Open Access **Baghdad Science Journal** **P-ISSN: 2078-8665**
Published Online First: July 2022 **2023, 20(1): 114-120** **E-ISSN: 2411-7986**

DOI: https://dx.doi.org/10.21123/bsj.2022.6584

Synthesis, characterization and bioactivity Study from azo – ligand derived frommethyl-2-amino benzoatewith some metal ions

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Received 28/9/2021, Revised 27/2/2022, Accepted 28/2/2022, Published Online First 20/7/2022, Published 1/2/2023

Abstract:

A Ligand (ECA) methyl 2-((1-cyano-2-ethoxy-2-oxoethyl)diazenyl)benzoate with metals of (Co^{2+}, Ni^{2+}, Cu^{2+}) were prepared and characterization using H-NMR, atomic absorption spectroscopy, ultra violet (UV) visible, magnetic moments measurements, bioactivity, and Molar conductivity measurements in soluble ethanol. Complexes have been prepared using a general formula which was suggested as [M $(ECA)_2$] Cl_2, where M = (Cobalt(II), Nickel(II) and Copper(II), the geometry shape of the complexes is octahedral.

Keywords: Bioactivity, complexes, ethanol, Molar conductivity, Transition Metals.

Introduction:

Azo compounds [1] are very important class of chemical compounds that is attracting study attention, they are highly colorful and have long been used as dyes and pigments. Transition metal azo compounds were instrumental in the development of coordination chemistry are widely used in industrial and biological systems. Azo compounds are very important molecules, these compounds derivatives and their metal complexes are very important pigments for synthetic leather and vinyl polymers. Coordination compounds (complexes) play a significant role in our life. Coordination compounds characteristics are the most important way in determining the chemistry of the transitional elements. Their study contributes in quietly understanding the chemistry of organometallic and inorganic compounds, and chemical bonds as a whole. The figure of possible coordination compound is almost infinite[2]. Inorganic compounds especially, transition metals, have played a significant part in the development of some cosmetic compounds and new metal-based drugs. Previously, complexes have been regarded as of interest only to the theoretical and to the inorganic chemists. However, these complexes are revealing a vital role in biochemistry, polymerization processes, and analytical chemistry through organic compounds preparation [3].

Transition metals, in particular, have played a key role in the creation of new metal-based pharmaceuticals and cosmetic compositions. Copper, for example, is one of many transition metals used in cosmetics (Cu). Nickel a transition metal is utilized as a skin sensitizer in cosmetics. Nickel, on the other hand, is one of the most poisonous transition metals[4].The aim of the work is preparation metal complexes from the Ligand (ECA) methyl 2-((1-cyano-2-ethoxy-2-oxoethyl)diazenyl)benzoate, Characterization of ligands and prepared complexes by different techniques and study of bioactivity of these complexes .

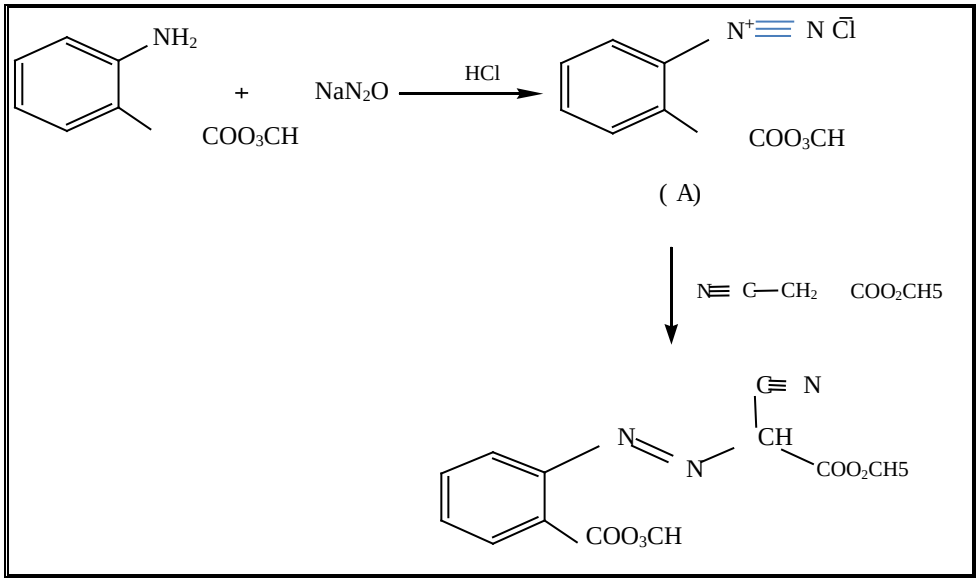
Materials and Methods:

