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Synthesis and Characterization of Trihydro mono and Dihydrobis(indole-3-acetic acid)Borate Ligands and Some of Their Metal Complexes

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Abstract

Two new ligands $Na_2[H_3B(BDIA)].0.05H_2O$ (L_1)(BDIA = 1-Boranyl-2,3-Dihydro-1H-Indol-3-yl)]Acetic Acid and $Na_3[H_2B(BDIA)_2].0.3H_2O.0.3CH_3Ph$ (L_2) were synthesized by reaction of $NaBH_4$ with indole -3- acetic acid (IAA) . The coordination properties of ligands were studied with Co(II) , Ni(II) , Cu(II) and Pt(IV) ions. Characterization and structural aspects of the prepared compounds were elucidated by ^{1}HNMR, FTIR electronic spectra, magnetic susceptibility, elemental and metal analysis, thermal analysis (TG & DTG) and conductivity measurements.

The obtained data for metal complexes suggested square planar geometry for copper complexes, octahedral geometry for nickel and platinium complexes and tetrahedral geometry for cobalt complex. The analytical data confirmed that the ligands were coordinated to the metals via oxygen atom of carboxylate groups and by agostic hydrogen of borate (B-H-----M agostic interaction).

Keywords: Borate ligands, Indole-3-acetic acid

تحضير وتشخيص ليكاندات بورات ثلاثي هيدرو احادي و ثنائي هيدرو ثنائي(اندول- 3- حامض الخليك) وبعض معقداتها الفلزية

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الخلاصة

حضر ليكاندان جديدان $Na_2[H_3B(BDIA)]0.05H_2O(L_1)$ و $Na_3[H_2B(BDIA)_2]0.3H_2O.0.3CH_3Ph(L_2)$ (BDIA = 1-Borany1-2,3-Dihydro-1H Indol-3-y1)] Acetic acid بواسطة تفاعل $NaBH_4$ مع indole-3-acetic acid (IAA). درست الصفات التناسقية لليكاندات مع الايونات Pt(IV), Cu(II), Co(II), Ni(II) . شخصت تراكيب المركبات المحضرة باستخدام أطياف الرنين النووي المغناطيسي للبروتون والأشعة تحت الحمراء والأطياف الالكترونية ، الحساسية المغناطيسية ، التحليل الدقيق للعناصر والفلزات ، التحليل الحراري (TG & DTG) وقياسات التوصيلية. النتائج المستحصلة تتفق مع الشكل الهندسي مربع مستوي لمعقدات النحاس والشكل الهندسي ثماني السطوح لمعقدات النيكل والبلاتين والشكل الهندسي رباعي السطوح لمعقد الكوبلت . نتائج التحاليل تتفق على ان الليكاندات كانت متناسقة مع الايونات الفلزية من خلال ذرة الأوكسجين لمجاميع الكاربوكسيل وأيضا عن طريق التآثر B-H-----M

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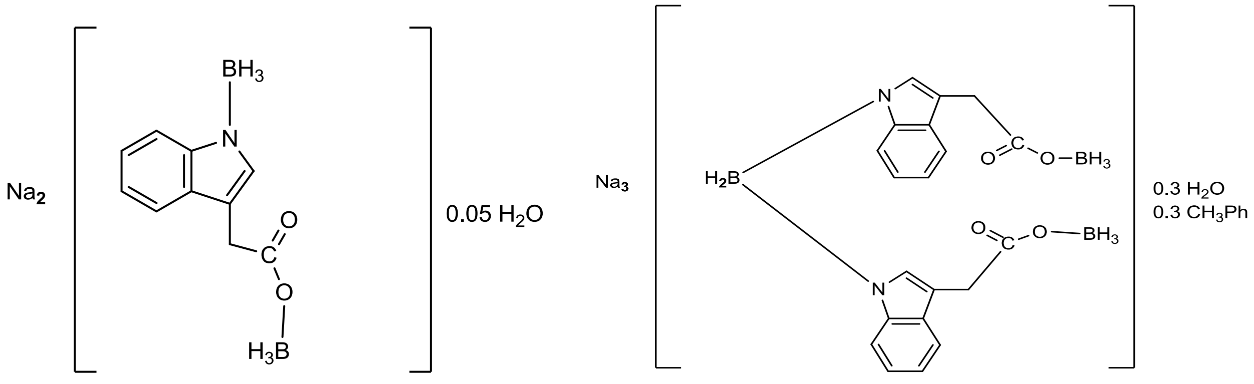
1. Introduction

