COBALT(II) AND NICKEL(II) COMPLEXES OF 2-(ARYLMETHYLENEACETYL)BENZIMIDAZOLE: SYNTHESES, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY

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Abstract

A series of Cobalt(II) and Nickel(II) complexes with 2-(Arylmethyleneacetyl)-benzimidazole (L_1-L_4) have been synthesized. These complexes were characterized using various physico-chemical techniques such as elemental analyses, UV-Vis, IR, thermal analyses and X-ray diffraction.

Also the complexes of Co(II) and Ni(II) with 2-(Arylmethyleneacetyl)benzimidazole in solution were studied by spectrophotometric methods which used for the determination of formation constants and the stioichiometries. The stoichiometry of the complexes is established as 1:2 (M : L) by Jobs and molar ratio methods. The composition and stability constants of the complexes were determined. The antibacterial activity of these complexes against Gram positive and Gram negative has also been tested.

Keywords: Cobalt(II) and Nickel(II) complexes; UV–Vis spectroscopy; thermal analyses; X-ray diffraction.

Introduction

Benzimidazole and its derivatives have interesting and useful biological properties. Benzimidazole as its 5,6-dimethyl derivative is present in vitamin B12 and related biomolecules and benzimidazole derivatives have found wide uses as antihelmintic agents for both human and veterinary purposes[(1)].

The chemistry and pharmacology of benzimidazoles have been of great interest to medicinal chemistry because its derivatives possessed various biological activities such as antioxidant, antimicrobial, antihelmintic, anticancer, antihypertensive, antineoplastic, anti-inflammatory, analgesic, antiprotozoal and anti-hepatitis B virus activity[(2)].

From the above literature the complexes of benzimidazoles have attracted considerable attention in recent years. Complex compounds of transition metal ions with benzimidazole and substituted compounds of these ligands have been studied extensively [(3-7)]. Benzimidazoles are also used extensively in industrial processes as

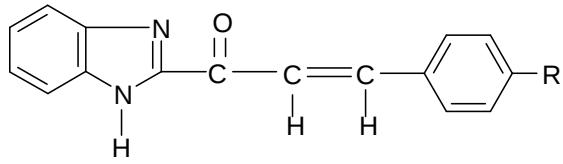
corrosion inhibitors for metal and alloy surfaces particularly of copper [8] and ion exchangers [9].

Isolation, Characterization and antimicrobial activities of different metal complexes wiith benzimidazole derivatives [10-13], as well as antimicrobial activity of cobalt(II), nickel(II), copper(II), zinc(II) and silver(I) complexes are studied with 2-aminobenzimidazole [14].

This paper describes the preparation of new Co(II) and Ni(II) complexes of 2-(Arylmethyleneacetyl)benzimidazole derivatives and their characterization by elemental analyses, conductance measurement, UV-Visible, IR, thermal analyses and X-ray diffraction. Antimicrobial and antifungal activities of the complexes were evaluated against a variety of bacteria such as Bacillus cereus, Staphylococcus aureus, Micrococcus luteus, Escherichia coli, Pseudomonas aeruginosa and serratia marcescens, and also against variety of fungi such as Candida albicans, Geotrichum candidum, Fusarium oxysporum, Aspergillus flavus, Scopulariopsis brevicaulis and Trichophyton rubrum.

Experimental

All the chemicals were AR grade; the ligands 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4) were prepared by procedure of Zeinab [15]. All solutions were prepared with doubly distilled water. The solutions were diluted as necessary to prepare standard working solution.



Where R = H (L_1), p-Cl (L_2), p- NO_2 (L_3), p-$N(CH_3)_2$ (L_4)

Fig. 1. Structure of the Ligand 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4).

Preparation of the solid complexes

The complexes were prepared in stoichiometric 1:2 (metal ion : ligand). A solution of Co(II) or Ni(II) chloride (0.01 mole dissolved in 25 ml ethanol) was added to a hot ethanolic solution of the ligands (L_1-L_4) (0.02 mole in 25 ml ethanol).