All the used chemical are supplied by either Fluka or Merck were of reagent grade and used as supplied. Ultra Shield 300 MHz (Bruker, Switzerland) was used to identify HNMR Spectra at University of Al-Bayt, Jordon. Shimadzu FT-IR infrared spectrophotometer was used to record absorption in the region of (4000-400cm^{-1}) by using a KBr disc. Shimadzu UV-Vis. (160A)

spectrophotometer was used to identify UV-Vis-spectra in ethanol solution. Shimadzu AA680G atomic absorption spectrophotometer was used to identify metal content atomic absorption technique of the complexes. A balanced magnetic susceptibility model (MSBKT) in the Faraday method was used to measure the magnetic moment (μ_{eff} B.M).Melting points were measured by the Stuart – melting point apparatus. Philips PW Digital conductivity meter was used to measure conductivity of the prepared compounds.

Preparation of the ligand (ECA) [5]

Methyl-2-amino benzoate solution (1.3ml, 0.01mole) in HCl (3ml) was concentrated and cooled to (0-5°C), then sodium nitrite (1.5gin 10ml of water) cooled solution was added drop by drop over 10 minutes. At the same temperature, the reaction mixture was agitated for 30 minutes. Drop by drop, over 15 minutes, the mixture was added to an ice-cold combination of ethyl cyanoacetate (0.01mole) and sodium acetate (4.1g, 0.05mole) in ethanol (30ml). After that, the solution was stirred for 30 minutes and then allowed to sit at room temperature for (2 hours). The solid product was recrystallized after it was produced and collected from ethanol to give the orange crystals (ECA), m.p (142-144˚C), and yield (75%). The reaction is shown in scheme 1.



Scheme 1. Preparation route of Ligand (ECA)

Preparation of complexes

A solution of metal chloride containing (0.11g, 0.11g and 0.076g) (1mmole) of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and $CuCl_2.2H_2O$ respectively was added to a solution of the ligand (ECA) (0.25g, 2mmole) in ethanol (5ml). After stirring for three hours, a colored precipitate was formed at room temperature. The rustling solids were filtered off from ethanol then dried at 50˚C in oven.

Result and discussion

The isolated compounds which are crystalline solids, were soluble ethanol, dimethyl formamide (DMF), and dimethyl sulphoxide (DMSO). The conductivity measurements in ethanol pointed out the electrolytic behavior. The molar ratio method was followed to measure the ratio of metal ion to ligand in complexes (M:L). Ethanol was used as a solvent. The (M: L) ratio was (1:2).

Table. 1 includes the physical properties; the magnetic measurements (μeff B.M) for the complexes.

Spectra studies

The ^{1}HNMR In DMSO, the spectrum of the ligand (ECA) was obtained, and Fig.1, shows the following signals: (DMSO) singlet (s) at (2.50) ppm, triplet (t) at (1.35) ppm for (3H, CH_3), singlet (s) at (3.9) ppm for (3H, OCH_3), quartet (q) at (4.34) ppm for (2H, OCH_2), and multiplet (m) at (7.2-8.0) ppm for (4H, Ar-H). The IR spectra of the ligand (ECA) and its complexes are shown in Table 2. In the free ligand, the prominent absorption bands were at (1701, 1583) cm^{-1} and (2222) cm^{-1}. The IR spectrum of the ligand (ECA) resulting from the (C=O) ester and (C=N) [4] in the complexes spectral

is shown in Fig .2. The IR spectra of the cobalt complex is shown in Fig. 3.

