

Preparation and Characterization of some Transition Metal Complexes with Two Mixed Ligands Macrocyclic and Ligands PPh₃

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ABSTRACT

A new ligand (3,4,6,14,15,17,23,24-octazaazatricyclo [17.3.1.1⁸,12] tetracos-1(23),8(24),9,11, 19, 21- hexaene - 2,5,7,13,16,18 – hexaone), (CHT) was been prepared from the reaction of pyridine-2,6-dicarboxylic acid with semicarbazide using microwave irradiation in solid state. The ligand is reacted with some transition metal(II) ions to form complexes of the type [Co(CHT)]Cl₂, [Fe(CHT) Cl]Cl and [M(CHT)Cl₂] where (M=Mn(II), Ni(II), Cu(II) and Zn(II)). Complexes of the type [Ni(CHT)(PPh₃)]Cl₂ and [M(CHT)(PPh₃)Cl]Cl where (M=Mn(II), Fe(II), Co(II), Cu(II) and Zn(II)), were prepared by the reaction of the above complexes with triphenylphosphine(PPh₃) in a 1:1 molar ratio. All the complexes were characterized by (C,H,N) analysis, metal content analysis, molar conductance, magnetic moment measurements, electronic and IR spectroscopy, as well as the ligand was characterized by ¹H, ¹³C -NMR. The electronic spectra and magnetic measurements indicate that the complexes have octahedral environment around the metal ions, except cobalt complex have square planer geometry.

Keywords: Macrocyclic Ligand, Microwave Irradiation.

تحضير وتشخيص بعض معقدات العناصر الانتقالية مع مزيج من ليكندين حلقي كبير وليكند ثلاثي فنيل فوسفين

الملخص

تم تحضير ليكاند جديد (3 , 4 , 6 , 14 , 15 , 17 , 23 , 24 - ثنائي آزا رباعي سايكلو [12, 1⁸.1. 3,17] كوسا-1(23), 8(24), 9, 11, 19, 21- هكساين-2,5,7,13,16,18 - هكساون)، (CHT) من تفاعل البردين-2,6- ثنائي الحامض الكربوكسيلي والسيميكاربازيد باستخدام أشعة الامواج الدقيقة في الحالة الصلبة، تم مفاعلة الليكاند مع بعض ايونات العناصر الأنتقالية لتكوين معقدات من النوع [Co(CHT)]Cl₂ , [Fe(CHT) Cl]Cl و [M(CHT)Cl₂] حيث Cu(II), حيث Zn(II), Ni(II), Mn(II)=M حضرت معقدات من النوع [Ni(CHT)(PPh₃)]Cl₂ , [M(CHT)(PPh₃)Cl]Cl حيث Cu(II), Ni(II), Mn(II)=M و Zn(II) من خلال تفاعل المعقدات المذكورة اعلاه مع ثلاثي فنيل فوسفين بنسبة مولية 1:1. شخصت جميع المعقدات بواسطة التحليل الدقيق للعناصر (C,H,N) وتقدير المحتوى الفلزي وقياسات التوصيلية الكهربائية المولارية و العزوم المغناطيسية والاطياف الألكترونية وطيف الأشعة تحت الحمراء، بالإضافة إلى ذلك فقد تم تشخيص الليكاند بواسطة طيف (¹³C, ¹H NMR). لقد اظهرت قياسات الطيف الألكتروني والقياسات المغناطيسية ان هذه المعقدات تمتلك بنية ثمانية السطوح حول الايون الفلزي. باستثناء معقد الكوبلت (II) الذي يمتلك بنية المربع المستوي.

الكلمات الدالة: ليكاند حلقي كبير، أشعة الأمواج الدقيقة.

INTRODUCTION

Macrocyclic compounds received much attention by many author's Robson macrocyclic (Lever, 1970; Dawood *et al.*, 2013; Xiaoqi *et al.*, 2018; Al-Daher *et al.*, 2018). Owing to their metal coordinating properties, metal ions are able in several favorable cases, to organize reacting molecular fragments according to specific geometry and drive the reaction toward the formation of cyclic compound. Transition metal macrocyclic compound have an active part of metalloenzymes as bionomic model compounds due to their resemblance with natural proteins like hemerythrin and enzymes (Zhang *et al.*, 2012).

