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Synthesis, Structural and Spectroscopic Study of Complexes of Tetradentate Schiff Base Derived from MalonylDihydrazide with Cr(III), Mn(II), Co(II), Cu(II) and Zn(II) Ions

Abstract*-This paper describes the synthesis of a new derivative dihydro-3H-indol-3-ylidene propane dihydrazide [L], which have been obtained from the reaction between malonyl di-hydrazide and an ethanollic solution of isatin. Tetradentatemacrocyclic ligand [L] was characterized by (C.H.N), (FT-IR), (UV-Vis), and 1H.NMR.A series of the used metal complexes have been synthesized by the prepared ligand [L] reaction with some transition metal ions. The isolated complexes were Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) also characterized using different techniques such as (FT-IR), and (UV-Vis) spectroscopies, (C.H.N), flam atomic absorption in addition to the magnetic susceptibility and molar conductivity measurement. Al complexes were octahedral in geometry except for Zn (II) complex, which was tetrahedral.*

Keywords: *Tetradentate Ligand, Transition Metals, Spectroscopic Studies.*

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1. Introduction

Malonyldihydrazide and isatin compounds are important class of polydentate ligands in coordination chemistry and find extensive applications in different fields [1], also, the presence of imine group (−N=C<), which imports in elucidating the mechanism of transformation and rasemination reaction in biological system [2]. The transition metal complexes of hydazone and its derivatives have been extensively examined due to its wide applications ranging from antimicrobial [3], anti-tubercular, carbonic anhydras inhibitors, and anti-inflammatory [4]. The developments of the field of bioinorganic chemistry have increased the interest in macrocyclic complexes containing oxygen and nitrogen atoms, since it has been recognized that many of these complexes may have some applications in industry and medicine [5,6]. The present paper describes some of the new Schiff base [L] applications, which is derived from isatinreaction with malonyldihydrazide. Ligand [L] provides four sites that are potential donor and forms complexes with Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The ligand [L] and its complexes have been fully characterized.

2. Experimental

All the chemicals were used as received (from Fluka and BDH) and they were of highest purity available by using metal chloride salts ($CrCl_3.6H_2O$, $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.2H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$.

2. Synthesis of 1N,3N-bis[(3E)-2-oxo1,2-di hydro-3Hindol-3-ylidene]popanedihydrozide

I. Physical Measurement and Analysis

The carbon, hydrogen and nitrogen contents were determined on Cario-Erba 1108, C.H.N, elemental analyzer at Al-Bait University, Jorden. FT-IR spectra were recorded on Shimadzu FT-IR-8100 spectrometer at Al-Mustansiriyah University. H-NMR spectra of the ligand [L] were measured in d^6-DMSO solvent using TMS as internal standard on Bruker 300 MHz at Al-Bait University, Jordan. The electronic spectra were measured using (UV-1650) PC Shimadzu spectrophotometer at 25°C. The results were recorded by using (10^{-3}M) concentration of the complex in the absolute ethanol. Molar conduct -ivity (μs.cm^{-1}) of the complexes were recorded at 25◦C for (1×10^{-3}M) solution of the samples in DMF, using a coming conductivity meter (220). Magnetic susceptibility results were also obtained at 25°C at the solid state by applying Gouy balance at Al-Mustansiriyah University. Moreover, all melting points results were recorded on (Gallen Kamp melting apparatus), and left uncorrected.

1. Synthesis of Malonyldihydrazide

This compound was prepared according to the literature preparations [7-9].

Ligand [L] was prepared from warm ethanol reaction with malonyldihydrazide solution

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(0.01Mole, 1.32g) with isatin (0.02Mole, 2.9g). The mixture was then refluxed for 6hrs. Then filtered, washed with ethanol and dried under vacuum, (yield 75%).

