Preparation and Identification of Mixed Ligand Complexes Derived From New Azo Quinoline Ligand

Jnan. A. Thabit
Abid Allah. M. Ali
College of Education for Women, University of Kufa
Raheem. T. Mahdi
College of Pharmacy, University of Kufa

ABSTRACT

This search included preparing of new mixed ligand complexes of Cobalt (II) and Nickel (II) and Copper (II) and Zinc (II) with new heterocyclic azo – quinoline ligand (HL_1) (P-TAQ) and ligand (HL_2)(2-Aminophenol), with the mole ratio metal: (HL_1): (HL_2) (1: 1: 1). The azo – quinoline ligand has been prepared in two steps, the first included preparation of the Schiff base (SB) (N-(1-(4-aminophenyl)ethylidene)-4-methylaniline) from condensation reaction of *P*-Toluidine with (*P*-Aminoacetophenone), while the second involved coupling of Schiff base's diazonium salt with (8-Hydroxyquinoline). The geometrical figures of prepared complexes, suggested depending upon the results of electronic spectra data, Infrared Spectra, magnetic susceptibility and molar conductivity.

INTRODUCTION

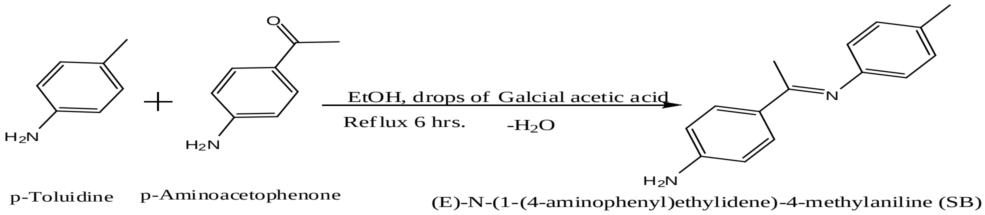
8-Hydroxyquinoline or (Oxine) has been widely used in deferent fields of chemistry(1-3). The nitrogen atom of the pyridine ring and oxygen atom of phenol ring, which present in Oxine molecule enable it to form stable five-membered metallic chelation ring with wide range of metal ions(4,5). The chemists also prepared various types of Oxine mixed ligand, by mixing it or one of its derivatives with other organic compounds(6-10). Azo quinolones are the most important quinolones derivatives(11), where used in solid phase extraction of Mercury(II) ion in water samples(12). Some of azo oxine derivatives used for extracting some heavy metal ions by cloud point extraction technics(13), while the others showed clear anticancer activity(14).

MATERIALS AND METHODS

All the used reagents and solvents had at least analytical grade . Melting points were determined by open capillary tube method and are uncorrected by using a Stuart melting point SMP10. Elemental analyses (C, H, N) were carried out using a C.H.N.O EA 3000 instrument by the Central Laboratory University of Kufa. The metal contents of the complexes was measured using atomic absorption technique by Shimadzu AA-6300. IR spectra were recorded on a Shimadzu 8000 FT-IR spectrophotometer in the (4000-400) cm^{-1} range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV spectrometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities were determined by faraday method at room temperature using Balance Magnetic (sherwood) apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant[19]. Molar conductance of the transition metal complexes were determined in ethanol using conductivity meter Alpha-800 at 25°C, the concentration of the solutions was (10^{-3} mol L^{-1}).