Poly aza macrocyclic compounds modified with tetraamide and hexaamide function a cyclic tetra peptide moieties in capsulate bind metal ions without deprotonation process of the amide group and are capable to stabilize even the low oxidation states of the metal ions (Kantekin *et al.*, 2010). On other hand not only the above macro molecules ligands form complexes with transition metals but also they were mixed with the phosphine. Macrocyclic phosphine hold promise as incredibly stable ligands for applications requiring robust complexes such as radio active transition metal complexes for use as radiopharmaceuticals. Because of this possibility, these ligand and their complexes have been synthetic targets since soon after the macrocyclic effect was discovered (Rajesh *et al.*, 2012).

Microwave techniques for preparation of organic substances have received a great deal of attention due to their various advantages such as selectivity, rapid and direct controllable internal reactions. This technique has been used to prepare an eighteen member ring ligand and it's reaction with transition metal ion's to form a new complexes of different geometries (Lever *et al.*, 1970).

In view of these interesting results and as continuation of our studies on transition metal complexes with macrocyclic ligand (Dawood, 2010; Dawood *et al.*, 2011; Dawood *et al.*, 2012), we have prepared new types of complexes containing different donor atoms using microwave technique.

EXPERIMENTAL

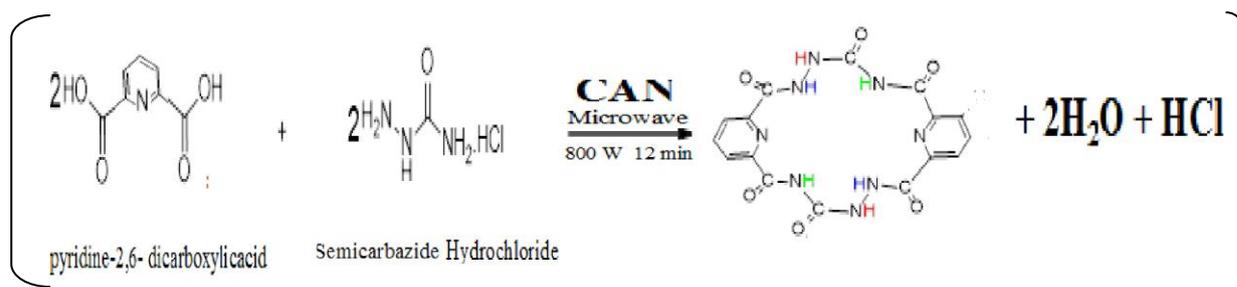
Materials and Methods

All chemicals used as supplied from BDH and Fluka companies. IR spectra were recorded on a Fourier-Transform (FT.IR) Spectrophotometer Tensor 27 Co. Bruker in the range (400 – 4000 cm^{-1}) using KBr discs. The CHN analysis carried out by (Euro Vactor Model E A 3000) in AL-Albeit University –Jordan. element analysis of the ligand and its complexes (PYE UNICAM SP9-Atomic Absorption Spectrophotometer) at the Department of Biology, Mosul University. Conductivity measurements were carried out on 10^{-3} M solution of the complexes in DMSO using (Conductivity Meter Model PCM3-JENWAY), electronic spectra were recorded on (Shimadzu-UV-Visible recording, UV-1650PC-spectrophotometer), using 10^{-3} M of the complexes in DMSO. The magnetic susceptibility were measured at 25 °C by Farady's method using Bruker BM6 instrument. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were carried out by(BRUKER 300 MHz (Switzerland)) and shimadzu QP 5050 A(JAPAN) at Al-Albeit University – Jordan. The ligands prepared in solid state using microwave oven type morph Richards EM 820 CPT. Melting points of all compounds were measured using electro thermal 9300 engineering apparatus and were uncorrected.

1. Preparation of the Ligand (CHT):

The ligand (CHT), (Scheme 1), Fig. (1), has been synthesized according to the following equation in below and procedure (Neerja *et al.*, 2010). A solid pyridine-2,6-dicarboxylic acid (3.34 g, 0.002 mol) was mixed with solid (0.15 g, 0.002 mol) semicarbazide and (0.005 g, 0.0001mol) of cerium ammonium nitrate (CAN) as a catalyst. The solid mixture was irradiated using a microwave 800 W for 10 minutes. The mixture cooled at room temperature, then ethyl acetate (20 ml) was added and the mixture stirred for about 1hr to dissolve the CAN which

separated from the mixture by filtration, the gray precipitate was washed with n-hexane, ethanol and dried under vacuum for several hours. The physical properties are listed in (Table 1).