3. Synthesis of Metal Complexes

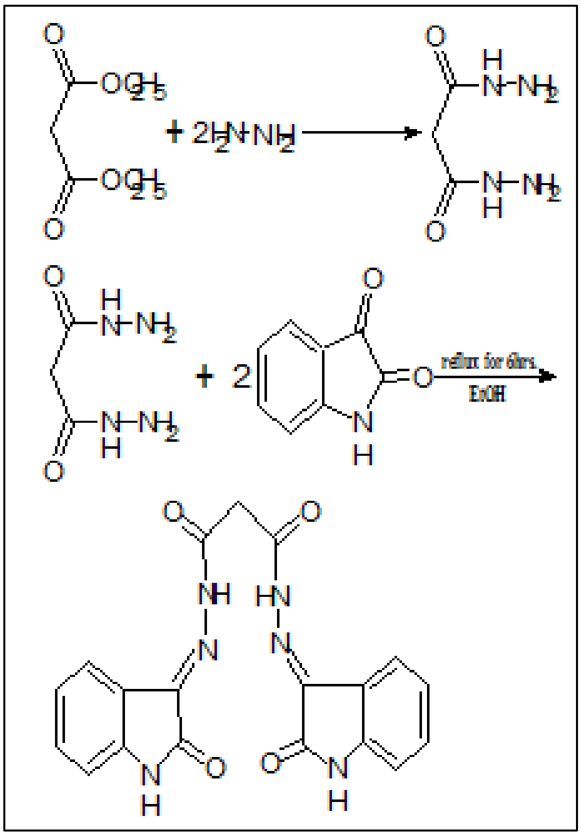
Ethanol solution (20ml) of metal chloride $CrCl_3.6H_2O$ (0.22g,1mmole), $MnCl_2.4H_2O$ (0.197g,1mmole),$CoCl_2.6H_2O$(0.237g,1mmole), $NiCl_2.6H_2O$ (0.237g, 1mmole), $CuCl_2.2H_2O$ (0.170g,1mmole), and $ZnCl_2$ (0.136g, 1mmole) were added with stirring to an ethanol solution of ligand (0.390g, 1mmole) and refluxed on water bath temperature for 2hrs., then the crude solid complexes were separated by filtration under suction, washed for several times with hot ethanol to afford colored purified metal complexes.

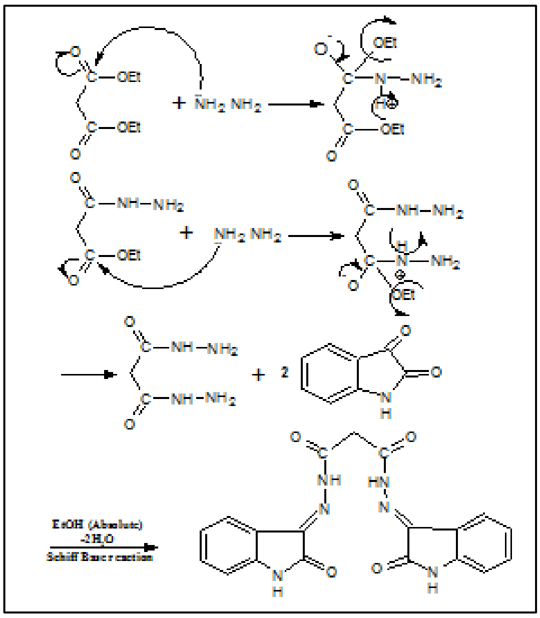
3. Results and Discussion

The reaction of one mole of malonyldihydrazide and two moles of isatin afforded the tetradentatemacrocyclic ligand [L] in good yield, scheme 1. The suggested mechanism of the formation of the ligand (L)can be shown in scheme 2.

I. Physical properties and micro elemental analysis

The physical properties and micro elemental analysis of the prepared ligand and its metal complexes are summarized in Table 1. Results are quite related to the suggested structural formula.





