

Synthesis and Identification of some New N-Tropylated Ligand Complexes with some Metallic Ions Co(II), Ni(II), Cu(II) and Zn(II)

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Received: 14th February, 2022; Revised: 13th April, 2022; Accepted: 10th May, 2022; Available Online: 25th June, 2022

ABSTRACT

In this contribution, modern metal ion complexes of the ions Co(II), Ni(II), Cu(II) and Zn(II) were gained through two steps. The first one involved a direct combination of tropylium tetrafluoroborate with some cyclic amino derivatives to produce N-tropylated ligands (M_1 - M_5). The second one involved the reaction of these synthesized N-tropylated ligands (M_1 - M_5) with the metal mentioned above ions in a molar ratio of 1:1 (except M_4) was 1:2. The gained complexes were identified by physical measurements such as melting points and color and by chemical properties such as carbon, hydrogen, nitrogen, sulfur (CHNS) analysis, fourier transform infrared spectroscopy (FTIR), ^{13}C -NMR spectroscopy, and magnetic susceptibility.

Keywords: Amino-Cycloheptatriene, N-tropylated amines, Tropylium tetrafluoroborate, International Journal of Drug Delivery Technology (2022); DOI: 10.25258/ijddt.12.2.50

How to cite this article: Al-Abbasee MJT, Shihab AS, Jebur AK. Synthesis and Identification of some New N-Tropylated Ligand Complexes with some Metallic Ions Co(II), Ni(II), Cu(II) and Zn(II). International Journal of Drug Delivery Technology. 2022;12(2):747-753.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

The substituents of aromatic amines and arylamines are the cornerstone of natural products and organic materials because they play a vital role as a significant center in various substrates possessing diverse activities such as amino acids, alkaloids, and various commercial medications.¹⁻⁴

N-alkylation of amines is an important class of reactions applied in synthesizing medications, insecticides and functional materials. Commercially, reactive alkyl halides have been used to synthesize N-alkylated amines, which often produce over alkylated products.^{5,6}

Coordination compounds with nitrogen in their structure are unique because of their numerous and interesting biological characteristics.⁷ The progress of efficacious fashion for the synthesis of C-N linkage has been the motif of interest, and various authenticated conventional and advanced techniques are currently available. However, the progress of an efficacious fashion for C-N linkage from accessible and available reagents continues to be an active subject of research.⁸ As well as Reductive amination of C=O derivatives with amines maintains a multi-purpose and valuable synthetic technique to synthesize amines and its substituents, which are laboratory beneficial organic intermediates in medicinal products and agricultural. This includes the production of an imine or iminium ion as an intermediate, subsequently in vessel hydrogenation. The tremendous number of the manufactural

applications of reductive amination reactions exemplifies the importance of these reactions.⁹

Amino-Cycloheptatriene substituents are widely used as ligands for synthesizing significant metal complexes.¹⁰ This interested cycloheptatriene scaffold engaged remarkable role for synthesizing different metal complexes¹¹ and as π -donor coordinate ligand.¹²

METHODOLOGY

Materials

Melting points of all gained ligands and complexes are determined and were uncorrected. The synthesized derivatives are recrystallized by hexane, and the proceeding of all reactions was monitored via thin layer chromatography. The gained structures were characterized via FT-IR, ^{13}C -NMR, C.H.N. elemental analysis and electrical molar conductivity.

Organic Synthesis

Preparation of Tropylium Tetrafluoroborate (M)^{13,14}

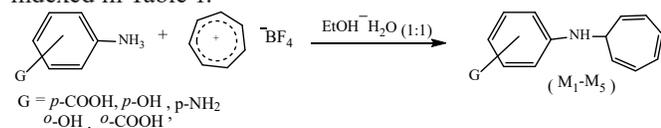
Place (1.9 mL, 1.8 mmole) of cycloheptatriene and (1.8 mmole, 6 g) of triphenylcarbenium tetrafluoroborate in a suitable Erlenmeyer flask with stirring. Acetonitrile with drop by drop added via few quantities even perfect solubility. When the solution has come into view, wait for some minutes; subsequently, remove the solvent via a rotatory evaporator. The solid precipitate that is produced is the tropylium

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tetrafluoroborate has been gained and treated via small fractions of cold ethanol afterward, cold ether to get white crystals yield (2.5 g, 78%) decompose at 198 °C.