Boron attached to nitrogen of heterocyclic compounds yields ligands of B-N bond that have a unique place in organoborate chemistry . Such ligands containing B-N bonds have been extensively exploited in coordination chemistry [1]. Interactions of KBH_4 with pyrazole , indazole , imidazole and indole have been shown to yield a variety of ligands which have exploited mainly in the synthesis of transition metal complexes [2]. The pyrazol borate ligands have found wide applications in coordination , organometalic and bioinorganic chemistry [2] . These ligands have become particularly important in the development of biomimetic coordination chemistry of metalloproteins[3]. Substitution on the pyrazole ring controls the steric environment of the binding site . Thus , a relationship between structure and reactivity in metal complexes is exhibited [1] . The chemistry of (pyrazolyl)borate complexes may critically depend on the pattern of the ring substitution[1] . The synthesis of mono and bis (pyrazolyl)borate ligands and their complexes have been reported earlier [4-7]. Only a few borate ligands other than pyrazole and their complexes have been reported , like trihydro(mercaptoazolyl)borate and their Tc ,Re complexes [8]. Dihydrobis(mercapto-benzimidazolyl)borate and Dihydrobis(mercapto-thiazolyl)borate and their sodium and bismuth complexes [9] . dihydrobis(thioxotriazolinyl)borato sodium salt and its zinc(II) ,bismuth(III) and Nickel(II) have been synthesized and characterized by X-ray crystallography [10] . Some literature research articles have provided some informations about the bonding of boron with oxygen atoms , potassium bis(phthalate)borate and its organo tin complexes which can be considered as a module system for metal ligand interaction in biological system [2] . Also O,O'Bis(Salicyldene)2,2'-Aminobenzothiazolyl borate and its Copper and zinc complexes were synthesized and their interaction with guanine, adenine and calf thymus DNA was studied [11].

Indole-3- acetic acid (IAA) is the most abundant naturally occurring plant hormone of the auxin class, which is well known for its regulating function in plant growth and development [12] and has been the subject of extensive studies by plant physiologists [12 -16]. Clinical significance of indol-3-acetic acid in gastric cancer patients is also well established [17]. In industrial applications, IAA has been used in the synthesis of polyindole [18]. Furthermore as chelating agent has hetero atoms N , O and can be used as potential corrosion inhibitors [19] . The coordination behaviour of Indole-3- acetic acid with transition and inner transition elements have also been reported [17, 20-22] **.**

In the present work, two new ligands $Na_2[H_3B(BDIA)].0.05H_2O$ (L_1) and $Na_3[H_2B(BDIA)_2].0.3H_2O.0.3CH_3Ph$($L_2$) (Figure-1) were synthesized from $NaBH_4$ and indole-3-acetic acid and their coordination behavior with Co(II) , Cu(II) , Ni(II) and Pt(IV) has been studied . The structures of the prepared compounds were elucidated depending on elemental analyses, UV-Vis, NMR, and FTIR spectra as well as, thermal analyses, atomic absorption, conductivity measurements and their magnetic susceptibility of metal complexes.



$Na_2 [H_3B(BDIA)]0.05 H_2O$ $Na_3 [H_2B(BDIA)_2] 0.3 H_2O . 0.3 CH_3Ph$

Figure 1- The structure of $L_1 = Na_2 [H_3B(BDIA)] 0.05H_2O$ and $L_2 = Na_3[H_2B(BDIA)_2] 0.3H_2O. 0.3CH_3Ph$

2. Experimental

Synthesis of $Na_2[H_3B(BDIA)].0.05H_2O$ (L_1)

Indol-3-acetic acid (0.4632g, 2.644 mmol) was mixed with a suspension of $NaBH_4$ (0.1 g, 2.644 mmol) in toluene (15mL) and refluxed for 15 h under dry conditions. The evolved hydrogen gas was collected over water. The reaction mixture with a white precipitate was left to stand overnight to allow for complete precipitation. The product was filtered, washed with hot toluene and toluene: acetone 1:1 then vacuum dried [1].

Synthesis of $Na_3[H_2B(BDIA)_2].0.3H_2O.0.3CH_3Ph$ (L_2)

This ligand was prepared by the same procedure as that described above by reacting Indol-3-acetic acid (0.9264 g, 5.288mmol) and $NaBH_4$ (0.1 g, 2.644 mmol) in 2:1 mole ratio. Evolved hydrogen gas was collected over water. A gray precipitate was formed. The resulting gray solid was washed with hot toluene and toluene: acetone 1:1 then vacuum dried [1].

Synthesis of metal complexes: $Na_2[(H_3B(BDIA))_2Cu].EtOH$($C_1$) and $[(H_3B(BDIA))_2Co_2].2H_2O$ (C_2)

Metal complexes of L_1 with Cu(II) and Co(II) ions produced C_1 and C_2 respectively by mixing (0.2g , 0.807 mmol) of L_1 with (0.403mmol) (0.0542 and 0.0958 g)of the metal salts $CuCl_2$ and $CoCl_2.6H_2O$ respectively dissolved in (13 ml) ethanol. Each mixture was heated under reflux with stirring for four hours .The color was changed from green to brown in C_1 and from violet to brown in C_2 .The products C_1 and C_2 were filtered, washed with hot ethanol then vacuum dried [1].