Scheme 1, 2: General Steps of Preparation of Ligand (L)

Table1:Ligand (L) and its Metal Complexes Physical and Analytical Data

Compound	Mol. Formula	Colour	M.P °C	Yield	%Elemental Analysis Found (Calc.)			
					M	C	H	N
$C_{19}H_{14}N_6O_4$	390	Light Green	203-205	75	-	58.35	3.32	21.52
						(58.46)	(3.59)	(21.54)
$[CrL(H_2O)_2]Cl_3$	584.5	Dark Green	235d*	70	9.022	39.22	3.21	14.13
					(8.896)	(39.01)	(3.08)	(14.37)
$[MnL(H_2O)_2]Cl_2$	551.9	Light Orange	166-168	65	10.242	41.00	3.43	15.12
					(9.947)	(41.31)	(3.26)	(15.22)
$[CoL(H_2O)_2]Cl_2$	555.9	Brown	220d*	73	10.233	41.32	3.30	15.22
					(10.595)	(41.01)	(3.23)	(15.11)
$[NiL(H_2O)_2]Cl_2$	555.7	Orange	210d*	76	10.952	41.21	3.22	15.00
					(10.563)	(41.03)	(3.24)	(15.12)
$[CuL(H_2O)_2]Cl_2$	560	Brown	146-148	80	11.40	40.03	3.00	15.21
					(11.250)	(40.71)	(3.21)	(15.00)
$[ZnL]Cl_2$	526.4	Light Green	190-192	76	12.424	40.41	3.18	14.55
					(12.021)	(40.54)	(3.20)	(15.94)

d*= decomposition

II.^{1}H-NMR Spectrum

^{1}H-NMR spectrum of the ligand in DMSO-d^6 solution was mentioned in addition to all experimental possible assignments [10]. Proton NMR spectrum showed peaks at 10.810ppm (4*H*, NH-C=O) 6.910-7.951 (m, 8*H*, Ar-H), 4.137-4.161ppm (s,-CH_2) [11]. The integration curves were used to calculate protons numbers and further details of the chemical shifts with their assignments can be found in Figure 1, which reveals the proposed structure of the ligand [L].

III. Infrared Spectra

The FT-IR provides very interesting information about the metal atom attached functional group nature. The free ligand [L] and its prepared metal complexes behave as a tetra dentate coordination with these ions of metal through the carbonyl oxygen and the nitrogen of azomethine group. FT-IR spectrum of free ligand band shows peculiar absorption at 1728cm^{-1} for υC=O in addition to a strong band in the 1612cm^{-1} region, due to υC=N which undergone to down shift in all spectra of metal complexes what indicates azomethine group nitrogen involvement in the coordination [12,13], as shown in Figure 2. Moreover, (–C=O) absorption negative shift gives a coordination significant investigation of the metal ions through carbonyl group oxygen atom [14]. Furthermore, the spectrum of each complex shows a weak to medium band in (530-619)cm^{-1}, and (420-474)cm^{-1} regions for (υM-N) and (υM-O) bands, respectively [15,16]. The spectrum of each complex except for Zn(II) complex exhibits a broad absorption band in (3412-3435)cm^{-1}regions that is attributed to (υO-H) of the coordinated water molecules and the coordinated water molecules O-H stretching [17,18]. Further details of the characteristic are shown in Figure 3 and Table 2.

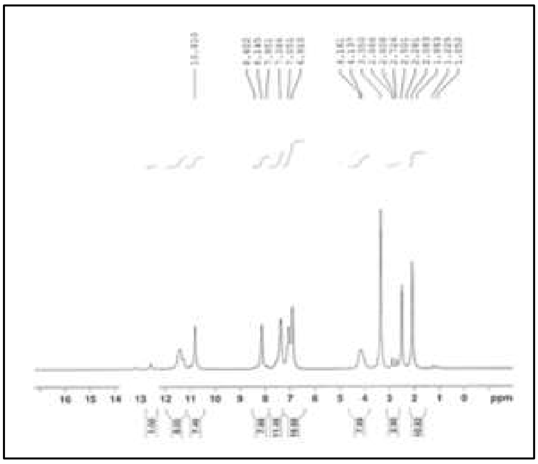


Figure 1:The ^{1}H-NMR Spectrum of the Ligand (L)

