

Preparation and X-ray powder diffraction investigation of some complexes with hydrazone ligands

Mustafa R. Albayati¹, Amira J. Al_Shaheen², Amal M. Ali³

¹Department of Chemistry, College of education for pure science, Kirkuk University, Kirkuk, Iraq

²Department of chemistry, College of Education, Mosul University, Mosul, Iraq

³Department of Chemistry, college of sciences, Mosul University, Mosul, Iraq

ABSTRACT

Two hydrazone ligands (L_1 and L_2) derived from ibuprofenyl hydrazide and benzaldehyde or salicylaldehyde have been synthesized and used in preparing the corresponding Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Calcium(II) complexes. The resulted complexes have been characterized by different physicochemical methods including elemental analyses, infrared and electronic spectroscopy, magnetic moment measurements and molar conductance. The structures of the complexes have been investigated by X-ray powder diffraction and the ligands have been investigated by ^1H , ^{13}C -NMR spectra. Infrared spectral data suggest that the ligand L_1 behaves, as a bidentate ligand with N,O donor atoms towards the metal ions, while the ligand L_2 behaves as a tridentate ligand with O,N,O donor atoms sequence towards the metal ions, except with cadmium ion it behaves as a bidentate ligand. On the basis of the above physicochemical measurements, the complexes have octahedral and tetrahedral geometries.

Keywords: Hydrazone, (NSAIDs), Metal complexes, X-ray powder diffraction

1. INTRODUCTION

It has been reported that complexes of metallic salts are more potent and less toxic in many cases as compared to the parent drugs (1). Ibuprofen 2-(4-isobutyl phenyl) propionic acid, is a member of non-steroidal anti-inflammatory drug (NSAIDs), known to relieve symptoms of arthritis, primary dysmenorrhea, fever and also possess mild anti-platelet effect (2). It is useful in sepsis-induced acute pneumonia, in retarding metastases of mammary carcinoma and in preventing oxidative lesions of lungs caused by phosgene. High doses of ibuprofen slow down the evolution of lung disease. It also protects prostaglandin H synthase of human endothelial cells from hydrogen peroxide (3). Hydrazones, a member of the Schiff base family with triatomic $>\text{C}=\text{N}-\text{N}<$ linkage, takes the fore front position in the development of coordination chemistry. Reports on the synthesis, characterization and structural studies on hydrazone ligands derived from aldehydes (benzaldehyde and salicylaldehyde) show the importance of hydrazone complexes in various fields including analytical and biological field (4,5). Hydrazone derivatives possessing anti-inflammatory, analgesic, antipyretic and antibacterial activities are also reported in the literature (6). These complexes which play an important role in reducing the toxicity of the parent drug and act as pro-drug (7).

2. EXPERIMENTAL

A. Materials and Measurements

All chemicals and solvent used for the syntheses were of analytical grade, the metal salts were commercially available pure samples and all chemicals used throughout this investigation from Merck, B.D.H., Aldrich or Fluka and used without further purification.

B. Analytical and physical measurements

Melting point and decomposition temperature were determined using STUART-SMPIO melting point apparatus, IR spectra measurements were recorded using Shimadzu FTIR-8400, as KBr pellets in the range ($400-4000\text{ cm}^{-1}$). UV-

Visible spectral measurements were recorded using Shimaduz 160 spectrophotomer for 10^{-3} M complexes in DMF solvent at room temp. using 1cm quartz cell in range (200-900)nm . Elemental analysis were carried out on a CHN analyzer type Vector, model EA 3000 V.3.0 single Euro .The NMR was recorded on broker shield 300 MHz using deuterated DMSO- d_6 as a solvent . Molar conductance of complexes were measured at room temp. for 10^{-3} M in DMF using (BC 3020 professional Bench top conductivity) .

Magnetic susceptibility of the complexes was carried out by (Magnetic Susceptibility Balance of Johnson Matthey catalytic system division, England) .Via Faradys method at room temperature. Metal contents were estimated spectro photo metrically using atomic absorption spectrometer NOVAA 350 Scientific Equipments. X-ray powder diffraction data for complexes (1,13) were measured at general company for Geological survey and mining-Baghdad by using Shimadzu x-ray diffraction 7000 model 2009 and the crystal data for complexes , were analyzed by using match program version 1.6 C .