Synthesis of metal complexes: $[(H_2B)_2(BDIA)_4Cu_4Cl_2].5H_2O$($C_3$) , $[(H_2B)_2(BDIA)_4Pt_2Cl_2]1.5EtOH$ (C_4) and $[(H_2B)_2(BDIA)_4Ni_4Cl_2(H_2O)_4$ (C_5)

Metal complexes of L_2 with Cu(II) , Pt(IV) and Ni(II) metal ions produced C_3, C_4 and C_5 respectively by mixing (0.205 mmol , 0.1g) of L_2 with (0.103 mmol) (0.0139 , 0.0501 and 0.0245 g)of the metal salts $CuCl_2$, K_2PtCl_6 and $NiCl_2.6H_2O$ respectively dissolved in (7ml ethanol) for C_3, C_5 and 20 ml (ethanol: water 1:3) for C_4 . The resulting mixtures were heated under reflux with stirring for four hours. The product of C_3 was filtered off, washed several times with ethanol and dried giving mustard product. The two complexes C_4 and C_5 were separated when a large part of the solvent was evaporated by gentle heating. The remaining solution was cooled to room temperature. Precipitation of the two products was achieved by adding the petroleum ether (40-60°). The products were filtered off, washed several times with petroleum ether and dried giving black product for C_4 and light brown product for C_5 **[1]**.

3. Results and Discussion

The reaction of $NaBH_4$ with indole -3- acetic acid (IAA) in 1:1 and 1:2 mole ratios in toluene yields L_1 and L_2 respectively .The completion of the reaction was ascertained by the release of requisite volume of the hydrogen gas according to the following equations

$$NaBH_4 + 1(IAA) \longrightarrow L_1 + H_2$$

$$NaBH_4 + 2(IAA) \longrightarrow L_2 + 2H_2$$

The metal complexes were prepared by the reaction of ligands with metal ions in 2:1 mole ratio with excess of metals. This excess is desirable to completion reaction and to produce a reasonable yield. The physical properties with metal and elemental analysis results are presented in Table-1.

Table 1- Analytical and physical data of the two ligands and their metal complexes

Symbol	Color	(m.p.) °C	Yield %	CHN Analysis Found(Calc.)			Metal % Found (Calc.)
				C%	H%	N%	
L_1	White	180 Dec.	78.23	48.459 (48.477)	5.085 (5.292)	6.206 (5.655)	-
C_1	Dark brown	> 280	74.33	46.853 (47.409)	5.482 (5.746)	5.981 (5.028)	12.35 (11.41)
C_2	Brown	> 280	46.76	43.857 (43.230)	5.733 (5.403)	6.219 (5.043)	20.83 (21.23)
L_2	Light gray	147	73.43	54.629 (54.293)	4.937 (5.118)	6.102 (5.732)	-
C_3	Mustard	192 Dec.	55.18	39.517 (40.397)	4.629 (4.544)	4.577 (4.713)	20.22 (21.40)
C_4	Black	122 Dec.	27.17	40.618 (39.589)	3.781 (4.066).	4.002 (4.296)	29.01 (29.95)
C_5	Light brown	138 Dec.	66.08	42.351 (41.714)	4.724 (4.519)	5.886 (4.866)	20.98 (20.40)

Dec.: decompose

3.1- Infrared Spectra

The important vibrational modes of IR spectra for the free ligands and their metal complexes are described in Table 2. The spectra of the free ligands ,cobalt complex(C_2) and copper complex (C_3) (Figure 2) displayed strong to moderate absorption bands in the wave number region 3280-3520 cm^{-1} which were assigned to stretching vibrational modes of lattice H_2O[23, 24] while the spectrum of the nickel complex (C_5) (Figure 2) showed bands at 3390, 790, 744 cm^{-1} which were attributed to coordinated H_2O[21,24] . Bands related to lattice ethanol were observed at 3471 and 3606 cm^{-1} in the spectra of copper (C_1) and platinum (C_4) complexes respectively [23]. The weak bands related to B-H vibration appeared at 2200-2460 cm^{-1} [2, 3, 8, 9, 25]. The strong intense band at 1701cm^{-1} present in the ligands was assigned to the vibrational modes due to ν C = O [21] . In all complexes, this band appeared at lower frequencies which refers to coordination of carbonyl oxygen with metal ions [1,21, 26] . Bands appeared at 1413-1461 cm^{-1} and 1456-1512 cm^{-1} were attributed to νB-N and νC-N respectively [1] .The absorption bands observed at 1388 and 1406 cm^{-1} for L_1 and L_2 respectively may be assigned to νB-O .This band was observed at lower frequencies in metal complexes indicating coordination of oxygen atom with metal ions [2,11]. The bands appeared at lower frequencies in the spectra of metal complexes were referred to M-O vibrational modes [24].