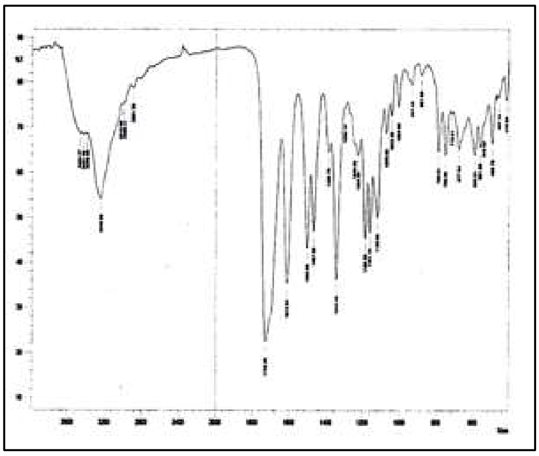


Figure 2: FT-IR Spectrum of the Ligand [L]

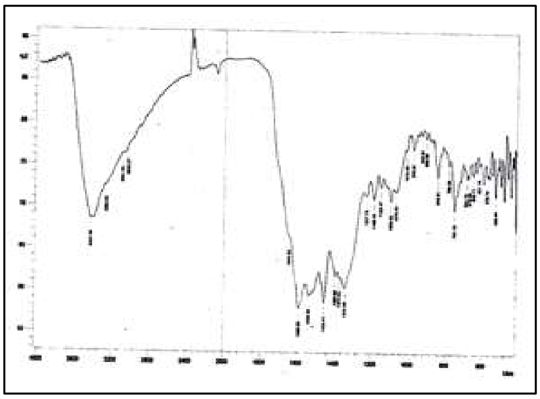


Figure 3: FT-IR Spectrum of Cu(II) Complex

Table 2: The Stretching Vibration Significant Frequencies (cm^{-1}) Situated in (L) and its Metal Complexes FT-IR spectra

Compound	υC=O	υC=N	M-N	M-O	υO-H
$C_{19}H_{14}N_6O_4$ [L]	1728	1612	-	-	-
$[Cr\,L\,(H_2O)_2]Cl_3$	(1693-1622)	1498	545	474	3412 br
$[MnL(H_2O)_2]Cl_2$	1616	1506	619	447	3429 br
$[CoL(H_2O)_2]Cl_2$	1680	1592	561	439	3435 br
$[Ni\,L\,(H_2O)_2]Cl_2$	(1651-1616)	1464	588	420	3419 br
$[CuL(H_2O)_2]Cl_2$	1645	1590	530	430	3431 br
$[Zn\,L]Cl_2$	1703	1502	619	470	-

IV. Electronic Spectra, Magnetic Susceptibility Measurements

The electronic spectroscopy is available tool for coordination chemists to obtain important information regarding structure of complexes.

The free ligand solution in ethanol (10^{-3}M) concentration showed high intensity absorption at (280, 320)nm, which are assigned to π→ π*, and n→π* respectively[19], Table 3, Figure 4.

The dark green chromium (III) complex gave three absorption bands that appeared at (15151, 18181, and 21739) cm^{-1} following octahedral field with [d^3] configuration. It was found that the effective magnetic moment at 25^{o}Cequals (3.79 B.M) which reveals an octahedral stereo chemistry of ligand around Cr(III) metal ion[20]. The prepared light orange Mn(II) complex showed two band at (16666,27777) cm^{-1} due to the transition $^6A_1g \xrightarrow{\upsilon_1} {}^4T_1g$, and $^6A_1g \xrightarrow{\upsilon_2} {}^4Eg_{(G)}, {}^4A_1g$ respectively, which associated withoctahedral Mn(II) complex spin-forbidden transition of high spin (5.08 B.M) [21]. The brown solution of cobalt(II) complex in the ethanol presented well resolved band at 172413cm^{-1} and 20408 cm^{-1} that maybe designated to $^4T_1g_{(F)} \rightarrow {}^4T_2g_{(F)}$, $^4T_1g_{(F)} \rightarrow {}^4T_1g_{(P)}$ transitions respectively, which confirm the high spin octahedral geometry for Co(II) ion [22].

