at 0.6, 1.2 and 2.4 μg/100 mL doses of M. canis and M. gipsium at the dose of 4.8 μg/100 mL, however, spore germination was not observed in both species. The effect of two ligands and their complexes in C. albicans was observed as a decrease in the number of colonies at doses of 0.6 and 1.2 μg/100 mL and as inhibiting of incubation at 2.4 μg/100 mL dose [32-38].

Pigmentation in M. canis and M. gipsium was observed with the effect of both ligand complexes. The inhibition effects of the ligand complexes were observed at 50 μg/mL in C. tropicals [39-40], at 355.87 μM in C. albicans [27], at 2.44 μg/mL in M. gypsium, at 78.12 μ/mL in C. albicans [24] and at 400 μ/mL in Aspergillus niger and Fusarium Sp [28] in the some literature. However, in the present study, the inhibition effects of the ligands and their complexes were seen at 4.8 μ/100 mL in M. gipsium and M. canis and at 2.4 μ/100 mL for Candida albicans. These results show that the ligands and their complexes are more effective compared to those used in the literature.

**Table 1** The Effect of Schiff Base Complexes on M. canis (X: Mycelle Diameter)*

| Compounds/Doses | 0.0 μg/100 mL (X ± SD) (Control) | 0.6 μg/100 mL (X ± SD) | 1.2 μg/100 mL (X ± SD) | 2.4 μg/100 mL (X ± SD) | 4.8 μg/100 mL (X ± SD) |
|---|---|---|---|---|---|
| $H_2L'$ | $2.50 \pm 0.35^{a}_{x}$ | $2.46 \pm 0.35^{a}_{x}$ | $1.40 \pm 0.10^{a}_{y}$ | $0.70 \pm 0.10^{c}_{z}$ | – |
| $CoL'$ | $2.50 \pm 0.35^{a}_{x}$ | $2.46 \pm 0.35^{a}_{x}$ | $1.23 \pm 0.15^{a}_{x}$ | $0.43 \pm 0.15^{a}_{z}$ | – |
| $ZnL'$ | $2.50 \pm 0.35^{a}_{x}$ | $2.46 \pm 0.35^{a}_{x}$ | $1.03 \pm 0.05^{b}_{y}$ | $0.53 \pm 0.06^{ba}_{z}$ | – |
| $CuL'$ | $2.50 \pm 0.35^{a}_{x}$ | $2.46 \pm 0.35^{a}_{x}$ | $1.40 \pm 0.17^{a}$ | $0.70 \pm 0.10^{c}$ | – |
| $NiL'$ | $2.50 \pm 0.35^{a}_{x}$ | $2.4 \pm 0.35^{a}_{x}$ | $1.53 \pm 0.15^{a}_{y}$ | $0.60 \pm 0.10^{c}_{z}$ | – |

*$^{a,b,c}$comporation column, $^{x,y,z}$comporation line

**Table 2** The Effect of Schiff Base Complexes on M. gipsium (X: Mycelle Diameter)*

| Compounds/Doses | 0.0 µg/100 mL (X ± SD) (Control) | 0.6 µg/100 mL (X ± SD) | 1.2 µg/100 mL (X ± SD) | 2.4 µg/100 mL (X ± SD) | 4.8 µg/100 mL (X ± SD) |
|---|---|---|---|---|---|
| $H_2L'$ | $3.20 \pm 0.45^{a}_{x}$ | $3.10 \pm 0.45^{a}_{x}$ | $2.10 \pm 0.14^{b}_{y}$ | $1.20 \pm 0.01^{c}_{z}$ | – |
| CoL′ | $3.20 \pm 0.45^{a}_{x}$ | $3.10 \pm 0.45^{a}_{x}$ | $1.50 \pm 0.14^{a}_{y}$ | $0.70 \pm 0.04^{a}_{z}$ | – |
| ZnL′ | $3.20 \pm 0.45^{a}_{x}$ | $3.10 \pm 0.45^{a}_{x}$ | $1.60 \pm 0.13^{a}_{y}$ | $1.03 \pm 0.04^{b}_{z}$ | – |
| CuL′ | $3.20 \pm 0.45^{a}_{x}$ | $3.10 \pm 0.45^{a}_{x}$ | $2.21 \pm 0.14^{b}_{y}$ | $1.02 \pm 0.04^{b}_{z}$ | – |
| NiL′ | $3.20 \pm 0.45^{a}_{x}$ | $3.10 \pm 0.45^{a}_{x}$ | $2.20 \pm 0.05^{b}_{y}$ | $1.03 \pm 0.01^{b}_{z}$ | – |