The mixture was reflux for about 4 hours, the precipitate was filtered, washed with ethanol several times and dried over P_4O_{10}.

Physical measurement and analyses

Electronic spectra of solutions of the complexes in DMF were recorded on a Perkin – elmer lambada 3B Spectrophotometer

The IR spectra were recorded on a shimadzu IR 470 (4000-400) spectrophotometer using KBr discs.

TGA, DTA measurements were carried out with a shimadzu thermal analyses 50, at heating rate of 20 ºC.

Conductivity was measured in solutions of the complexes in DMF (10^{-3} M) using Hana instrument conductivity bridge (Model) HI 8819 at 25 ºC.

Microanalyses for C, H, N were carried out at the Microanalytical center , Assiut university.

X-ray was carried out with Philips X-ray PW 1710 diffractometer using Ni-filtered CuKα radiation.

Result and discussion:

The complex formation reaction of the ligands (L_1-L_4) with Co(II) and Ni(II) halides can be represented by the following equations:

$MX_2 + L \rightarrow [MLX_2]$

$MX_2 + 2\ L \rightarrow [ML_2X_2]$

Where M= Co(II) and Ni(II)

X= Cl

They are soluble in DMF, DMSO, Acetone and slightly soluble in Ethanol, methanol.

The complexes were characterized by chemical analyses, IR and visible spectra, thermal analyses and conductivity measurements.

The molar conductivity values in 1×10^{-3} M DMF solution of the solid complexes measured for 1:2 (M:L) solution are quite law, which indicates the non-electrolytic nature of these complexes [16].

Infrared spectra

The IR spectra of the free ligands and its metal complexes were given in Table (1). The IR spectrum of the free ligand display a stretching band at 3150-3450 cm^{-1} attributed to vNH [15]. Also the free ligands spectrum exhibits a strong band at 1600-1670 cm^{-1} is due to C=O stretching frequency and is shifted to higher or lower frequencies in the metal complexes. Also other absorption band in the IR spectra of the free ligands at 1540-1595 cm^{-1} attributed to the C=N group and band is shifted to higher or lower frequencies in the meta complexes [17].

The IR spectrum also exhibits stretching band of the free ligand at 1475-1540 cm^{-1} attributed to the C=C of skeletal benzonoid moieties of these ligand, but these band in the complexes are slightly shifted compared to the free ligands.

Table 1. Characteristic infrared bands and λ_{max} electronic absorption bands of the 2 (Arylmethyleneacetyl)benzimidazole (L_1-L_4) and its complexes.

Compound	vNH	C=O	C=N	C=C	λ_{max} nm
L_1	3250	1650	1580	1510	330
$[Co(L_1)_2Cl_2]2H_2O$	3450	1625	1540	1505	352
$[Ni(L_1)_2Cl_2]4H_2O$	3400	1627	1550	1475	340
L_2	3420	1662	1595	1485	332
$[Co(L_2)_2Cl_2]$	3180	1635	1550	1490	338
$[Ni(L_2)_2Cl_2]2H_2O$	3410	1638	1595	1485	335
L_3	3300	1658	1585	1508	340
$[Co(L_3)_2Cl_2]2H_2O$	3420	1635	1595	1515	596
$[Ni(L_3)_2Cl_2]4H_2O$	3400	1670	1595	1518	560
L_4	3450	1658	1595	1540	436
$[Co(L_4)_2Cl_2]3H_2O$	3150	1600	1595	1520	440
$[Ni(L_4)_2Cl_2]4H_2O$	3400	1625	1590 1580	1525 1520	456

X-ray powder diffraction

X-ray diifraction patterns of the complexes of Co(II) and Ni(II) with 2-(Arylacetyl)benzimidazole were obtained. They indicate that the Ni(II) complexes with L_1 and L_2 are crystalline (Fig. 2), also the Co(II) complex with L_3 is crystalline, while the Co(II) complex with L_2 is amorphous (Fig. 3). This indicates that the polymeric structure of Ni(II) complexes with L_1, L_2 and Co(II) complex with L_3 are more convenient, while the Co(II) complex with L_2 has a monomeric structure.