Scheme-1- Preparation of the Ligand (CHT)

2. Preparation of $[\text{Co}(\text{CHT})\text{Cl}_2]$, $[\text{Fe}(\text{CHT})\text{Cl}]\text{Cl}$ and $[\text{M}(\text{CHT})\text{Cl}_2]$

(where $\text{M}=\text{Mn}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$):

The solution of the ligand (CHT) (0.42 g, 0.001 mole) in (10 ml) DMF and ethanol solution of (0.001 mole) of metal chloride [$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.198 g); $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.198 g); $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g); $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.234 g); $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.170 g); $[\text{ZnCl}_2$ (0.132 g)] were mixed together with stirring. The mixture was refluxed for 2 hr. After cooling the precipitate was filtered off washed with cold ethanol then dried under vacuum.

3. Preparation of mixed ligand complexes $[\text{Ni}(\text{CHT})(\text{PPh}_3)]\text{Cl}_2$ and $[\text{M}(\text{CHT})(\text{PPh}_3)\text{Cl}]\text{Cl}$ (where $\text{M}=\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$)

The metal complexes $[\text{Fe}(\text{CHT})\text{Cl}]\text{Cl}$ (0.54 g, 0.001 mol) was dissolved in (10 ml) DMF and added to a solution of triphenylphosphine (0.26 gm, 0.001 mol) in (10 ml) ethanol, the mixture was refluxed for 1h. The precipitate that formed was filtered off, washed with diethylether and dried under vacuum. Same procedure was carried out to prepare the other complexes of (Co(II), Ni(II), Cu(II), Zn(II)).

RESULTS AND DISCUSSION

Microwave irradiation of a mixture of the semicarbazid, dicarboxylic acid and CAN catalyst afforded the ligand (CHT) in 90% Yield, which is stable in air, non-hydroscopic at room temperature. C.H.N analyses, melting point, and other physical properties for the ligand are listed in (Table 1). The complexes and the mixed ligand complexes are stable, non-hydroscopic and have high melting points, the physical properties are listed in (Table 1).

The ligand (CHT) characterized by ^1H NMR (Table 2) Fig. (2) and the chemical shift's data are listed in. Table (2) the band at $\delta(8.6 \text{ ppm})$ attributed to 6H (H- py ring) assisted by the integration. The band at $\delta(8.6 \text{ ppm})$ and $\delta(7.2 \text{ ppm})$ attributed to 4H for the NH-NH-CO-pyr group, and $\delta(11.2 \text{ ppm})$ attributed to 2H for the (N-H) group (Sternhell *et al.*, 1969).

Table (3), Fig. (3) contains ^{13}C -NMR chemical shift's (160 ppm) for (N-CO-N), (165 ppm) for (-CO-py) and (140 ppm) for (C-py meta), (148.9 ppm) for (C-py ortho), (128 ppm) for (C-pyr Para), the atom carbon of solvent (DMSO) to show at (40 ppm) in (Table 3), and Fig. (3) assist the structure of the ligand (Levy *et al* 1972).

The conductivity measurements indicated that the complexes (1,4,5,6) are nonelectrolytes, while the complexes (2,7,8,9,11,12) and (3,10) are electrolytes as (1:1) and (1:2) respectively (Table 1).

