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Synthesis, Characterization and Biological Activity Study of Cobalt(II), Nickel(II) and Copper(II) Complexes Derived from Mixed Bi dentate Ligands of Oxime and Phenanthroline

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Abstract

The present work involves the synthesis and characterization of cobalt (II), nickel (II) and copper (II) complexes derived from (1:1:1) mole ratios of coumarine-oxime:1,10-phenanthroline:metal ions with respect to the continuous variation method of Job via spectroscopic studies. The isolated metal complexes were characterized with their ligands of 3-acetoxime-coumarine by elemental analyses, FT-IR, EI-MS and NMR spectra. The flame atomic absorption spectroscopy, molar conductivity in DMF and magnetic moment measurements were also employed to determine the supposed molecular weights and their geometry. Furthermore the gravimetric thermal analysis (TG-DTA) was estimated for copper(II) and nickel(II) complexes and the observed data form weight loss percents confirmed the suggested chemical formulas and structures of complexes. The results observed from UV-Visible spectra and elemental analyses together with mass spectra confirmed the octahedral geometry around the cobalt(II) and copper(II) ions whereas the diamagnetic complex of nickel(II) was square-planner in $[Ni(Phen)(L)]Cl_2$ formula. As well as the biological activities of complexes solutions were tested against two types of bacteria and the inhibition zones data proved that all solutions were active compared with standard drugs of 10 ppm concentrations.

Keywords: Mixed ligands, metals complexes of oxime, biological activity of mixed ligands

1. Introduction

The continuous interest in functionalization of oxime ligands have been attributed to the versatile and broad applications of their complexes in the fields of dyes [1,2] and drugs [3,4]. The ligands derived from 4-hydroxy coumarine and 3-acetylcoumarine area vital component of various drugs employed in medicine as anti-tumor, sedatives, antiepileptic's, anti-inflammatory, antibacterial, anti-tuberculosis [5-7] and antiviral [8,9]. The DNA binding to the chiral mixed ligands complexes of europium(III) have stuied extensively by Haruki, M. *etal* [10] and the anti-oxidation activity encouraged many researchers to synthesized novel complexes of this type of oxime complexes . The phenanthroline is a poly aromatic hetro cyclic compound and considered as classic ligand in co-ordination chemistry [11] which couples in a very versatile manner with different metal atoms/ions to give different peculiar characteristics to the metal complexes formed by it such as metal complexes with nitrogenic ligands that they can be showed to develop new molecular " Chromo sensors" for metal cations and anions, ionophores as well as new intercalating agents for polynucleotide's especially in case of DNA cleavage [12]. All the literatures mentioned of mixed ligands with their significance have encouraged us to prepare new complexes of cobalt(II),nickel(II) and copper(II) with varying the stoichiometry ratios of the reactants in order to get special physical and chemical properties of the isolated complexes with their biological activity against certain types of Gram-positive and Gram-negative bacteria.

2. Experimental

2.1. Chemicals and Instrumentation

Elemental analyses (C, H and N) were realized with an Elemental Combustion System CHNS-O, using a Costech device, type ECS 4010All starting materials were of analytical grade and were used without further purification. Compounds are characterized in the laboratory, Department of Chemistry, College of Science, Mustansiriyah University. The melting points were determined using the Gallen Kamp melting point apparatus, Model number 8899339 and were uncorrected. The elemental micro-analyses (C, H and N) of the oxime derivatives and its mixed complexes

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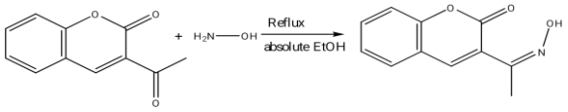
with 1,10-phenanthroline were realized with an Elemental Combustion system CHNS-O, using Carlo-Erbal Elemental analyzer Italy model. The electronic spectra were determined in ethanol and DMF solvents using the Shimadzu UV-1800 spectrometer with absorption maxima given in nanometers (nm) and log Ɛ is the figure in parenthesis. The FT-IR spectra was determined using Shimadzu 8400 S Fourier Transform Infrared (FT-IR) spectrophotometer and the absorption given in wave number (cm^{-1}). The H NMR spectra were determined in deuterated DMSO solvent using Bruker 400 MHz instrument at Al-Bait University, Amman, Jordan. The magnetic susceptibility of solid complexes were carried out at laboratory service of chemistry department, college of science, Mustansiriyah university with Sherewood Magnetic balance apparatus *via* Farady 's method at 290 K^0 temperature. The TG-DTA analyses of metal complexes were carried out in helium gas with heating rate 10 ^{0}C/min. on Mettler Todelo TGA/DTA 851 e thermal analyzer within temperature range (298-973) ^{o}K.