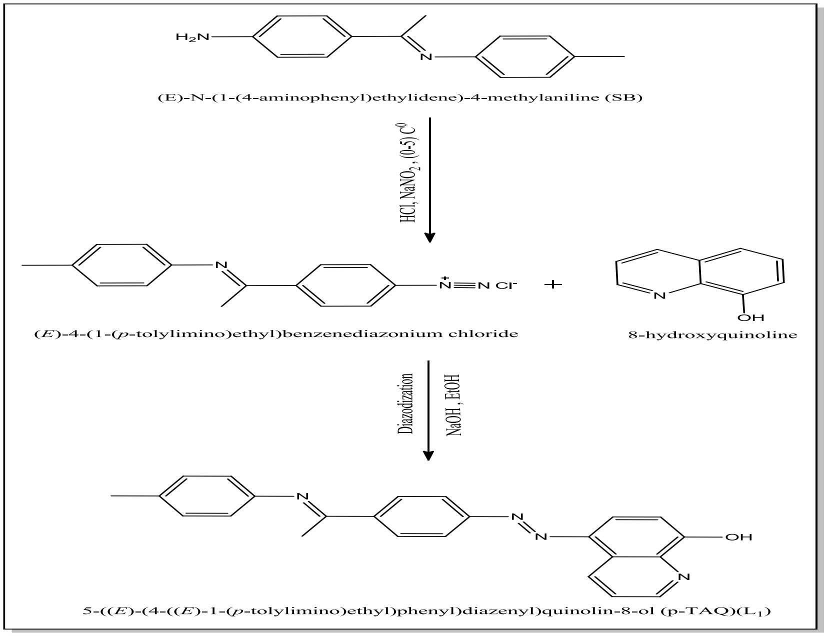
Preparation of the ligand (P-TAQ)(HL_1)

(P-TAQ)(HL_1) ligand was prepared according to the following. 4-Aminoacetophenone (1.35 g, 10 mmol) was dissolved in 20 mL of absolute ethanol and mixed with solution (1.07g, 10 mmol) from (p-Methylaninline) dissolved in 20 ml from same solvent and add 3 drops of glacial acetic acid (Scheme1) .The reaction mixture reflexed for 6 hrs. The solution left to cool, then poured into ice to obtain the product as pale yellow crystals(15) . This product filtered and dried and finally re-crystalized from hot ethanol .



Scheme (1): Synthetic rout of Schiff base (SB)

The second step included the azotization of Schiff base's derivative (SB), where (2.24 g, 10 mmol) of the Schiff base (SB) (N-(1-(4-aminophenyl) ethylidene)-4-methylaniline) dissolved in (20 ml) of alcohol ethanol followed by adding (3 ml) of (12N) hydrochloric acid and (20 ml) of distilled water, the mixture cooled to ambient temperature ($0-5C^0$) and added a solution (0.69 g, 10 mmol), of sodium nitrite dissolved in (10 ml) distilled water, gradually with stirring and note the lack of warming up($5C^0$), leave the solution to settle for 15 minutes to complete the process of diazotized. The diazonium added gradually with stirring to the solution (1.45 g, 10 mmol) of (8-Hydroxyquinoline), which dissolved in a mixture of (100 ml) of ethanol and (50 ml) of sodium hydroxide solution (10%) It was noted the solution brown discoloration left combination interaction to the next day and acidic function was modified by adding hydrochloric acid until (pH = 7) observed going down brown precipitate, left to stagnate and then filtrated it and wash with distilled water to remove salt sodium chloride output of the equalizer, and after making sure of the dry salt in the air and re-crystalized from the hot ethanol. Collected the precipitate and dry in electric oven under (80 C^0) for 24 hours.



Preparation of complexes

Addition of ethanolic solution of azo – quinoline ligand (HL1) (P-TAQ) and ligand (HL_2)(2-Aminophenol) to an aqueous solution of the hydrated metal chloride Co(II) and Ni(II) and Cu(II) and Zn(II) in (1: 1: 1) (metal: ligand: ligand) molar ratios. After stirring for (30 min), colored precipitates formed at room temperature, the rustling solids were filtered off, washed with hot ethanol to remove any traces of the unreacted starting materials dried and recrystallized from ethanol and dried at 90°C.

RESULTS AND DISSCUSION

Identification of ligand and its metal complexes

The azo-quinoline ligand was brown powder, but the chelates complexes of this ligand vary in color depended on metal ions. The experimental results of the elemental analysis of the prepared ligand and its metal chelates are in good agreement with theoretical values. The elemental analysis of the complexes indicate that the metal-ligand ratios were (1: 1:

1) chelate complexes. The ligand and its complexes were insoluble in water but soluble in most organic solvents such as methanol, ethanol, acetone, chloroform, and pyridine giving stable solutions at room temperature. The synthesized ligand and its complexes were soluble in water giving stable solutions at room temperature. However, some physical and analytical data given in Table.1.