Adequate Routine for Synthesis of N-tropyliated Ligands (M_1 - M_5)¹⁵

In 5 mL:5 mL of ethanol : distilled water (0.25 g, 1.4 mmole) of tropylium tetrafluoroborate was dissolved. Subsequently, (0.13 g, 1.4 mmole) of substituted amino pyridine was added to the solution. The mixture was stirred for half an hour and then monitored by TLC (n-hexane 4:1 ethylacetate) and then treated with 10% of NH_4OH for neutralization until solidifying. The gained products were purified and recrystallized from hexane. The physical constants and yield for gained ligands (M_1 - M_5) indexed in Table 1.



Adequate Routine for Synthesis of Complexes (M_6 - M_{25})¹⁶

2 mmole of one of the synthesized ligands, (M_1 - M_5) except (M_4) was dissolved in an appropriate volume of ethanol in a round bottom flask and drop by drop added to a solution of (1 mmole) of used metal ion solution in ethanol ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2). The gained solution was magnetically stirred for (30 minutes) until the completion of the reaction. The produced precipitate collected, washed, dried and recrystallized from hexane. All gained complexes

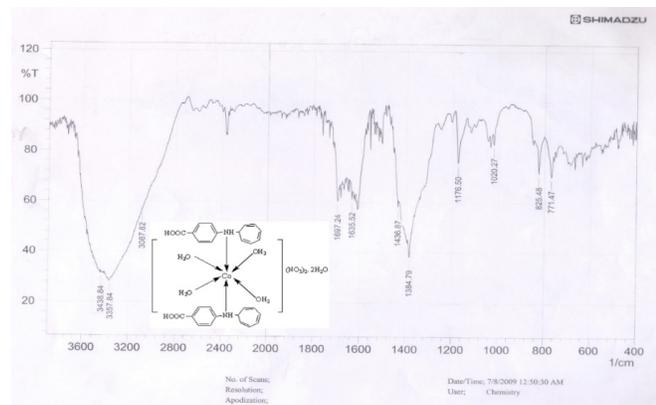


Chart 1: IR chart of complex (M_6)

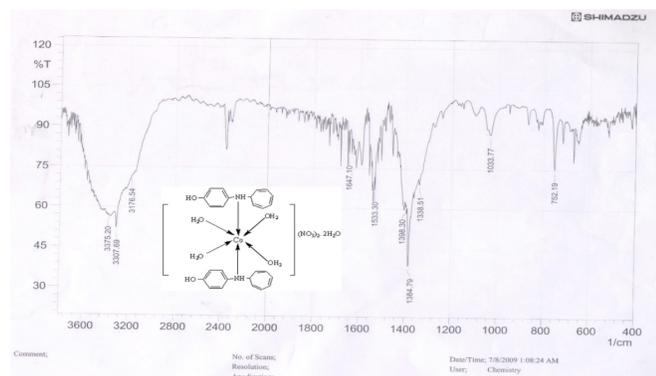
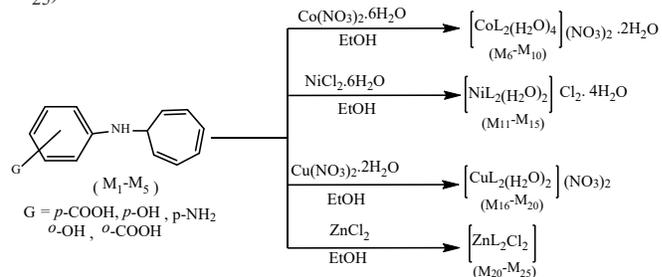