3. PREPARATION OF THE LIGANDS AND THE COMPLEXES

Synthesis of 2(4-isobutyl phenyl) propionic acid ethyl ester (Ibuprofenyl ethyl ester)

The Ibuprofene was esterified(8)by dissolving(6.18 g, 0.03 mole) of it in 20ml of ethanol and then to that 2.0 ml of sulfuric acid was added . The mixture was refluxed for 6-8hrs . After completion of reaction, solvent was removed by adding 100m of cold water , followed by extracting with sodium bicarbonate and separated in the organic layer . The yield (80%) , b.p 250-252 °C , empirical formula $C_{15}H_{22}O_2$.

	%C	%H	%N
Calc.	76.92	9.40	-
Found	77.0	9.50	-

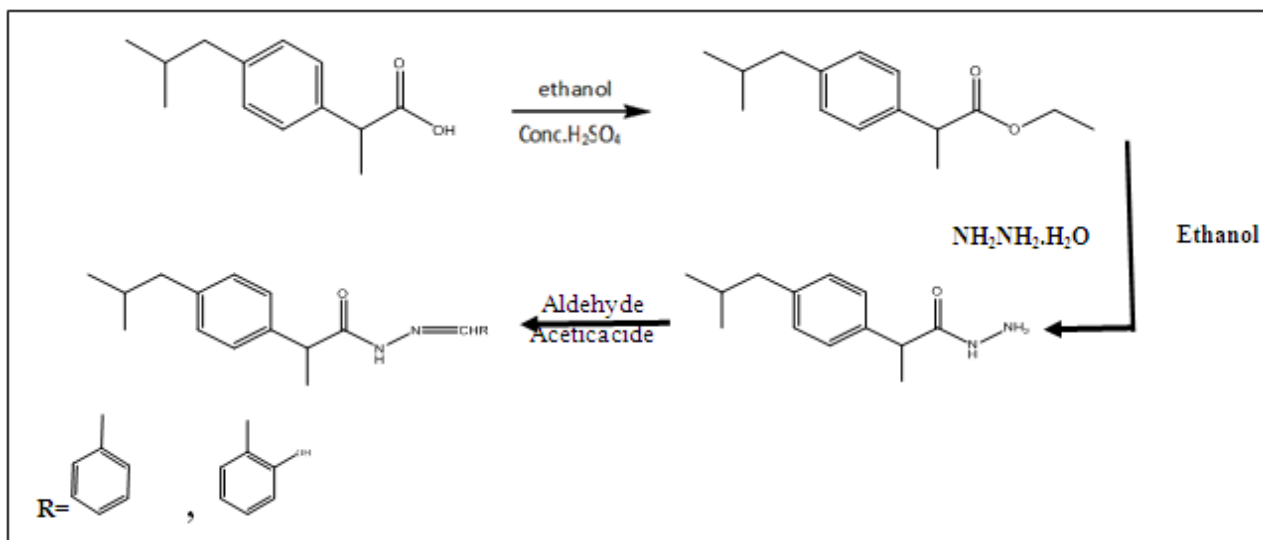
Synthesis of 2-(4-isobutylphenyl) propionic acid hydrazide

The hydrazide was prepared(9)by refluxing (4.68g , 0.02mol) of 2-(4-isobutyl phenyl) ethyl propanate in 15ml ethanol with an excess of hydrazine hydrate $NH_2 \cdot NH_2 \cdot H_2O$ (85%) for 24h , the reaction mixture was then left to stand overnight The compound precipitated on standing over night, filtered and washed with cold distilled water . The pure white solid hydrazide was obtained by recrystallization from ethanol and dried in an oven at(70-80)C , yield(81%), mp 76-78°Cempirical formula $C_{13}H_{20}N_2O$.