The bands were in a range between (1637-1508) cm^{-1} and deviated from lower frequencies by (64-193) cm^{-1}. This shows that the oxygen atom at the (C=O) group in methyl ester [5] is coordinated. A band of (C=N) was missing, indicating that the nitrogen atom of (C=N) was not coordinated. (N=N) [6] caused a band in the ligand spectra at (1454) cm^{-1}. Complex spectra show that this band was around (1436-1373) cm^{-1} and that it deviated to lower frequencies by (81-18) cm^{-1}. This shows that the ligand (ECA) is coordinated through the azo nitrogen [7] atom, and new bands formed in the spectra of metal complexes at (530-510) cm^{-1} and (462-415) cm^{-1}, respectively, attributable to the (M-O) and (M-N).[8]

The spectrum of the ligand

Table. 3 shows the assignments and absorptions that were related to the ligand and its complexes Fig. 4, displays an electronic spectra of ligand (ECA) with absorption bands at 253 nm 39525 cm^{-1} and 361 nm 27710 cm^{-1}, which might be attributed to ($\pi \longrightarrow \pi^*$) and($n \longrightarrow \pi^*$) transitions [9].

Spectra of Complexes

$[Co(ECA)_2]Cl_2$ complex

The bands at (250)nm (40000) cm^{-1}, (364)nm (27472) cm^{-1}, (665) nm (15037)cm^{-1} , and (841) nm (12285) cm^{-1} in the spectra of deep green Co(II) complex were assigned to (C.T), $^4T_{1g(F)} \longrightarrow {}^4T_{1g(P)}$, $^4T_{1g} \longrightarrow {}^4A_{2g}$ and $^4T_{1g} \longrightarrow {}^4T_{2g}$respectively [10]. The value of ($\acute{B}$) was determined to be (376.93) nm, and the value of $\beta = \acute{B} / B_\circ$ is (0.388), indicating the presence of a covalent bond in the complex. The magnetic moment of the cobalt (II) complex is (4.34) B.M in the octahedral range**.**

$[Ni(ECA)_2]$ Cl_2 complex

The absorptions at (251) nm (39840)cm^{-1}, (360) nm (27777)cm^{-1}, (502) nm (19920)cm^{-1}, and (765) nm (13071)cm^{-1} were ascribed to (C.T), 3A2g $\longrightarrow {}^3T_{1g(P)}$, $^3A_{2g} \longrightarrow {}^3T_{1g(F)}$ and $^3A_{2g} \longrightarrow {}^3T_{2g}$ respectively [11], in the spectra of red complex Fig. 5. The value of (*B)* was determined to be (565.6) nm, and the value of $\beta = \acute{B} / B_\circ$ is (0.543), indicating the presence of a covalent bond in the complex. The moment of induction is (3.29). The above-mentioned geometry was confirmed by B.M. From these results, the distorted Octahedral structure was proposed for this complex.

$[Cu(ECA)_2]$ Cl_2 complex

The absorption bands observed at (254)nm(39370)cm^{-1}, (363)nm(27548)$cm^{-1}$and (520)nm (19231) cm^{-1}, which were attributed to the (C.T) , $^2Eg \longrightarrow {}^2T_{2g}$transition respectively [12] . The spectrum of deep red showed absorption bands at (39370) nm and (27548) nm, which were assigned to charge transfer transitions (C.T). The magnetic moment of the copper (II) complex is (1.75) B.M in the octahedral range.

Table 1. The results of microanalysis and some physical properties of ligands and their complexes

Formula of compound	Molecular weight	Colour	M.p˚C or dec.	C.H.N% Found (Calc.)			Metal % Found (Calc.)	Molar conductivity ($S.cm^2mole^{-1}$) in Ethanol (10^{-3} M)	μeff (*β*.M) Found (Calc)	Suggested Structure
$C_{13}H_{13}O_4N_3$ [ECA]	275	Orange	142-144˚C	56.7 (56.2)	4.7 (4.2)	15.2 (15.4)	-	2.4	-	-
$[Co(ECA)_2]Cl_2$	679.93	Deep green	95(dec.)	22.5 (22.3)	1.8 (2.3)	6.06 (6.2)	8.50 (8.66)	80	4.34)4.39)	octahedral
$[Ni(ECA)_2]Cl_2$	679.69	Red	100(dec.)	19.8 (19.4)	1.6 (1.8)	1.6 (1.9)	7.46 (8.64)	75	3.29 (3.35)	octahedral
$[Cu(ECA)_2]Cl_2$	684.54	Deep red	98(dec.)	24.7 (25.7)	2.06 (3.4)	6.6 (5.9)	10.07 (9.28)	81	1.75 (1.85)	octahedral