Table-1: Some physical and analytical data of the ligand and its complexes

Compound	**Formula**	**m.p. °C**	**Yield%**	**Color**	**Found (*calc.*) %)**			
					C	**H**	**N**	**M**
(HL_1)	$C_{24}H_{20}N_4O$	217	78	Brown	75.70 (75.76)	5.25 (5.29)	14.71 (14.72)	----
(HL_2)	C_6H_7NO	170-175	---	Pale Yellow	----	----	----	----
(C_1)	$[Co(C_{30}H_{29}N_5O_4]$	59-61	80	Brown	61.81 (61.86)	4.97 (5.53)	12.01 (12.02)	10.11 (10.89)
(C_2)	$[Ni(C_{30}H_{29}N_5O_4]$	>300	82	Dark Purple	61.83 (61.89)	4.98 (5.02)	12.02 (12.02)	10.08 (11.54)
(C_3)	$[Cu(C_{30}H_{29}N_5O_4]$	>300	76	Brown	61.32 (61.37)	4.94 (4.97)	11.92 (11.93)	10.82 (11.07)
(C_4)	$[Zn(C_{30}H_{25}N_5O_2]$	147-150	78	Brown	65.11 (65.17)	4.52 (4.55)	12.66 (12.66)	11.82 (10.77)

Infrared spectra

The mode of bonding between the azo-quinoline ligand and the titled metal ions was elucidated by examining the IR spectra of the metal complexes in comparison to those of the free ligand. The stretching vibrations of (O─H) bond, which appear in the IR spectra of (HL_1) and (HL_2) at 3275 cm^{-1} and (2500-3200) cm^{-1}, respectively, disappeared in all mixed ligands complexes spectra(16,17), also the stretching vibrations of $v(C=N)$ for (HL_1) and $v(-NH_2)$ for (HL_2) which observed at 1585 cm^{-1} and (3337 cm^{-1}), (3306 cm^{-1}), respectively, suffered from noticed changes in position and or shape. All these, indicated that azo-quinoline ligand attached to assign metal ions via azomethine and hydroxyl groups after removing the proton of last one(17,18), also the these results proved that (HL_2) attached to assign metal ions through amino and hydroxyl groups after removing the proton of the last one. The IR spectra of (C_1-C_3) complexes showed a broad bands at the frequencies (3294, 3404, 3385) cm^{-1}, respectively, assigned to the stretching vibrations of (O-H) bond of the coordinated water molecule(20,21). The spectra of all mixed ligand complexes revealed new bands at the frequencies (459-431) cm^{-1} and (569-588) cm^{-1} , which attributed to the stretching vibrations of (M-O) and (M-

N) bonds, respectively(22,23). The Table (2), shows IR data of important functional groups in two ligands with their mixed complexes.

Table (2): IR data of (HL_1), (HL_2) and (C_1-C_4) complexes

Comp.	***v*(O-H)**	***v(N-H₂)***	***v(C=N)Imin. v(C=N)Qxin.***	***v*$_{as}$(C=O) *v*$_{s}$(C=O)**	***v(C-O)L₂. v(C=N)Qxin.***	***v*(M-O) *v*(M-N)**
(HL_1)	3275	---	1674, 1585	---	1162	---
(HL_2)	2500- 3200	3373, 3306	---	---	1267	---
(C_1)	---	3294, ---	1672, 1585	---	(1502) (1138)	588 431
(C_2)	---	3404, 3379	1656, 1600	---	1263 1136	569 445
(C_3)	---	3385, 3167	1668, 1570	---	1261 (1178)	570 459
(C_4)	---	3454, 3308	1652, 1591	---	1263 (1174)	581 431

