Synthesis and Spectral Study of Mixed Ligand Complexes of N, N-bis(4-nitro phenyl) Malonyl Dihydrazide and 1, 10-Phenanthroline with Cr(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Ions

Enaam Majeed Rasheed, Sarab Mahdi Saleh and Sinan Madhat Mohammed
Al-Mustansiriyah University, College of Science, Department of Chemistry

Received 11 June 2013 ; Accepted 21 October 2013

Abstract

Tetradentate macrocyclic ligand (L) having nitrogen and oxygen atoms was prepared by condensation of the diethyl malonate with 4-nitro phenyl hydrazine in ethanol. An ethanolic solution of ligand (L) and an ethanolic solution of 1, 10-phenanthroline were reacted with ethanolic solution of metal salts to give complexes with the general formula [M(L)(phen)]X, where L=N,N-bis(4-nitro phenyl) malonyl dihydrazide, phen= 1,10-phenanthroline and M= Cr(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The resulting product was solid, which have been characterized using FT-IR and UV-Vis spectroscopy. Elemental analysis have been performed using C.H.N and atomic absorption technique, the magnetic susceptibility and the conductivity have also, been measured. From these measurements, mixed structures of the complexes were proposed to be octahedral geometry and to study the coordination behavior and spectral.

Keywords: Synthesis, Tetradentate ligand, 1,10-phenanthroline, Mixed ligands complexes, Characterization.

Synthesis and Spectral Study of Mixed Ligand Complexes of N, N-bis (4-nitro phenyl) Malonyl Dihydrazide and 1, 10-Phenanthroline with Cr(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Ions

Enaam Majeed Rasheed, Sarab Mahdi Saleh and Sinan Madhat Mohammed

تحضير ودراسة طيفية لبعض معقدات العناصر الإنتقالية مع مزيج N،N-بس (4-نايتروفنيل) مالونيل ثنائي هيدرازيد و1،10-فينانثرولين

أنعام مجيد رشيد وسراب مهدي صالح وسنان مدحت محمد

الجامعة المستنصرية، كلية العلوم، قسم الكيمياء

الخلاصة

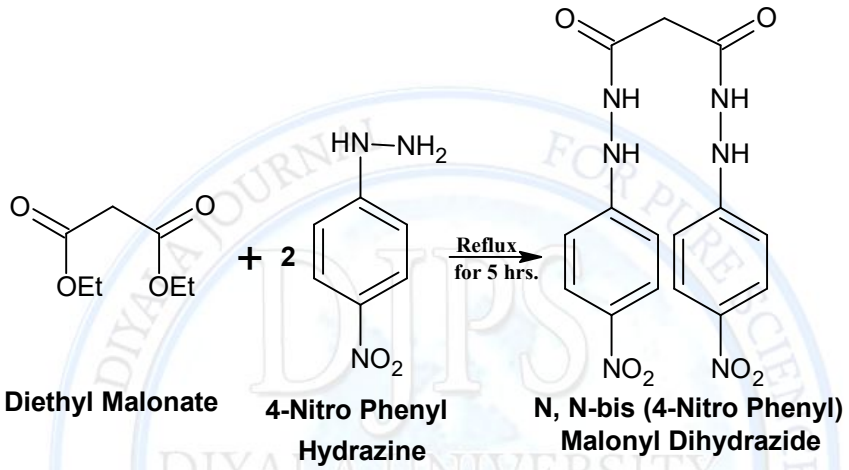
تم في هذا البحث تحضير ليكاند رباعي السن (L) من تكاثف ثنائي أثيل مالونيت مع 4-نايتروفنيل هيدرازين في مذيب الإيثانول. بعد ذلك تم تحضير معقدات الأيونات الفلزية لكل من الكروم (III) والكوبلت (II) والنيكل (II) والنحاس (II) والخارصين (II) والكادميوم (II) مع مزيج الليكاندين (L) و1،10-فينانثرولين. وجرى تشخيص الليكاند (L) والمعقدات المحضرة بإستعمال أطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية والمرئية بالإضافة إلى التحليل الدقيق للعناصر C.H.N وحساب نسبة الفلز بإستعمال تقنية الإمتصاص الذري اللهبي فضلا عن قياس الحساسية المغناطيسية للمعقدات في الحالة الصلبة وقياس التوصيلية المولارية الكهربائية لمحاليلها في مذيب ثنائي مثيل فورماميد بتركيز 10^{-3} مولاري.

الكلمات الدالة: تحضير ووليكاند رباعي السن و1،10-فينانثرولين ومعقدات لمزيج ليكاندين وتشخيص.