The IR spectrum data of (CHT). Table (4) exhibited absorption frequencies assignable to $\nu(\text{N}-\text{H})$ stretching as a strong band at (3250 cm^{-1}) , $\delta(\text{N-H})$ appears at (1306 cm^{-1}) , $\nu(\text{N}-\text{N})$ stretching vibration appears at (1001 cm^{-1}) , and the frequency assignable to $\nu(\text{C}=\text{O})$ band at (1708 cm^{-1}) as medium intensity (Nakamoto, 1997). The IR spectrum characteristic to $\nu(\text{N}-\text{N})$, $\nu(\text{CO}-\text{NH}-\text{CO})$ and $\nu(\text{C}=\text{O})$ stretching frequencies confirm the condensation reaction between

the carboxylic acid and semicarbazide, to form a 20 membered hexa amide macrocycle CHT, as shown in Fig. (1). On complication, the stretching frequencies of $\nu(\text{N-H})$, $\delta(\text{CO-NH-CO})$ and $\nu(\text{N-N})$ shifted to lower frequency, which may indicate the coordination of two (NH) from the semicarbazide group Fig. (1), other support of this coordination comes from the appearance of new bands attributed to $\nu(\text{M-N})$ stretching at $(434 - 492 \text{ cm}^{-1})$. However, the position of $\nu(\text{C=O})$ stretching vibration has not been shifted frequencies in all complexes (Sulekh, 2005 ; Zafar, 2004). New bands in the spectrum of the complexes appeared between $(434 - 501) \text{ cm}^{-1}$ vibration of $\nu(\text{M-N})$ group in all complexes may prove the coordination nitrogen atoms with metal ions.