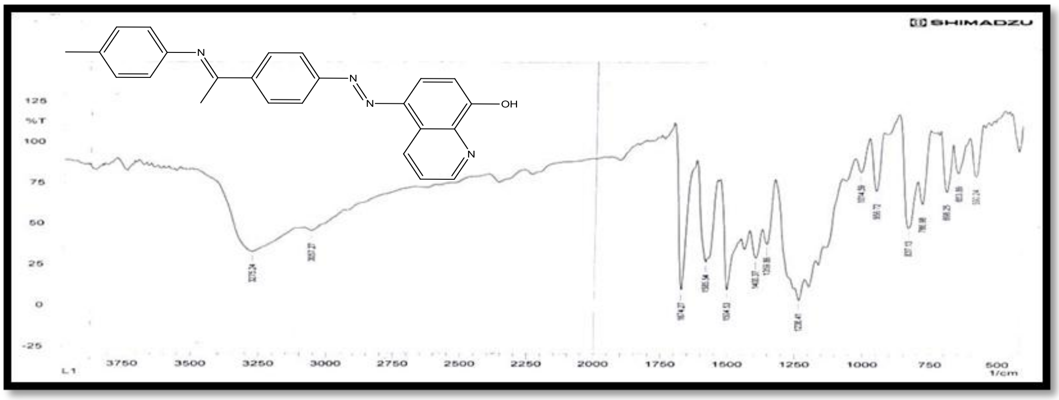


Fig.(1): The infrared spectrum of ligand (P-TAQ)(HL_1)

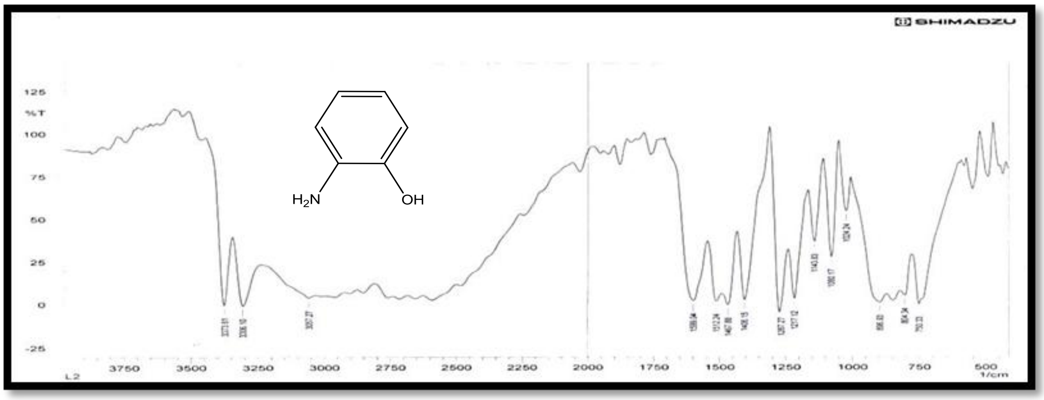


Fig.-2: The infrared spectrum of ligand (*o*-Aminophenol) (HL_2)

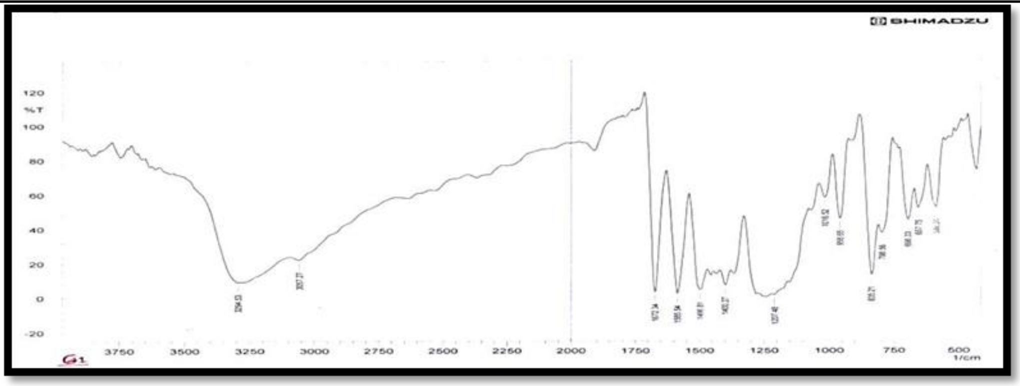


Fig.(3): The infrared spectrum of the complex (C1)

