



Synthesis and Characterization of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2-Carboxy benzaldehyde Aroylhydrazones

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Abstract

A new metal complexes have been synthesized by a reaction of metal compounds contained Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with two kinds of ligands that are 2-carboxy benzaldehyde 4-methylbenzoylhydrazone (CBMH) and 2-carboxy benzaldehyde picolinoyl hydrazine (CBPH), the ligands (CBMH and CBPH) were prepared by condensation of 2-carboxy benzaldehyde with 4-methylbenzoyl hydrazide or picolinoyl hydrazide, respectively. In fact, complexes $[M(L-H)_2] \cdot xH_2O$ were characterized by elemental analysis, molar conductance, magnetic susceptibility, and spectral measurements (UV-Vis, IR.). The hydrazones CBMH and CBPH act as monobasic tridentate ligands, in all their complexes. The ligand CBMH coordinated to the metal ions through the azomethine nitrogen, the carboxyl group oxygen, and the amide carbonyl group oxygen atoms, while the ligand CBPH coordinated through the carboxyl group oxygen, the azomethine nitrogen, and the pyridine ring nitrogen atoms. Physico-chemical studies suggest octahedral geometry for all metal(II) complexes.

Keyword: Complexes, Hydrazones, Transition metals, Octahedral complexes

Introduction

Interest in the study of hydrazones has been growing up because of their biological importance included antituberculosis, antibacterial and antitumor activities [1-5]. Aroylhydrazones play an important role in coordination chemistry, as they stable metal complexes with various transition metal ions [6,7].

Many metal complexes with hydrazones proposed as models for species of biological importance [8]. In addition, aroylhydrazone coordination compounds have also been observed to act as enzyme inhibitors and used as medicines because of their various pharmacological activity [9,10]. furthermore, some hydrazones are important analytical reagents for determining various metal ions using various analytical methods. [1,12].

Some interesting facts were reported that hydrazone metal complexes, have the ability to behave as polydentate chelating ligands, these ligands exhibit keto-enol tautomerism [13] and can coordinate in neutral mono anionic, or dianionic forms to the metal ions, to produce mononuclear or binuclear complexes Nevertheless, they rely on the

reaction conditions, included basicity of the medium, solvent used, structure of the hydrazone ligand and the nature of the metal ion [14]. In earlier research [14-16] we have described the synthesis, characterization, and antibacterial activity of a number of aroylhydrazones and their metal complexes. The results of those studies showed the diversity of mode of coordination of aroylhydrazones with metal ions; the complexation with enhance the antibacterial activity.

In fact, the hydrazones derived from aroylhydrazides and 2-carboxy benzaldehyde and their coordination behaviours with metal ions have seldom been examined. [17,18]. A new class of polydentate ligands is expected and interesting complexes with uncommon structural characteristics may be obtained, since carboxylate is structurally a very diverse group in coordination compounds. Deferent coordination mode of carboxylate containing ligands lead to the formation of mono and polynuclear complexes with metal ions [19-21].

In this work the synthesis and characterization of metal complexes with aroylhydrazones were achieved. The hydrazones were derived from 2-carboxy

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benzaldehyde and aroylhydrazides as shown in (Scheme 1).

2. Experimental part

2.1. Materials and methods

All chemicals that used in this work were purchased from Fluka and B.D.H companies. Melting points were determined using melting point apparatus model Electrothermal 9300. IR spectra were recorded using Tensor 27 Bruker FT-IR spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$) with KBr disc. By the Labo Med, inc 1650Pc spectrophotometer and using DMF as a solvent in 1cm quartz cruets, the UV-Vis spectra ($1100\text{--}200\text{ nm}$) were measured ambient temperature. Molar conductance was measured at ambient temperature using PMC3 Jeneway conductivity meter. Magnetic susceptibility was determined at ambient temperature with the Sherwood scientific Cambridge balance. Using Pascal's tables, the appropriate diamagnetic corrections for ligands were performed. The C.H.N. elemental analyses were performed using Euoro EA 3000 Instrument. The complexes were determined using Shimadzu AA670 atomic absorption spectrophotometer, or volumetrically (Ni and Zn) using standard EDTA solution and suitable indicator [22].

