



Synthesis and evaluation of the biological activity for some new metal ion complexes with ligand (E)-3-(((2-amino-4-methylphenyl)imino)methyl)-4H-chromen-4-one

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Abstract

Complexes of Co(II), Ni(II), Cu(II) Zn(II), and Cd (II) with the ligand 3-(((2-amino-4-methylphenyl)imino)methyl)-4H-chromen-4-one derived 3-formyl chromone with 4-methyl-O-phenylenediamine were synthesized and characterized by elemental analysis, FTIR, electronic spectra, magnetic moment and molar conductance. The prepared complexes have the general formula $[M(C_{17}H_{14}N_2O_2)_2]Cl_2$, where M represents the ions of metals elements such as Co(II), Ni(II), Cu(II) and Zn(II) except complex of cadmium it has the formulae $[Cd(C_{17}H_{14}N_2O_2)Cl]Cl$. The results obtained showed that the proposed geometric shape of the complexes is octahedral around the metal center except for the cadmium complex exhibit tetrahedral geometry. *E.coli* and *S. aureus* bacteria used to estimate the biological activities for the complexes.

Keyword: 3-formylchromone, new complexes, biological activities, *E.coli*, *S. aureus*.

Introduction

Heterocyclic compounds contain one or more hetero atoms in their structure [1]. The compounds have wide applications, as they are mostly used as medicines, veterinary products and agricultural products [2]. They can also be used in other applications such as antioxidants, disinfectants, dyestuffs and corrosion inhibitors [3]. It is also used to synthesize other organic compounds [4]. In nature, heterocyclic compounds are included in the structure of many



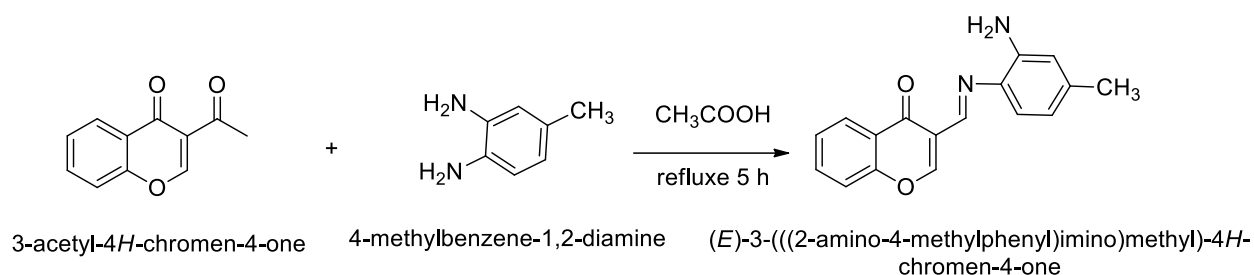
important molecules of life such as DNA, enzyme and vitamins such as vitamin C, vitamin B1 and biotin (vitamin H) [5-6]. Heterocyclic compounds are of biological importance as they are used as anti-inflammatory, antifungal, antiviral, antibacterial, enzyme inhibitor, human immunodeficiency, antidiabetic, and anticancer activity [7]. The compounds resulting from the fusion of a benzene ring with a pyran ring together to give a compound called benzopyrans. It is of two types depending on the position of the double ligament of the pyran ring the first 1-benzopyrans and the second 2-benzopyrans [8]. Chromone is a benzopyran containing a substituted keto group on the pyran ring [9]. Schiff bases for aromatic aldehydes are more stable than those of aliphatic aldehydes which are comparatively unstable and are easily polymerizable. The existence of an electron lone pair on the atom of nitrogen for the azomethine is of large chemical and biological prominence. Schiff bases over the years have played an animated role as chelating ligands in coordination chemistry, because of their immutability with different oxidation and reduction conditions difference, as well as the imine ligands are considered the borderline between soft and hard Lewis bases[10]. Complexes of transition elements with Schiff bases used as ligands have wide applications such as medicinal and industrial chemistry, biological and pharmaceutical studies, catalysis properties, bioinorganic modeling studies, polymer chemistry and material science [11]. Therefore, we objective to synthesize of 3-(((2-amino-4-methylphenyl)imino)methyl)-4H-chromen-4-one and its complexes. We think that our compounds will display good antibacterial activity.