Table 2. Infrared spectrum bands of the ligand (ECA) and its metal complexes

Compounds	υ (N=N)	υ(C=O) Ester	υ(C≡N)	M-N	M-O
C13H13O4N3 [ECA]	1454	1701, 1583 (s)	2222(s)	-	-
$[Co(ECA)_2]Cl_2$	1435(m)	1627(s)	2220(s)	420(w)	526(w)
$[Ni(ECA)_2]Cl_2$	1436(m)	1637(s)	2215(s)	424(w)	530(w)
$[Cu(ECA)_2]Cl_2$	1404(w)	1620(s)	2210(s)	418(m)	520(w)

Where:
s = (strong)
m = (medium)
w = (weak)

Baghdad Science Journal
2023, 20(1): 114-120
P-ISSN: 2078-8665
E-ISSN: 2411-7986

Table 3. In ethanol solvent, electronic spectral data of ligand (ECA) and its complexes

Compound	λmax nm	Wave number cm^{-1}	εmax $Molar^{-1}cm^{-1}$	Assignment
Ligand [ECA]	253	39525	567	π→ π*
	361	27710	1207	n→ π*
$[Co(ECA)_2]Cl_2$	250	40000	428	C.T
	364	27472	870	$^4T1g(F)$→
	665	15037	10	$^4T1g(P)$
	814	12285	8	$^4T1g→^4A2g$
				$^4T1g→^4T2g$
$[Ni(ECA)_2]Cl_2$	251	39840	365	C.T
	360	27777	869	3A2g→3T1g(P)
	502	19920	12	3A2g→3T1g(f)
	765	13071	8	3A2g→3T2g
$[Cu(ECA)_2]Cl_2$	254	39370	1178	C.T
	363	27548	1497	C.T
	520	19231	143	2Eg→2T2g