2.2. Synthesis of the ligands

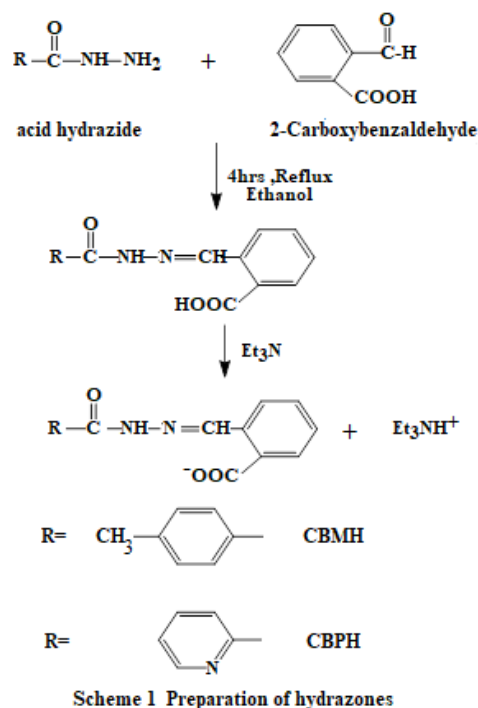
2.2.1. Preparation of hydrazides:

4-Methylbenzoyl hydrazine (MBH), picolinoyl hydrazine (PH) were prepared by the reaction of hydrazine hydrate with the corresponding ethyl ester in ethanol, according to the literature [14,23]. To (0.05mol, 7.5g ethylpicolinate, or 8.2g ethyl 4-methylbenzoate) in ethanol (30mL), excess hydrazine hydrate (80%) (5g, 0.08mol) was added with continuous stirring. The mixture was then heated under reflux for 7hrs. On cooling white crystalline precipitate formed, filtered, washed with cold ethanol (5ml) then with diethyl ether (5mL) and dried, m.p. PH, 144-145°C; MBH, 115-117°C.

2.2.2. Synthesis of hydrazones:

2-Carboxy benzaldehyde 4-methylbenzoyl hydrazone (CBMH), and 2-carboxy benzaldehyde picolinoylhydrazone (CBPH) were prepared according to the literature [17] (Scheme 1) by reacting an ethanolic solution (20 mL) of acid hydrazide (0.03 mol) (4.50g, MBH or 4.11g, PH) with 2-carboxybenzaldehyde (4.5g, 0.03 mol) in absolute ethanol (20 mL) under reflux with constant

stirring for 4hrs upon which white solid separated. The solid was filtered off, washed with absolute ethanol (5mL), and dried in an oven at 80-90°C.



2.3. Synthesis of metal complexes:

To stirred hot ethanolic solution (10 mL) of the appropriate metal salt (0.001mole) [0.20g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.25g $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.25g $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.20g $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, or 0.22g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] was added (0.002mol) of the ligand [0.564g CBMH or 0.538g CBPH] in (10 mL) of absolute ethanol and (0.202g, 0.02mol) triethylamine. The resulting mixture was refluxed for 3hs, upon which the solid complexes were separated, filtered off and washed with ethanol (5 ml) then dried in an oven at 80-90°C.

3. Results and discussion

3.1. Synthesis and characterization of ligands

The ligands were synthesized in good yield and purity by condensation of equimolar quantities of 4-methylbenzoyl hydrazide or picolinoyl hydrazide with 2-carboxy benzaldehyde (Scheme 1). The molecular structure of the ligands were established using IR and elemental analyses (Table 2). The IR spectra of the free ligands exhibited characteristic bands of the functional groups (Table 3). The weak broad bands at the range $2400\text{--}3113\text{ cm}^{-1}$ in the spectra of ligands are attributed to the free stretching of the hydrogen bonded (νOH) of the carboxylic moiety. The strong

absorption bands observed at the range 1689-1688 cm^{-1} are assignable to the carboxylic group carbonyl frequency $\nu(\text{C}=\text{O})_{\text{car}}$.

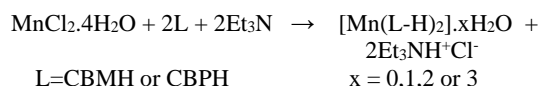
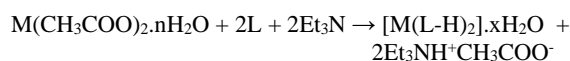
The amide-I carbonyl $\nu(\text{C}=\text{O})_{\text{(hydraz)}}$ and the azomethine stretching $\nu(\text{C}=\text{N})$ frequencies were observed at the ranges 1637-1622 cm^{-1} and 1610-1599 cm^{-1} , for CBMH and CBPH respectively. Medium to weak intensity band appeared at the ranges 3209-3165 cm^{-1} and 1012-947 cm^{-1} are due to $\nu(\text{NH})$ and $\nu(\text{N}-\text{N})$ stretching vibrations, respectively [17,18].