2.2. Synthesis of (Z)-3-(1-(hydroxyimino)ethyl)-2*H*-chromen-2-one

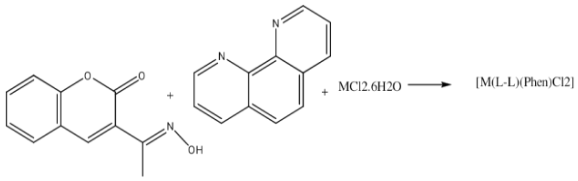
The oxime ligand was prepared according to the modified procedure mentioned in literature [12]. A measuring cylinder was used to measure benzene (100 ml) and transferred into a three-necked flask. 3-acetylcoumarine (2.30 g, 5 mmole) was dissolved in the mixture of $CHCl_3$/Benzene (20 ml), followed by addition of anhydrous sodium carbonate (0.92 g) and the mixture was warmed to boiling temperature in the three necked flask. Then hydroxylamine (3.4 g, 3.10 moles) was added and the mixture refluxed on a water bath with magnetic stirring for 3 hours at a temperature of 80 ^{o}C. The reaction mixture was allowed to cool and then poured into a beaker containing crushed ice. The precipitate formed was air dried on the filter paper and the crude product recrystallized from ethanol-water (3:1) mixture to obtain dark yellow solid. The purity of the product was ascertained using thin layer chromatography m.p.175-177 ^{o}C (Lit. 182 ^{o}C). Yield 2.5 g, UV-visible (ethanol), λ_{max}: 360 (1200), 250 (12000). IR (V_{max}, cm^{-1}, KBr): 3450 (-OH), 1690(C=O), 1630 (C=N), 1596 (C=C), 1460 (C=C-Ar), 1200 (C-O-C). ^{1}H NMR (400 MHz, d_6-DMSO):3.77(s, 3H , -CH_3) 7.77 (s, 1H-coumarin), 6.88 (s, 1H, coumarin-C4), 9.22 (s, 1H,OH), molecular formula: $C_{11}H_9NO_3$. Elemental analysis; Calc. (Obs.%): C: 65.02 (64.80), H: 4.46(4.22) and N: 6.89 (5.90). MS (ESI), m/z (% relative intensity): 96.90 (190.40), 206.00 (80.00), 204.0 (60.0), 188.0 (25).



Scheme1. Synthesis of oxime ligand

2.3. Synthesis of cobalt (II),nickel (II) and copper(II) complexes

A mixture of metal chloride hexahydrate of cobalt(II), (34 mg, 10 m mole) or $CuCl_2.2H_2O$, (1.70 g, 10 m mole) dissolved in (10 ml) hot methanol was added gradually to (1.81 g, 10 m mole) of 1,10-phenanthroline with stirring followed the addition of (0.206 g, 10 m mole) of primary oxime ligand (L) dissolved in minimum hot ethanol. The mixture was refluxed on water bath with constant stirring for 30 minutes and a green to an olive precipitates were separated, filtered off and dried in oven for several hours. The purification of complexes was done by washing the crudes with hot distilled water, ethanol and diethyl ether, Table (1).



Scheme2. Synthesis of complexes with mixed ligands

2.4. Antimicrobial activity study

The antimicrobial activity of the synthesized compounds was evaluated in form of minimum inhibitory concentration (MIC) against the tested microbes via micro-broth dilution method following the procedure stipulated by Clinical Laboratory Standard Institute [10,11]. The microorganisms in this study are *Staphylococcus aureus, Streptococcus pneumonia, E. Coli, Salmonella typhi, klebsiella pneumonia.* These are clinical isolates obtained from the Department of Pharmaceutical Microbiology and Biology Laboratory, University of Mustansiriyah, College of Science. The standard antibiotics used were ciprofloxacin. The inhibition zones were measured in counter with respect to holes of millimeters *via* diffusion method [12].