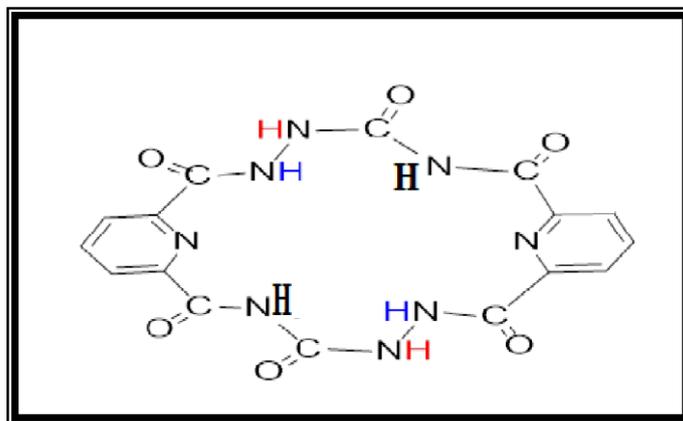


Fig. 1 : Structure of the ligand CHT

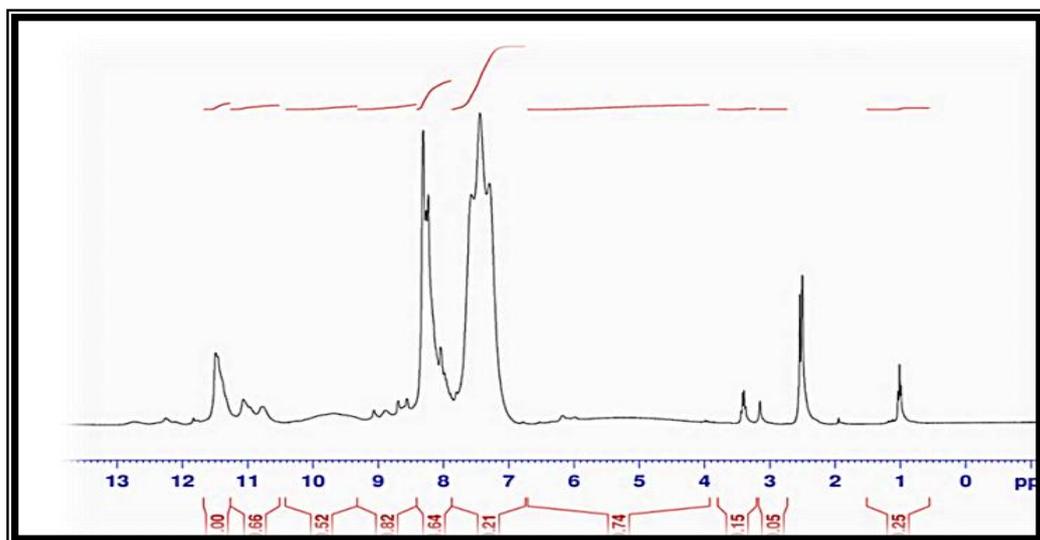


Fig. 2 : $^1\text{H-NMR}$ for CHT ligand

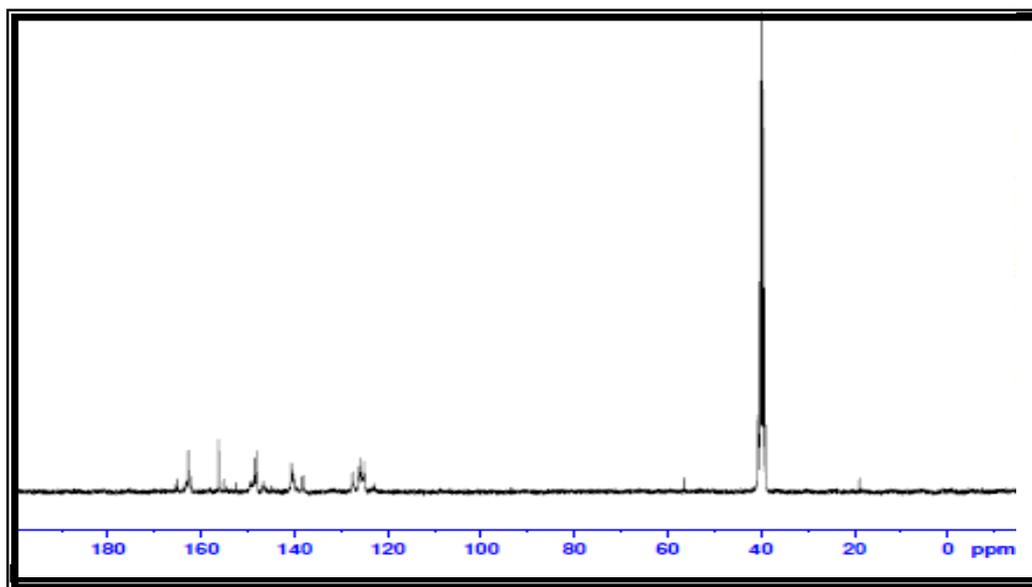


Fig .3 : ^{13}C - NMR for CHT ligand

Electronic Spectra and Magnetic Measurements

The magnetic moments and electronic spectra data for all the complexes are given in (Table 5). The spectrum of the CHT ligand has bands in the U.V spectra at (45871 and 36760 cm^{-1}), assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively. These values are shifted to lower frequencies ($328 - 1229$; $264 - 4080$) cm^{-1} respectively in the spectrum of the complexes.

The two manganese complexes number (1 , 7) have a magnetic moment (5.99 , 5.88 B.M) corresponding to five unpaired electrons, while the U.V – visible spectrum show bands at ($34482 - 48543\text{ cm}^{-1}$), (30121 , 37962 cm^{-1}) which may be due to charge transfer, indicating octahedral structure (Lever, 1970).

The magnetic moment values for the Fe(II) complexes number (2 ,8) have a magnetic moment values (4.87 , 5.12 B.M) as well as the electronic band at ($10526 - 10224\text{ cm}^{-1}$) one attributed to the $^5\text{T}_{2g} \rightarrow ^5\text{E}_g$ transition, show bands at (32679 , 34482 cm^{-1}), (929230 , 36764 cm^{-1}) which may be due to charge transfer, indicating octahedral structure (shakir *et al.*, 1995).

The cobalt complexes number (3, 9) have a magnetic moment values (2.61, 4.80 B.M). Complex (9) is corresponding to three unpaired electrons (Table 5).The U.V– visible spectra show three bands at (10245 cm^{-1}), (15625 cm^{-1}), (16889 cm^{-1}) due to the transition $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ ν_1 , $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ ν_2 and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ ν_3 , respectively, and (32051 cm^{-1}) which may be due to charge transfer. These data may of complex number 9 attribute to octahedral structure but complex (3) the U.V– visible spectra show bands at (18181 cm^{-1}) due to the transitions $^2\text{A}_{1g} \rightarrow ^2\text{E}_g$, (32679 cm^{-1}) which may be due to charge transfer, indicating square planer and similar results were found else where (Sulekh *et al.*, 2004).