Table 2 - FTIR spectral data (cm^{-1}) for the ligands and their metal complexes

compounds	ν H_2O lattice(coord)	νB-H	νC=O	νC-N	νB-N	νB-O	νM-O
L_1	3280-3520	2225,2280,2360	1701	1489	1454	1388	–
C_1	–	2310,2385	1612	1460	1420	1340	457
C_2	3500	2365, 2410	1614	1461	1421	1344	430
L_2	3440	2200, 2320	1701	1487	1456	1406	–
C_3	3440	2340, 2320	1612	1493	1461	1340	450
C_4	–	2320,2420,2460	1616	1512	1460	1321	435
C_5	(3390,790,744)	2327, 2370	1699	1456	1413	1340	448

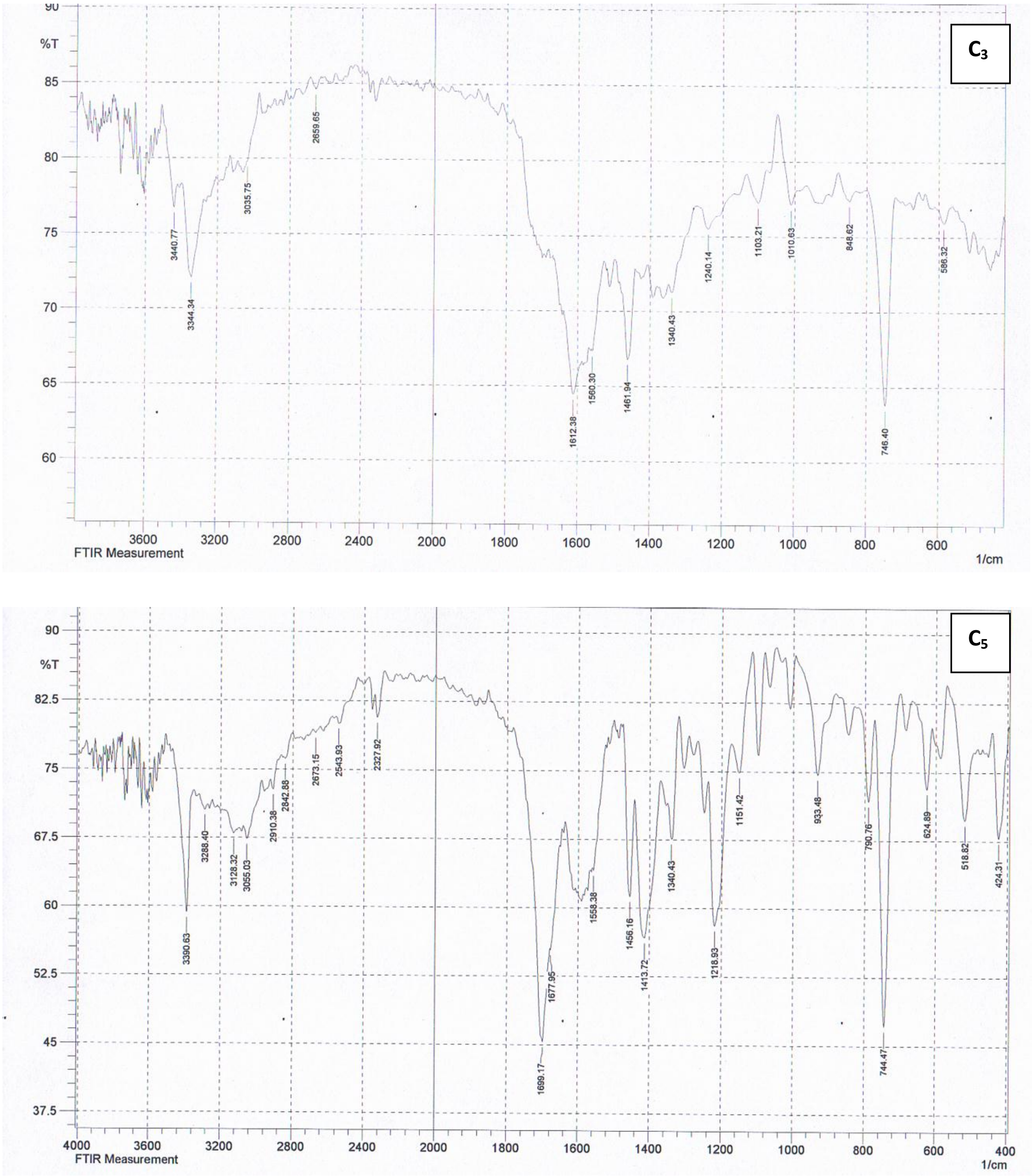


Figure 2- FTIR Spectra of C_3 and C_5 Complexes

3.2- ^{1}H NMR Spectra

The ^{1}H NMR spectra of the two ligands L_1 and L_2 Figure-3 were recorded in DMSO .The chemical shifts and peak assignments are given in Table-3. The two spectra exhibited multiplet signals of aromatic protons which were observed in the chemical shift range (δ= 7.004-7.538 and 7.032 - 7.534 ppm respectively) [2, 23] . Another signal appeared at (δ 6.352- 6.549 ppm) which was due to proton of (HCN ring)[9] . The spectra showed a peak at δ 4.5 ppm attributed to lattice H_2O [23] . Chemical shifts of B-H protons were observed at δ = 3.467 and 3.562 ppm. For the two ligand respectively [2,9, 20, 21] . The signals appeared at δ 3.258 and 3.353 ppm respectively were due to chemical shift of CH_2 protons [20] . The peak at δ 2.5 ppm was attributed to DMSO [23].