Experimental

Instruments and chemical materials

The chemicals (3-formyl chromone, 4-methyl-O-phenylenediamine, ethanol, glacial acetic acid, and metal salt were equipped from a number of companies like (Fluka, ACS, Macklin, Scharlu, BDH, SCRC, CDH, and Aldrich). The instrumentations used in this study were FT-IR spectroscopy (PERKIN ELMER SPEACTRUM-65/Germany), UV-Vis double beam spectrophotometer (JASCO V-650, Japan). The elemental analysis (C.H.N) (EM-017 mth instrument), atomic absorption (Shimadzu Atomic Absorption 680 Flam Spectrophotometer), NMR-spectrum (Bruker 400 MHz spectrometer), and magnetic magnetic sensitivity (Johnson Matthey catalytic systems Division Engineered products)

Preparation of ligand (E)-3-((2-amino-4-methylphenyl)imino)methyl)-4H-chromen-4-one (8.61mmol) of 3-formylchromone was dissolved in 50ml ethanol and added to (8.61mmol) of 4-Methyl-O-phenylenediamine which dissolved in 50 ml of ethanol. After that 1 ml of glacial acetic acid was added. The mixture was refluxed in a water bath at 80°C. The completion of the reaction was achieved after 5 h, and leaving the mixture for stirring at room temperature overnight; forming a yellow precipitate followed by filtration and washing using ethanol. The scheme of synthesis is given below Scheme (1)



Scheme 1: synthesis of ligand

Preparation of complexes

The complexes of $[\text{Co}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2] \text{Cl}_2$, $[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2] \text{Cl}_2$, $[\text{Cu}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2] \text{Cl}_2$, $[\text{Zn}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2] \text{Cl}_2$ were prepared by mixing a solution of ligand (2.2 mmol) in ethanol (30 ml) with a solution of metal chlorides such as $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 (1.1mmol) in ethanol (20 ml) [molar ratio(2:1, ligand: metal)]. Then added 5% of KOH (a few drops) to a mixture and leave to refluxed in a water bath with a degree of at a temperature of 78 ° C for two hours, then leave for 4 hours, filter and wash in sufficient quantity in ethanol. The same procedure was used to preparation of $[\text{Cd}(\text{C}_{17}\text{H}_{14}\text{N}_2 \text{O}_2)\text{Cl}]\text{Cl}$ complex except the molar ratio(1:1, ligand: metal)] by utilized (2.2mmol) from ligand with (2.2mmol) of ligand. Figure (1) shows the structure of complexes.

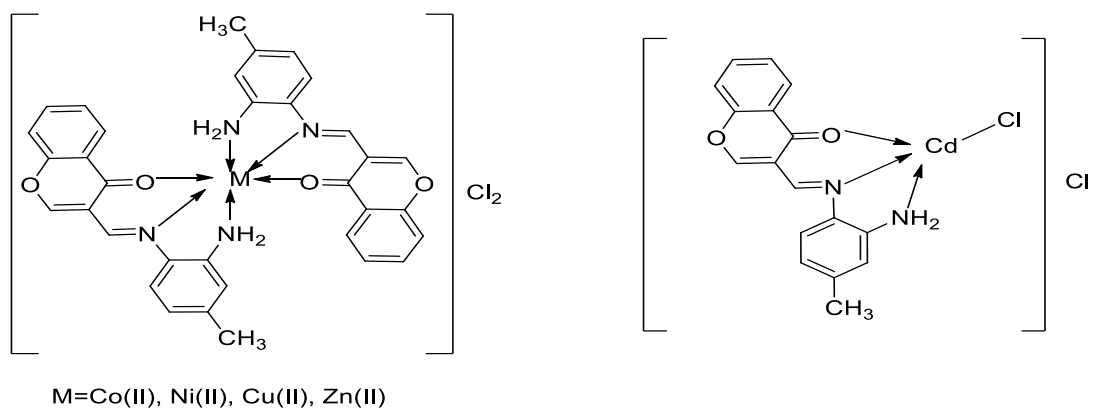


Figure 1: The structure $[M(C_{17}H_{14}O_2N_2)_2]Cl_2$ and $[Cd(C_{17}H_{14}O_2N_2)Cl]Cl$

Biological estimation of complexes

Staphylococcus aureus was grown on agar of blood, agar of mannitol salt, agar of methylene blue, and eosin, while *E. coli* isolates were grown on macCkonky agar. The preparation solution supplied by the company (biomerix) was utilized to calibrate the number of bacterial cells since it approximates 1.5×10^8 cells/ml. Muller Hinton Agar may be made by dissolving 38 grams of agar in 1L of distilled water, sterilizing it in an autoclave for 15 minutes at 121 C° and 15 pounds of pressure. Bacterial colonies were carried via a loop to make the suspended bacteria and charge them in tubes containing brain heart infusion broth. The tubes were incubated at 37 C° for (18-24 hours). The muller hinton agar-coated plates were then covered with the bacteria suspension and allowed to dry for a period of time. To drill holes in the culture medium, a sterilized cork borer was employed. 100ml of the complexes (concentration 100/150/200) was delivered to each hole individually using a micropipette. Following that, incubate the plate for 24 hours at 37 C° . As a positive control, sterilized dimethyl sulfoxide (DMSO) was used. The potency of every concentration was determined by measuring the inhibition zone diameter surrounding each hole.