The UV – visible spectra of the Ni (II) complexes number (4,10) shows three bands at (10181 , 10111cm^{-1}), (14679 , 15337cm^{-1}) and (23412 , 22676 cm^{-1}) corresponding to three spin allowed transition $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})(\nu_1)$, $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})(\nu_2)$, and $^2\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})(\nu_3)$, respectively, (35211 , 36761 cm^{-1}) which may be due to charge transfer. The magnetic moment values (3.04 , 2.99 B.M) agree with high spin configuration indicating an octahedral environment around the Ni(II)ions (San *et al.*, 2007).

The magnetic moment of the Cu(II) complexes number (5,11) lie in the range (2.16,1.94 B.M), corresponding to one unpaired electron and electronic spectra have a band in the range (16667 , 17391 cm^{-1}) assigned to the $^2\text{E}_{2g}(\text{F}) \rightarrow ^2\text{T}_{2g}$, (32051 , 32679 cm^{-1}) which may be due to charge transfer , indicating distorted octahedral environment (Lever *et al.*, 1970).

The μ_{eff} values of the two Zn(II) complexes number (6, 12) were diamagnetic as expected, while the U.V – visible spectrum show bands at (30121, 37962 cm^{-1}), (33121, 41025 cm^{-1}) which may be due to charge transfer, indicating an octahedral environment around the Zn (II)ions

Table 1: Some physical properties including molar conductance and elemental analysis data of the all complexes

No	Compound	Color	M.P, °C	CHN Elemental analysis data found (Calculated %)				Molar conductance $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
				%C	%H	%N	Metal %	
CHT	$\text{C}_{16}\text{H}_{12}\text{N}_8\text{O}_6$	Gray	158	51.18 (51.58)	6.16 (6.47)	19.90 (20.34)	—	—
1	[Mn(CHT)Cl ₂]	Pale yellow	63	—	—	—	10.21 (10.01)	21
2	[Fe(CHT)Cl]Cl	Deep brown	80	35.65 (34.93)	2.24 (2.04)	20.79 (19.61)	10.36 (10.28)	48
3	[Co(CHT)Cl ₂]	Deep green	105	—	—	—	10.87 (10.77)	86
4	[Ni(CHT)Cl ₂]	Pale brown	70	—	—	—	10.83 (10.80)	16.5
5	[Cu(CHT)Cl ₂]	Deep brown	60	—	—	—	11.62 (11.51)	19
6	[Zn(CHT)(CHT)Cl ₂]	Light Gray	175	35.03 (34.21)	2.20 (2.10)	20.43 (19.85)	11.92 (11.80)	5.6
7	[Mn(CHT)PPh ₃ Cl] Cl	Pale brown	75	—	—	—	6.68 (6.56)	42
8	[Fe(CHT)PPh ₃ Cl]Cl	Green Cloud	110	50.74 (50.94)	13.37 (13.16)	13.37 (13.15)	6.97 (6.77)	34
9	[Co(CHT)(PPh ₃ Cl)Cl]	Blue	60	50.76 (51.21)	13.33 (13.22)	3.36 (3.26)	7.33 (7.11)	35.5
10	[Ni((CHT))(PPh ₃)Cl ₂]	Light Green	80	50.78 (51.51)	13.33 (12.85)	3.36 (3.19)	7.30 (7.25)	70.5
11	[Cu(CHT)PPh ₃] Cl]Cl	Dark Green	70	—	—	—	7.85 (7.58)	44.5
12	[Zn(CHT)(PPh ₃ Cl)Cl]	Pale yellow	65	—	—	—	8.06 (7.95)	35

Table 2: Chemical shift for ¹H-NMR

compound	NH-NH-CO-pyr	NH-NH-CO-pyr	N-H	H- pyr
CHT	7.2	8.1	11.2	8.6

Table 3: Chemical shift for ¹³C –NMR

compound	N-CO-N	-CO-pyr	C-pyr meta	C-pyr ortho	C-pyr Para
CHT	160	165	140	148.9	128