Table 3- ^{1}H NMR data of the ligands in DMSO

L_1		L_2	
Chemical shift δ (ppm)	Assignments	Chemical shifts δ (ppm)	Assignments
(7.004-7.538, 4H, m)	aromatic protons	(7.032-7.534, 10.4H, m)	aromatic protons
(6.488-6.549 , 1H , b)	HCN proton	(6.352-6.546,2H, b)	HCN proton
(4.500, 0.1H, s)	protons of $0.05H_2O$	(4.500, 0.6H,s)	proton of $0.3H_2O$
(3.467, 6H, s)	protons of B-H	(3.562, 8H,s)	protons of B-H
(3.052-3.258, 2H, b)	proton of CH_2	3.353-3.472 , 4H,b)	proton of CH_2
(2.5, 6H , s)	protons of DMSO	(2.5, 6H, s)	protons of DMSO

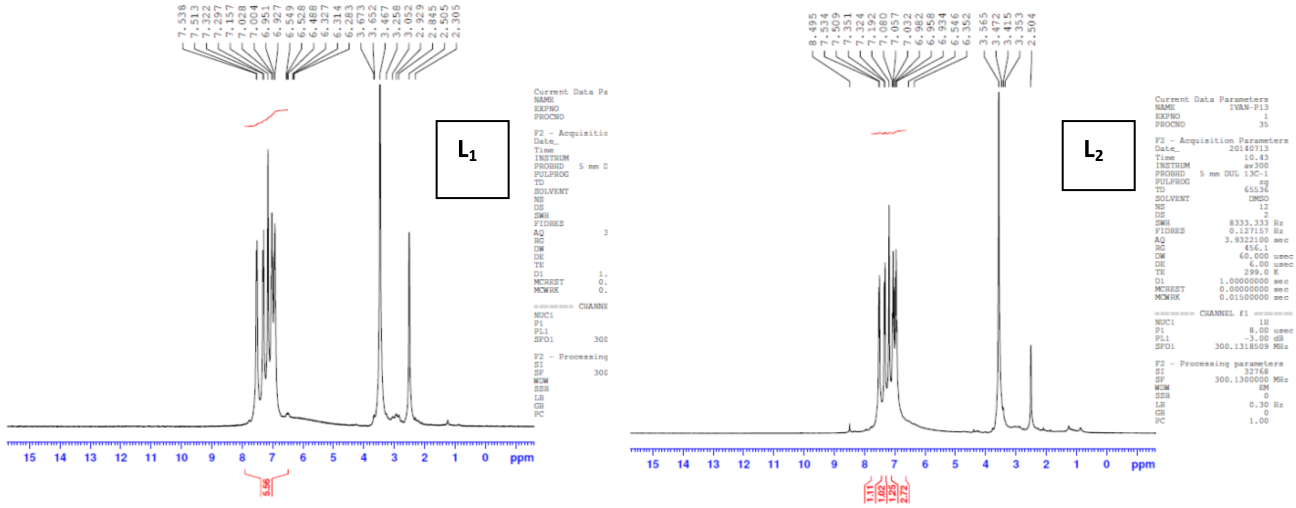


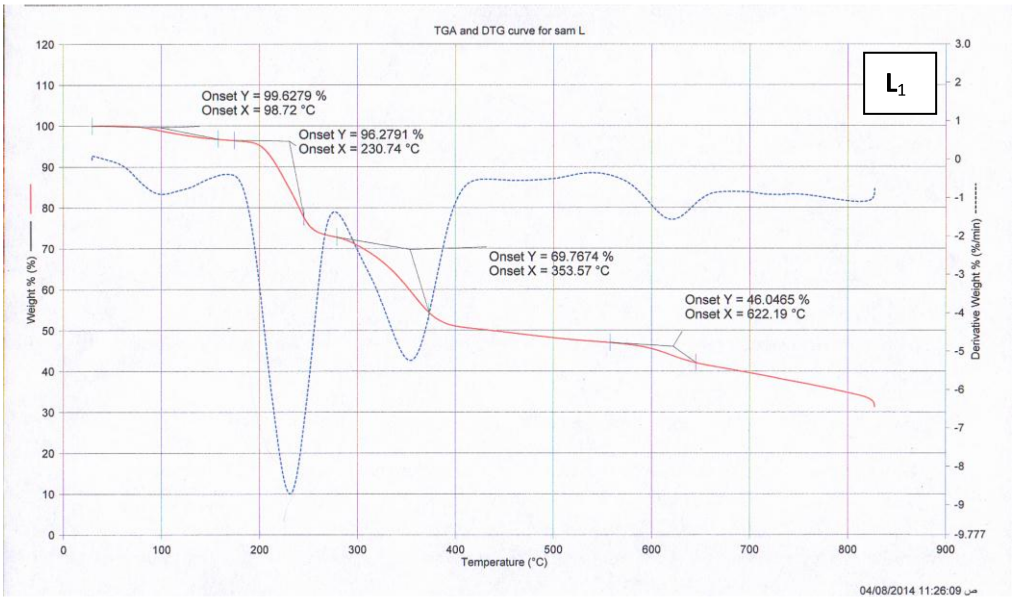
Figure 3- ^{1}HNMR spectra of L_1 and L_2