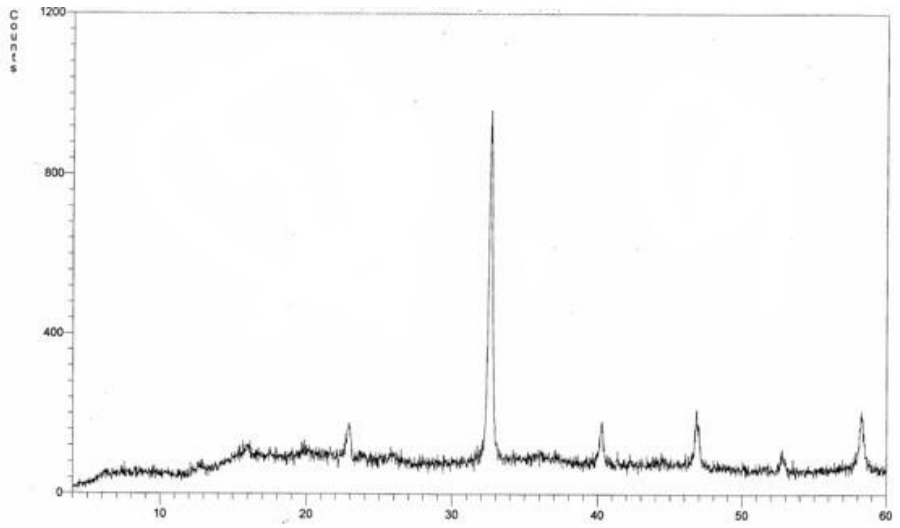


Fig. 2. X-ray powder diffraction pattern of $[Ni(L_1)_2Cl_2]4H_2O$ complex.

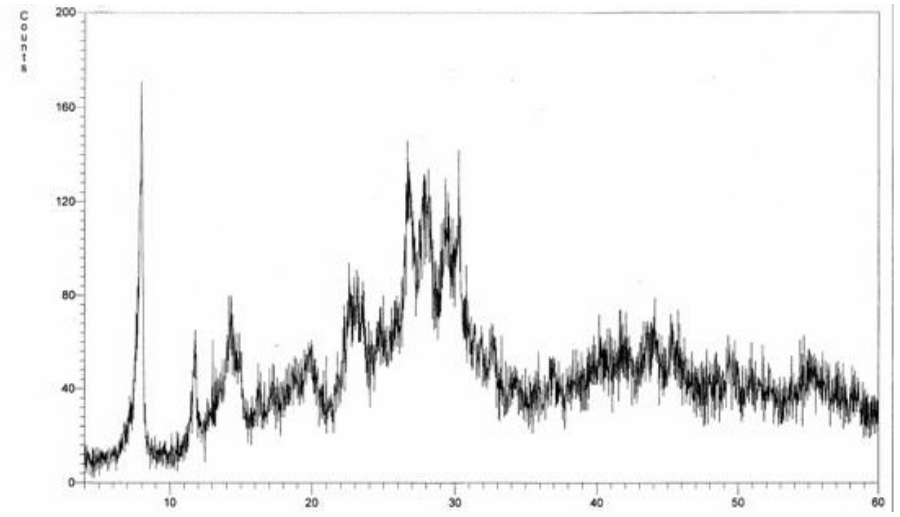


Fig. 3. X-ray powder diffraction pattern of [Co $(L_2)_2Cl_2$] complex.

Microanalysis :

The elemental analyses data (Table 2) of the isolated complexes of Co(II) and Ni(II) with 2-(Arylacetyl)benzimidazole (L_1 - L_4) are in good agreement with the stoichiometry of the metal complexes. These were ascertained by the continuous variation and molar ratio methods. The results reveal that the stoichiometry is 1:2 (M-L).

Table 2. Elemental analysis result of the Co(II) and Ni(II) complexes with 2-(Arylmethyleneacetyl)benzimidazole derivatives.