Magnetic Measurement and Electronic Spectra

The spectral data and the magnetic moment of prepared complexes are listed in Table (3). The magnetic moment of the Co(II) (C_1) and Ni(II) (C_2) complex have been found to be (5.2 B.M) and (2.93 B.M), respectively, which confirm the high spin characters of this complexes(24). The Cu(II) (C_3) complex shows low magnetic moment value (1.68 B.M), when compared with spin only value (1.73 B.M)(24) .The low value may be assigned to experimental error. The magnetic moment of Zn(II) (C_4) at room temperature was found to be (0.0 B.M), as a result of presence ten electrons in 3d orbital. The electronic spectra of four complexes (C_1-C_4) in ethanol solution, revealed absorption peaks at (206, 264)nm, (207, 265)nm (204, 241)nm and (206, 242, 271), respectively assigned to ($\pi \rightarrow \pi^*$) transitions for aromatic rings(25,26) The peak related to ($n \rightarrow \pi^*$) transition of (HL_1), which observed at (376 nm), absent in spectra of complexes, this explained on the bases of stabilizes of non-bonding loin pair of azomethine group nitrogen atom of the ring as a result of donation of this non-bonding loin pair to metal ion through the coordination(27). The spectra of (C_1), (C_2) (C_3) and (C_4) complexes exhibited new absorption peaks at (477 nm), (484 nm), (409 nm) and (504 nm), respectively, which are assigned to the (CT) transitions(28,29). The electronic spectrum of (C_3) displays three new peaks at (347 nm), (455 nm) and (492 nm) which are assigned respectively to ${}^2B_1g \rightarrow {}^2Eg$, ${}^2B_1g \rightarrow {}^2B_2g$ and ${}^2B_1g \rightarrow {}^2A_1g$, which confirm the distorted geometry around C(II) ion(30,31).

Table.-4: Electronic spectra, conductivity and magnetic moment of complexes

Compound symbol **Color in (Solid State) (Ethanol Solution)**	***λ_{max} nm ($\bar{\upsilon}$ cm^{-1})***	***Assignment***	***Conductivity*** S. cm^2 .mol^{-1}	**μ_{eff} B.M**	***Geometry***
C_1 (Brown) (Brown)	206 (48544) 264 (37879) 321 (31153)	($\pi\rightarrow\pi^*$) ($n\rightarrow\pi^*$) (CT)	13.73	5.2	O.h
C_2 (Dark Purple) (Purple)	207 (48309) 265 (37736) 307 (32573) 484 (20661)	($\pi\rightarrow\pi^*$) ($\pi\rightarrow\pi^*$) ($n\rightarrow\pi^*$) (CT)	11.95	2.93	O.h
C_3 (Brown) (Brown)	204 (49020) 241 (41494) 409 (24450) 437 (22883) 455 (21978) 492 (20325)	($\pi\rightarrow\pi^*$) ($\pi\rightarrow\pi^*$) ($n\rightarrow\pi^*$) $^2B_1g\rightarrow{}^2Eg$ $^2B_1g\rightarrow{}^2B_2g$ $^2B_1g\rightarrow{}^2A_1g$	7.89	1.68	O.h
C_4 (Brown) (Brown)	206 (48544) 242 (41322) 271 (36900)	Intraligand ($\pi\rightarrow\pi^*$)	9.88	Dia.	**T.h**
	317 (31546) 390 (25641)	($n\rightarrow\pi^*$)			
	504 (19841)	(CT)			