3.3 - Thermal Analysis

Thermo gravimetric (TG) and differential thermo gravimetric (DTG) analysis for the two ligands L_1 and L_2 were performed under helium atmosphere as inert gas in heating rate of 20 ml / min in the temperature range 30 - 900ºC at 20ºC /min . Thermo grams of the ligands are given in Figure-4 and the decomposition temperature and the weight losses are described in Table-4 .The TG curves of L_1 showed four distinct weight losses. The first weight loss of L_1 occurring in the temperature range 30 - 156 ^{o}C and at peak temperature 98.72 ^{o}C was due to loss of lattice water . Then the degradation of L_1 took place in the temperature range 157 - 900 ^{o}C leaving 46.060 % residue . Thermo gram of L_2 exhibited two steps refer to the weight losses attributed to the loss of lattice water and toluene in the temperature range 30 - 137 ^{o}C and 138-274 ^{o}C respectively at peak temperature 110.63 and 238.54 ºC respectively. Two steps of thermal decomposition occurred at temperature ranges 275 -407 and 408 - 826 ºC respectively at peak temperature 382.59 and 732.91 ºC respectively. The remaining residue was 19.815 % .These results show that the thermal stability of L_1 is higher than L_2. The results obtained from TG and DTG gave a supportive evidence to the suggested structures of ligands L_1 and L_2[2,27] .

Table 4-Thermal decomposition steps of the two boron ligands L_1 and L_2

Ligands	Temp.range ºC (TG)	Temp.ºC (DTG)	Weight lost %		Moiety lost	Residue % Found (Calculated)
			Found	Calculated		
L_1	30-156 157-241 242-374 375-645	98.72 230.74 353.57 622.19	0.372 3.348 26.511 23.721	0.363 2.423 27.324 23.430	0.05 H_2O 6H 2Na + 2B $C_2H_2O_2$	46.060 (46.457) C_8H_5N
L_2	30-137 138-274 275-407 408-826	110.63 238.54 382.59 732.91	0.930 7.255 50.511 21.488	1.105 7.288 50.083 20.640	0.3 H_2O [0.3 toluene +8H] [3Na+$C_7H_6O_4B_2$] C_6H_4NB	19.815 (20.882) C_7H_4N



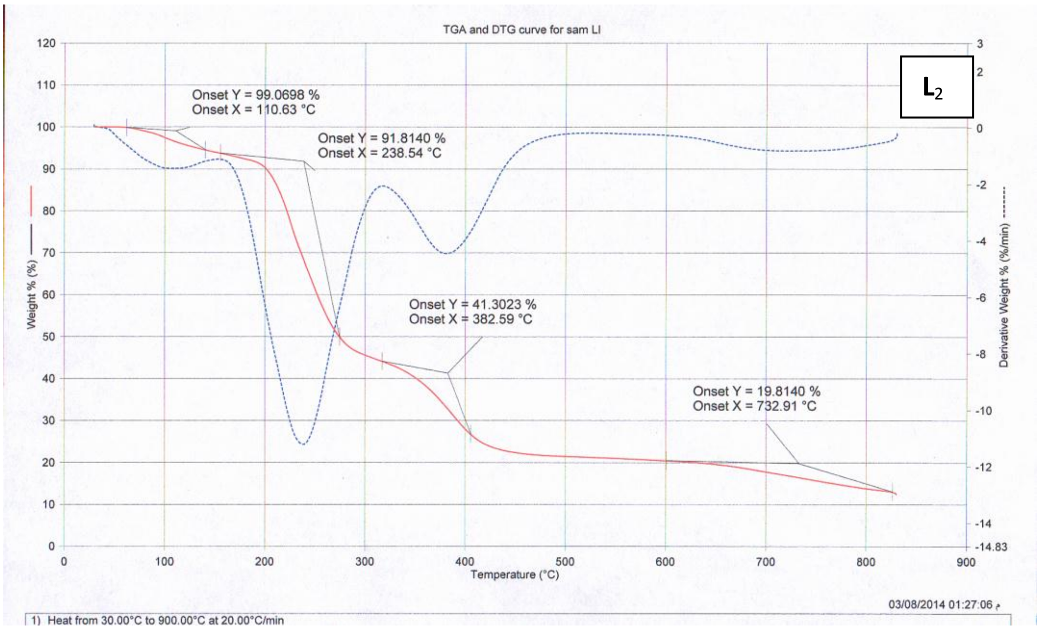
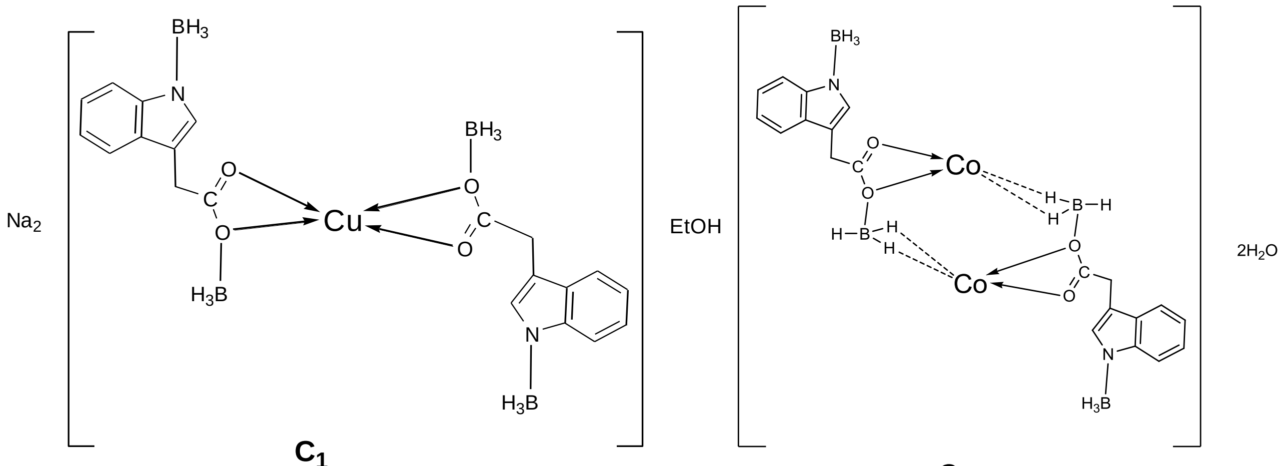