3.2. Synthesis and Characterization of Complexes

Analytical data and some physical properties of the synthesized hydrazones and their complexes are listed in Tables (1 and 2). For all complexes, the elemental analysis results indicate 1:2 (metal: ligand) stoichiometry. The results of the analyses are in good agreement with those required by the formulas proposed. Molar conductivity (Λ_m) of the complexes as 10^{-3}M solutions in DMF at ambient temperature were determined and all prepared complexes were found to have non-electrolytic nature, (Λ_m) was in the range of 5.6-21.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ [24]. All the complexes have been obtained as solids. They are insoluble in most organic solvents like chloroform, benzene, and diethyl ether and they have low solubility in ethanol but more soluble in DMF and DMSO. All of the prepared complexes melt in the temperature range 162 -275 $^{\circ}\text{C}$ which may indicate the non-polymeric nature of complexes, Complexes 6

and 8-10 with decomposition.

The complexes reported here were obtained by reaction of hydrated M(II) salts with suitable ligand in basic medium, using 1:2:2 (metal: ligand: triethyl amine) molar ratio in absolute ethanol. The ligands were deprotonated and neutral complexes of the general formulas $[\text{M}(\text{L}-\text{H})_2] \cdot x\text{H}_2\text{O}$ were obtained. The reactions may be written as:



L=CBMH or CBPH

x = 0, 1, 2 or 3

3.2.1. Infrared Spectra

IR spectra usually provide many valuable information on coordination compounds. The characteristic band frequencies for the complexes and ligands presented in Table (3) (Fig.1). In all complexes, the absence of the bands due to $\nu(\text{OH})$ of the carboxylic group suggests its deprotonation on complexation. The involvement of the carboxylate group in complex formation is also confirmed by the disappearance of the bands due to carboxyl group carbonyl group stretching vibration $\nu(\text{C}=\text{O})_{\text{car}}$. The appearance of two new bands at 1558-1529 and 1390-1377 cm^{-1} assignable to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{sy}}(\text{COO})$, respectively and $\Delta(\nu_{\text{as}}(\text{COO}) - \nu_{\text{sy}}(\text{COO})) < 200 \text{ cm}^{-1}$. This indicates that the carboxylate group behave as a mononegative unidentate group [18,20,24,26].

Table (1): Physical data for ligands and the complexes.

Comp.,No	Formula	Colour	M.p.,($^{\circ}\text{C}$)	Yield,%	$\Omega \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
L ₁	CBMH(C ₁₆ H ₁₄ N ₂ O ₃)	White	192-194	82
1	[Mn(CBMH-H) ₂].2H ₂ O	Pink	162-164	55	14.4
2	[Co(CBMH-H) ₂].2H ₂ O	Yellowish orange	216-218	78	18.7
3	[Ni(CBMH-H) ₂].3H ₂ O	Green	240-242	84	15.6
4	[Cu(CBMH-H) ₂].2H ₂ O	Green	273-275	57	9.3
5	[Zn (CBMH-H) ₂]. H ₂ O	White	172-174	65	16.8
L ₂	CBPH(C ₁₄ H ₁₁ N ₃ O ₃)	White	177-179	76
6	[Mn(CBPH-H) ₂].H ₂ O	Creamy White	260 d*	72	21.3
7	[Co(CBPH-H) ₂].2H ₂ O	Reddish brown	266-268	58	7.4
8	[Ni(CBPH-H) ₂].3H ₂ O	Green	250 d*	56	11.8
9	[Cu(CBPH-H) ₂]	Greenish orange	218 d*	53	10.5
10	[Zn(CBPH-H) ₂].3H ₂ O	White	262 d*	66	5.6

*d: decomposition

Table 2: C.H.N. analytical results of metal complexes and the ligands.