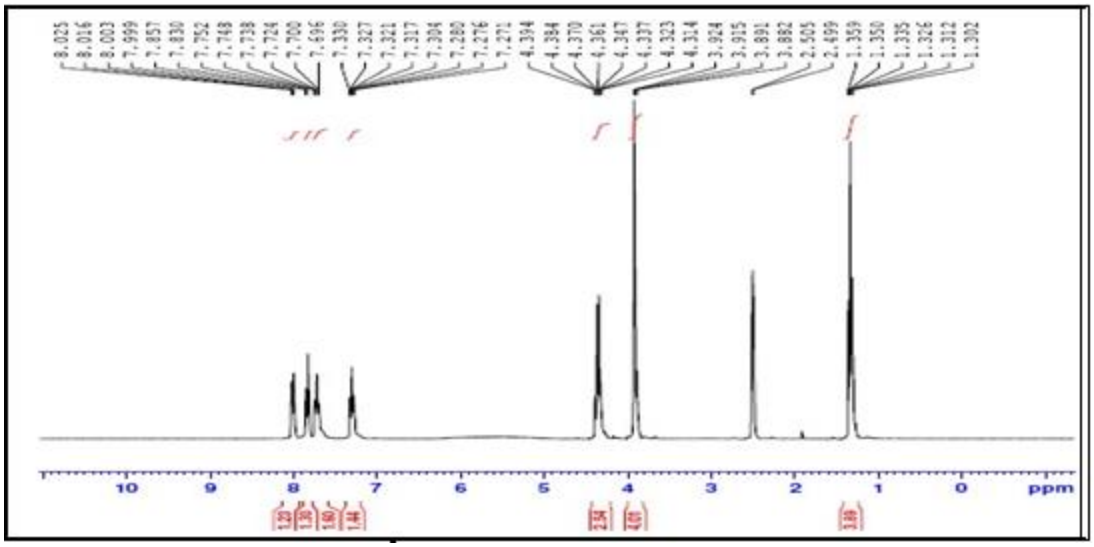


Figure 1. Ligand(ECA)HNMR Spectrum

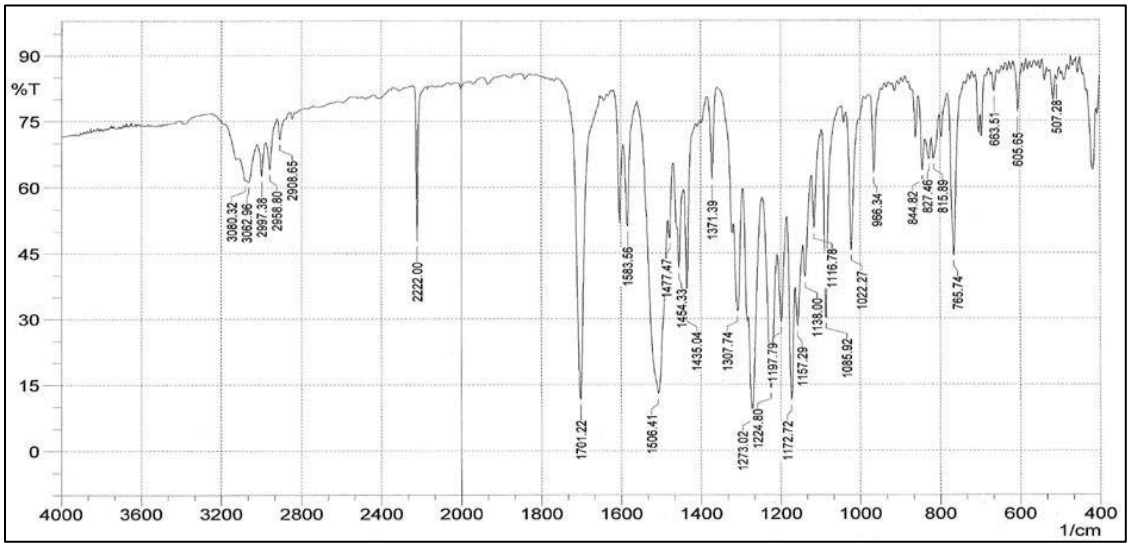


Figure 2. Ligand (ECA)Infrared Spectrum

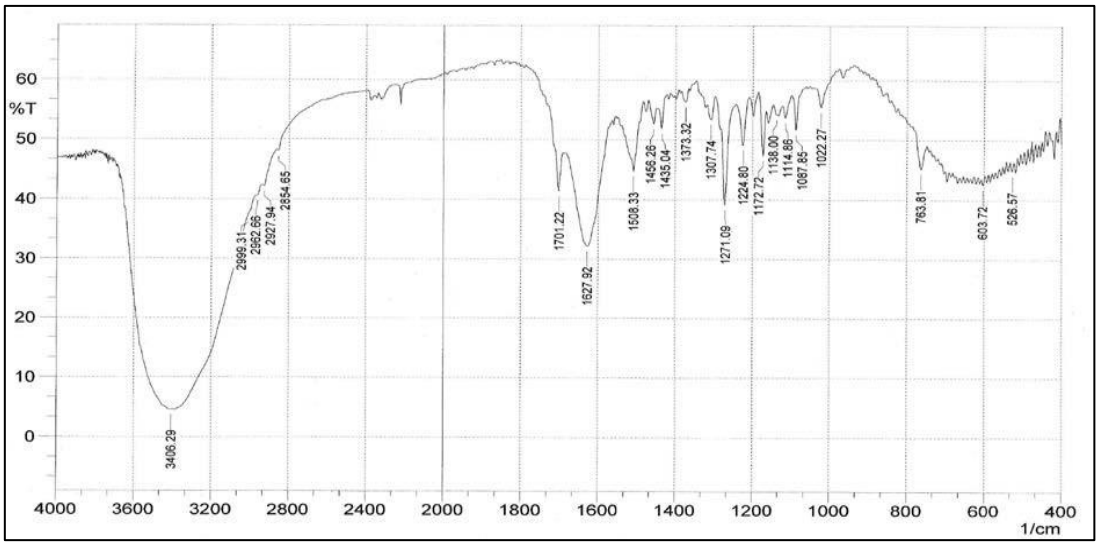


Figure 3. Co complex of IR spectrum

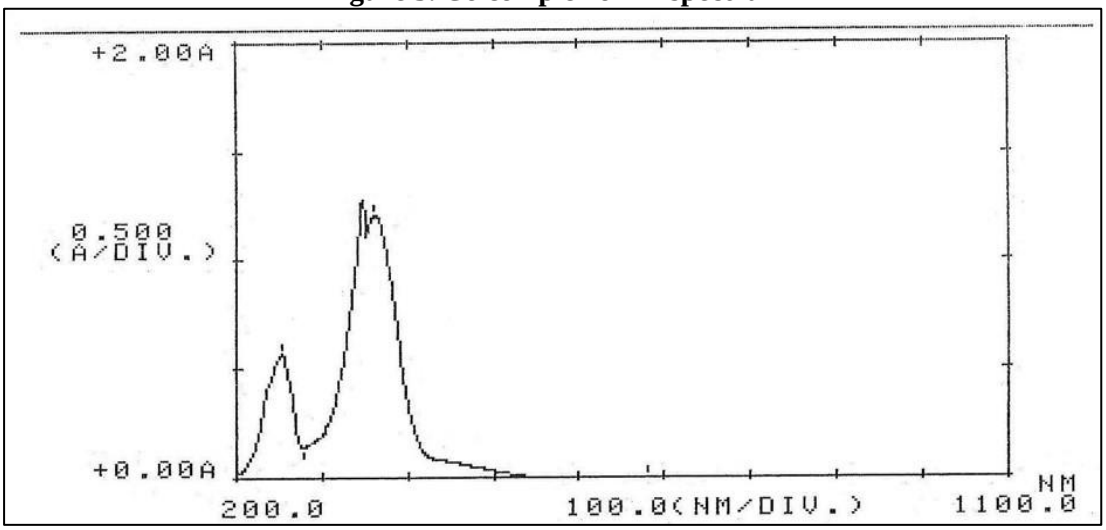


Figure 4. Electronic spectrum of ligand (ECA)