Table 4 : Selected I.R bands and their assignment in cm^{-1}

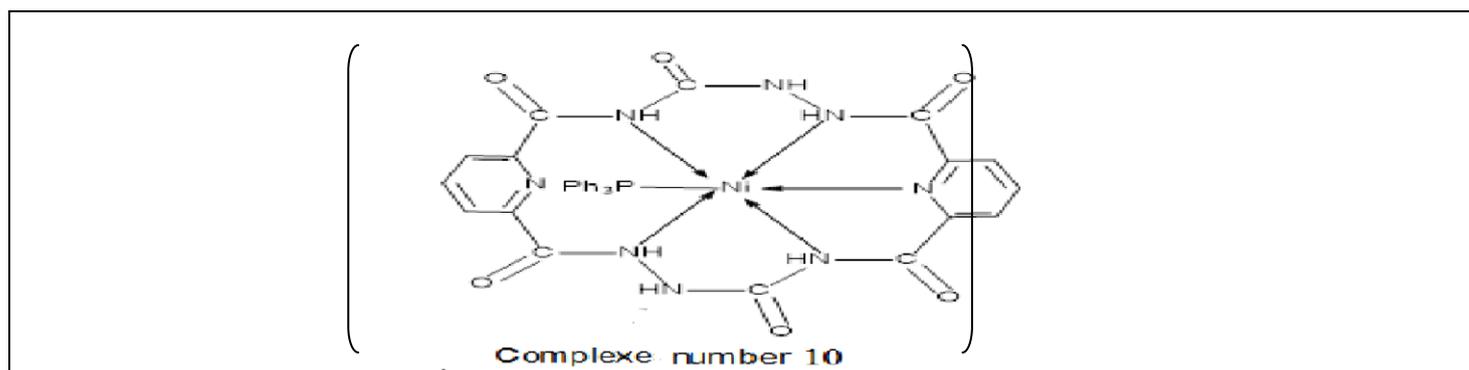
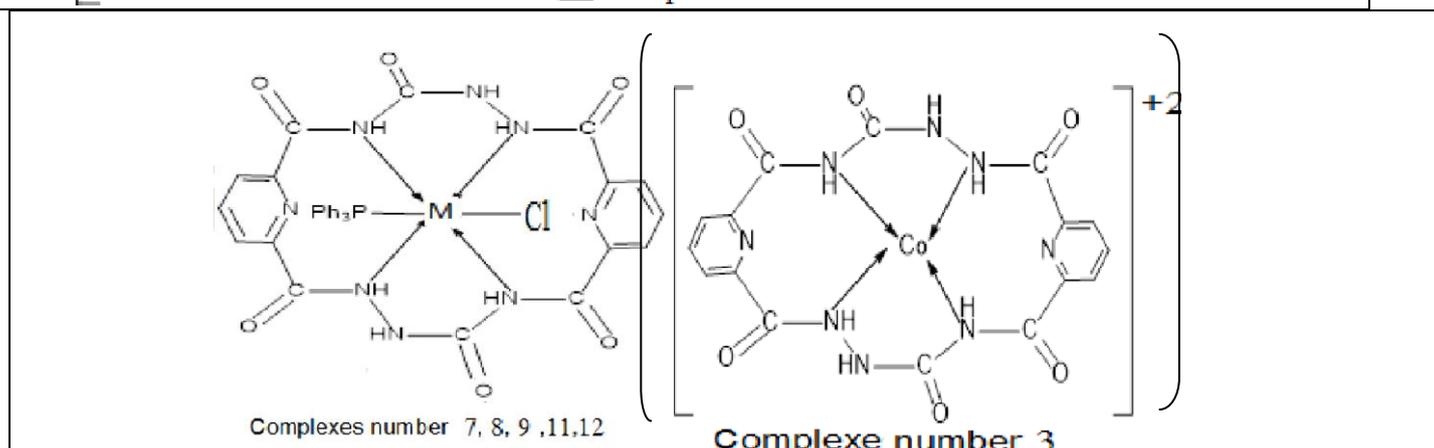
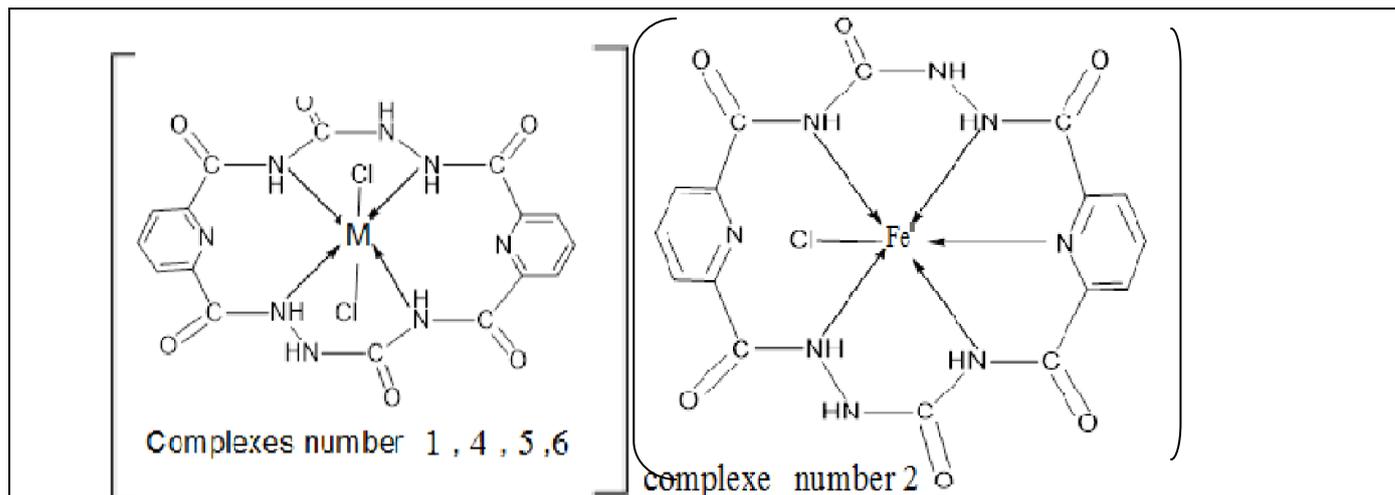
No	I.R spectra					
	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{N-N})$	$\nu(\text{C=O})$	$\nu(\text{N-Pyr})$	$\nu(\text{M-N})$
CHT	3250	1306	1001	1708	1520	—
1	3168(w)	1295(s)	943(s)	1709(m)	1520	434(m)
2	3124(w)	1267(m)	999(m)	1705(m)	1481	453(m)
3	3167(w)	1286(w)	951(m)	1708(m)	1516	476(w)
4	3172(w)	1298(s)	999(s)	1705(m)	1518	465(m)
5	3197(w)	1275(w)	951(m)	1707(m)	1518	484(m)
6	3211(m)	1277(m)	951(s)	1705(s)	1522	430(m)
7	3192(w)	1281(m)	999(s)	1707(m)	1518	542(s)
8	3170(m)	1290(m)	941(s)	1706(s)	1522	453(m)
9	3190(w)	1279(s)	997(s)	1704(m)	1523	457(m)
10	3201(w)	1280(s)	951(s)	1705(m)	1482	465(s)
11	3145(m)	1271(m)	951(s)	1707(m)	1518	501(m)
12	3180(w)	1281(m)	999(m)	1709(m)	1520	492(m)