	%C	%H	%N
Calc.	70.90	9.09	12,72
Found	70.78	9.22	12.81

Synthesis of hydrazone ligands (L_1 & L_2)

The ligands were synthesized according to the method described in the literature(10) . by reacting equimolar amount of Ibuprofenyl hydrazide and benzaldehyde or salicylaldehyde. A hot ethanolic solution of the ligand made by dissolving (2.2g, 0.01 mole) of Ibuprofenyl hydazide in 15 ml of ethanol, and has been slowly mixed with a hot ethanolic solution containing (1.06g , 0.01 mole) of benzaldehyde or (1.22g, 0.01 mole) of salicylaldehyde .The resulting mixture has been refluxed for about 6 hrs. The mixture has been left to stand for nearly two hours. The precipitated compound was filtered . recrystallized from ethanol, washed with ether and dried under vacuum.



The structures of the ligands are shown in Fig. (1)

Table 1: physical properties and analytical data of the ligands

Ligands	Empirical formula = M. wt	Colour	m.p (C)	Yield	Elemental analysis calcu. (found)		
					% C	% H	% N
L ₁	C ₂₀ H ₂₄ N ₂ O 308	White	180-182	%72	77.92 78.01	7.79 (7.83)	9.09 (8.87)
L ₂	C ₂₀ H ₂₄ N ₂ O ₂ 324	White	167-169	%79	74.07 (73.87)	7.40 (7.61)	8.64 (8.70)

Synthesis of the complexes

All complexes were obtained according to the following procedure(11) , an ethanolic solution of (0.005mol) metal(II) chloride or nitrate was mixed with a hot clear ethanolic solution of the ligand L₁(3.08 gm , 0.01mol) or L₂(3.24gm , 0.01mol) in the mole ratio 2:1 (L:M) after Mixing, The mixture has been refluxed for 5hrs . Then cooled down to room temperature. A precipitates were filtered, washed successively with water and ethanol , followed by diethyl ether and dried in an oven at (70-80)C° .

Table 2: Weight of metal salts used to prepare complexes.

Metal salt	Wt(g) metal salt	metal salt	Wt(g) metal salt
CoCl ₂ .6H ₂ O	1.19	CuCl ₂ .2H ₂ O	0.85
Co(NO ₃) ₂ . 6H ₂ O	1.45	Zn Cl ₂	0.68
NiCl ₂ . 6H ₂ O	1.18	Cd Cl ₂	0.91
Ni(NO ₃) ₂ .6H ₂ O	1.45	Ca Cl ₂	0.55

Table 3: Characterization, analytical, molar conductance and magnetic susceptibility data of the complexes.

NO.	Formula	Molecular Weight	Colour	Yield %	m.p C°	Meff B.M	Δ _M DMF Cm ² . Ohm ⁻¹ .mol ⁻¹	Calculate(Found)%			
								%C	%H	%N	%M
1	[Co(L ₁) ₂ Cl ₂]	746	Brown	69	>300	4.67	18	64.34 (64.22)	6.43 (6.11)	7.50 (7.23)	7.90 (7.72)
2	[Co(L ₁) ₂ (H ₂ O) ₂](NO ₃) ₂	835	Green	74	281- 283	4.75	150	57.48 (57.21)	6.22 (6.03)	10.05 (9.92)	7.05 (6.86)

3	[Ni(L ₁) ₂ Cl ₂]	745	Brown	68	239-241	3.28	17	64.42 (64.11)	6.44 (6.17)	7.51 (7.24)	7.78 (7.63)
4	[Ni(L ₁) ₂ (H ₂ O) ₂](NO ₃) ₂	834	Olive	61	257*	2.92	143	57.55 (57.21)	6.23 (6.11)	10.07 (9.78)	6.95 (6.76)
5	[Cu(L ₁) ₂ Cl ₂]	750	Black	69	254*	2.15	22	64.00 (63.85)	6.40 (6.23)	7.46 (7.35)	8.40 (8.33)
6	[Zn(L ₁) ₂ Cl ₂]	752	White	81	>300	Dia	25	63.82 (63.45)	6.38 (6.10)	7.44 (7.21)	8.64 (8.46)
7	[Cd(L ₁) ₂ (H ₂ O) ₂]Cl ₂	835	White	72	295*	Dia	133	57.48 (57.31)	6.22 (6.01)	6.70 (6.44)	13.41 (13.32)
8	[Ca(L ₁) ₂ Cl ₂]	727	White Yellowish	85	275-277	Dia	16	66.02 (65.88)	6.60 (6.45)	7.70 (7.65)	-
9	[Co(L ₂) ₂]	706	Red	69	292-294	4.65	13	67.98 (67.87)	6.65 (6.47)	7.93 (7.69)	8.35 (8.22)
10	[Ni(L ₂) ₂]	705	green	66	206-208	3.31	15	68.08 (67.77)	6.66 (6.76)	7.94 (7.71)	8.22 (8.03)
11	[Cu(L ₂) ₂]	710	Brown	78	290*	1.99	27	67.60 (67.40)	6.61 (6.34)	7.88 (7.94)	8.87 (8.67)
12	[Zn(L ₂) ₂]	712	Pale Yellow	65	270-272	Dia	18	67.41 (67.22)	6.60 (6.40)	7.86 (7.40)	9.12 (8.88)
13	[Cd(L ₂) ₂]	759	White	69	>300	Dia	12	63.24 (62.89)	6.19 (5.81)	7.37 (6.91)	14.75 (14.43)
14	[Ca(L ₂) ₂]	687	White	80	285-287	Dia	28	69.86 (69.66)	6.84 (6.62)	8.15 (7.64)	-