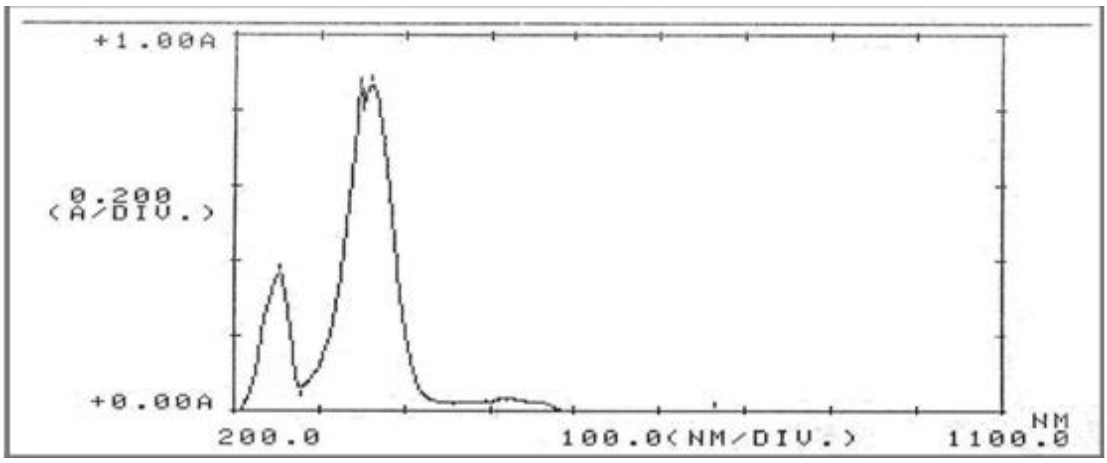


Figure 5. Electronic spectrum of $[Ni(ECA)_2]Cl_2$

General Proposed Stereo Chemistry Structure of Complexes:

According to the results obtained from the elemental analysis, spectral studies, magnetic and conductivity measurements, the general structure of the prepared complexes can be illustrated as follows in Fig. 6.