Table 5 : Magnetic moment and electronic spectral data of the complexes

No	Compound	μ_{eff} , B.M(25 °C)	λ_{max} (cm^{-1})
1	[Mn(CHT)Cl ₂]	5.99	34482 , 45543
2	[Fe(CHT)Cl]Cl	4.87	10526 , 32679 , 34482
3	[Co(CHT)Cl ₂]	2.61	18181 , 32679
4	[Ni(CHT)Cl ₂]	3.04	10181,14679 , 23412 , 35211
5	[Cu(CHT)Cl ₂]	2.16	16667 , 32051
6	[Zn(CHT)(CHT)Cl ₂]	diamagnetic	30121 , 37962
7	[Mn(CHT)PPh ₃]Cl Cl	5.88	33112 , 44642
8	[Fe(CHT)PPh ₃]Cl]Cl	5.12	10224 , 29230 , 36760
9	[Co(CHT)(PPh ₃)Cl]Cl	4.80	10245 , 15625, 16889, 32051
10	[Ni((CHT))(PPh ₃)Cl ₂]	2.99	10111 ,15337, 22676 , 36496
11	[Cu(CHT)PPh ₃] Cl]Cl	1.94	17391 , 32679
12	[Zn(CHT)(PPh ₃)Cl]Cl	diamagnetic	33121 , 44525

COUNCLUSION

On the basis of the above results, we proposed the following structures [for all the complexes].



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