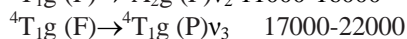
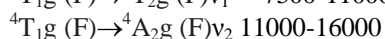
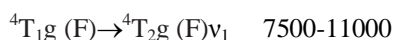
4. RESULTS AND DISCUSSION

The two ligands and their metal complexes are solid and most of them are coloured, insoluble in water but soluble in organic solvents such as DMF at 10⁻³ M. The molar conductance values of all complexes are in the range (12-28) ohm⁻¹ cm² mol⁻¹ indicating non electrolytic nature. While the molar conductance values of the complexes 2,4 & 7 are in the range (133-150) ohm⁻¹ cm² mol⁻¹ indicating a (1:2) electrolytic nature of these complexes. The molar conductance values are in a good agreement with given formulations(12). the metal percentage in the complexes and physical data of complexes are given in table (3).

Electronic Spectra and magnetic moment

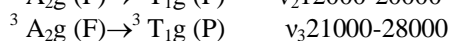
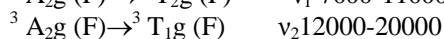
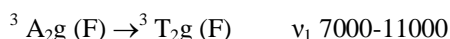
The ultraviolet spectra for the ligands exhibited two bands in the UV intervals at (27173-29069) cm⁻¹ and (30487- 38461) cm⁻¹, assigned to n → π*, and π → π* transitions respectively. All these transitions were also found in the spectra of the complexes but they were shifted to lower frequencies confirming the coordination of the ligand to the metal ions(13) (table 4).

The electronic spectra of Co(II) complexes 1,2 and 9 exhibit bands at (11157-12820) cm⁻¹ due to ν₁ and (14947-15625) cm⁻¹ due to ν₂, and (16366-20533) cm⁻¹ due to ν₃, which are assigned to following transitions:



and these values agreed with high spin octahedral configuration. The value of magnetic moment obtained for these complexes are (4.65-4.75)B.M. and this value greater than the the ortal value (3.87) B.M due to orbital contribution(14).

While Ni(II) complexes 3,4 and 10 exhibit electronic spectrum bands at (11100 – 12468)cm⁻¹, (14513 – 20449) cm⁻¹ and (20533 – 24752) cm⁻¹ respectively, and assigned to transitions:



The octahedral geometry of Ni(II) ion in the complexes is confirmed with the measured magnetic moment values(2.92–3.31)B.M(15).

The Cu(II) complexes 5 & 11 show one broad band peaking at 16780 or 18845 cm^{-1} . This band may arise from the ${}^2E_g \rightarrow {}^2T_{2g}$ transition of 2D state. This band has been comparable both in position and width with the earlier reported octahedral complexes. Because the eg state has been highly affected by Jahn tellar effect, therefore, copper complex had distorted octahedral geometry. The magnetic moment value obtained for Copper (II) complexes (2.15, 1.99) B.M respectively (16), which may suggest an distorted octahedral structure.