*$^{a,b,c}$comporation column, $^{x,y,z}$comporation line

**Table 3** The Effect of Schiff Base Complexes on M. canis (X: Mycelle Diameter)*

| Compounds/Doses | 0.0 µg/100 mL (X ± SD) (Control) | 0.6 µg/100 mL (X ± SD) | 1.2 µg/100 mL (X ± SD) | 2.4 µg/100 mL (X ± SD) | 4.8 µg/100 mL (X ± SD) |
|---|---|---|---|---|---|
| HL | $3.30 \pm 0.30^{a}_{x}$ | $2.00 \pm 0.10^{a}_{y}$ | $1.40 \pm 0.20^{a}_{z}$ | $0.70 \pm 0.10^{a}_{w}$ | – |
| $CuL_2$ | $3.30 \pm 0.30^{a}_{x}$ | $2.00 \pm 0.10^{a}_{y}$ | $1.30 \pm 0.10^{a}_{y}$ | $0.60 \pm 0.10^{a}_{w}$ | – |
| $NiL_2$ | $3.30 \pm 0.30^{a}_{x}$ | $1.90 \pm 0.20^{a}_{y}$ | $1.40 \pm 0.10^{a}_{y}$ | $0.70 \pm 0.10^{a}_{w}$ | – |

*$^{a,b,c}$comporation column, $^{x,y,z}$comporation line

**Table 4** The Effect of Schiff Base Complexes on M. gipsium (X: Mycelle Diameter)*

| Compounds/Doses | 0.0 µg/100 mL (X ± SD) (Control) | 0.6 µg/100 mL (X ± SD) | 1.2 µg/100 mL (X ± SD) | 2.4 µg/100 mL (X ± SD) | 4.8 µg/100 mL (X ± SD) |
|---|---|---|---|---|---|
| HL | $4.20 \pm 0.30^{a}_{x}$ | $2.10 \pm 0.10^{b}_{y}$ | $2.00 \pm 0.10^{b}_{z}$ | $1.20 \pm 0.20^{b}_{w}$ | – |
| $CuL_2$ | $4.20 \pm 0.60^{a}_{x}$ | $3.00 \pm 0.30^{a}_{y}$ | $2.6 \pm 0.20^{a}_{z}$ | $0.80 \pm 0.10^{b}_{w}$ | – |
| $NiL_2$ | $4.20 \pm 0.40^{a}_{x}$ | $3.00 \pm 0.20^{a}_{y}$ | $2.50 \pm 0.10^{a}_{z}$ | $1.30 \pm 0.10^{a}_{w}$ | – |

*$^{a,b,c}$comporation column, $^{x,y,z}$comporation line

**Table 5** The Effect of Schiff Base Complexes on *Candida albicans* (X: Mycelle Diameter)*

| Compounds/Doses | 0.0 (Average colony number%) (Control) | 0.6 (Average colony number%) | 1.2 (Average colony number%) | 2.4 (Average colony number%) |
|---|---|---|---|---|
| HL | 100 | 50 | 30 | – |
| $CuL_2$ | 100 | 50 | 30 | – |
| $NiL_2$ | 100 | 50 | 30 | – |

**Table 6** The Effect of Schiff Base Complexes on Candida albicans (X: Mycelle Diameter)*

| Compounds/Doses | 0.0 (Average colony number%) (Control) | 0.6 (Average colony number%) | 1.2 (Average colony number%) | 2.4 (Average colony number%) |
|---|---|---|---|---|
| $H_2L'$ | 100 | 50 | 70 | – |
| CoL′ | 100 | 50 | 70 | – |
| ZnL′ | 100 | 50 | 70 | – |
| CuL′ | 100 | 50 | 70 | – |
| NiL′ | 100 | 50 | 70 | – |

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