INTRODUCTION

Malonoyl dihydrazide compounds are important class of ligands in coordination chemistry and find extensive application in different fields [(1)]. Hydrazide derivatives are well known as polydentate ligands coordinating in neutral forms [(2)]. The transition metal complexes of hydrazone and its derivatives have been extensively examined due to wide application in various fields like anti-inflammatory and analgesic [(3)]. They have been investigated due to their diverse biological properties as antibacterial and antifungal [(4)]. The development of the field of bioinorganic chemistry has increased the interest in macrocyclic complexes containing oxygen and nitrogen atoms, since it has been recognized that many of these complexes may serve as models for analytical, industrial and medical applications [(5, 6)]. The present paper describes the preparation of N, N-bis (4-nitro phenyl) malonyl dihydrazide

produced from the reaction of the diethyl malonate and 4-nitro phenyl hydrazine to be used a ligand (L), that provide four potential donor sites to form complexes with some transition metal ions. The ligand (L), 1,10-phenanthroline and their complexes have been fully characterized and their structures were determined as out lined below, scheme (1).



Scheme (1): The synthesis route of the ligand

Experimental

All the chemicals and solvents used in this work were of analytical reagent grade (AR/Aldrich), including $CrCl_3.6H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2$, Diethyl malonate, 4-Nitro phenyl hydrazine, 1,10-phenanthroline, ethanol, DMF were obtained from Fluka, BDH and of the highest purity available.

Physical Measurements and Analysis :

Melting points were recorded on Gallen kamp melting point apparatus and were uncorrected. FT-IR spectra were recorded using FT-IR 8300 Shimadzu in the range of (4000-200)cm^{-1}. Samples were measured as CsI disc. Electronic spectra were obtained using UV-1650pc. Shimadzu spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3}M of the complex in ethanol as solvent. Micro analytical data for C.H.N were obtained using EA-034, mth. Metals in the complexes were

estimated by flame atomic absorption-Shimadzu AA, 670. Conductivity measurements were obtained using corning conductivity meter 220. These measurements were obtained in dimethyl formamide (DMF) as a solvent using concentration of 10^{-3}M at 25°C. Magnetic susceptibility measurements were obtained at 25°C on the solid state applying Faraday's method using Bruker BM6 instrument.

Preparation of the Ligand (L) N,N-bis (4-nitro phenyl) malonyl dihydrazide:

The ligand was prepared by the condensation of the diethyl malonate (1.74g, 0.01mole) with 4-nitro phenyl hydrazine (3.0g, 0.02 mole) in ethanol 25ml. the resulting mixture was then refluxed for 5 hrs., the solvent was removed and the solid product was collected and recrystalised from absolute ethanol. The ligand was characterized using elemental analysis and (FT-IR). The physical properties of the prepared ligand is described in table (1).

General Method for Preparation of the Complexes:

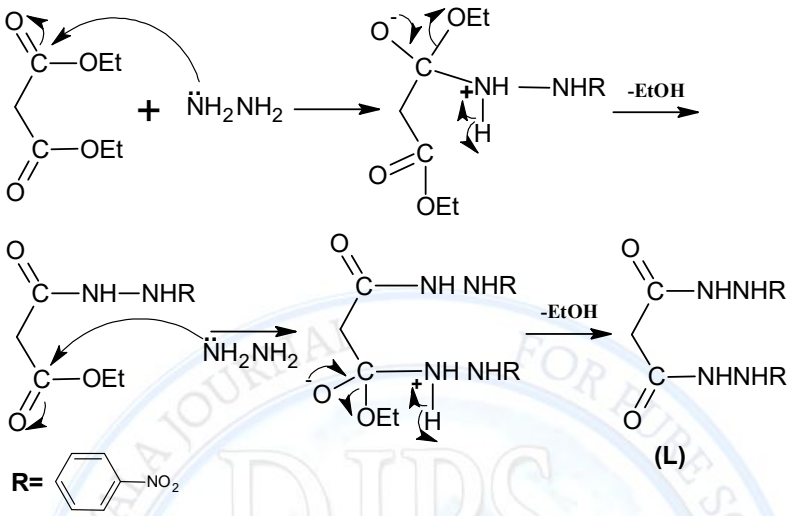
An ethanolic solution of ligand (L) (0.37g, 1 mmole) and an ethanolic solution of ligand 1, 10-phenanthroline (phen) (0.18g, 1 mmole) were added respectively to an ethanolic solution of each of the following metal ion salts (1mmole) [$CrCl_3.6H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $CdCl_2$] with stirring. The mixture was heated under reflux for two hours during this time aprecipitate was formed. The product was isolated by filtration, washed several times with hot ethanol then dried under vacuum. The physical data of the prepared complexes are shown in table 1.

RESULTS AND DISCUSSION

Reaction between one mole from diethyl malonate and two mole from 4-nitro phenyl hydrazine afforded the tetradentate macrocyclic ligand (L) in good yield this compound was formed through the following suggested mechanism, scheme 2.