Figure 4- TG and DTG Curves of L_1 and L_2

3.4- Electronic spectra, conductivity and magnetic susceptibility measurements

The electronic spectra of L_1 and L_2 in DMSO exhibited high intensity band at 35211 cm^{-1} which was assigned to $\pi \rightarrow \pi^*$ transition of conjugated system and low intensity bands at 29498 and 28735 cm^{-1} for L_1 and L_2 respectively which assigned to $n \rightarrow \pi^*$ transition [23]. The spectra of copper complexes (C_1 and C_3) exhibited blue shift of ligand bands and this was attributed to the formation of complexes [22,27]. The charge transfer bands were observed at 24154 and 23923 cm^{-1} for C_1 and C_3 respectively [28]. The additional bands appeared in the visible region at (15243 and 14858 cm^{-1}) and (12658 and 12936 cm^{-1}) were assigned to ($^2B_1g\rightarrow {}^2B_2g$) and ($^2B_1g\rightarrow {}^2A_1g$) transitions for C_1 and C_3 respectively . These bands were attributed to square planar Cu(II) complexes[28,29] .The magnetic moment ($\mu eff = 1.97$ and 1.87 B.M) for C_1 and C_3 respectively were consistent with the value for square planar Cu(II) complexes [1,28,29]. The spectrum of di nuclear cobalt complex (C_2) exhibited change in profile compared with the spectrum of L_1 and this change due to formation of complex [22, 27]. The band appeared at 23923 cm^{-1} was assigned to charge transfer transition [28] . Two bands appeared in the visible region, the first was multiple band with an average value of 15873 cm^{-1} . This band corresponds to the transition $^4A_2\rightarrow {}^4T_1$ (P) .The second band appeared at 9319 cm^{-1} was assigned to $^4A_2\rightarrow {}^4T_1$ (F) transition . The value of third band (5010 cm^{-1}) was calculated from Tanaba-Sugano diagram . The spectral data and the value of magnetic moment ($\mu eff = 4.57$ B.M) supported a high spin tetrahedral geometry of Co(II) complex [28,30]. The spectrum of tetra nuclear nickel complex(C_5) showed changes in positions of ligand bands and this was due to formation of complex [22,27] . A charge transfer band was observed at 27397 cm^{-1} . Three additional bands were observed in visible region at 24213 , 14005(average value) and 12135 cm^{-1} which were attributed to $^3A_2g\rightarrow {}^3T_1g(P)$, $^3A_2g\rightarrow {}^3T_1g(F)$ and $^3A_2g\rightarrow {}^3T_2g$ transitions respectively . The spectral data and the effective magnetic moment of nickel complex ($\mu eff = 3.84$ B.M) was consistent with the value for octahedral Ni(II) complexes [2,28] . In order to obtain further structural information for Co (C_2) and Ni(C_5) complexes , the spectral data (B' , Dq / B' , 10Dq and nephelauxetic ratio β) were calculated by applying band energies on Tanaba Sugano diagram . For Co complex : B' = 835 cm^{-1}, Dq / B' = 0.625 , 10Dq = 5220 cm^{-1} , $\beta = 0.86$ and for Ni complex B' = 810 cm^{-1}, Dq / B' = 1.54 , 10Dq = 12474 cm^{-1} and $\beta = 0.78$. The values of nephelauxetic ratio of Co(II) and Ni(II) complexes (0.86 and 0.78 respectively) refer to a covalent bonding in the cobalt and nickel complexes [2,28] . The spectrum of di nuclear platinium (IV) complex (C_4) (diamagnetic complex) exhibited change in profile due to formation of complex. Two absorption bands appeared at 23310 and 17605 cm^{-1} which were assigned to $^1A_1g\rightarrow {}^3T_2g$ and $^1A_1g\rightarrow {}^3T_1g(H)$ transitions of octahedral Pt(IV) complexes [30]. The molar conductivities were (0.013, 0.064 , 0.010 , 0.016 , 0.057 , 0.035 , 0.071 $s.mol^{-1}. cm^2$) for L_1 , C_1 , C_2 , L_2 , C_3 , C_4 and C_5 respectively . These values showed the non electrolytic nature for all studied compounds [1,31] . The suggested structures of complexes Figure-5 and -6 showed the coordination of ligands with metal ions through the oxygen atoms and agostic interaction (B - H…M).