Chart 2: IR chart of complex (M_7)

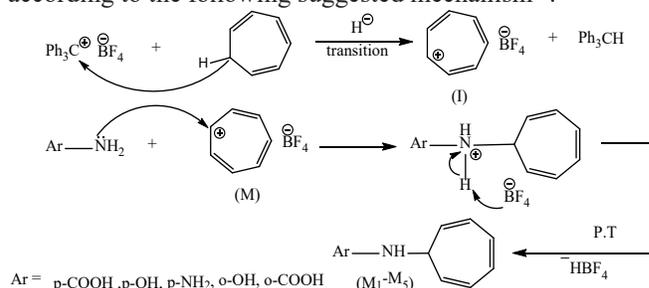
were synthesized in the ratio of 1:2 metal-ligand (except M_4 1:1). The physical properties for synthesized compounds (M_6 - M_{25}) are indexed in Table 2.



RESULTS AND DISCUSSION

The reaction of triphenyl tetrafluoroborate with cycloheptatriene produced Tropylium tetrafluoroborate (M).

Tropylation of derivatives of aniline was prepared according to the following suggested mechanism¹⁷:



The resulted monodentate N-tropyliated amine have been coordinate with (Co(II), Ni(II), Cu(II), Zn(II)) in a mole ratio of 1:2 while the bidentate N-tropyliated amine coordinated in a mole ratio of 1:1 metal-ligand.

Physico-chemical data indicate the presence of new N-tropyliated complexes of the adequate formula $[\text{M}(\text{L})_4]$ ($\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$).

All the obtained complexes are stable, dissolved in dimethylsulfoxide (DMSO) and DMF completely. The new ligand were detected by melting point, FTIR, ¹HNMR, ¹³C-NMR and C.H.N. elemental analysis, while its complexes via melting point, FTIR, magnetic measurement, and conductance. The resulted data correspond with the suggested formulas.

FT-IR Spectra

FT-IR stretching bands for complex (M_6) referred the reveal of wide signal (-COOH) at 3357 cm^{-1} , olefinic (=CH-) at 3087 cm^{-1} , (-C=O) at 1697 cm^{-1} , (-C=C) at 1635 cm^{-1} , aromatic (C=C) at 1610 cm^{-1} that showed in Table 4 and Chart 1.¹⁸

The FT-IR spectrum of complex (M_7) shown a wide signal (-OH) at 3375 cm^{-1} , (-NH-) band at 3307 cm^{-1} , aromatic (-CH-) at 3176 cm^{-1} , olefinic (-C=C) at 1647 cm^{-1} , and aromatic (C=C) at 1620 cm^{-1} that showed in Table 4 and Chart 2. The FT-IR spectrum of complex (M_{11}) shown appear of wide (-COOH) band at 3496 cm^{-1} , (-NH-) band at 3400 cm^{-1} , (-C=O) at 1680 cm^{-1} , (-C=C) at 1652 cm^{-1} , aromatic (C=C) at 1604 cm^{-1} that showed in Table 4 and Chart 3.¹⁸

The FT-IR spectrum of complex (M_{13}) shown appear of

Table 1: Physical constants for gained ligands (M₁-M₅)

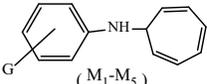
Ligand No.	substituent G	 (M ₁ -M ₅)	Chemical formula of product	Color	Melting point °C	Yield %
M ₁	<i>p</i> -COOH	4-(cyclohepta-2,4,6-trien-1-ylamino)benzoic acid	C ₁₄ H ₁₃ NO ₂	Bright yellow	125-127	50
M ₂	<i>p</i> -OH	4-(cyclohepta-2,4,6-trien-1-ylamino)phenol	C ₁₃ H ₁₃ NO	yellow	178-181	61
M ₃	<i>p</i> -NH ₂	4-(cyclohepta-2,4,6-trien-1-ylamino)aniline	C ₁₃ H ₁₄ N ₂	Pale yellow	128-130	56
M ₄	<i>o</i> -OH	2-(cyclohepta-2,4,6-trien-1-ylamino)phenol	C ₁₃ H ₁₃ NO	Pale yellow	140-141	57
M ₅	<i>o</i> -COOH	2-(cyclohepta-2,4,6-trien-1-ylamino)benzoic acid	C ₁₄ H ₁₃ NO ₂	yellow	113-115	56