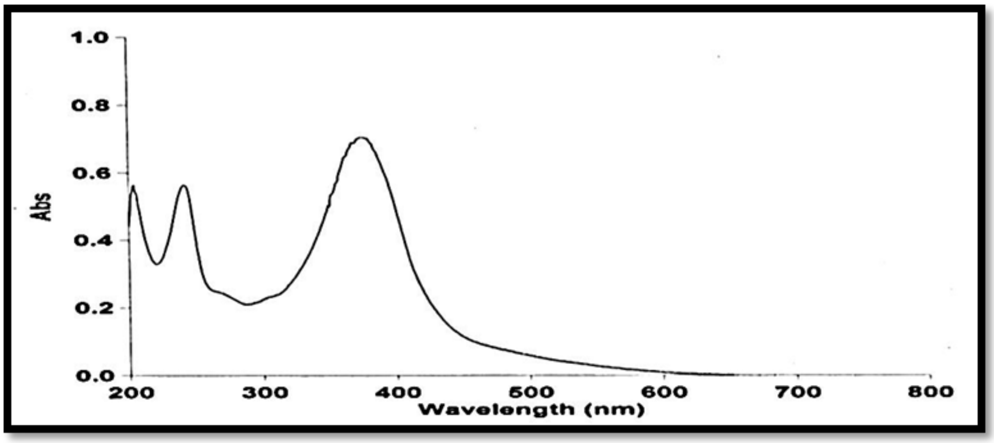


Fig.(4):Spectrum UV-visible ligand (HL_1) in ethanol

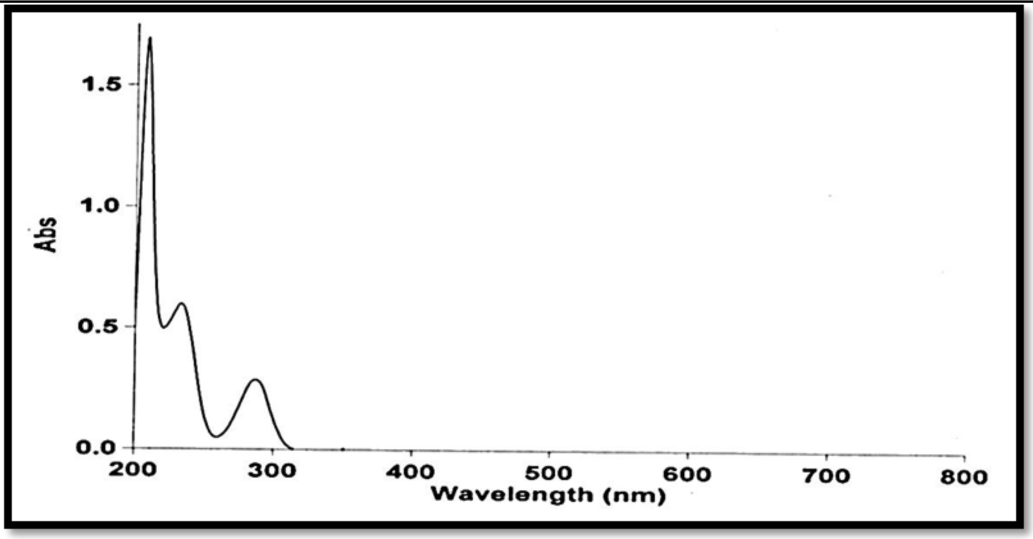


Fig.(5): Spectrum UV-visible ligand (HL_2) in ethanol

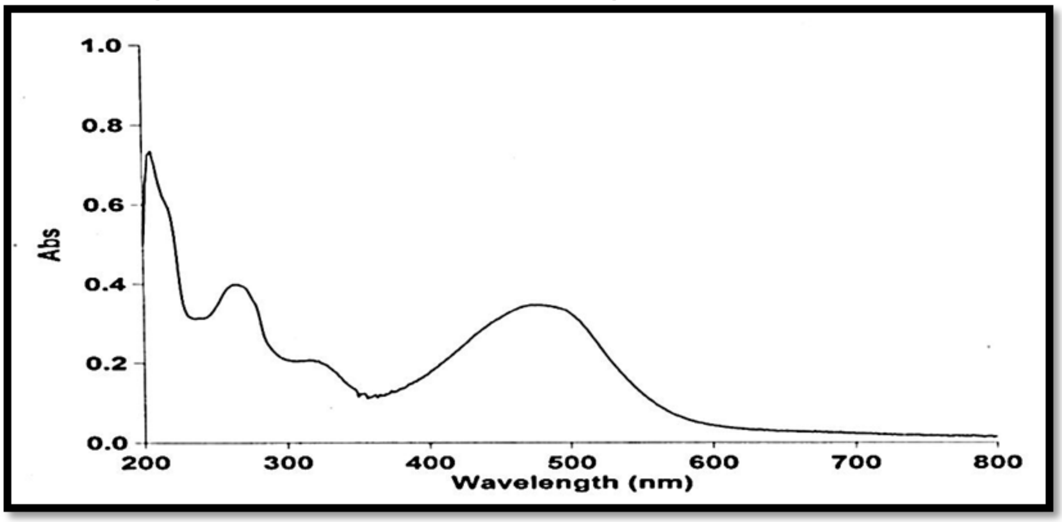


Fig.(6): Spectrum UV-visible for complex(C_1) in ethanol

Conductivity Measurement

The values of the complexes (C_1) to (C_4) in ethanol were within the range (9.88-13.73) S. cm^2. mol^{-1}, indicated the non-electrolyte nature[(32)] of these complexes.