Comp. No.	Formula	%C Calculated (Found)	%H Calculated (Found)	%N Calculated (Found)	%M Calculated (Found)
L1 (CBMH)	C ₁₆ H ₁₄ N ₂ O ₃ (Mwt,282)	68.09(67.95)	4.96(5.11)	9.93(9.75)	
1	[Mn(CBMH-H) ₂].2H ₂ O	58.80(58.58)	4.59(4.45)	8.58 (8.21)	8.42(8.15)
2	[Co(CBMH-H) ₂].2H ₂ O	58.45(57.98)	4.57(4.65)	8.52 (8.38)	8.97(9.31)
3	[Ni (CBMH-H) ₂].3H ₂ O	56.91 (57.19)	4.74(5.05)	8.30 (7.66)	8.70(9.15)
4	[Cu(CBMH-H) ₂].2H ₂ O	58.05(57.89)	4.53(4.75)	8.47 (8.15)	9.60(11.02)
5	[Zn (CBMH-H) ₂].H ₂ O	59.50 (59.29)	4.34(4.35)	8.67 (8.57)	10.13(9.68)
L2 (CBPH)	C ₁₄ H ₁₁ N ₃ O ₃ (Mwt,269)	62.45(67.95)	4.09(5.11)	15.61(9.75)	
6	[Mn(CBPH-H) ₂].H ₂ O	55.17(55.58)	3.61(3.45)	13.79(13.51)	9.03(9.35)
7	[Co(CBPH-H) ₂].2H ₂ O	53.25(53.52)	3.80(4.05)	13.31(13.02)	9.34(8.95)
8	[Ni (CBPH-H) ₂].3H ₂ O	51.80 (51.59)	4.01(3.95)	12.95 (12.66)	9.05(9.37)
9	[Cu(CBPH-H) ₂]	56.04(55.89)	3.34(3.55)	14.01 (13.75)	10.60(11.31)
10	[Zn (CBPH-H) ₂].3H ₂ O	51.27 (51.53)	3.97(3.71)	12.82(12.74)	9.97(10.43)

In unreacted ligand CBMH, the carbonyl group of the hydrazide moiety found at 1622cm^{-1} was moved to lower frequencies by $(6-12\text{cm}^{-1})$ in CBMH-complexes(1-5) which indicates the participation of the carbonyl of hydrazide moiety $\nu_{(\text{C}=\text{O})_{\text{hydraz}}}$ in coordination to the central metal ion in these complexes [27]. This band observed at 1637cm^{-1} in the spectrum of the unreacted CBPH but shifted to higher frequencies by $(4-30\text{cm}^{-1})$ in its complexes (6-10) which indicates the non-participation of the carbonyl of hydrazide moiety $\nu_{(\text{C}=\text{O})_{\text{hydraz}}}$ in coordination in these complexes. The azomethine stretching vibration $\nu_{(\text{C}=\text{N})}$ in all complexes was shifted to lower frequency $(12-30\text{cm}^{-1})$ than the unreacted ligands indicating the coordination of azomethine(C=N) group with metal [4]. The $\nu_{(\text{N}-\text{N})}$ stretching vibrations observed at $1012-947\text{cm}^{-1}$ in the spectra of the ligands, shifts to higher frequency by $(5-27\text{cm}^{-1})$ in their complexes, suggesting the coordination of the nitrogen atom of the (N-N) group with metal. The shift to a higher wave number upon complexation is due to reduced repulsion among the lone pairs of neighbouring nitrogen atoms [28]. The ligand CBPH exhibits a band at 633cm^{-1} due to deformation vibration $\delta(\text{Py})$ of pyridine ring this was observed at higher frequencies $(9-33\text{cm}^{-1})$ suggesting the involvement of the nitrogen atom pyridine in coordination of the CBPH-complexes (6-10). The appearance of non-ligand bands in the spectra of the complexes (1-10) at the ranges $(495-453\text{cm}^{-1})$ and $(436-401\text{cm}^{-1})$ which may be appointed tentatively to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ respectively is another evidence for the bonding of

the ligand with the metal ions [25,28].

The spectra of all complexes except (9) exhibit a broad band centered around 3400cm^{-1} due to the symmetric and asymmetric stretching modes of uncoordinated water molecule. Furthermore, no bands in the regions of the bending deformation modes of coordinated water [29].