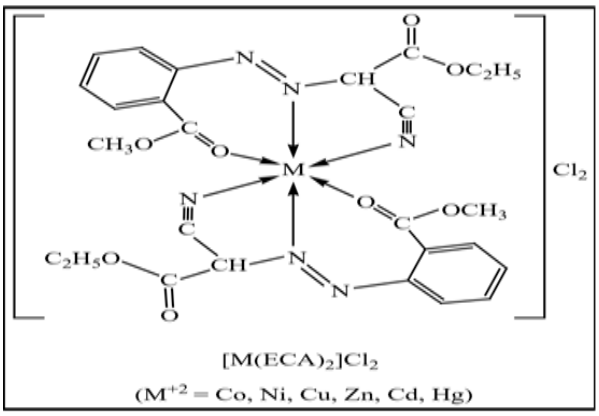


Figure 6. The proposed structural formula of the complexes

Biological activity of the ligand and its complexes

The ligand (ECA) combined with Co, Ni, or Cu complexes showed biological activity which was studied by using the inhibition method for four types [13] of pathogenic bacteria and *Candida albicans fungi*. *Staphylococcus aureus* and *Bacillus subtilis*are two forms of gram-positive bacteria. *Escherichiacoli* and *Pseudomonas aeruginosa* were the second and third gram-negative bacteria, respectively. To all species of bacteria, the chemicals show no inhibitory diameter. Under similar experimental settings, the results suggest that the complexes are more active than the ligand because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring such.

The results for the compounds**,** the results as modified to the literature [13] are shown in table 4 and Figure 7.

Table 4. The results of compounds

Bactra comp.	*Staphlococcus aureu* (a)	*Psedomonas aeruginosa*(b)	*Bacillus subtilis*(c)	*Escherichi a coli*(d)	*Candida albicans fungi*(e)
Ligand [ECA]	-	-	-	-	-
$[Co(ECA)_2]Cl_2$	-	-	-	-	-
$[Ni(ECA)_2]Cl_2$	-	-	-	-	-
$[Cu(ECA)_2]Cl_2$	-	-	-	-	-

Where: (-) No significant Zone

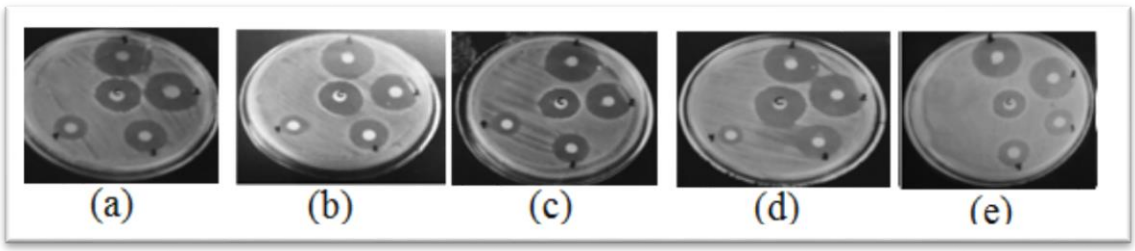


Figure 7. (a-e) below shows bioactivity of the ligand and their compounds (L,Co,Ni and Cu) for types bacteria

Conclusions:

In this study new novel complexes are synthesized and recognized by a variety of spectral and physicochemical analyses. The findings show that the synthesized ligand behave as tridented coordinating with metal ions through three donor atoms (O in C = O, N in N=N and N in C**=N),** the complexes prepared have geometry octahedral, therefore the study of bioactivity for all compounds prepared show No significant Zone for all types bacteria *Staphlococcus aureu*, *Psedomonas aeruginosa,Bacillus subtilis ,Escherichia coli*and *Candida albicans fungi*.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions statement:

The role of first authors I. H. I., Prepared higands and complexes did IR tset and data analysis, The role of second authors N. S. M. (UV visble test, measure molarity conductivity and study biological activity) for the complexes, the role of the third and fourth authors writing the manuscript, drafting and designing the Ms .

References:

1.Geersing A, Ségaud N, Monique G P, Van der Wijst M G, Rots M G , Roelfes G, Importance of metal-ion exchange for the biological activity of coordination complexes of the biomimetic ligand N4Py. Inorg.Chem. 2018; 57(13), 7748-7756.