Synthesis and Spectral Study of Mixed Ligand Complexes of N, N-bis (4-nitro phenyl) Malonyl Dihydrazide and 1, 10-Phenanthroline with Cr(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Ions

Enaam Majeed Rasheed, Sarab Mahdi Saleh and Sinan Madhat Mohammed



Scheme (2)

A- Elemental Analysis:

The analytical data of (L) and its metal complexes are given in table (1), which a satisfactory agreement with the calculated values.

The physical properties and data of the ligands (L) and (phen) with their metal complexes are given in table (1).

Table 1: The Physical data for (L) and its Metal Complexes

Compound	Color	M.p.°C	Yield%	%Elemental Analysis Found (Calc.)			
				M	C	H	N
$C_{15}H_{14}N_6O_6$(L)	Brownish red	110	85	-	48.46 (48.12)	3.41 (3.74)	22.29 (22.45)
[Cr(L)(phen)]Cl_3	Deep green	125	76	7.39 (7.29)	45.56 (45.47)	3.00 (3.08)	15.40 (15.71)
[Co(L)(phen)]Cl_2	Deep brown	212	69	8.70 (8.61)	47.16 (47.37)	3.42 (3.21)	16.56 (16.37)
[Ni(L)(phen)]Cl_2	Deep	220	72	8.51	47.45	3.30	16.31

	yellow			(8.58)	(47.39)	(3.21)	(16.38)
$[Cu(L)(phen)]Cl_2$	Deep red	210	80	9.38 (9.22)	47.36 (47.05)	3.29 (3.19)	16.33 (16.26)
$[Zn(L)(phen)]Cl_2$	Red	186	78	9.52 (9.47)	46.69 (46.92)	3.34 (3.18)	16.40 (16.22)
$[Cd(L)(phen)]Cl_2$	Pale red	194	66	15.13 (15.24)	43.82 (43.93)	2.76 (2.98)	15.35 (15.18)

B- Infrared Spectral Studies:

1- Infrared Spectra of Free Ligands:

The characteristic vibrations and assignments of ligand (L) and (phen) and their complexes as CsI disc are described in table 2.

The spectrum of ligand (L), figure (1), bands at 3319 cm^{-1} and 3064 cm^{-1}, could be attributed to υ_{N-H} and υ_{C-H} aromatic respectively. While the strong band at 1597 cm^{-1} which belongs to $\upsilon_{C=O}$ and the other bands belong to the $\upsilon_{C=C}$, υ_{C-N} and υ_{N-N} were found at 1512 cm^{-1}, 1276 cm^{-1} and 837 cm^{-1} respectively [7, 8].

In the spectrum of ligand (phen), it was noticed that the band at 3063 cm^{-1} which could be attributed to υ_{C-H} aromatic. The other bands are appeared at 1645 cm^{-1}, 1387 cm^{-1} and 1502 cm^{-1} which attributed to $\upsilon_{C=N}$, υ_{C-N} and $\upsilon_{C=C}$ respectively [9].