Complex	Formula	%Found (Calc.)		
		%C	%H	%N
$2H_2O$[Co $(L_1)_2Cl_2$]	$C_{32}H_{28}Cl_2CoN_4O_4$	57.95 (58.00)	4.21 (4.23)	8.95 (8.46)
$4H_2O$[Ni $(L_1)_2Cl_2$]	$C_{32}H_{30}Cl_2NiN_4O_6$	55.5 (55.00)	4.80 (4.58)	8.80 (8.02)
[Co $(L_2)_2Cl_2$]	$C_{32}H_{22}Cl_4CoN_4O_2$	55.92 (55.09)	3.05 (3.44)	7.65 (8.03)
$2H_2O$[Ni $(L_2)_2Cl_2$]	$C_{32}H_{26}Cl_4NiN_4O_4$	52.88 (52.38)	3.75 (3.82)	8.05 (7.64)
$2H_2O$[Co $(L_3)_2Cl_2$]	$C_{32}H_{26}Cl_2CoN_6O_8$	50.88 (50.92)	3.2 (3.71)	11.14 11.14) (
$4H_2O$[Ni $(L_3)_2Cl_2$]	$C_{32}H_{30}Cl_2NiN_6O_{10}$	49.15 (48.60)	3.52 ((4.05	10.64 10.63) (
$3H_2O$[Co $(L_4)_2Cl_2$]	$C_{36}H_{40}Cl_2CoN_6O_5$	56.80 (56.25)	5.45 (5.46)	11.32 10.93) (
$4H_2O$[Ni $(L_4)_2Cl_2$]	$C_{36}H_{42}Cl_2NiN_6O_6$	55.30 (55.10)	5.25 (5.61)	10.90 10.71) (

Thermal Analyses

The TGA thermogram characteristic of the [Ni$(L_4)_2Cl_2$]$4H_2O$ complexe (Fig. 4) have three decomposition steps, The first step within the temperature range from 50 to 280 ºC corresponds to the loss two hydrated, two coordinated water molecules and two HCl molecules (18.2%). The second step at the 280- 440 ºC range was recorded and corresponds to the loss of PhCH and $N(CH_3)_2$ molecules (15%). The third step of decomposition occures at 440 – 700 ºC can be attributed to complete decomposition of metal chelate (85%) leaving the NiO as a final solid black product.

The TG thermogram of the $[Co(L_2)_2Cl_2]$ complex (Fig. 5) displays two steps, the first step in the range 200-300 ºC corresponding to the loss of four HCl molecules (20%). The second step in the temperature range 300-800 ºC the mass loss reaches to 87% attributed to complete decomposition of parent molecule leaving cobalt oxide (CoO) as stable end product.

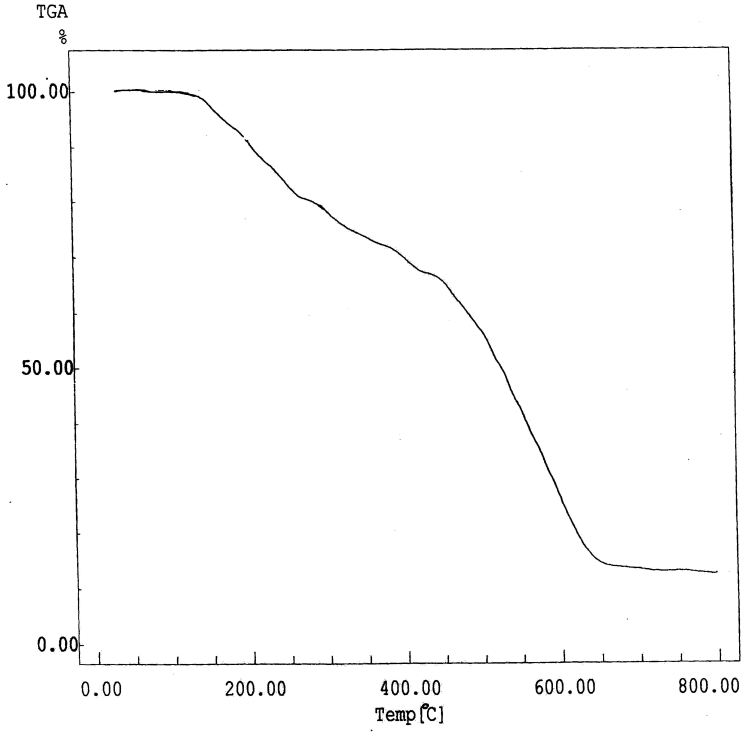


Fig. 4. TG diagram of $[Ni(L_4)_2Cl_2]4H_2O$ complex.