Table 2: Physical constants for gained complexes (M₆-M₂₅)

Complex No.	Suggested formula	Color	Melting point (°C)	Yield %
M ₆	[Co(L ₁) ₂ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	Pale black	256 (d)	62
M ₇	[Co(L ₂) ₂ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	Red-brown	244 (d)	66
M ₈	[Co(L ₃) ₂ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	Pale red	223-225	63
M ₉	[CoL ₄ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	brown	163-165	55
M ₁₀	[Co(L ₅) ₂ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	Pale black	136-139	51
M ₁₁	[Ni(L ₁) ₂ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	Light Green	255 (d)	70
M ₁₂	[Ni (L ₂) ₂ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	Gray	225(d)	68
M ₁₃	[Ni (L ₃) ₂ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	Brown-black	213-215	72
M ₁₄	[Ni L ₄ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	Pale Green	160-162	62
M ₁₅	[Ni (L ₅) ₂ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	Brown	144-146	69
M ₁₆	[Cu(L ₁) ₂ (H ₂ O) ₂] (NO ₃) ₂	Pale black	238 (d)	61
M ₁₇	[Cu (L ₂) ₂ (H ₂ O) ₂] (NO ₃) ₂	Green	194-196	73
M ₁₈	[Cu (L ₃) ₂ (H ₂ O) ₂] (NO ₃) ₂	Pale yellow	215 (d)	70
M ₁₉	[Cu L ₄ (H ₂ O) ₂] (NO ₃) ₂	Deep green	173-175	66
M ₂₀	[Cu (L ₅) ₂ (H ₂ O) ₂] (NO ₃) ₂	Pale black	133-135	59
M ₂₁	[Zn(L ₁) ₂ Cl ₂]	Deep brown	216 (d)	58
M ₂₂	[Zn (L ₂) ₂ Cl ₂]	black	194-196	61
M ₂₃	[Zn (L ₃) ₂ Cl ₂]	blue	174-177	52
M ₂₄	[Zn L ₄ Cl ₂]	Pale black	181-183	55
M ₂₅	[Zn (L ₅) ₂ Cl ₂]	Deep brown	134-136	67

d = decompose

(-NH₂) band at 3338 cm⁻¹, (-C-H) aromatic at 3134 cm⁻¹, (-C-H) olefinic at 3064 cm⁻¹, olefinic (-C=C) at 1625 cm⁻¹, aromatic (C=C) at 1600 cm⁻¹ that showed in Table 4 and Chart 4.¹⁸

The FT-IR spectrum of complex (M₁₆) shown appear of wide (-COOH) band at 3427 cm⁻¹, (-NH) band at 3300 cm⁻¹, (-C=O) at 1685 cm⁻¹, (-C=C) at 1618 cm⁻¹, aromatic (C=C) at 1600 cm⁻¹ that showed in Table 4 and Chart 5.¹⁸

The FT-IR spectrum of complex (M₁₉) shown appear of wide signal (-OH) at 3398 cm⁻¹, (-NH-) band at 3250 cm⁻¹, (-C-H) aromatic at 3107 cm⁻¹, olefinic (-C=C) at 1608 cm⁻¹, aromatic (C=C) at 1571 cm⁻¹ that showed in Table 4 and Chart 6. The FT-IR spectrum of complex (M₂₄) shown a wide signal (-OH) band at 3346 cm⁻¹, (-NH-) band at 3360 cm⁻¹, (-C=C) at 1649 cm⁻¹, aromatic (C=C) at 1606 cm⁻¹ that showed in Table 4 and