Table 3: Ligand (L) and its Metal Complexes Electronic Spectrum, Molar Conductance in (DMF) and Magnetic Moments (B.M)

Compound	λmax nm	Bands Cm^{-1}	Transitions	μ_{eff}. B.M	Molar Cond. μs.cm^{-1}	Suggested Structure
$C_{19}H_{14}N_6O_4$ [L]	280 320	35714 31152	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
$[CrL(H_2O)_2]Cl_3$	660 550 460	15151 18181 21739	$^4A_2g \xrightarrow{\upsilon 1} {}^4T_2g$ $^4A_2g \xrightarrow{\upsilon 2} {}^4T_1g$ $^4A_2g \xrightarrow{\upsilon 3} {}^4T_1g(P)$	3.79	223	Octahedral
$[MnL(H_2O)_2]Cl_2$	600 360	16666 17777	$^6A_1g \xrightarrow{\upsilon 1} {}^4T_1g$ $^6A_1g \xrightarrow{\upsilon 2} {}^4Eg(G)$, ^4A_1g	5.08	155	Octahedral
$[CoL(H_2O)_2]Cl_2$	580 490 340	17241 20408 29411	$^4T_1g(F) \xrightarrow{\upsilon 1} {}^4T_2g(F)$ $^4T_1g(F) \xrightarrow{\upsilon 2} {}^4T_1g(P)$ $^4T_1g(F) \xrightarrow{\upsilon 2} {}^4A_1g$	4.05	132	Octahedral
$[NiL(H_2O)_2]Cl_2$	650 530 430	15384 18867 23255	$^3A_2g(F) \xrightarrow{\upsilon 1} {}^3T_2g(F)$ $^3A_2g(F) \xrightarrow{\upsilon 2} {}^3T_1g(F)$ $^3A_2g(F) \xrightarrow{\upsilon 3} {}^3T_1g(P)$	2.80	150	Octahedral
$[CuL(H_2O)_2]Cl_2$	620	16129	$^2Eg \rightarrow {}^2T_2g$	1.79	140	Octahedral
$[ZnL]Cl_2$	280 390	35714 25641	L.MCT L.MCT	0.0	130	Tetrahedral

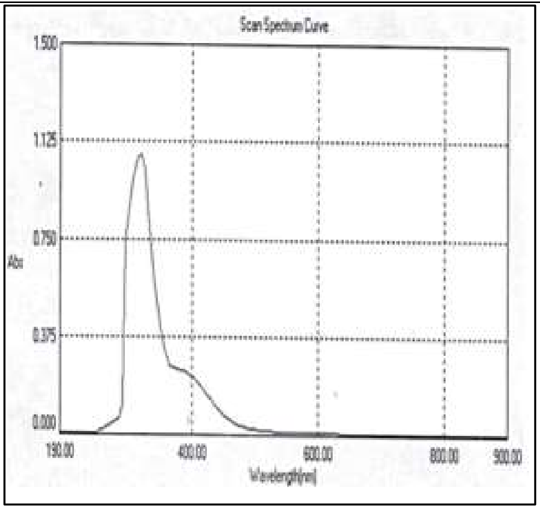


Figure 4: UV-Vis Spectrum of the Ligand[L]

The high intensity band at (29411cm^{-1}) has been allocated to the charge transfer from the metal to the ligand [23], which would support the high delocalization between the groups of C=O, and C=N with the ion of Co(II) that maybe referred to high covalence factor of Co-O and Co-Nb and in complex [22], with (4.05 B.M) magnetic moment for Co(II) complex in the solid state. The Ni(II) complex electronic spectrum exhibited three bands at(15384,18867,23255)cm^{-1}, which have been 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, that indicates an octahedral geometry [23]. Ni(II) complex magnetic moment value equals of (2.80)B.M, which confirmed its high spin octahedral geometry [24], Figure 5, Table 3.

Copper (II) complex electronic spectra in ethanol demonstrated a band that is low energy and weak at (16129) cm^{-1}with high intensity one at (26315)cm^{-1}, the visible region of the first band is typically expected for 10Dq, which corresponds to $^2Eg \rightarrow {}^2T_2g$ transition [25]. Moreover, the magnetic moment (1.79B.M) corresponds to one unpaired electron, which offers possibility of an octahedral geometry [26]. On the other hand, Zinc(II) complex showed two high intensity absorption band at 35714cm^{-1} , and 25641 cm^{-1} regions that are assigned to ligand field (L.MCT) transition [27], Table 3.