Results and Discussion

Characterization of (E)-3-((2-amino-4-methylphenyl)imino)methyl)-4H-chromen-4-one
 $^1\text{H NMR}$ (DMSO- d_6 /TMS) δ (ppm) (Figure 1): 8.603 (s, 1H, $\text{CH}=\text{N}$), 7.592 (s, 1H, (O- $\text{CH}=\text{C}$), 7.588-6.936 (m, 7H, Ar-H), 6.929 (s, 2H, NH_2) 1.562 (s, 3H, CH_3). While the $^{13}\text{C NMR}$

(DMSO-*d*₆/TMS) δ (ppm) (Figure 2): 177.22 ($\underline{C=O}$), and 162.56 ($O-\underline{CH=C}$), 152.37($\underline{CH=N}$), 102($O-C=\underline{C}-C=N$), 156.70, 144.87, 138.21, 137.70, 137.12, 134.80, 131.26, 125.90, 122.56, 122.37, 115.55, 115.15 ($12\underline{C}$ atom of aromatic ring) and 21.3 ($Ar-\underline{CH}_3$). The characteristic FT-IR bands in (cm^{-1}) (Figure 3) and Table (1): 3274 and 3120 (νNH_2), 1640 ($\nu C=O$) and 1589 ($\nu HC=N$). Anal. Calc. (Found) for $C_{17}H_{14}O_2N_2$ (MWt 278.3): C =73.37 (72.81), H= 5.07(4.87), and N= 10.07 (9.22) [12-14].

FT-IR Spectra of complexes

The FT-IR spectra of each compound that was created when compared to the spectrum of the free ligand, Table (1) shows changes in the shape and location of the vibration for the $C=N$ group value, the vibration for the ($C=O$) carbonyl group and NH_2 . This indicates that the ligand coordinates with the metal ion through the atoms of (nitrogen an azomethine, oxygen of carbonyl and nitrogen of NH_2). In the spectra, new bands that imply M-O vibration occurred at (501-516) and M-N vibration at (405-450) [15-16].