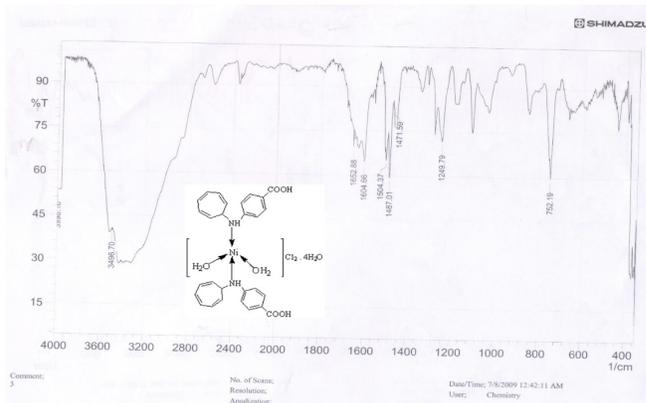

Chart 3: IR chart of complex (M₁₁)

Chart 7. The FT-IR spectrum of complex (M_{25}) shown a wide signal (-COOH) band at 3250 cm^{-1} , (-NH-) band at 3200 cm^{-1} , (-C-H) aromatic at 3147 cm^{-1} , (-C-H) olefinic at 3062 cm^{-1} , (-C=O) at 1700 cm^{-1} , olefinic (-C=C) at 1615 cm^{-1} , aromatic (C=C) at 1590 cm^{-1} that showed in Table 4 and Chart 8.¹⁸

¹³C-NMR data

The ¹³C-NMR spectrum of derivative (M), (in DMSO as a solvent) revealed a signal at δ 115.7 ppm attributed to carbon atoms marked as (a), a signal at δ 115.99 ppm attributed to carbon atoms marked as (b), a signal at δ 141.12 ppm attributed to carbon marked as (c), a signal at δ 148.66 ppm attributed to carbon atoms marked as (d), showed in Chart 9.¹⁸

The ¹³C-NMR spectrum of compound (M_1), revealed a signal at δ 59.05 ppm attributed to carbon marked as (a), a signal at δ 121.05 ppm attributed to carbon atoms marked as (b), a signal at δ 126.05 ppm attributed to carbon marked as (c), a signal at δ 121.96 ppm attributed to carbon atoms marked as (d), a signal at δ 131.36 ppm attributed to carbon atoms marked as (e), a signal at δ 135.61 ppm attributed to carbon atoms marked as (f), a signal at δ 137.24 ppm attributed to carbon atoms marked as (g), a signal at δ 142.03 ppm attributed to carbon atoms marked as (h), a signal at δ 187.65 ppm attributed to carbon marked as (i), showed in Chart 10.¹⁸

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Sensitivity measurements are considered one of the techniques specialized for single electrons, as they are considered one of the simple and successful methods that complement the diagnostic methods in their results, To suggest the geometrical forms of the complexes.¹⁹ The magnetic value of Co(II) complexes in the range (4.01–3.38) B.M compatible with octahedral aspect. The magnetic value of Ni(II) complexes in the range (3.59–2.22) B.M compatible with tetrahedral aspect. The

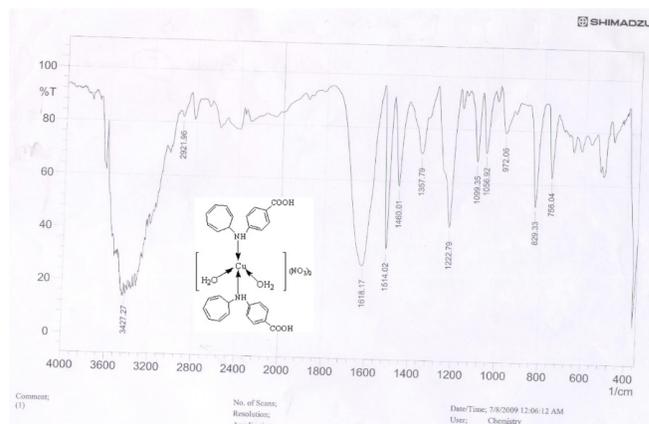


Chart 5: IR chart of complex (M_{16})