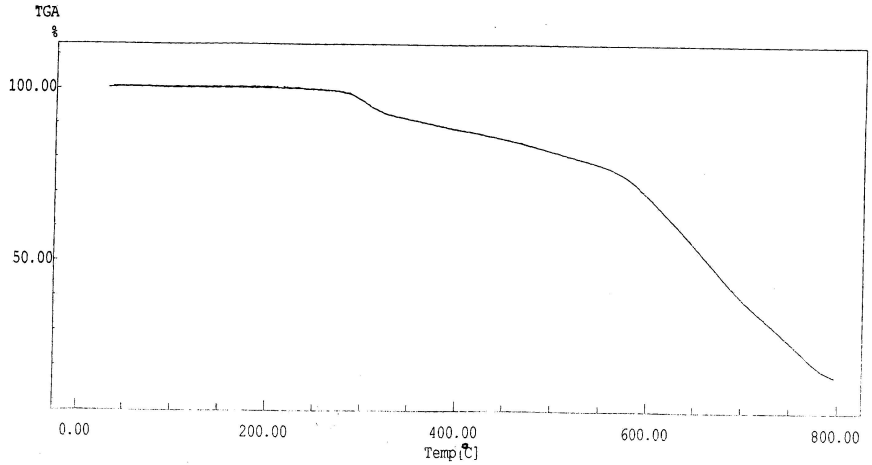


Fig. 5. TG diagram of $[Co(L_2)_2Cl_2]$ complex.

Electronic spectra

The absorption spectra of the 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4) in ethanol exhibit a main absorption at 330 nm , 332 nm, 340 nm and 436 nm for L_1-L_4 respectively. These bands undergo a reasonable shift to longer wavelengths on addition of metal ion solution, which is an evidence for the formation of the coordination compounds. The maximum absorption of bands of the Co(II) and Ni(II) complexes with 2-(Arylacetyl)benzimidazole (L_1-L_4) are recorded in Table (1).

The difference in λ_{max} absorption bands between the free ligand (L_3) and its Co(II) and Ni(II) complexes are being at 340, 596 and 560 nm respectively, which Indicating that L_3 can be readily utilized as a sensitive reagent for microanalytical determination of metals.

Determination of the stoichiometry of the complexes :

The stoichiometry of the different Co(II) and Ni(II) complexes with 2-(Arylmethyleneacetyl)benzimidazole (L_1-L_4) in solution was determined by using the two spectrophotometric methods

i- Molar ratio method [18] ii- Jobs continuous variation method [19]

The results from the two methods indicate that the stoichiometry of the different complexes formed in solution from the reaction of each of the ligand (L_1-L_4) with Co(II) and Ni(II) metal ions are 1:2 (metal to ligand) complex (Fig. 6).

From Fig. 6, we can show the formation of 1:1 and 1:2 (Metal to ligand) this return to form 1:1 at first and then form 1:2 by increasing the concentration of ligand.

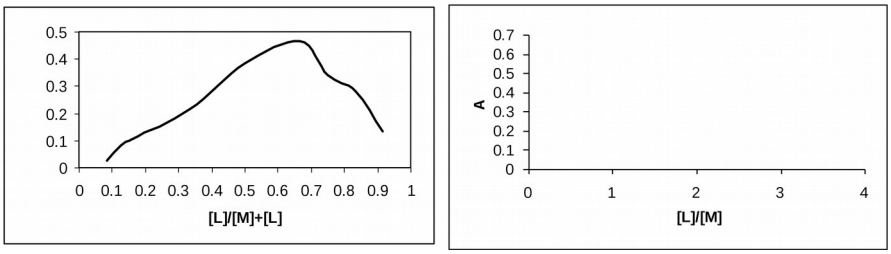


Fig.6. Molar ratio and continuous variation curve for Co (II) L_1 complex.