C_1 C_2

Figure 5- The structures of L_1 complexes

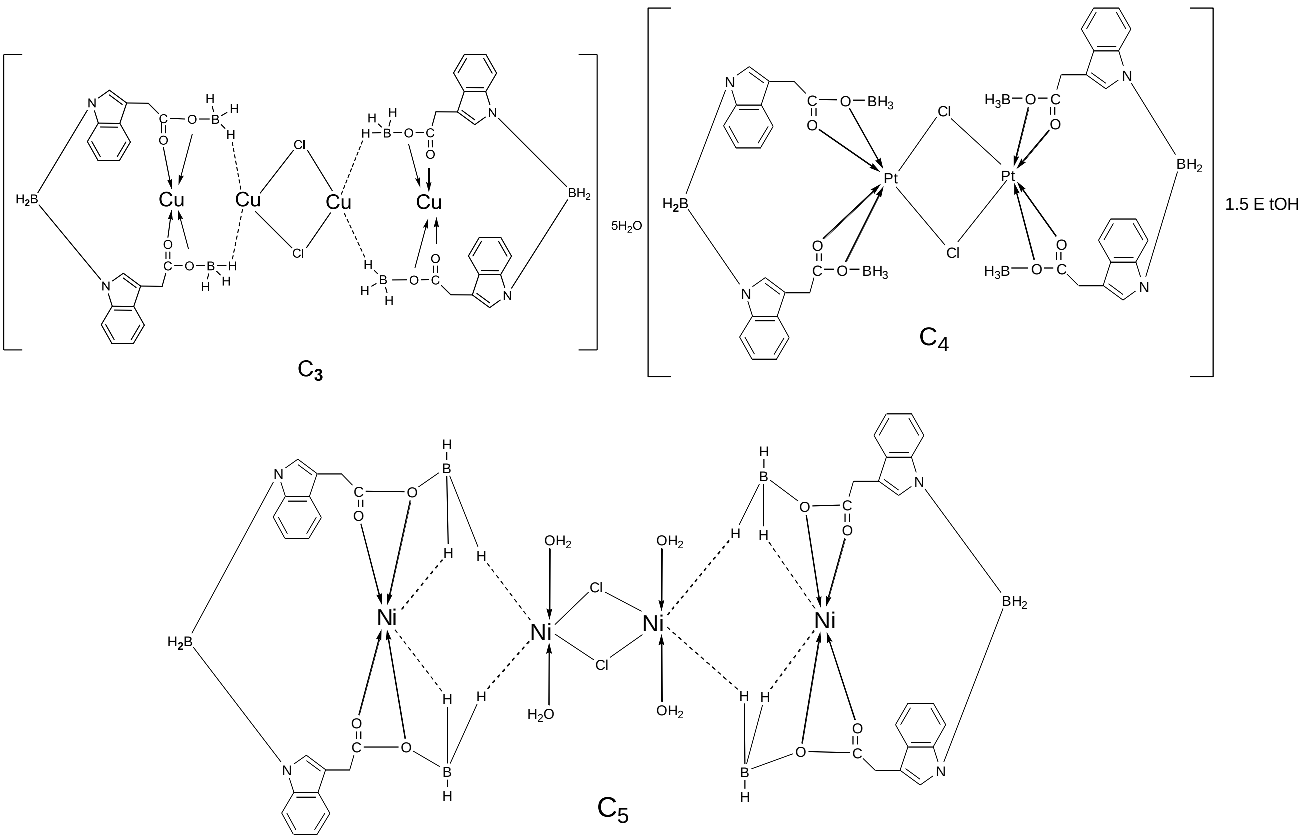


Figure 6-The structures of L_2 complexes

Conclusion

Two new boron ligands have been successfully prepared and their structures were confirmed by ^{1}HNMR and FTIR spectra, elemental and thermogravimetric analyses. The FTIR spectra of the ligands referred to the bonding of boron atom with both nitrogen of indole ring and oxygen of carboxyl group. Coordination of the two ligands with the metal ions (Co(II) , Ni(II) , Cu(II) and Pt(IV)) gave mono, di and tetranuclear complexes in which occurred through the oxygen of carboxylate anion and B-H …M agostic interaction .All complexes showed non electrolytic nature . The spectral data, elemental analyses and magnetic susceptibility measurements suggested square planar geometry of copper complexes, octahedral geometry of nickel and platinum complexes and tetrahedral geometry of cobalt complexes. The results obtained are in good agreement with those calculated for the suggested formula.

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