Table 4: Electronic spectra data of the complexes

Complex. No.	Electronic transition of d-d cm^{-1}			CT
	ν_1	ν_2	ν_3	
1	12820	15337	16366	35714
2	12297	15625	20533	24154
3	12468	14513	24752	28169
4	11100	20449	22935	37764
9	11157	14947	18103	33557
10	12468	14517	26638	28169

CT = Charge transfer band

Infrared Spectra

The coordination sites of the ligand involved in the bonding with metal ions had determined by careful comparison of the infrared spectra of these complexes with that of the parent ligand. The ligand basically composed of different groups of potent ability to coordinate with the metal ion. The IR spectra of the ligands (L_1 and L_2) show band at (3182, 3120) cm^{-1} due to NH stretching vibration (17) respectively, and a new absorption bands appeared at (1672, 1662) cm^{-1} which has been attributed to frequency of C=O amide group. The IR spectra of the ligands L_1 and L_2 show a strong band in the region (1608, 1614) cm^{-1} , which is a characteristic of the azomethine (stretching vibration of C=N) group and, these bands in complexes are shifted to lower frequency indicating coordination of carbonyl oxygen atom and azomethine nitrogen atom to the metal (18).

In the spectra of the ligands L_1 and L_2 showed, a weak band at (2952, 2950) cm^{-1} due to sym & asym. C-H aliphatic of CH_2 group and this band remains unaltered on complexation. Also the spectra of L_1 and L_2 showed a broad band at (1066, 1050) cm^{-1} due to N-N group shifted towards lower frequency (954-1033) cm^{-1} on complexation (19). The aqua complexes contain a weak to medium broad band at (3450 – 3464) cm^{-1} due to OH stretching vibration of H_2O . Water molecules are coordinated, confirmed by occurrence of additional strong band at (846 – 875) cm^{-1} due to OH rocking vibration. The spectra of the complexes showed bands in the region (514 – 591) cm^{-1} and (420 – 500) cm^{-1} are assigned to M-O and M-N stretching bands of the metal complexes.

In addition the coordination of chloride could not be inferred from infrared spectra of the complexes, because the band due to these group occurred beyond the range of our instrument, whereas for Cl- ligand has been checked by AgNO_3 . The chloride complex 7 shows a band at 570 cm^{-1} has been attributed to ionic Cl (Table 5). The band located at 1380, cm^{-1} in nitrate complexes, were attributed to ionic nitrate group (20, 21).

${}^1\text{H}$ NMR & ${}^{13}\text{C}$ NMR Spectra

The coordination of the ligands have been further substantiated by ${}^1\text{H}$ NMR & ${}^{13}\text{C}$ NMR spectra of the ligands and some of their complexes in DMSO- d_6 as a solvent.

${}^1\text{H}$ NMR data

The ligands exhibit a sharp singlet at δ 8.2 ppm due to the proton azomethine group were shifted down field in the spectra of the complexes (δ 8.5, 8.7) ppm. This deshielding is possibly due to the donation of the lone pair of electrons by the azomethine nitrogen to the metal atom resulting in the formation of a coordination.

The spectrum of the L_1 & L_2 showed singlet broad signals at (δ =11.2, 11.1) ppm due to amide proton NH-CO- and, this signal remained unaltered in the complexation which indicates non participation of NH- in coordination to metal ion, also there is no conversion of the ligand to enolic form and confirmed the bonding through the C=O group. The OH proton of L_2 exhibits singlet signals at δ 11.8 ppm, this signal in the spectra of complex disappeared due to the deprotonation that takes place and to the coordination between oxygen and the metal atom. The aromatic ring proton show a multi signals at (δ =7.1- 8.0) for L_1 , (δ =6.9-7.6) for L_2 , while the aliphatic protons show signals at 0.8-2.4 ppm

in a free ligand, the spectra show none change in these signal values for the prepared complexes which indicate non-participation in the coordination (22,23).

¹³CNMR data

The ¹³CNMR was recorded in d6-(DMSO) solution. The two ligands show signals at (18-44), ppm due to the carbon atom of the aliphatic L₁ and L₂ respectively, and signals in range (126-147), (116-157) ppm due to the aromatic ring. No change appeared in these signals in complexes formation. And this refers to uncoordinated aliphatic and aromatic carbons in the metal complexes. While the signals due to azomethine carbon and carbonyl carbon were appeared at 169 ppm and 174 ppm and these signals were altered in coordination(24,25) (table 5).