2.Yousif Q I, Alia F M ,Synthesis,Strctural study Antimicrobial activity and theoretical treatment of 3d-metal complexes involiving schuff base of piperonal derivative AJPS. 2018;13(1):1-13

3.Sodhi R K, Paul S , Metal Complexes in Medicine an Overview and Update from Drug Design Perspective. Cancer Ther Oncol Int J. 2019; 14(1), 25-32.

4.Karwan O A, Hikmat A M, Synthesis, Characterization, and Antibacterial Activity of Ni(II), Pd(II), and Pt(II) Complexes with 2-benzoylthiobenzimidazole. Zanco J Pure Appl .2020; 32 (2): 15-23.

5. Ana A B, Supramolecular Assembly of Benzimidazole Derivatives and Applications., DOI: 10.5772/intechopen . 2019; 85333 (Review).

6.Husain A, Varshney M, Rashid M , Akhter A, benzimidazole : A Valuable Insight into the recent Advances and Biological Activities J.Pharm Rese. 2016; 4(2) ,413-419.

7. Waleed A , Israa H , Synthesis and Spectral Analysis of Mn(II), Cu(II) Ni (II) and Cd(II) Complexes with Mixed Ligand containing 1,10- phenanthroline and Schiff base derived of 4- aminoantipyrine. Baghdad Sci J . 2014 ; 11(4): 1519-1521.

8. Hawraa M, Maha AL-T , Israa H,Muna S , Surfactant Cloud Point Extraction as a Procedure of Preconcentrating for Metoclopramide Determination Using Spectro Analytical Technique, Baghdad Sci J . 2020; 17(1): 57-65.

9. Mahasn F A , Doaa H M , 2015.Synthesis , Spectral Study and Theoretical Treatment of Mixing Benzimidazole Derivatives and Phenanthroline Complexe.ANJS.2016;19 :6056-6068.

10. A-Hammdani A, Al –Zoubi W,New metal complexes N3 tridentate ligand Synthesis ,spectral studies and biological activity .Spectrochim Acta A Mol Biomol Spectrosc. 2016; 137: 75-89.

11. Anamm M, Sinan M, Rehab A, Muna A, Synthesizing Structure and Characterizing Bioactivites of Cr (III), La(III) and Ce(III)Complexes with Nitrogen ,Oxygen and Sulpher donor bidentate Schiff base ligands. Baghdad Sci.J. 2021; 18 (4) 1547.

12. Devi O,Basavaiah K, Vinay K, Revanasiddappa H, Sensitive spectrophotometric determination of metoclopramide hydrochloric in dosage forms and spiked human urine using vanilline .Arab J Chem. 2016; 9: S64-S72.

13. Sahar S H, Nidhal M H , Shaymaa RB, Asmaa MS , Biological Evalution and Therotical Studay of Bi-dentate Ligand for Amoxicilline Derivative with Some Metal Ions .Baghdad Sci.J. 2021; 18 (4)1269.

تحضير وتشخيص ودراسة الفعالية البايولوجيه لليكاند ازو مشتق من مثيل 2- امين بنزوات مع بعض الايونات الفلز

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الخلاصة:

حضرت بعض المعقدات الفلزية الجديدة من الليكاند مثيل -(1- سيانو-2- ايثوكسي)بنزوات مع ايونات ((Co(II)، Ni (II)، Cu(II)) وشخصت بالطرائق الطيفية وهي طيف الاشعة تحت الحمراء، وطيف الاشعة فوق البنفسجية والمرئية فضلا" عن تعيين نسبة الفلز في المعقدات بوساطة طيف الامتصاص الذري، وقياس التوصيلية المولارية لمحاليل المعقدات في مذيب الايثانول، وتحديد النسبة المولية لليكاند الى الفلز، وقياس العزم المغناطيسي للمعقدات المحضرة ودرست الفعاليه البايولوجية للمركبات . وفي ضوء التشخيصات اعلاه اقترح الشكل الثماني السطوح لهذه المعقدات.

الكلمات المفتاحية: معقدات ، ايثانول ، فعالية بايولوجيه ، توصيليه مولاريه ، عناصر انتقاليه