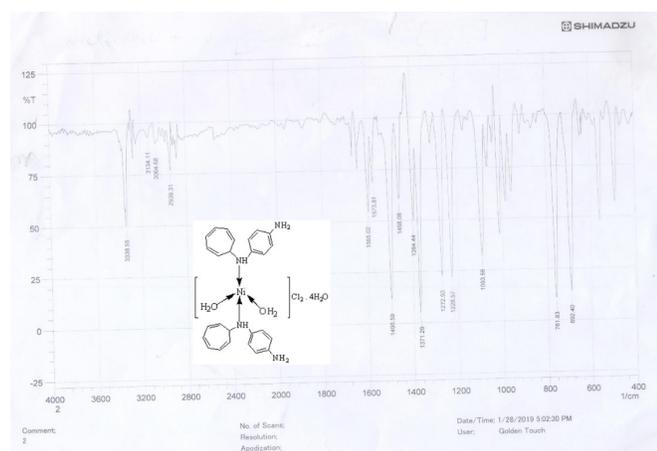


Chart 4: IR chart of complex (M_{13})

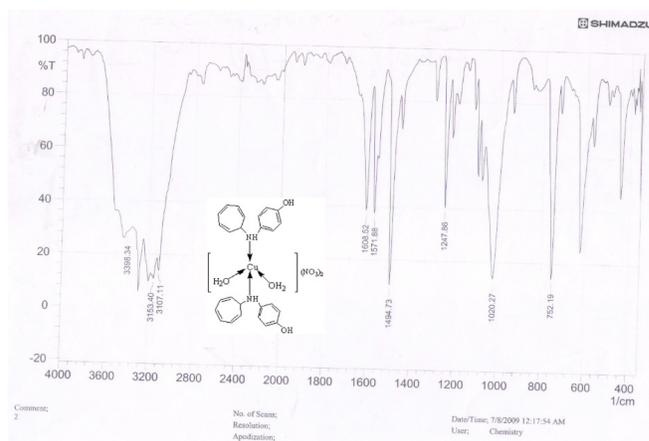
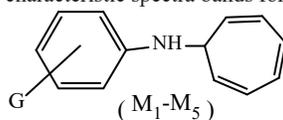


Chart 6: IR chart of complex (M_{19})

Table 3: The FT-IR characteristic spectra bands for the ligands (M_1 - M_5)



Lignds	substituent <i>G</i>	IR(KBr), γ (cm^{-1})					
		<i>C=C</i> aromatic	<i>C=C</i> cycloheptatriene	<i>C=O</i>	<i>N-H</i>	<i>COOH</i>	<i>OH</i>
M_1	<i>p</i> -COOH	1585	1660	1700	3325	3350	---
M_2	<i>p</i> -OH	1510	1600	---	3350	---	3053
M_3	<i>p</i> -NH ₂	1593	1623	---	3377	---	---
M_4	<i>o</i> -OH	1500	1585	---	3250	---	3500
M_5	<i>o</i> -COOH	1600	1666	1700	3361	3400	---

Table 4: The FT-IR characteristic spectra bands for the complexes

Complex No.	IR(KBr), γ (cm^{-1})					
	Functional group					
	C=C aromatic	C=C cycloheptatriene	C=O	N-H	COOH	OH
M ₆	1610	1635	1697	3357	3438	---
M ₇	1620	1647	---	3307	---	3375
M ₈	1602	1681	---	3460	---	---
M ₉	1614	1632	---	3325	---	3345
M ₁₀	1615	1685	1701	3335	3400	---
M ₁₁	1604	1652	1680	3400	3496	---
M ₁₂	1608	1644	---	3349	---	3333
M ₁₃	1600	1625	---	3338	---	---
M ₁₄	1596	1620	---	3323	---	3367
M ₁₅	1605	1613	1710	3336	3445	---
M ₁₆	1600	1618	1685	3300	3427	---
M ₁₇	1585	1610	---	3318	---	3354
M ₁₈	1580	1609	---	3310	---	---
M ₁₉	1571	1608	---	3398	---	3250
M ₂₀	1595	1615	1708	3390	3335	---
M ₂₁	1611	1620	1703	3320	3325	---
M ₂₂	1602	1630	---	3363	---	3340
M ₂₃	1598	1633	---	3324	---	---
M ₂₄	1606	1649	---	3360	---	3346
M ₂₅	1590	1615	1700	3200	3250	---