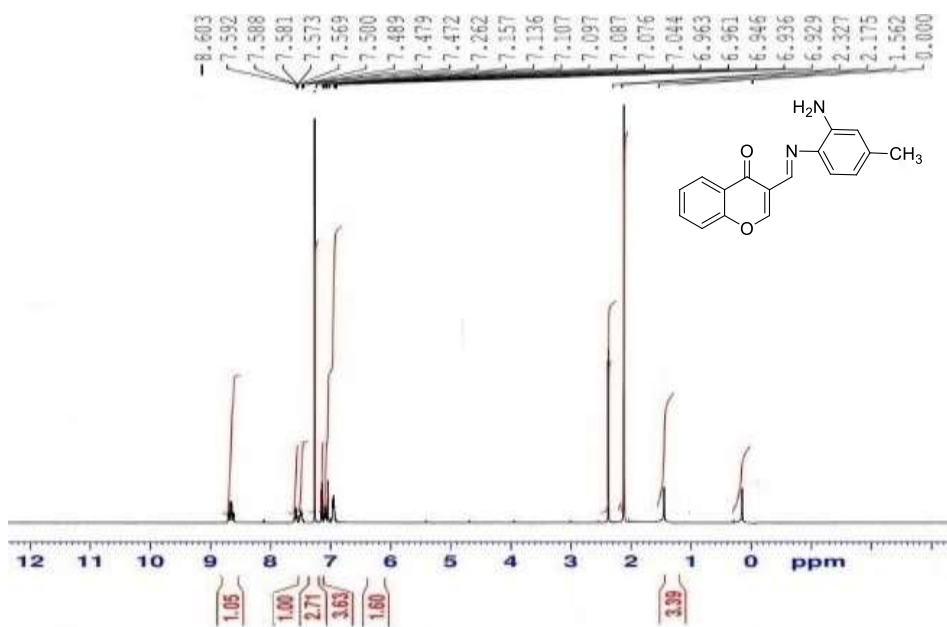


Figure 1: 1H NMR of ligand

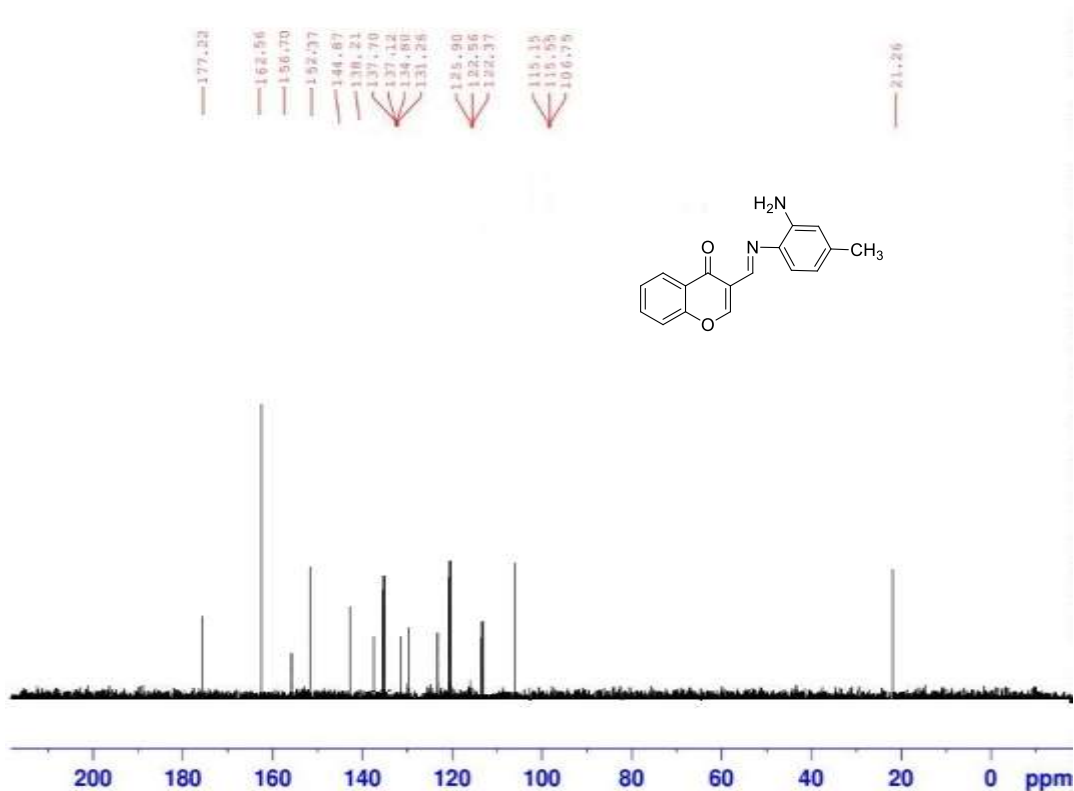


Figure 2: ^{13}C NMR of ligand

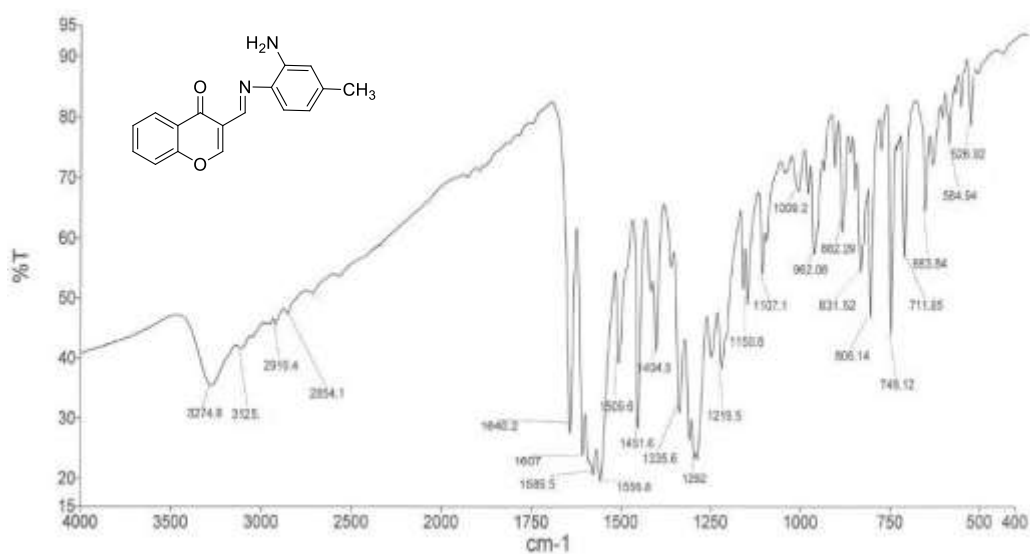


Figure 3: FT-IR of ligand



UV-Vis, magnetic properties and molar conductance

The UV-Vis spectrum was measured in DMSO. The spectrum of the ligand showed three absorption bands: appeared first peak in the UV region at (259 nm, 38610cm^{-1}) was assigned to transition ($\pi \rightarrow \pi^*$), while the second and third absorption bands appeared at (358 nm, 27932cm^{-1}) and (392 nm, 25510cm^{-1}) due to ($n \rightarrow \pi^*$). Electronic transitions with their assignments for ligand and complexes are summed up in Table (2).