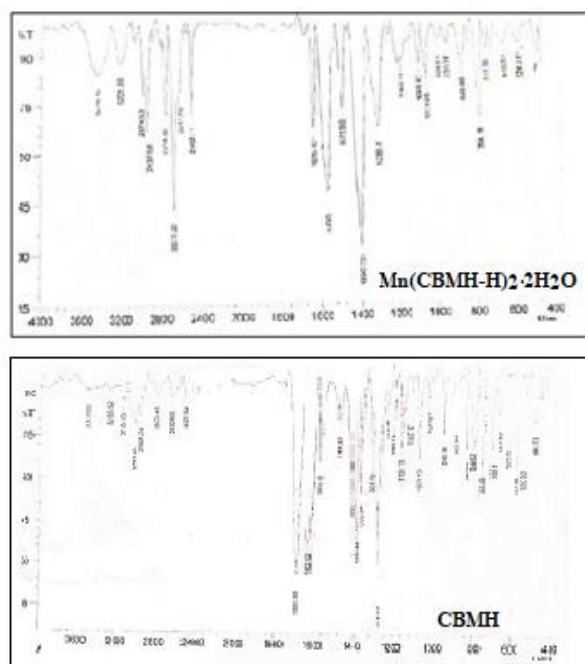


Fig. 1 Infrared spectra of the ligand CBMH and its Mn(II) complex

Table (3) Characteristic IR spectral frequencies of the ligands and complexes.

Comp. No.	$\nu(\text{C=O})$ carbox.	$\nu(\text{C=O})$ hydraz.	$\nu(\text{C=N})$	$\nu(\text{N-N})$	$\nu(\text{N-H})$	ν as(COO)	ν sy(COO)	$\delta(\text{Py})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L ₁	1688 (vs)	1622(s)	1610 (sh)	947 (m)	3165(m)
1	1616(s)	1578 (sh)	962 (w)	3205(m)	1556(s)	1390(s)	465(w)	412(w)
2	1612(s)	1572(sh)	974 (w)	3200(m)	1554(s)	1381(s)	479(w)	425(m)
3	1610(s)	1583(sh)	968(m)	3199(m)	1548(s)	1383(s)	472(m)	420(m)
4	1612(m)	1580(m)	965 (w)	3210(m)	1529(s)	1388(s)	495(w)	420(m)
5	1615(s)	1585(s)	958 (m)	3232(m)	1558(s)	1379(s)	453(w)	401(m)
L ₂	1689(vs)	1637(sh)	1599 (s)	1012 (m)	3209 (m)	633(m)
6	1653(s)	1587(s)	1015(m)	3232(m)	1548(vs)	1390(vs)	653(m)	461(w)	420(w)
7	1657(sh)	1579(s)	1019(m)	3205(sh)	1545(vs)	1384(vs)	642(m)	462(w)	421(w)
8	1641(m)	1585(s)	1024(m)	3215(sh)	1547(vs)	1382(vs)	644(m)	457(w)	428(w)
9	1645(sh)	1582(s)	1028(m)	3220(m)	1556(s)	1377(vs)	666(m)	495(w)	420(m)
10	1667(m)	1573(m)	1022(m)	3226(sh)	1547(vs)	1383(vs)	644(m)	471(w)	436(w)

w = weak, m = medium, s = strong, vs = very strong

3.2.2. Electronic spectra and magnetic behaviour

The magnetic moments at ambient temperature and the electronic spectra of the complexes are described in Table (4). The electronic spectra reliable information about the electronic structure of the compounds. The ligand spectra in DMF show strong bands at 34246-33898 cm^{-1} and 31948-30674 cm^{-1} due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand transitions of the aromatic moiety and (-C=N-NH-CO) chromophore respectively. These bands moved to lower wave numbers in the electronic spectra of the complexes at the regions 33557-29498 cm^{-1} and 28901-26809 cm^{-1} respectively, suggesting the complexation of the hydrazone ligands to the metal atoms [30]. The new strong spectral band of all complexes (1-10) at the region 26455-23474 cm^{-1} may be related to the charge transfer transition [31].

The Mn(II) complexes (1,6) exhibit 5.90- 5.60 B.M. magnetic moments. For five unpaired electrons, which are significantly close to the computed spin-only value, and reveals a high spin state. In the visible region Mn(II) complexes and the diamagnetic Zn(II) complexes reveal no notable absorption because Mn(II) complexes of high-spin d^5 electronic configuration and Zn (II) of d^{10} have no d-d transitions.