Table 5: Magnetic moment, Hybridization and geometrical forms for some complexes

Complex No.	Suggested formula	$\mu_{eff.}$ (B.M) founded	$\mu_{eff.}$ (B.M) calculated	Correction factor $10^{-6} \times (D)$	Atomic sensitivity $\chi_A \times 10^{-6}$	Hybridization	Shape
M ₇	[Co(L ₂) ₂ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	4.01	4.7-5.20	272.88-	6758.16	sp ³ d ²	Octahedral
M ₈	[Cu (L ₂) ₂ (H ₂ O) ₂] (NO ₃) ₂	2.19	1.9-2.18	292.02-	2023.77	sp ³ d ²	Tetrahedral
M ₉	[CoL ₄ (H ₂ O) ₄] (NO ₃) ₂ .2H ₂ O	3.38	4.7-5.20	155.84-	4794.08	sp ³ d ²	Octahedral
M ₁₄	[Ni L ₄ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	2.22	2.83-3.50	158.77-	2078.27	sp ³	Tetrahedral
M ₁₅	[Ni (L ₅) ₂ (H ₂ O) ₂] Cl ₂ . 4H ₂ O	3.59	2.83-3.50	163.16-	5414.09	sp ³	Tetrahedral
M ₁₉	[Cu L ₄ (H ₂ O) ₂] (NO ₃) ₂	2.96	1.9-2.18	155.84-	3689.72	sp ³	Tetrahedral
M ₂₁	[Zn(L ₁) ₂ Cl ₂]	Dia.	---	---	0	dsp ²	Square planer
M ₂₄	[Zn L ₄ Cl ₂]	Dia.	---	---	0	dsp ²	Square planer