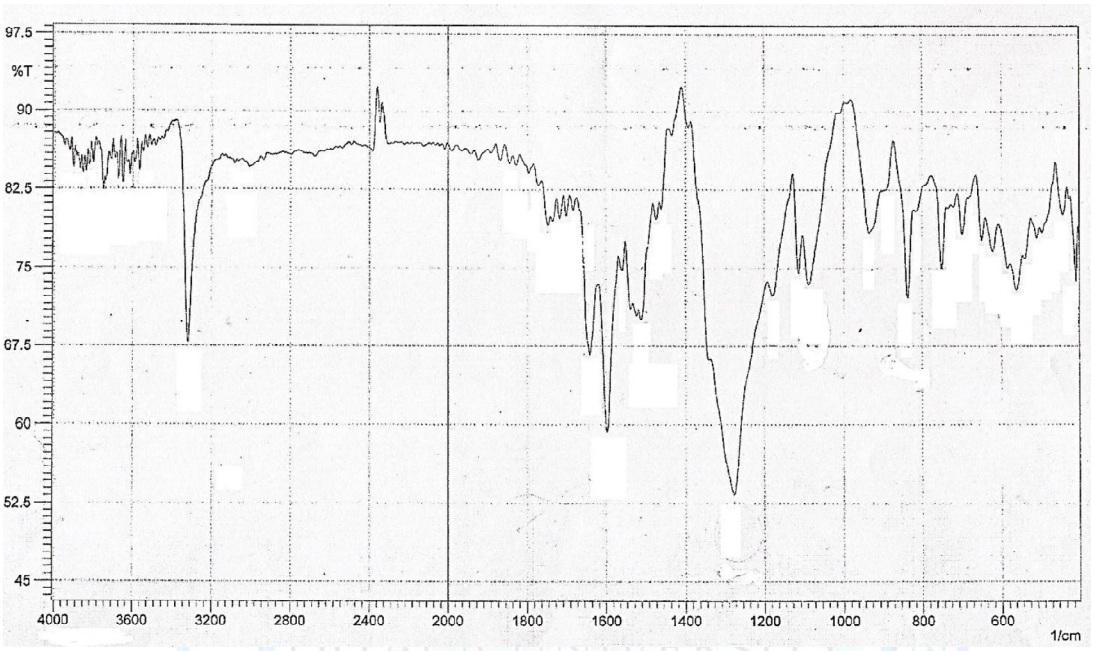


Figure (1): FT-IR Spectrum of Ligand (L)

2- Infrared Spectra of Complexes:

The infrared spectra of the prepared complexes exhibited $\upsilon_{C=O}$ in the range of 1585-1590 cm^{-1} which shows a shifting to the lower frequencies by 12-7 cm^{-1}, also exhibited υ_{N-N} in the range of 847-854 cm^{-1} which shows a shifting to the higher frequencies between 10-17 cm^{-1} but the bands of υ_{N-H} which was shifted to higher frequencies 3331-3406 cm^{-1} in compared with ligand (L), which indicated the coordination of ligand (L) with metal ions through the Oxygen and the Nitrogen atoms in their structures. The other bands are exhibited $\upsilon_{C=N}$ in the range of 1600-1630 cm^{-1} which shows a shifting to lower frequencies by 45-15 cm^{-1} in comparison with ligand (phen), it is which indicated the coordination of metal ions with the nitrogen atoms in the ligand 1,10-phenanthroline [10, 11]. Figure (2).

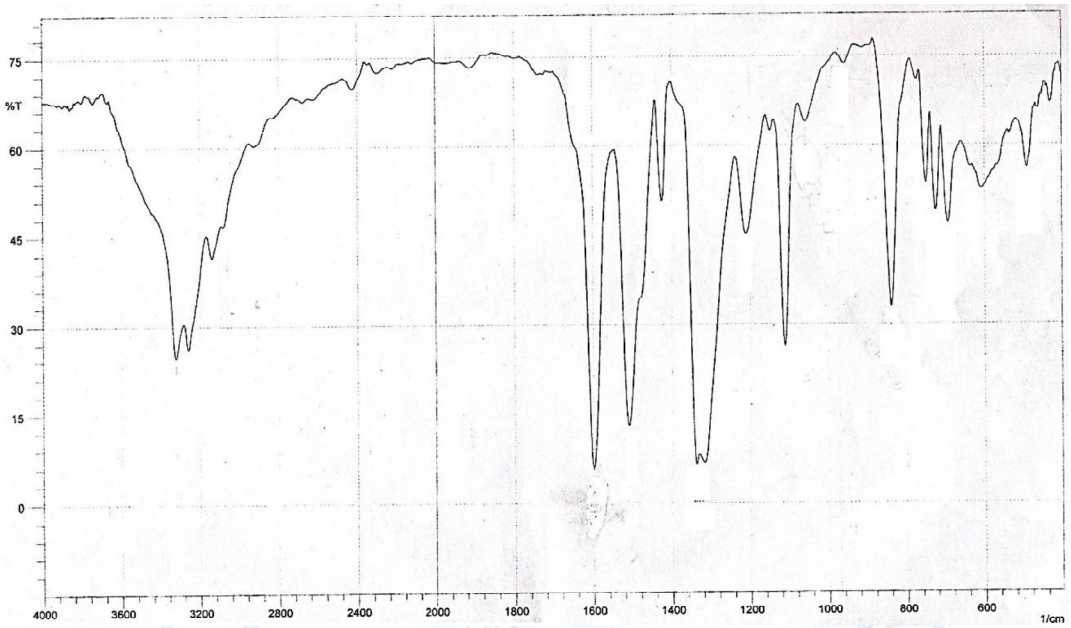


Figure (2): FT-IR Spectrum of Ni(II) Complex

3- M-Ligand Bond:

The infrared of prepared complexes have shown weak bands in the range of 501-536 cm^{-1} and 485-495 cm^{-1} which was attributed to the υ_{M-O} and υ_{M-N} respectively [12, 13].