Table 5: Selected I.R. bands of the ligands and its complexes (in cm)⁻¹

Comp No.	ν (OH)	ν (N-H)	ν (C=O)	ν (N-N)	ν (C=N)	ν (C-O)	ν (M-N)	ν (M-O)	Other
L ₁	--	3182	1672	1066	1608	--	--	--	ν (C-H)2952
L ₂	3197	3120	1662	1060	1614	1274	--	--	ν (C-H)2950
1	--	3178	1636	1030	1555	--	420	560	
2	--	3187	1640	1022	1570	--	455	550	ν (OH ₂)3450 , 875 ν (NO ₃)1383 , 750
3	--	3185	1643	995	1578	--	478	586	
4	--	3184	1620	1022	1556	--	422	530	ν (OH ₂)3464 , 850 ν (NO ₃)1389 , 777
5	--	3180	1653	1022	1557	--	421	533	
6	--	3177	1612	1043	1564	--	467	514	
7	--	3180	1653	1022	1557	--	421	533	$\nu_{\text{ionic Cl}}$ 625 ν (OH ₂)3421 , 846
8	--	3185	1655	1005	1583	--	447	567	
9	--	3115	1600	1000	1539	1298	426	590	
10	--	3118	1613	1021	1591	1251	500	567	
11	--	3122	1630	1010	1584	1240	500	569	
12	--	3124	1610	1002	1539	1238	551	588	
13	--	3117	1660	946	1550	1247	447	567	
14	--	3123	1646	1009	1543	1260	491	551	

X-ray Powder Diffraction Analysis

The XRD patterns indicate a crystalline nature for complexes. Indexing of the diffraction patterns was performed using High Score Plus software Match(26) program, and their Miller indices (hkl) along with observed and calculated 2θ angle, d values, and relative intensities, From the indexed data the unit cell parameters were also calculated. The Powder XRD patterns of the compounds are completely different from those of the starting materials, demonstrating the formation of coordination compounds. It is found that complexes have orthorhombic and tetragonal structure As shown in Tables (6). Moreover, using diffraction data, the mean crystallite sizes of the complexes, were determined according Scherrer equation ($D = 0.9 \lambda / (\beta \cos \theta)$), where λ X-ray wavelength (1.5406 \AA), θ is Bragg diffraction angle, and β is the full width at half maximum of the diffraction peak(27).

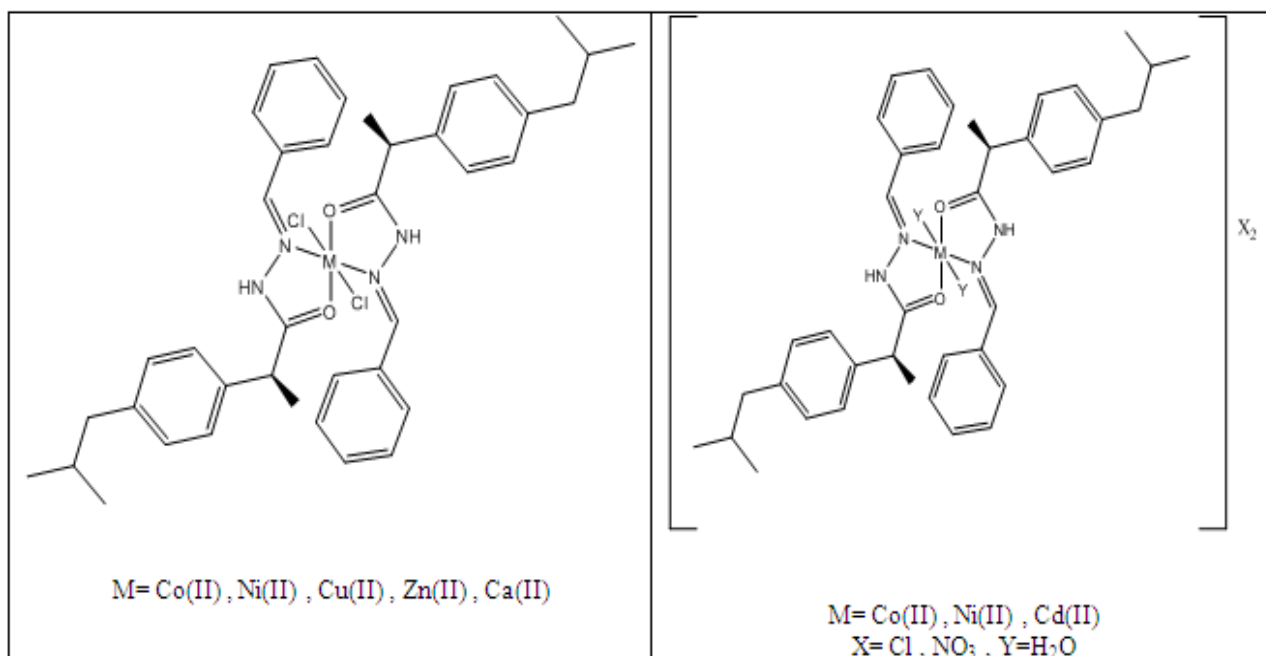
Table 6: Crystal data and structure refinement for complex 1&13