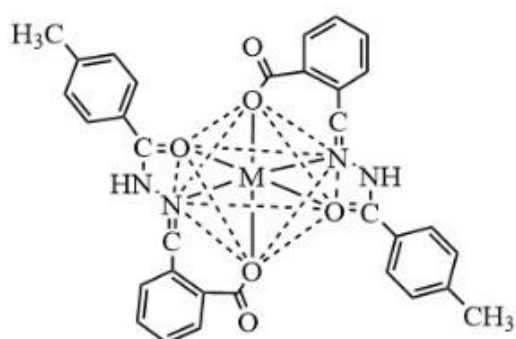
The electronic spectra of Co(II) complexes (2,7) show three bands at the ranges 20703-18867, 15337-14388 and 10183-10141 cm^{-1} corresponding to the

${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_1(F) \rightarrow {}^4T_2g(F)$ transitions respectively, favouring octahedral geometry around the central ion [32]. The magnetic moments values of Co(II) complexes are in the rang 4.90-4.50 B.M, which further support the presence of octahedral geometry around the Co(II) ions. The higher values than that for spin only for high spin d^7 system(3.87B.M.) is due to large orbital contribution [33]

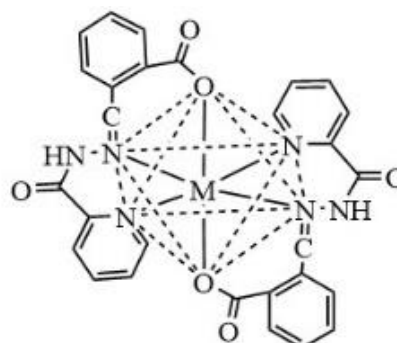
The electronic spectra of Ni(II) complexes (3,8) exhibit three bands at the regions 23752-21739, 13192-12468 and 10121-9633 cm^{-1} . these are interpreted to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions, respectively. These transitions revel an octahedral geometry around Ni(II) ions. This finding was further emphasized by the measured magnetic moment of Ni(II) complexes at 3.08-2.92 B.M., which lies in the range (2.9–3.3 B.M.) of the Ni(II) octahedral complexes [33]. The electronic spectra of Cu(II) complexes (4,9) contains a broad band at the region 14471-14025 cm^{-1} . This band is typical for distorted octahedral stereochemistry of Cu(II) complexes and can be attributed to two or three transition ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2A_{2g}$ [26,27]. The magnetic moment of the complexes (4,9) are in the range (2.20-2.02 B.M.) suggest a monomeric octahedral geometry [34] (Fig. 2).

Table (4) : Magnetic susceptibility and electronic spectra of the ligands and the complexes

Compound No.	M _{eff} BM	Electronic spectra cm ⁻¹
CBMH		33898 , 31948
1	5.90	30303, 28901 , 26455
2	4.50	30674 ,26809,24390,20703,14388,10183
3	3.08	32786 ,28409 ,25974 ,23752 ,13192 ,9633
4	2.02	31575 ,27027 ,25125 ,14025
5	Dia	30864 ,26737 ,23474
CBPH		34246 ,30674 ,
6	5.60	33557 , 28818 ,23980
7	4.90	30395 ,27173 ,24390 ,18867 ,15337 ,10141
8	2.92	32476 ,28248 ,25575 ,21739 ,12468 ,10121
9	2.20	29498 ,28571 ,24096 ,14471
10	Dia	32362 ,27100 ,24213



$[M(L_1-H)_2].XH_2O$, $L_1=CBMH$,
 $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$



$[M(L_2-H)_2].XH_2O$, $L_2=CBPH$
 $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)$.

Fig.2 Proposed Structure of the prepared complexes.

4. Conclusion

A novel tridentate hydrazone ligands and their Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) complexes were synthesized and characterized by various spectroscopic techniques. The hydrazones derived from 2-carboxy benzaldehyde and 4-methyl benzoyl hydrazine (CBMH) or picolinoyl hydrazine (CBPH) act as monobasic tridentate ligands, coordinated to the M(II) metal ions in two different modes of coordination (Fig.2). CBMH coordinates via azomethine nitrogen, hydrazide moiety carbonyl group oxygen, and carboxylate group oxygen atoms (NOO). On the other hand CBPH coordinates via carboxylate group oxygen, azomethine nitrogen, and pyridine ring nitrogen atoms (ONN). On the basis of spectral data, it is observed that all the synthesized complexes possess an octahedral geometry.

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