CONCLUSIONS

The spectral, Spectrophotometric and magnetic studies of the prepared mixed ligands complexes of two ligands reveal, that Co(II)and Ni(II) and Cu(II) metal complexes are having octahedral geometry and the (metal : ligand: ligand) ratio is 1:1:1 . But Zn(II) metal complex is having tetrahedral geometry and same ratio . The ligand can be good analytical reagent for some metal ions. According to the above data the structural formula of metal complexes may be proposed in Figs.

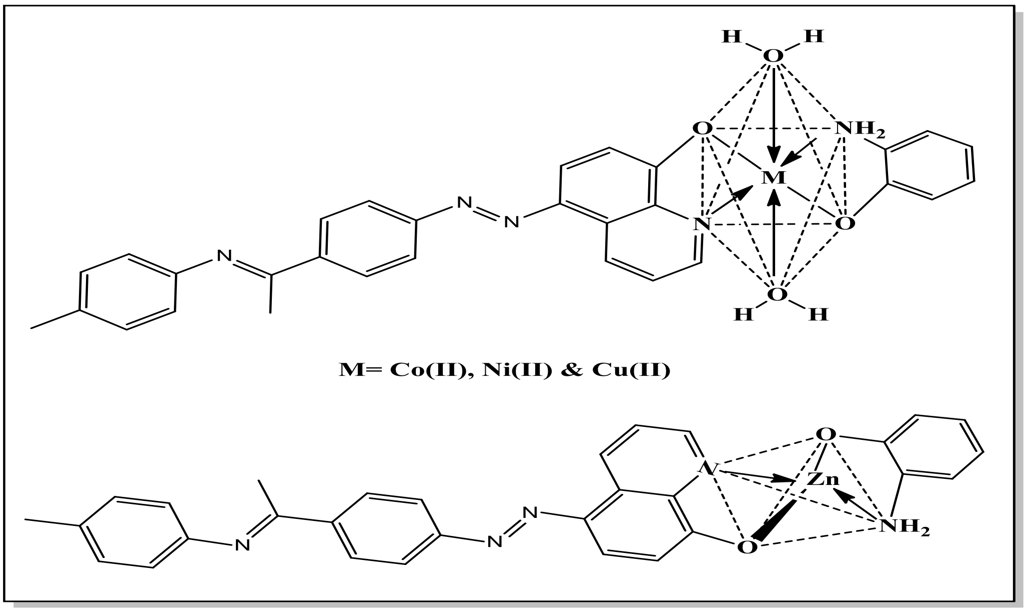


Fig.(6): The Stereochemistry of mixed ligands complexes (C_1-C_4)

REFERENCES

1. G. A. Shar and G. A. Soomro;" ***J. Chem. Soc. Pakis***.", 27, 5, 471-475, (***2005***).
2. Z. A-A Khammas, and A. A. Ghali;" ***Iraqi National Journal of Chemistry***",49, 25-37, (***2013***).
3. V. S. Shivankar, S. P. Yadav and N. V. Thakkar;" ***IOSR Journal of Applied Chemistry***", 3(6), 31-39, (***2013***).
4. J. Marthinus;" ***Ph.D. Thesis***", University of the Free State, (**2008**).
5. Leipoldt, J. G., Basson, S.S. and Dennis, C.R.;" ***Inorg. Chim. Acta.***", 50, 121, (***1981***).
6. Y. Malgher, R. C. Prabhu and R. W. Raut;" ***Acta Poloniae Pharmaceutica ñ Drug Research***", 66, 1, 45-50, (***2009***).
7. S. S. Patil, G. A. Thakur and M. M. Shaikh;" ***International Scholarly Research Network***", (***2011***).
8. A. S. Bodkhe, S. S. Patil and M. M. Shaikh;" ***Acta Poloniae Pharmaceutica - Drug Research***", 69, 5, 871-877, (***2012***).
9. Sreekanth B., Gopinath S.M. and Sridhara V.;" ***Research Journal of Pharmaceutical, Biological and Chemical Sciences***", 4, 4, 217-225, (***2013***).
10. Ammar J. Alabdali and Farah M. Ibrahim;" ***IOSR Journal of Applied Chemistry***", 6, 6, 60-63, (***2014***).
11. Huges, D. L. and Truter, M. R. J.;" ***Chem. Soc. Dalton Trans***.", 520, (***1979***).
12. M. Daye, B. Ouddane and M. Hamzeh;" ***The Scientific World Journal***", (***2013***).
13. Z. A-A Khammas, and A. A. Ghali;" ***Iraqi National Journal of Chemistry***",49, 25-37, (***2013***).
14. A. Pretorius;" ***Msc. thesis***", University of Pretoria (***2011***).
15 . A. R. H. Al-Muraabi;" ***Msc.thesis***", Kufa University, (***2009***).
16 . A. A. Osunlaja, N. P. Ndahi and J. A. Ameh," ***African Journal of Biotechnology***", 8 (1), 4-11, (***2009***).
17 . D. S. Wankhede, S. Hussain and O. Shankarrao;" ***Der Chemica Sinica***", 4(5), 79-85, (***2013***).
18 . S. S. Patil, G. A. Thakur and M. M. Shaikh;" ***International Scholarly Research Network***", (***2011***).
19 . Tank M.F. and Acharya G.D.;" ***Universal Journal of Pharmacy***", 2(6), 78-82, (***2013***).
20 . Ketan B. Patel, Raksha B.Patel, and Kiran S. Nimavat;" ***Der Pharmacia Sinica***". 3 (4):501-506, (***2012***).