No	Complex	1
1	Molecular Formula	C ₄₀ H ₄₈ Cl ₂ O ₂ N ₄ Co
2	Molecular weight	746

3	Crystal system	Orthorhombic
4	Space group	P2 ₁ 2 ₁ 2 ₁
5	Unit cell parameters (Å ^o)	a=9.1440(1) Å, b = 12.0110(1) Å, c = 33.5670 (4) Å
6	Cell Volume (Å ^{o3})	726.62 (6) Å ³
7	Z	8
8	θ range , deg	2.50– 31.7
9	Index ranges	27 ≤ h ≤ 30, 12 ≤ k ≤ 6, 15 ≤ L ≤ 3
No	Complex	13
1	Molecular Formula	C ₄₀ H ₄₆ N ₄ O ₄ Cd
2	Molecular weight	759
3	Crystal system	Pi Tetragonal
4	Space group	P-4(85)
5	Unit cell parameters (Å ^o)	a= 20.1 Å ^o , c= 5.33 Å ^o
6	Cell Volume (Å ^{o3})	784.37 Å ^{o3}
7	Z	4
8	θ range , deg	25.14 – 46.13
9	Index ranges	16 ≤ h ≤ 20 16 ≤ k ≤ 4 13 ≤ L ≤ 2

5. CONCLUSION

From the above discussion of various physicochemical, spectral and according to the measurements of XRD analysis, the crystal geometries of some complexes has been established, and we concluded that the metal ions are hexa coordinate with most probable octahedral structure has been suggested for most complexes. Whereas cadmium complex has tetrahedral geometry. The analytical and spectroscopic data showed that ligand L₁ act's as bidentate coordinated to the metal ions through oxygen carbonyl and azomethine nitrogen atoms while, L₂ act's as tridentate ligand with O,N,O donor atoms sequence towards the metal ions, except with cadmium ion it behaves as bidentate ligand .