Table 2: The Characteristic Bands of Infrared Spectra of the Ligands and their Complexes

Compound	$\upsilon_{C=O}$	υ_{N-H}	υ_{N-N}	$\upsilon_{C=N}$	υ_{M-N}	υ_{M-O}
$C_{15}H_{14}N_6O_6$(L)	1597	3319	837	-	-	-
$C_{12}H_8N_2$(phen)	-	-	-	1645	-	-
[Cr(L)(phen)]Cl_3	1590	3331	848	1627	495	536
[Co(L)(phen)]Cl_2	1588	3340	847	1630	490	520
[Ni(L)(phen)]Cl_2	1590	3381	850	1600	491	509
[Cu(L)(phen)]Cl_2	1585	3406	854	1626	488	501
[Zn(L)(phen)]Cl_2	1588	3380	850	1620	492	525
[Cd(L)(phen)]Cl_2	1586	3365	852	1625	485	515

C- Electronic Spectra, Magnetic Moment and Conductance Studies :

The UV spectrum of ligand (L), figure (3), showed intense bands at 237 nm and at 380 nm, which belong to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively[14], table (3).

The electronic spectra of the mixed ligand complexes were recorded for their solution in ethanol in the range (200-1100) nm, while the molar conductance was measured in dimethyl formamide (DMF) as a solvent.

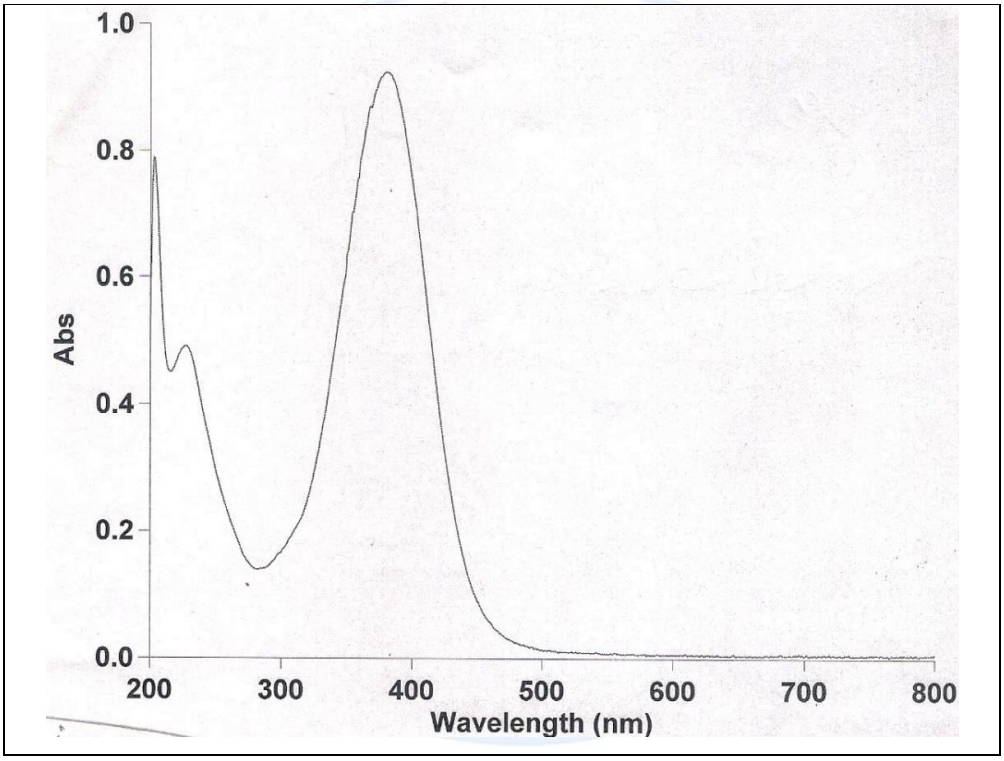


Figure (3): UV-Visible Spectrum of Ligand (L)

[Cr(L)(Phen)]Cl_3 Complex:

The Electronic spectrum of Cr(III) complex exhibits three transitions at 16528, 25380 and 38461 cm^{-1} assignable to $^4A_{2g(F)} \rightarrow {}^4T_{2g(F)}$, $^4A_{2g(F)} \rightarrow {}^4T_{1g(F)}$ and $^4A_{2g(F)} \rightarrow {}^4T_{1g(P)}$ transitions, respectively, suggesting octahedral environment around Cr(III) ion. The magnetic moment value was found to be 3.81 B.M, which is also agree well with the known values for Cr(III)

complex in octahedral geometry [15]. The conductance measurements indicate that complex was to be an electrolyte behavior, table (3).

[Co(L)(phen)]Cl_2 Complex: The electronic spectrum of Co(II) complex show three bands at 11876, 18518 and 22471 cm^{-1}. These bands assigned to $^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$, $^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$ and $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ transitions respectively characteristic of octahedral geometry [16]. The magnetic moment value was found to be 4.79 B.M., which agrees well with the expected value for a high-spin Co(II) ion in an octahedral environment[17]. Conductivity measurement in (DMF) showed an electrolyte behavior of the complex, table (3).