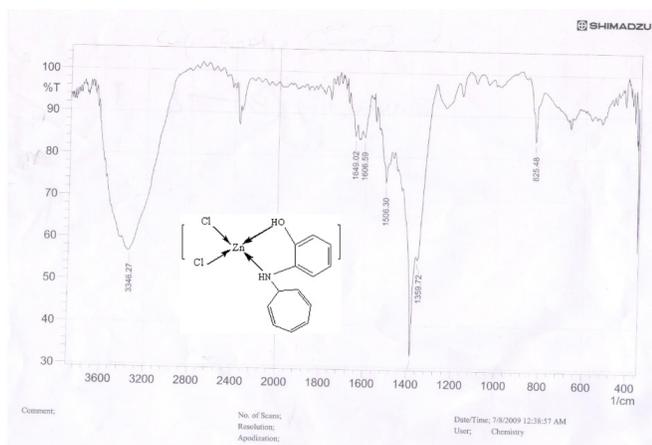
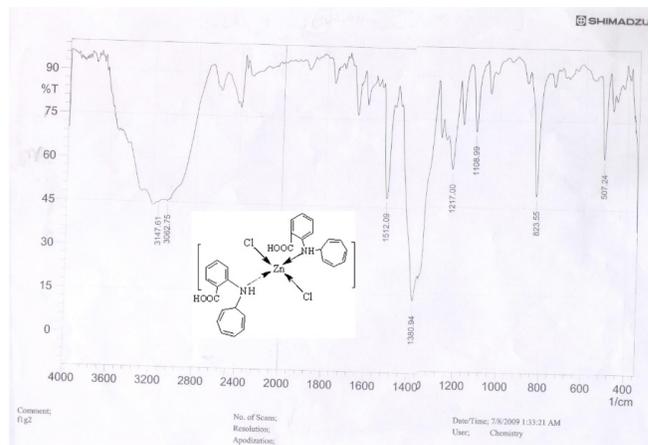
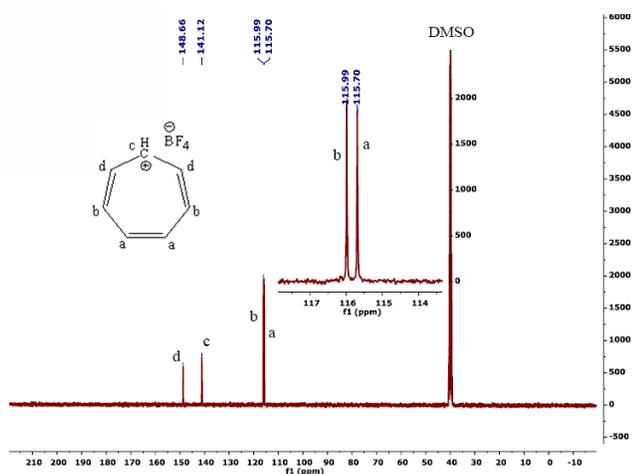
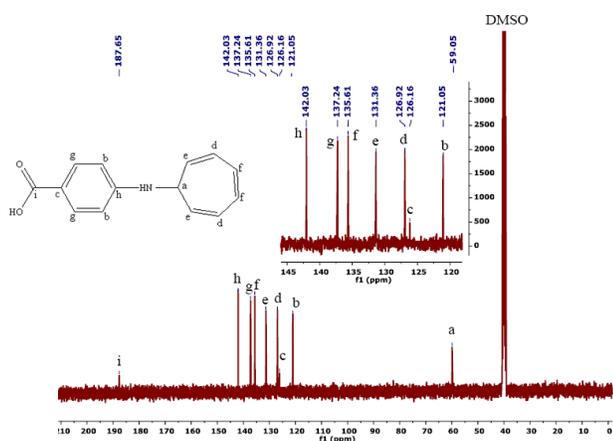
Table 6: (C.H.N.) Elemental Analysis for the Gained Ligands (M₁-M₅)

Ligand No.	Chemical formula	%C Cal. (found)	%H Cal. (found)	%N Cal. (found)
M ₁	C ₁₄ H ₁₃ NO ₂	73.99 (73.68)	5.77 (5.45)	6.16 (6.09)
M ₂	C ₁₃ H ₁₃ NO	78.36 (77.13)	6.58 (6.44)	7.03 (7.10)
M ₃	C ₁₃ H ₁₄ N ₂	78.75 (78.14)	7.12 (6.97)	14.13 (14.03)
M ₄	C ₁₃ H ₁₃ NO	78.36 (77.79)	6.28 (6.49)	7.03 (7.08)
M ₅	C ₁₄ H ₁₃ NO ₂	73.99 (73.40)	5.77 (5.55)	6.16 (6.10)

magnetic value of Cu(II) complexes in the range (2.19–2.96) B.M is compatible with tetrahedral aspect. As expected, the Zn(II) complexes are diamagnetic, and the metal likely favors the square planer aspect.²⁰⁻²² The results as in Table 5.

ELEMENTAL ANALYSIS (C.H.N.)

CHN elemental analysis technique was used to determine the chemical formula for the synthesized ligands. The results as in Table 6.


 Chart 7: IR chart of complex (M_{24})

 Chart 8: IR chart of complex (M_{25})

 Chart (9): ^{13}C -NMR spectrum for compound (M)

 Chart (10): ^{13}C -NMR spectrum for compound (M_1)

CONCLUSION

Our work aims to develop a facile and simple protocol for synthesizing some new N-tropyliated complexes with well-known tropylium tetrafluoroborate salt as a core.

ACKNOWLEDGEMENTS

The authors are grateful to (SDI) company in Samarra-Iraq for its financial participation and support of chemicals.

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