The observed value of magnetic moment for cobalt(II), nickel(II), and copper(II) complexes display ($\mu_{\text{eff}}=3.89, 2.86, 1.74$) B.M respectively, that refer to paramagnetic characteristic (high spin) and octahedral geometry[17]. But the prepared Cd(II) and Zn(II) complexes were diamagnetic which was expectant for the d^{10} ion.

The conductivity of prepared complexes was measured at room temperature in dimethyl sulfoxide solvent, and the data obtained from that indicates that the complexes $[\text{M}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2]\text{Cl}_2$, $\text{M} = \text{Co(II), Ni(II), Cu(II) and Zn(II)}$ were ionic with (1 ion of the complex: 2 ions of chloride) ratio [18], except for the complex of cadmium $[\text{Cd}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)\text{Cl}]\text{Cl}$ was ionic with (1 ion of the complex: 1 ion of chloride) ratio [19]. Magnetic susceptibility and values of molar conductance of complexes were listed in Table(2).

Table 1: FT-IR spectrum of ligand and its complexes in cm^{-1} (stretching vibration)

Compound	NH ₂	C-H Alph.	C=O	C=N	M-O	M-N	Other Peak
$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$	3274 3125	2919	1640	1589	----	----	(1607) C=C chromone (1556, 1509, 1451) C=C aromatic
$[\text{Co}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2]\text{Cl}_2$	3282 3115	2924	1643	1580	501	405	(1607) C=C chromone (1559, 1508, 1452) C=C aromatic
$[\text{Ni}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2]\text{Cl}_2$	3282 3109	2972 2918	1646	1580	506	433	(1607) C=C chromone (1559, 1508, 1484) C=C aromatic
$[\text{Cu}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2]\text{Cl}_2$	3270 3131	2918	1648	1570	501	438	1607 C=C chromon (1553, 1508, 1455) C=C aromatic
$[\text{Zn}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2]\text{Cl}_2$	3276 3109	2918	1649	1577	507	438	(1607) C=C chromon 1559, 1505, 1481) C=C aromatic
$[\text{Cd}(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)\text{Cl}]\text{Cl}$	3270 3109	2918	1655	1580	516	450	(1607) C=C chromon (1559, 1508, 1455) C=C aromatic, (327) M-Cl



Table 2: Electronic spectrum, molar conductivity, and magnetic properties

Comp.	λ nm ($\bar{\nu}$ cm ⁻¹)	Transition	μ_{eff} BM	Conductivity in DMSO S.cm ² .mol ⁻¹	Suggested Geometry
C ₁₇ H ₁₄ O ₂ N ₂	259 (38610) 358 (27932) 392 (25510)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$	-----	-----	-----
[Co(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	261(38314) 349(28653) 404(24753) 520(19230) 677(14771) 740(13513)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T ${}^4T_{1g} \rightarrow {}^4T_{1g(p)}$ ${}^4T_{1g} \rightarrow {}^4A_{2g(F)}$ ${}^4T_{1g} \rightarrow {}^4T_{2g(F)}$	3.89	71	Octahedral
[Ni(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	254(39370) 351(28490) 394(25380) 483(20703) 688(14534) 774(12919)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^3A_{2g} \rightarrow {}^3T_{1g(p)}$ ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$	2.86	77	Octahedral
[Cu(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	268(37313) 361(27700) 397(25188) 402(24875) 410(24390) 680(14705)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n \rightarrow \pi^*$ ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ${}^2B_{1g} \rightarrow {}^2E_g$	1.74	73	Distorted octahedral environment (<i>Jahn-Teller effect</i>)
[Zn(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	263(38022) 361(27700) 389(25706)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T	0	79	Octahedral
[Cd(C ₁₇ H ₁₄ O ₂ N ₂)Cl]Cl	265(37735) 368(27173) 399(25062)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ C.T	0	57	Tetrahedral

Physical characteristics, elemental analysis, and atomic absorption for new complexes

The percentage for (carbon, hydrogen, nitrogen, and metal in all prepared complexes (calculated and discovered) were compatible with each other and were in agreement with the structure of the synthesized compounds. Analytical data and physical characteristics for all complexes were provided in Table (3).