[Ni(L)(phen)]Cl_2 Complex: The electronic spectrum of Ni(II) complex exhibited three bands at 12987, 24691 and 26178 cm^{-1}, which are attributed to $^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$, $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ and $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)}$ transitions respectively indicating octahedral geometry [18]. The Ni(II) complex has a magnetic moment value of 3.42 B.M., which indicates that it is high spin octahedral geometry [19]. Conductivity measurement in (DMF) showed an electrolyte behavior of the complex, table (3).

[Cu(L)(phen)]Cl_2 Complex: The electronic spectrum of Cu(II) complex, figure (4), exhibited absorption band at 14084 cm^{-1} assignable to $^2Eg \rightarrow {}^2T_2g$ transition indicating octahedral geometry [20]. The Cu(II) complex showed magnetic moment 1.79 B.M. corresponds to one unpaired electron, which offers possibility of an octahedral geometry [21]. Conductivity measurement in (DMF) showed the complex to be electrolyte behavior, table (3).

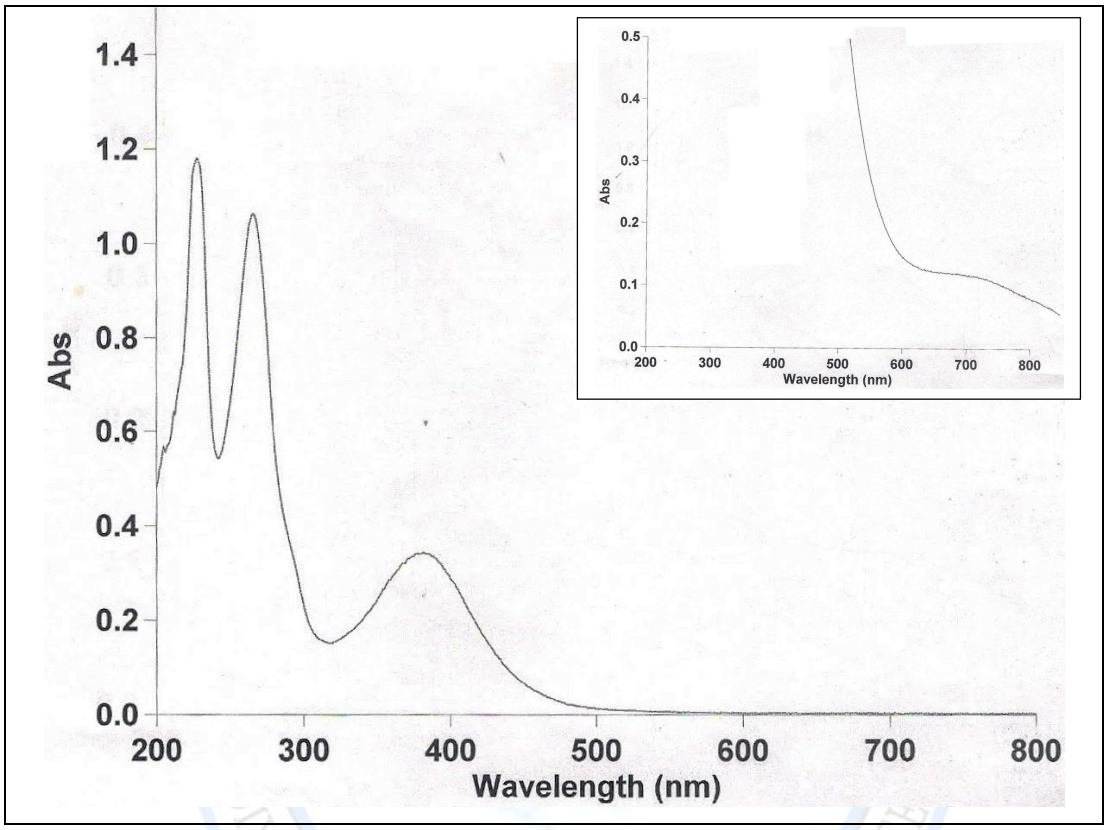


Figure 4: UV-Visible Spectrum of Cu(II) Complex

[Zn(L)(phen)]Cl_2 and [Cd(L)(phen)]Cl_2 Complexes: The electronic spectrum of Zn(II) and Cd(II) complexes show no absorption peak to range (380-1000) nm that are indicated no (d-d) electronic transition happened (d^{10}-system) in visible region, these are good results of Zn(II) and Cd(II) octahedral complexes [22, 23]. Conductivity measurement in (DMF) showed an electrolyte behavior of the complexes, table (3).