Evaluation of the apparent Formation Constants of the Complexes:

The curvature around the inflection point of the molar ratio plot as well as the continuous variation plot have been used to establish the stoichiometry of the metal complexes in solution , was utilized to calculate the formation constant (K_f) of each complex. Two mathematical relations were used to evaluate K_f [20], the first is for 1:1 complex (MX) and the second is for 1:2 complex (MX_2).

$$K_f = \frac{A/Am}{(1 - A/Am)^2 C} \quad \text{.....(1)}$$

$$K_f = \frac{A/Am}{4C^2(1 - A/Am)^3} \quad \text{.....(2)}$$

Results of the formation constant determination for the complexes:

The K_f values obtained for the metal complexes under investigation, by applying the above relation (2) to the data of the continuous variation and molar ratio methods. The results in Table (3) reveal the following features:

(I) The order of the stability of the 1:2 complexes of the same ligand runs according to the following sequence :

Ni (II) > CO (II)

This is in agreement with the general order of stability of the complexes of these

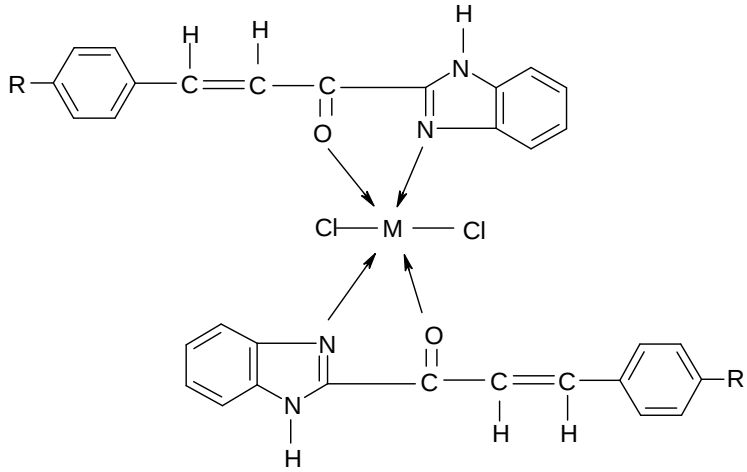
metal ions which was established before by Grinberg and Yatsimirki [21] and by Irving and Williams [22].

(II) The complex stability of the same metal with the different ligands used decreases according to the sequence :

L_4 (R= p-N$(CH_3)_2$) > L_1 (R= H) > L_3 (R= p-NO_2) >L_2(R= p-Cl)

This is in agreement with decreasing electron releasing character of the substituent in the same direction which results in a decrease in the basicity of the azomethine nitrogen of the ligand and consequently the tendency toward complex formation is expected to decrease.

Based on the elemental analyses and various physico-chemical studies, the structure shown in Fig. 7 is tentatively proposed for the complexes.



Where M = CO (II), Ni (II) and R = L_1 (H), L_2(p-Cl), L_3 (p-NO_2), L_4 (p-N$(CH_3)_2$)

Fig. 7. Proposed structure of the complexes.

Table. 3. Apparent formation constant values (K_f) of the different Co(II) and Ni(II) complexes with 2-(Arylmethyleneacetyl)benzimidazole derivatives.

Complex	Molar Ratio	Continuous Variation	Mean
Co- L_1	4.54×10^{10}	7.1×10^{10}	5.82×10^{10}
Co- L_2	3.23×10^{10}	6.54×10^{10}	4.885×10^{10}
Co- L_3	4.13×10^{10}	6.81×10^{10}	5.47×10^{10}
Co- L_4	5.12×10^{10}	7.3×10^{10}	6.21×10^{10}
Ni – L_1	4.82×10^{10}	8.41×10^{10}	6.615×10^{10}
Ni – L_2	4.16×10^{10}	6.87×10^{10}	5.515×10^{10}
Ni – L_3	4.71×10^{10}	7.19×10^{10}	5.95×10^{10}