3. Results and Discussion

3.1. Chemistry and Characterization

The synthesis of the oxime was followed by TLC technique and the structure and formula was confirmed by mass spectrum, and elemental analyses which are in good agreement with the literature results respectively [13], Table(1). The molar conductance measurements in DMF solution (10^{-3} M) supports the electrolytic behavior of NiL complex with value 75

ohm^{-1}.cm^2 per mole whereas the complexes of cobalt(II) and copper(II) showed molar conductivity values around (15-22) ohm^{-1}.cm^2 per mole which are associated with the neutral properties since the chloride ions are bonded covalently to the central metal ions of Co^{2+} and Cu^{2+} within the inner-sphere of complexes [13]. The experimental analytical data of (C,H,N) were in good agreement with the theoretical assigning the proposed chemical structures of oxime ligand and it's metal complexes.

Table (1) Some Physical Properties and Elemental Analysis of the prepared Oxime Ligand and its Mixed Ligands Complexes

Compound/ Color	Ω S.cm^2/mole	M.P ^{0}C	Elemental analysis % Found % (Calc.)				
			C	H	N	Cl	M[a]
$C_{11}H_9NO_3$ Dark yellow	-	175-177	64.80 (65.02)	4.22 (4.46)	6.96 (6.89)	-	-
$C_{23}H_{17}N_3O_3NiCl_2$ [CoL(Phen)Cl$_2$] Green	15	250-252	53.22 (53.82)	3.20 (3.34)	8.22 (8.19)	11.78 (11.44)	13.54 (13.82)
[NiL(Phen)]Cl$_2$ Orange	75	295 Dec	53.50 (53.82)	3.29 (3.34)	8.49 (8.19)	13.55 (13. 82)	11.17 (11.44)
[CuL(Phen)Cl$_2$] Olive	22	305 Dec	53.01 (53.34)	3.27 (3.31)	8.30 (8.11)	13.73 (13.96)	12.05 (12.27)
a= analyses of %M by flame atomic absorption spectroscopy (FAAS), and Dec=decomposed							

[10, 12]. The thermal decomposition of all complexes are lie at around (278-290) ^{o}C temperature and are greater than the free ligands which mainly show good indication for the formation of covalent character among bi dentate 1,10-phenanthroline and oxime ligands with cobalt(II), nickel(II) and copper(II) ions

3.2. LC-Mass Spectra of Oxime and Complexes:

mass spectra data of (L) are as presented in the experimental section. The molecular ions are in agreement with the proposed molecular formula of the compounds. The observed fragments were appropriately assigned. However, some fragments not assigned are most likely due to un-identified fragments of the parent compound, Figure (1).

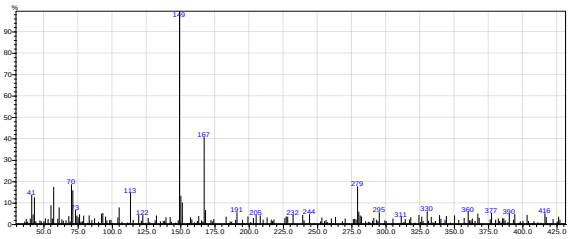


Figure (1). Mass spectrum of oxime ligand, L.

Furthermore, the mass spectrum of nickel (II) complex exhibited *m*/e=442 with low intensity due to the molecular ion of complex and the other peaks at around 398, 356, 266, 184 and 85 may be assigned to breaking of weak bonds of –OH, Ni-Cl and cleavage of 10-phenanthroline ligand in the next steps of decomposition in the gas phase of analysis [10,14].