Table 3: Physical characteristics, elemental analysis (C.H.N.) and atomic absorption (A.A.) data for compounds

Compounds	Color	m.p. °C	Yield %	M.Wt g.mol ⁻¹	Elemental analysis Found (Calc.)			M % Found (Calc.)
					C %	H %	N %	
C ₁₇ H ₁₄ O ₂ N ₂	Orang sovereign	242-244	90	278.3	72.98 (73.37)	4.96 (5.07)	9.92 (10.07)	---
[Co(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	Light orange	205-207	85	686.4	59.69 (59.49)	4.29 (4.11)	8.00 (8.16)	8.26 (8.59)
[Ni(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	Burnt Orange	228-230	90	686.2	59.71 (59.51)	3.98 (4.11)	8.36 (8.16)	8.66 (8.55)
[Cu(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	Brown	296-298	83	691.1	58.89 (59.09)	3.95 (4.08)	8.21 (8.11)	9.35 (9.20)
[Zn(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	yelow	248-250	82	692.9	59.10 (58.94)	4.10 (4.07)	8.39 (8.09)	9.66 (9.44)
[Cd(C ₁₇ H ₁₄ O ₂ N ₂)Cl]Cl	yelow	237-240	80	461.6	44.44 (44.23)	3.16 (3.06)	6.28 (6.07)	24.52 (24.35)

Antibacterial activity

Bacteria (*E.coli*, and *S. aureus*) were selected to be tested against [M(C₁₇H₁₄O₂N₂)₂]Cl₂ and [Cd(C₁₇H₁₄O₂N₂)Cl]Cl (Figure 4). The function of DMSO in the biological screening was clarified by separated studies adopted with the solutions of DMSO alone, which exhibited no activity towards any microbial strain. The results of antibacterial activity for [Cd(C₁₇H₁₄O₂N₂)Cl]Cl complex exhibited activity against two kinds of bacteria in all concentrations were used in this study at the time of exposure 24 h and [Zn(C₁₇H₁₄O₂N₂)₂]Cl₂ complex exhibited activity against *E.coli* in all concentrations while appear activity against *S.aureus* in concentrations [150 and 200 mg/ml] only. The complex [Co(C₁₇H₁₄O₂N₂)₂]Cl₂ do not show activity against *E. coli* bacteria but exhibited activity against *S.aureus*. in all concentrations, either [Cu(C₁₇H₁₄O₂N₂)₂]Cl₂ was not active against *E. coli* bacteria but exhibited activity against *S. aureus*. In concentrations [150 and 200 mg/ml] only. Also, the complex of [Ni(C₁₇H₁₄O₂N₂)₂]Cl₂ exhibited activity against *E. coli* bacteria at [150 and 200 mg/ml] only and against *S. aureus* in 200 mg/ml. The obtained results show in Table (4).

Table 4: antibacterial activities of the experience complexes (inhibition zones in mm)

Microorganism \ Tested complexes	<i>E. Coli</i>			<i>S. aureus</i>		
	100	150	200	100	150	200
[Co(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	---	---	---	16	19	21
[Ni(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	---	11	14	---	---	15
[Cu(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	---	---	---	---	11	12
[Zn(C ₁₇ H ₁₄ O ₂ N ₂) ₂]Cl ₂	11	11	13	---	12	16
[Cd(C ₁₇ H ₁₄ O ₂ N ₂)Cl]Cl	19	21	22	22	24	27
DMSO	---	---	---	---	---	---