Table 3: Electronic Spectra, Conductance (in DMF) and Magnetic Moment (B.M) for (L) and Its Metal Complexes

Compound	λ_{max} nm	Bands cm^{-1}	Transitions	μeff B.M.	Molar Cond. $Ohm^{-1}.cm^2.mol^{-1}$	Suggested Structure
$C_{15}H_{14}N_6O_6$(L)	237 380	42194 26315	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	5.63	-
[Cr(L)(phen)]Cl_3	605 394 260	16528 25380 38461	$^4A_2g_{(F)} \rightarrow {}^4T_2g_{(F)}$ $^4A_2g_{(F)} \rightarrow {}^4T_1g_{(F)}$ $^4A_2g_{(F)} \rightarrow {}^4T_1g_{(P)}$	3.81	207	Octahedral
[Co(L)(phen)]Cl_2	842 540 445	11876 18518 22471	$^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$ $^4T_1g_{(F)} \rightarrow {}^4A_2g_{(F)}$ $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$	4.79	159	Octahedral
[Ni(L)(phen)]Cl_2	770 405 382	12987 24691 26178	$^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$ $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ $^3A_2g_{(F)} \rightarrow {}^3T_1g_{(P)}$	3.24	170	Octahedral
[Cu(L)(phen)]Cl_2	710	14084	$^2Eg \rightarrow {}^2T_2g$	1.79	150	Octahedral
[Zn(L)(phen)]Cl_2	281 365	35587 27397	Charge Transfer	Zero	162	Octahedral
[Cd(L)(phen)]Cl_2	275 390	36363 25641	Charge Transfer	Zero	160	Octahedral

CONCLUSION

In this paper new mixed ligand complexes containing ligand (L) and ligand (phen) with the general formula [M(L)(phen)]x, where L= N,N-bis(4-nitro phenyl) malonyl dihydrazide and phen= 1,10-phenanthroline were synthesized. According to the obtained results from elemental and spectral analysis as well as magnetic moment and the molar conductivity of the complexes in DMF solution were electrolyte and configurations were performed to coordinate the ligand N,N-bis(4-nitro phenyl) malonyl dihydrazide and 1,10-phenanthroline through the nitrogen and oxygen atoms. Therefore, from the presented results the complexes have octahedral configuration, figure (6).

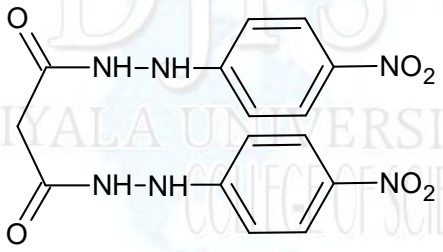


Figure (5): The Structure of Ligand (L)