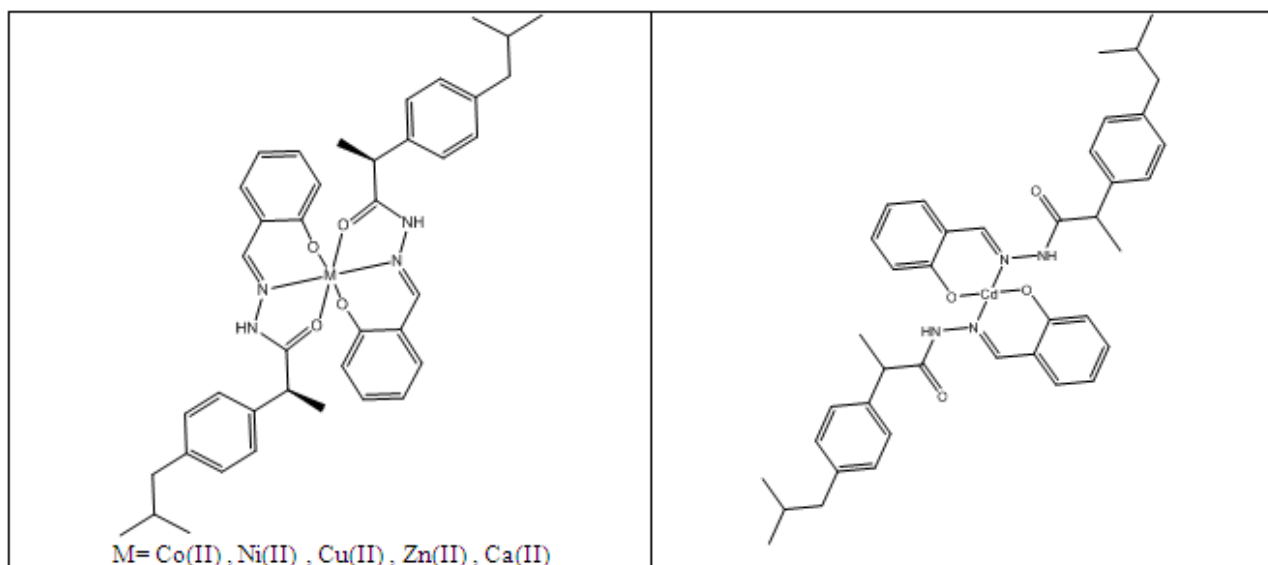
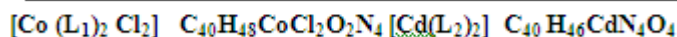
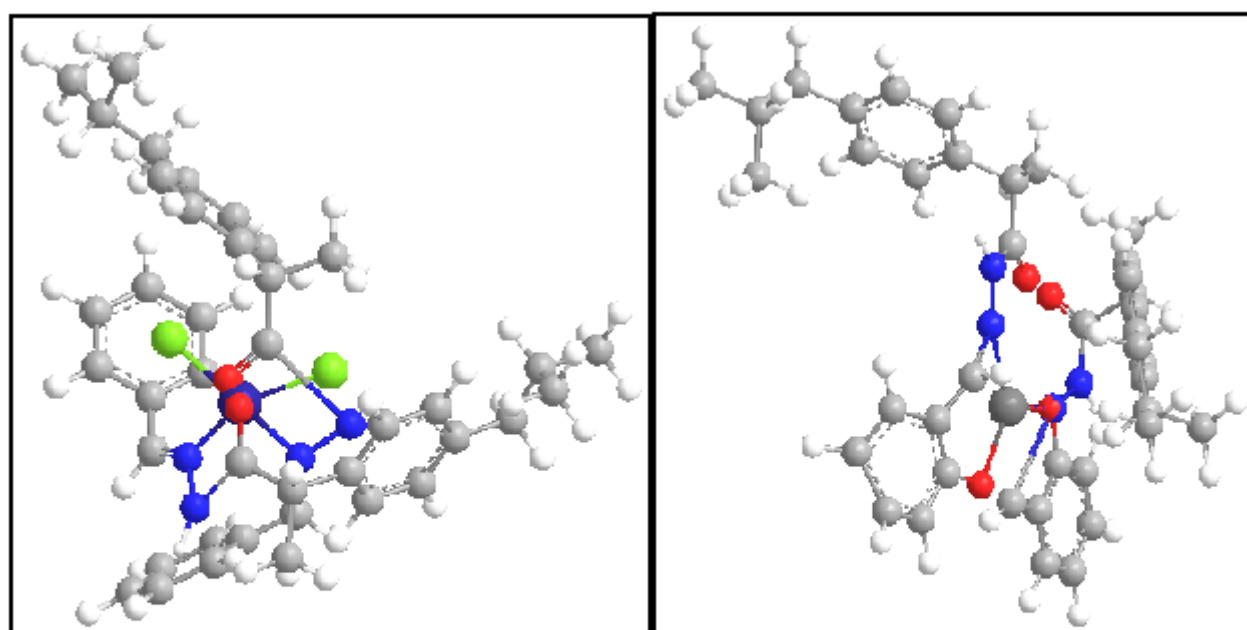


Fig. (2): The structure of the prepared complex



Mol. Wt.:746

Mol. Wt.:759



Fig. 3: The structures of complexes 1&13 Cheme Office. Version. Ultra 8.0. 3D

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