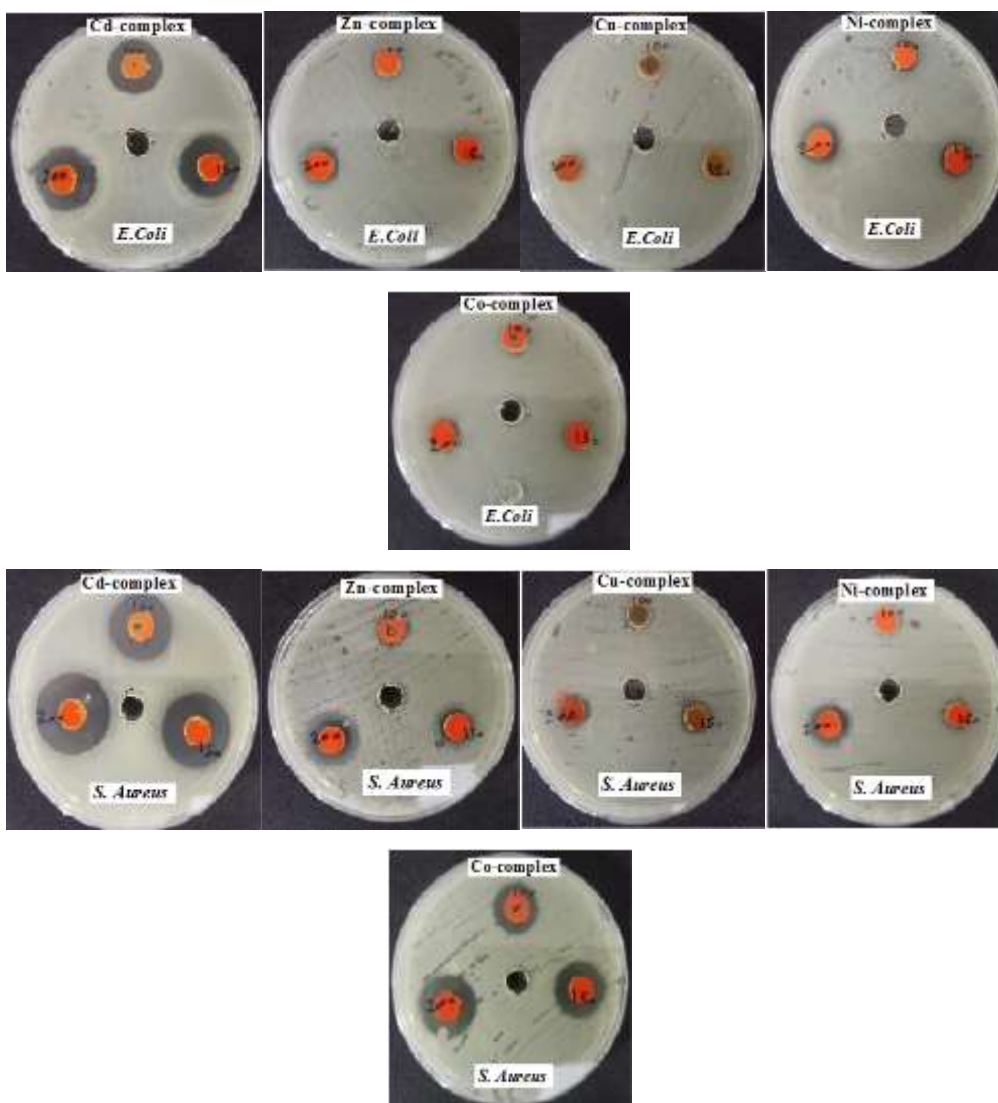


Figure 4: Images of antibacterial activities for complexes



Conclusion

The new metal complexes of the ligand (E)-3-(((2-amino-4-methylphenyl)imino)methyl)-4H-chromen-4-one were prepared and characterized by FTIR, UV-Vis spectra, conductivity measurements, magnetic susceptibility and atomic absorption. The data obtained from magnetic susceptibility for cobalt(II), nickel(II), and copper(II) complexes refer to paramagnetic properties. But the prepared Cd(II) and Zn(II) complexes were diamagnetic and the molar conductance of the all synthesized complexes appeared to be ionic. The proposed geometrical structure for all complexes were octahedral except Cd(II) complex was tetrahedral geometry. The results of antibacterial activity for $[\text{Cd}(\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2)\text{Cl}]\text{Cl}$ complex exhibited activity against two kinds of bacteria in all concentrations were used in this study and it has larger activity when compared with other complexes.

References

1. P. Arora, V. Arora, H. S. Lamba, D. Wadhwa, Importance of heterocyclic chemistry: a review, International Journal of Pharmaceutical Sciences and Research, 3(9), 2947(2012), DOI([http://dx.doi.org/10.13040/IJPSR.0975-8232.3\(9\).2947-54](http://dx.doi.org/10.13040/IJPSR.0975-8232.3(9).2947-54))
2. P. K. Shukla, A. Verma, P. Mishra, Significance of nitrogen heterocyclic nuclei in the search of pharmacological active compounds, New perspective in agricultural and human health, (Bharti publication. New Delhi, 2017), 100-126
3. T. Qadir, A. Amin, P. K. Sharma, I. Jeelani, H. Abe, A review on medicinally important heterocyclic compounds, The Open Medicinal Chemistry Journal, 16(1), 1-32(2022), DOI(<http://dx.doi.org/10.2174/18741045-v16-e2202280>)
4. B. Eftekhari-Sis, M. Zirak, A. Akbari, Arylglyoxals in synthesis of heterocyclic compounds, Chemical Reviews, 113(5), 2958-3043 (2013), DOI(<https://doi.org/10.1021/cr300176g>)
5. T. B. Fitzpatrick, L. M. Chapman, The importance of thiamine (vitamin B1) in plant health: From crop yield to biofortification, Journal of Biological Chemistry, 295(34), 12002-12013(2020), DOI(<https://doi.org/10.1074/jbc.rev120.010918>)