Ni – L_4	5.2×10^{10}	8.75×10^{10}	6.975×10^{10}

Antimicrobial activity

The complexes ($[Ni(L_3)_2Cl_2]4H_2O$, $[Ni(L_1)_2Cl_2]4H_2O$, $[Co(L_2)_2Cl_2]$, $[Co(L_4)_2Cl_2]3H_2O$) were tested against a variety of bacteria such Bacillus cereus, Staphylococcus aureus, Micrococcus luteus, Escherichia coli, Pseudomonas aeruginosa and serratia marcescens. The complex $[Ni(L_3)_2Cl_2]4H_2O$ was highly active against Micrococcus luteus and Pseudomonas aeruginosa. These results are shown in Table 4.

Antifungal Activity

The experimental data (Table 5) indicate that the complexes which tested show a varying degree of activity against fungi such as Candida albicans, Geotrichum candidum, Fusarium oxysporum, Aspergillus flavus, Scopulariopsis brevicaulis and Trichophyton rubrum. Also The complex $[Ni(L_3)_2Cl_2]4H_2O$ was highly active against Candida albicans and Trichophyton rubrum.

Table. 4. Antimicrobial activity of some Co(II) and Ni(II) complexes with 2-(Arylmethyleneacetyl)benzimidazole derivatives.

Complex	Organisms					
	Gram-positive bacteria			Gram-negative bacteria		
	Staphylococcus aureus	Bacillus cereus	Micrococcus luteus	Serratia marcescens	Pseudomonas aeruginosa	Escherichia coli
$[Ni(L_3)_2Cl_2]4H_2O$	17	24	26	16	17	18
$[Ni(L_1)_2Cl_2]4H_2O$	14	10	0	14	0	16
$[Co(L_2)_2Cl_2]$	12	12	10	15	0	14
$[Co(L_4)_2Cl_2]3H_2O$	12	12	12	18	0	12
Control*	22	34	18	22	12	26

Control* = Choramphenicol as antibacterial standard.

Table. 5. Antifungal activity of some Co(II) and Ni(II) complexes with 2-(Arylmethyleneacetyl)benzimidazole derivatives.

Complex	Candida albicans	Geotrichum candidum	Fusarium oxysporum	Aspergillus flavus	Scopulariopsis brevicaulis	Trichophyton rubrum
$[Ni(L_3)_2Cl_2]4H_2O$	18	17	8	12	16	26
$[Ni(L_1)_2Cl_2]4H_2O$	8	13	12	0	0	18

0 $[Co(L_2)_2Cl_2]$	0	14	10	0	0	12
$[Co(L_4)_2Cl_2]3H_2O$	12	16	8	0	0	16
Control*	18	21	16	24	24	38

Control* = Clotrimazole as antifungal standard.

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الملخص العربى

تحضير وتوصيف ودراسات بيولوجيه على متراكبات أيونات الكوبلت الثنائى والنيكل الثنائى مع مشتقات 2-أريل مثيلين اسيتيل بنزاميدازول.

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تم فى هذا البحث تحضير ثمانية متركبات من الكوبلت الثنائى والنيكل الثنائى مع اربع مشتقات 2-اريل مثيلين اسيتيل بنزاميدازول.
تمت دراسة التحليل العنصرى والتكسير الحرارى ودراسة أطياف الأشعه تحت الحمراء والأشعه المرئيه وأشعة أكس للمشتقات ومتراكباتها لتحديد صيغ التراكيب الجزيئيه وطريقة الترابط بين الفلزات وهذه المشتقات.
أيضا تم دراسةهذه المتراكبات فى المحاليل بالطرق الطيفيه مثل طريق التغير المستمر والنسبه المولاريه لدراسة نسبه تكون المتراكب وتبين من الدراسه ان نسبة تكون المتراكبات 1:2 (الليجند : الفلز) وتم حساب ثوابت التكوين لهذه المتراكبات. أثبتت الدراسات البيولوجيه على المتراكبات المحضره ان لها تأثير حيوى قوى مضاد لنمو العديد من أنواع البكتريا والفيروسات.