21 . Tank M.F. and Acharya G.D.;" ***Universal Journal of Pharmacy***", 2(6), 78-82, (***2013***).

22 . D. S. Wankhede, S. Hussain and O. Shankarrao;" ***Der Chemica Sinica***", 4(5), 79-85, (***2013***).

23 . Y. MALGHE, R. C. PRABHU and R. W. RAUT;" ***Acta Poloniae Pharmaceutica ñ Drug Research***", 66, 1, 45-50, (***2009***).

24 . A. P. Mishra, R. K. Mishra;" ***J. Serb. Chem. Soc***.", 74(5) 523-535 (***2009***).

25 .T. H. Al-Noor, K. F. Ali, A. J. Jarad and A. S. kindeel;" **Chemistry and Materials Research**", 3, 3, (***2013***).

26 . T. H. Al-Noor , A. J. Jarad and A. O. Hussein;" ***Chemistry and Materials Research***", 6, 3, (***2014***).

27 . P. E. Aranha, M. P. dos Santos;" ***Polyhedron***" 26 (***2007***) 1373–1382.

28 . G. S. Kurdekar, S. M. Puttanagouda;" ***Med Chem Res***" (***2011***) 20:421–429.

29 . D. Sakthilatha and R. Rajavel;" ",***Journal of Chemical and Pharmaceutical Research***", (***2013***), 5(1):57-63.

30 . N. S. Abdel-Kader and R. R. Mohamed; " ***Therm Anal Calorim***", (***2013***).

31 . C. Zhou, J. Wang;" ***Catal Lett***", (***2010***) 135:120–125.

32 .S. A. Kettle “***Coordination Compound***” Thomas Nelson and Sons,London, p.3, 186, 212 (***1975***).

الخلاصة

تضمن البحث تحضير معقدات كلابية لكل من الكوبلت (II) والنيكل (II) والنحاس (II) والخارصين(II) مع كل من ليكاند الآزوكوينولين ألجديد (HL_1)(P-TAQ) وليكاند (HL_2)(اورثوأمينوفينول) وبنسبة فلز:ليكاند:ليكاند (1:1:1) . حضر ليكاند الآزوكوينولين بخطوتين تضمنت الخطـوة الاولـى تحضير قاعدة شف (SB)N-(1- (4- أمينو فنيل) أثليدين) مثيل أنلين من تفاعل تكثيفي بين البارا أمينو أسيتوفينون وما يكافئـها مـوليـا (1:1) من الـبارا تلويدين وفي الثانية تم إزواج ملح الديازونيوم لقاعدة الشف (SB) مع المركب 8-هيدروكسي كوينولين. أما ألأشكال الفراغية لهذه المعقدات فقد تم أقتراحها بالأستناد ألى معطيات التحليل الدقيق للعناصر وقياسات الحساسية المغناطيسية وألتوصيل الكهربائي المولاري وأطياف ألأشعة تحت الحمراء والأطياف الألكترونية .