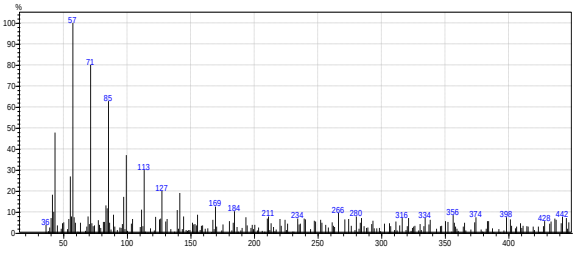


Figure (2). Mass spectrum of [NiL(Phen)]Cl$_2$ complex

3.2. FT-IR, UV-Visible spectra and magnetic susceptibility measurements:

The comparison of vibration modes of oxime primary ligand (L), secondary phenanthroline with the IR spectra of complexes were strong evidence for identification the metal-ligand bonds in the low frequency regions (200-600) cm^{-1}. The free oxime ligand showed strond absorptions at around 1635 cm^{-1} and (145-1500) cm^{-1} beside a broad band at 3500 cm^{-1} which are assigned to functional groups of –C=N- ,-C=C- of coumarine ring and –OH group respectively [11,15]. All complexes exhibited lowering in the absorptions of isomthine –HC=N- in the region (1550-1605) cm^{-1} confirming the participation nitrogen atom in coordination with the central metal ions [15]. As well as the shift of OH absorption to (3100-3250) cm^{-1} revealed the coordinatrion of OH to metal ions with out deprotonation. However the appearance of shoulder bands at (1510-1533) cm^{-1} supports the bi dentate behavior of 1,10-phenanthroline secondary ligand in coordination with Ni^{2+},Co^{2+} and Cu^{2+} ions [13,16]. The weak and medium bands in the regions (550-

490) and (410-380) cm^{-1} are ascribed to (M-N),(M-O) and (M-Cl) bonds [2,3,15].

1. The UV-Vis spectrum of the ligand (L) in ethanol within the range (250-800) nm, display mainly two peaks. The first at (360 nm) was assigned to the moderate energy $n\rightarrow\pi^*$ transition of the aromatic rings. The shoulder (λ_{max}) peak at (250 nm) was related to the $\pi\rightarrow\pi^*$ transition of intermolecular charge-transfer taken place through the azo group (-C=N-) [15,16].The solutions of Co(II), Cu(II) and Ni(II) complexes in DMF with the oxime ligand (L) and 1,10-phenanthroline secondary ligand were studied spectrophotometrically over a wide molar concentrations. The interaction between the metal ion and the ligand manifests itself by the change in color from red to violet, reddish-violet and blue-violet for the previous ions and by the great bath chromic shift which was detected in the visible region for the complex solution with respect to that of the free ligand. The high shift in the (λ_{max}) give a good indication for coordination and complex formation. The complexes recorded d-d spectra at around (300-450), (480-600) and (600-750) nm respectively which are considered spin-allowed transitions and *Laporte* forbidden [16]. The magnetic moments of cobalt (II) complex displayed 4,80 BM value due to orbital contribution of (S+L) spin-orbital criteria that is proved the octahedral environment. As well as the copper (II) complex was distorted octahedral due to paramagnetic character with 1.90 BM valu. The zero value of *X*g for nickel (II) complex at room temperature gives us strong evidence for the low-spin of square-planner geometry with dsp^2 hybridization. In order to give more details of d-d spectra for cobalt(II) complex in DMF solution Three transitions were usually assigned to these types of complexes in the following ranges [15,16].The possible spin-allowed transitions in octahedral complexes of cobalt(II) are : $^4T_1g_{(F)} \rightarrow ^4T_2g_{(F)}$ (ν_1) (15037-10200) cm^{-1} ,$^4T_1g_{(F)} \rightarrow ^4T_1g_{(P)}$ (ν_2) (16970-13086) cm^{-1} and $^4T_1g_{(F)} \rightarrow ^4A_2g_{(p)}$ (ν_3) (25455-22200) cm^{-1}. In the $[Ni(L)(Phen)]Cl_2$ spectrum, three peaks were observed at 600 nm ,480nm and 300 nm. The first and second peaks, may belongs to the ν_1.The splitting of this peak may pointed out for the presence of some mixing of F-P spectroscopic terms then it would have been consistent with the orbital contribution if (t_2g^5) (eg^2) configuration which is in well magnetic moment value of 3.80 BM [17,18].

3.3. Determination of Mole-Ratio

The determination of mole ratios of primary to metal ions and secondary ligand, 1,10-phenathroline were estimated on the mole ratio method through variable concentrations of ligand to metal ions and recording the absorbance data verse the M/L on x-axis and the observed results from figure(3) it is concluded that the non-integer value intercept of mole ratio confirms the formation of nickel(II) complex on mixed secondary ligand of phenanthroline then supports the expected chemical skeletal of all structures.