V. Molar Conductivity Measurements

The results of the molar conductance is (130-223)ohm^{-1}.cm^2.mol^{-1}for all complexes, that were carried out in DMF solvent, which indicates that all of the study complexes are (1:2) electrolytic nature [28, 29] and Cr(III) is (1:3).These results suggest that all of the study complexes are electrolytes, thereby showing the chloride ions in counter ion, Table3.

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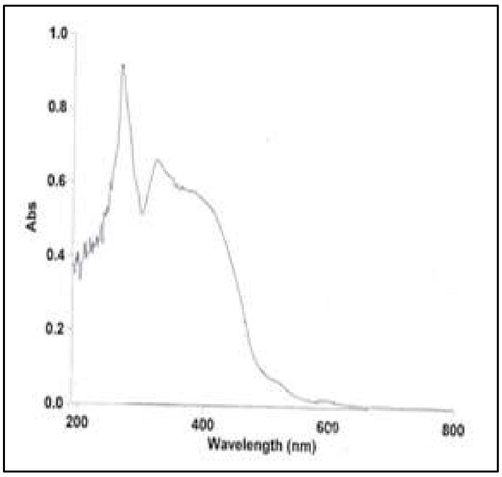

Figure 5: UV-Vis Spectrum of Ni(II) Complex

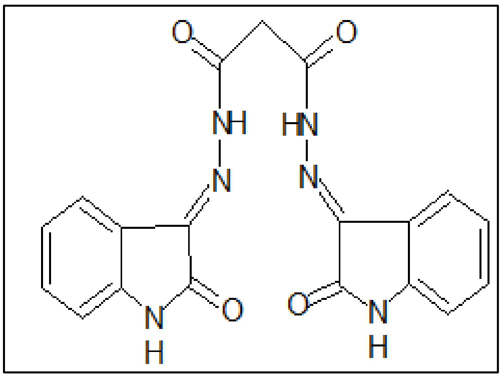

Figure 6: The Structure of Ligand [L]

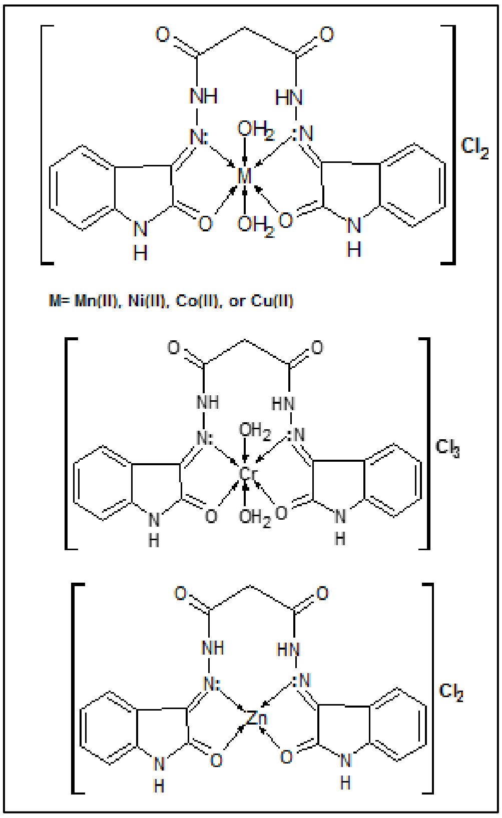

Figure 7: The Structure of the Complexes

4. Conclusion

In this study, all spectral data demonstrated that the prepared Schiff base compound behaves as tetra dentate ligand and binding to the metal ion through the oxygen of the carbonyl and nitrogen of azomethine group. Moreover, the analytical data demonstrated that the ratio of M:L is 1:1in all the prepared complexes and consequently suggest a mononuclear structure for all complexes. Depending on the results that obtained from the spectral and elemental analysis in addition to the magnetic moment and the molar conductivity of the complexes in DMF solution, all complexes were electrolyte and have octahedral configuration except for Zn(II) complex, which has tetrahedral geometry, Figure 7.

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