6. C. Foti, G. Calogiuri, E. Nettis, A. De Marco, L. Stingeni, K. Hansel, A. Barbaud, Allergic contact dermatitis from vitamins: A systematic review, *Health Science Reports*, 5(6), e766(2022), DOI(<https://doi.org/10.1002/hsr2.766>)
7. P. Tandon, Q. Jin, L. Huang, A promising approach to enhance microalgae productivity by exogenous supply of vitamins, *Microbial cell factories*, 16(1), 1-13(2017), DOI(<https://doi.org/10.1186/s12934-017-0834-2>)
8. A. M. Rayar, N. Lagarde, C. Ferroud, J. F. Zagury, M. Montes, M. Sylla-Iyarreta Veitia, Update on COX-2 selective inhibitors: Chemical classification, side effects and their use in cancers and neuronal diseases, *Current topics in medicinal chemistry*, 17(26), 2935-2956(2017), DOI(<https://doi.org/10.2174/1568026617666170821124947>)
9. Y. Xu, Q. L. Mi, Y. K. Li, W. L. Zeng, Q. Gao, C. M. Song, J. Wang, Three new anti-tobacco mosaic virus prenyl chromone derivatives from *Cassia nomame*, *Heterocycles*, 98(3), 444-450(2019), DOI(<https://doi.org/10.3987/com-19-14041>)
10. A. A. Jarullah, F. L. Faraj, H. S. Lateef, N. A. Imran, S. M. Salih, Synthesis a new series of complexes from the ligand (**LOH**), In: *AIP Conf. Proc.* 2475, 040019-1-040019-12(2023), DOI(<https://doi.org/10.1063/5.0105263>)
11. A. M. Abu-Dief, I. M. Mohamed, A review on versatile applications of transition metal complexes incorporating Schiff bases, *Beni-suef University Journal of Basic and Applied Sciences*, 4(2), 119-133(2015), DOI(<https://doi.org/10.1016/j.bjbas.2015.05.004>)
12. O. E. Sherif, El-Fattah, M. Hussein, M. M. El-Ajily, Characterization of transition metal ion chelates with 8-(arylazo) chromones using thermal and spectral techniques, *Journal of Thermal Analysis & Calorimetry*, 74(1), (2003), DOI(<https://doi.org/10.1023/A:1026390105986>)
13. N. D. Resen, B. F. Abbas, T. M. Alkhaisy, N. Majed, Structural study and antimicrobial evaluation of some transition metal complexes with 3-(2-amino-4-methylphenyl)-2-thioxo-2, 3-dihydroquinazolin-4 (3H)-one, *Periodicals of Engineering and Natural Sciences*, 8(3), 1548-1554(2020)



14. J. E. Philip, S. A. Antony, S. J. Eeettinilkunnathil, M. P. Kurup, M. P. Velayudhan, Design, synthesis, antimicrobial and antioxidant activity of 3-formyl chromone hydrazone and their metal (II) complexes, *Inorganica Chimica Acta*, 469, 87-97(2018), DOI(<https://doi.org/10.1016/j.ica.2017.09.006>)
15. J. E. Philip, M. Shahid, M. P. Kurup, M. P. Velayudhan, Metal based biologically active compounds: design, synthesis, DNA binding and antidiabetic activity of 6-methyl-3-formyl chromone derived hydrazones and their metal (II) complexes, *Journal of Photochemistry and Photobiology B: Biology*, 175, 178-191(2017), DOI(<https://doi.org/10.1016/j.jphotobiol.2017.09.003>)
16. N. H. Al-Shaalan, Synthesis, characterization and biological activities of Cu (II), Co (II), Mn (II), Fe (II), and UO₂ (VI) complexes with a new Schiff base hydrazone: O-Hydroxyacetophenone-7-chloro-4-quinoline hydrazine, *Molecules*, 16(10), 8629-8645(2011), DOI(<https://doi.org/10.3390/molecules16108629>)
17. B. Geeta, K. Shrivankumar, P. M. Reddy, E. Ravikrishna, M. Sarangapani, K. K. Reddy, V. Ravinder, Binuclear cobalt (II), nickel (II), copper (II) and palladium (II) complexes of a new Schiff-base as ligand: Synthesis, structural characterization, and antibacterial activity, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 77(4), 911-915(2010), DOI(<https://doi.org/10.1016/j.saa.2010.08.004>)
18. B. M. Sarhan, S. M. Lateef, E. J. Waheed, Synthesis and characterization of some new metals complexes of [N-(3-acetylphenylcarbamothioyl) -4- methoxy- benzamide, *Diyala Journal for Pure Sciences*, 12(1), 28-42(2016)
19. W. H. Mahmoud, N. F. Mahmoud, G. G. Mohamed, A. Z. El-Sonbati, A. A. El-Bindary, Synthesis, spectroscopic, thermogravimetric and antimicrobial studies of mixed ligands complexes, *Journal of Molecular Structure*, 1095, 15-25(2015), DOI(<https://doi.org/10.1016/j.molstruc.2015.04.004>)