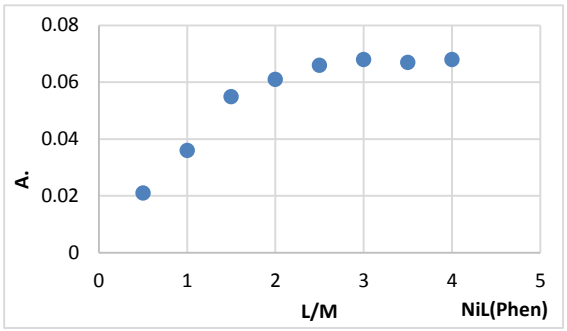


Figure (3). Mole ratio in nickel (II) complex at 400 nm

3.4. Thermal Gravimetric Analyses:

The thermal gravimetric analysis of nickel(II), C_2 and copper(II), C_3 complexes were determined their thermal stability in helium atmosphere and the thermo grams displayed steps of decomposition with expected losing of weight percent's. The TG-DTA thermo grams of C1 showed exothermic process at around (350-400) °C and (469-500) °C with 27.05 % and 28.62 % weight loss which definitely prove the breaking the M-L bonds of Ni-O and Ni-N=CH- ,2Cl and cleavages of 1,10-phenanthroline secondary ligand which confirms the thermal stability of complex with strong points of M-OH bonding and M-N=CH- moieties of primary ligand [3,22]. As well as the expected weight percent of metal oxide (NiO) and (CuO) were compared with the exothermic processing at 650-700) ^{0}C, Figure (4).

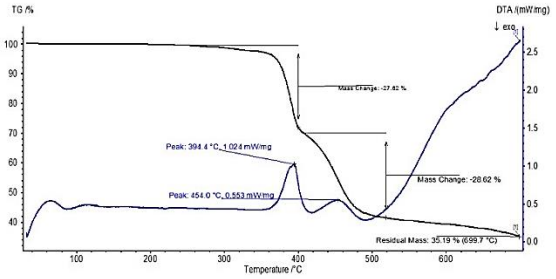


Figure (4). TG-DTA analysis of [NiL(Phen)] complex in He gas

3.5. Antimicrobial activity

The copper (II), $[CuL(Phen)Cl_2]$ showed good and varying inhibition activity against the test microbes. The MICs of $[NiL(Phen)]Cl_2$ showed less inhibition zones with (10-22) mm in compared with cobalt(II) complex and the free ligands due to the high polarity of complex and high electrolytic behabior of counter ions of chlorides anions which corrupted the passing

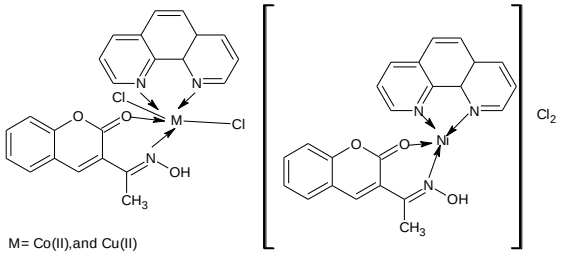
of biological part across the lipo layer of bacteria [18,19]. The MIC values of the ligand and complexes are recorded in the ranges from 10 to 30 ppm while those of *Ciprofloxacin* was 25 ppm. Although ciprofloxacin was more active than most of the oxime and complexes, it was apparent that copper(II) complex has MIC (25 µg/ml) comparable to those of ciprofloxacin[22,23].

Table (2). Inhibition zones (mm) for the primary and secondary ligands and its complexes in 10 ppm concentrations

Compound	*Staph aureus*	*Strep pneu*	*E.Coli*	*Kleb pneu*
L	35	12	13	19
(1,10-Phen)	27	24	82	23
CoL	38	40	45	78
NiL	18	24	30	13
CuL	24	35	65	90

4. Conclusion

New mixed ligands of 1,10-phanthroline and (Z)-3-(1-(hydroxyimino)ethyl)-2*H*-chromen-2-one and their ternary Co(II),Ni(II) and Cu(II) complexes were designed, synthesized, and physical studied. Based on FT-IR,NMR and ES-IMS spectral and analytical data, they adopt octahedral geometry around Co(II) and Cu(II) whereas the nickel(II) complex was adopted as low-spin square-planner geometry.The TG investigations were able to show the expected thermal stability in helium gas through the exothermic decomposition at around (365-700) ^{o}C temperature range.. Based on these observations, metal ions coordinate *via* coumarine oxime oxygen and azomethine nitrogen of Schiff bases (L), Scheme (3). The biological activity of the complexes solutions in 10 ppm concentration against two types of bacteria and fungi were greater than the free ligands in consideration DMSO as blank solution by diffusion method.



Scheme (3). Octaheral and square-planner geometry of complexes

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