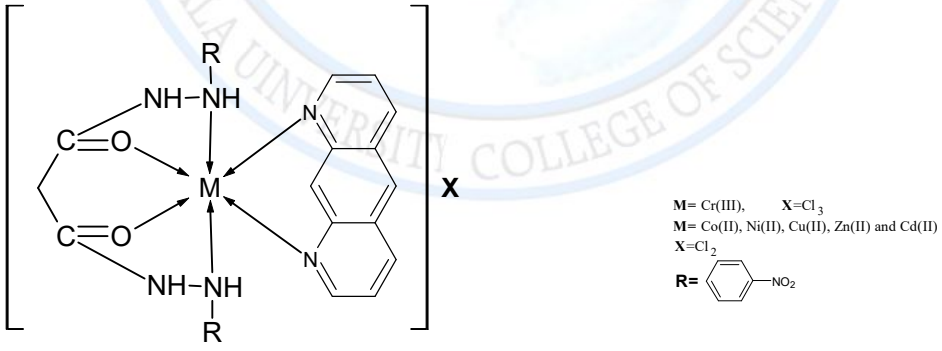


Figure (6): The Suggested Structure of the Complexes

REFERENCES

1. G. Prakash, K. C.H. Vinod and A. P. Sangamesh, "Synthesis, Spectral Characterization, in-Vitrmicrobiological Evaluation and Cytotoxic Activities of Novel Macrocyclic bis Hydrazone", Medicinal Chemistry, 1-8, 2009.
2. A. Kriza, L. V. Ababel and N. Cioatera, "Synthesis and Structural Studies of Complexes of Cu, Co, Ni and Zn with Isonicotinic Acid Hydrazide and Isonicotinic Acid (1-naphthyl Methylene) Hydrazide", J. Serb. Chem. Soc., 75(2) :229-242, 2010.
3. S. Sondhi, M. Dinodia and A. Kumar, "Synthesis, Anti-Inflammatory and Analgesic Activity Evaluation of Some Amidine and Hydrazone Derivatives", Bio. Org. Med. Chem., 14, 4657, 2006.
4. D. P. Singh, V Malik and R. Kumar, "Synthesis Characterization and Antibacterial and Antifungal Studies of Some Tetraazamacrocyclic Complexes", J. Serb. Chem. Soc., 75(10) :1369-1380, 2010.
5. K. Gloe, "Current Trends and Future Perspectives", 1st Ed. Springer, Amsterdam, 2005.
6. E. C. Constable, "Coordination Chemistry of Macrocyclic Compounds", 1st Ed., Oxford University Press, Oxford, 1999.
7. R. M. Silverstein, G. C. Bassler and T. G. Morrill, "Spectrometric Identification of Organic Compounds", 4th Ed., John-Wiley and Sons Inc., New York, London, 1981.
8. L. D. Rajib, B. Indrajit, G. Subhadra and M. Alko, "Synthesis and Reactivity of the Copper(II) Complexes of N-α-Acetophenyl-X-Salicylaldimines (α=4 or 3, X=H, 5-Br or 3-COOH) Molecular Structure of Bis (N-4-Acetophenyl-Salicylaldiminato) Copper(II)", Indian J. of Chemistry, 41A, 1380-1384, 2002.
9. N. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds", 4th Ed., Wiley, Inerscience, New York, 1986.
10. K. Nakamoto, "Infrared and Roman Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, 1997.

11. M. L. Vukadin, V. Ljijanas, M. S. Katalin and C. Valerijal, "Transition Metal Complexes with Thiosemicarbazide-Based Ligands Part 46-Synthesis and Physico-Chemical Characterization of Mixed Ligand Cobalt(II) Complexes with Salicylaldehyde Semi-Thiosemi and Isothiosemicarbazone and Pyridine", J. Serb. Chem. Soc., 68 :919-927, 2003.
12. S. Belaid, A. Landreau, S. Djebbar, O. Benali-Baitich and G. Bouet, "Synthesis, Characterization and Antifungal Activity of a Series of Manganese(II) and Copper(II) Complexes with Ligands Derived from Reduced N,N-O-Phenylene bis(Salicylideneimine)", J. Inorg. Biochem., 102 :63-69, 2008.
13. K. Dey and K. Chakraborty, "Synthesis and Characterization of Some Chromium(III) Complexes with N, S, O-Donor Thiohydrazones", Indian J. Chem., 39A, 1140, 2000.
14. A. E. Goeta, J. A. K. Howard, D. Maffeo, H. Puschmann, J. A. G. Williams and D. S. Yufit,"Copper(II) Complexes of the Isomeric Tetraazamacrocyclic Ligands 1,11- and 1,8-Bis-(2-Pyridylmethyl)-1,4,8,11-Tetraazacyclotetradecane and of the 1,4,8,11-Tetraazacyclotetradecane and of the 1,4,8,11-Tetraazacyclotetradecane-5-12-Dione Analogue at Neutral and Basic pH", J. Chem. Soc. Dalton Trans., 1873-1880, 2000.
15. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1984.
16. D. Sutton, "Electronic Spectra of Transition Metal Complexes", 1st Ed., Mc Graw-Hill Publishing, London, 1968.
17. X. W. Douglas, A. A. Nassar, F. A. El-Saied and M. I. Ayad, "Cobalt(II) Complexes with 2-Aminoacetophenone N(4)-Substituted Thiosemicarbazones", Trans. Met. Chem., 24, 617, 1999.
18. M. Tumer, D. Ekinci, F. Tumer and A. Bulut, "Synthesis, Characterization and Properties of Some Divalent Metal(II) Complexes: Their Electrochemical, Catalytic, Thermal and Antimicrobial Activity Studies", Spectrochimica Acta Part A:Molecular and Biomolecular Spectroscopy, 67(3-4) :916, 2007.
19. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley-Interscience, New York, 1998.

20. S. Chandra, D. Jain and A. K. Sharma, "Mass, Electronic, IR Spectroscopic and Thermal Studies of Bimetallic Copper(II) Complexes with Tetradentate Ligand, 1,4-Diformyl Piperazine Bis (Carbohydraone)", Spectrochim. Acta., Part A, 71, 1712-1719, 2009.
21. G. G. Mohammad and Z. H. A. El-Wahab, "Mixed Ligand Complexes of Bis (Phenylimine) Schiff Base Ligands Incorporating Pyridinium Moiety: Synthesis, Characterization and Antibacterial Activity", Spectrochim Acta Part A, (61) :1059, 2005.
22. M. S. Suresh and V. Prakash, "Preparation, Characterization and Microbiological Studies of Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} Chelates of Schiff Base Derived from Vanillin and Anthranilic Acid", Int. J. Phys. Sci., 5(9) :1443-1449, 2010.
23. O. W. Salawu and A. O. Abdulsalam, "Synthesis, Characterization and Biological Activities of Cd(II) Complexes with Hydrazide Ligands", Der Pharma Chemica., 3(4) :298-304, 2011.