

IMIDAZOLIUM FUNCTIONALISED IONIC LIQUIDS (EMIM),CL AND METAL COMPLEXES

Pd and Cu

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ABSTRACT

The infrared spectra of the prepared complexes $\text{EtMeim}_2[\text{CuCl}_2\text{Br}_2]$, $[\text{EtMeim}_2[\text{PdCl}_2\text{Br}_2]$ show the strong bands assigned to (C-H) and (C-N) Amination reaction supported by medium intensity band at IR and NMR spectrum .The stretching frequency of (C=C)and (C-N) stretching vibration assigned to(M-Cl) for the complexes.These data indicate that the ligands is coordinated with the metal atom . The NMR spectrum of these complexes $\text{EtMeim}_2[\text{CuCl}_2\text{Br}_2]$, $[\text{EtMeim}_2[\text{PdCl}_2\text{Br}_2]$ was measured by using DMSO-d₆ as solvent.A suitable palladium and copper catalyst system for the imidazolium supported ionic liquids has been developed.

INTRODUCTION

C_N cross coupling of Metal-promoted aromatic reactions provide a excellent and convergent approach to the amines. There are a few successful reports of arylsilanes, despite their low toxicity and abundance which are similar to those of organoboron compound. - Electrophilic amination of aryl[(2-hydroxymethyl)phenyl]dimethylsilanes with O-acylated hydroxylamines has been developed with copper catalyzed - to afford the corresponding anilines in good yields. This smooth catalytic reaction under mild conditions to tolerates a wide range of functional groups. In the amination reaction the functional groups allows various arylsilanes by copper catalysis tolerates and adopted efficiently from the synthesis of arylamines. such an arylsilane is capable of selective aryl group transfer such an arylsilane through facile formation of an intramolecularly penta coordinated arylsilicate, despite its high stability associated with a tetra organo silane structure. cyclic amines showed somewhat lower efficiency: the reaction of six-membered piperidine and morpholine provided the corresponding anilines and in moderate yields, whereas the seven-membered azepane as transformed into 78% yield.

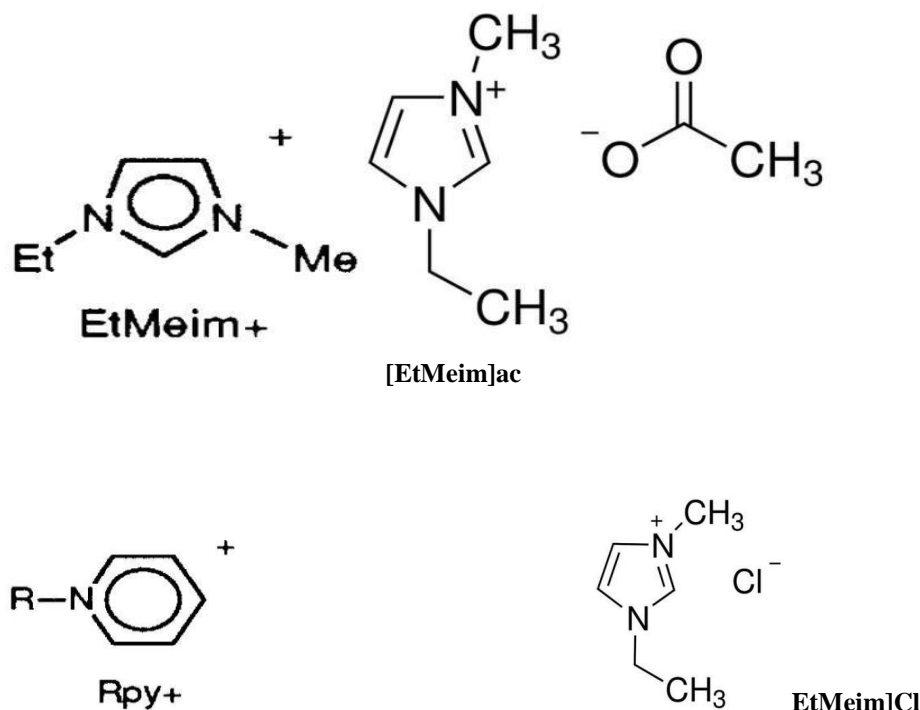
Any salt that melts without decomposing or vaporizing usually yields an ionic liquid. Sodium chloride (NaCl). The ionic bond is usually stronger than the Van der Waals forces between the molecules of ordinary liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. Some salts are liquid at or below room temperature. Examples include compounds based on the 1-Ethyl-3-methylimidazolium (EMIM) cation and include: EMIM:Cl, EMIM dicyanamide,

Low-temperature ionic liquids can be compared to ionic solutions, liquids that contain both ions and neutral molecules, and in particular to the so-called deep eutectic solvents, mixtures of ionic and non-ionic solid substances which have much lower melting points than the pure compounds. Certain mixtures of nitrate salts can have melting points below 100 °C.

The term "ionic liquid" in the general sense was used as early as 1943 When Tawny crazy ants (*Nylanderia fulva*) combat Fire ants (*Solenopsis invicta*), the latter spray them with a toxic, lipophilic, alkaloid-based venom. The Tawny crazy ant then exudes its own venom, formic acid, and self-grooms with it, an action which de-toxifies the Fire ant venom.

The palladium-catalyzed cross-coupling reactions to form C–C bonds are very powerful synthetic tools in modern organic synthesis .With their increasing applications in the synthesis of pharmaceuticals, natural products and functional materials moving these useful transformations to occurring in aqueous media became more and more attractive .Despite there are several strategies for palladium-catalyzed cross-coupling reactions in water, such as microwave heating , ultrasonic irradiation and ligand-free methodology , the more efficient and preferable one is the use of water-soluble ligated palladium catalysts. This approach not only enhances the water solubility of the catalyst, but also facilitates the recovery of the catalyst by separating the aqueous phase and subsequently for the potential reuse of catalyst .Initially, such catalysts have been obtained through modifying traditional palladium–phosphine catalysts by grafting various hydrophilic substituents on phosphine ligands

Ionic liquids are attracting considerable attention as versatile media and materials due to their peculiar physicochemical properties, thermal stability, and easy recycling . I have received great attention as potential solvents to replace volatile organic solvents in a wide variety of chemical reaction, separation, and manufacturing processes to provide excellent protocols for clean and green ideology.



ILs has received much attention of late because of their potential applications in green chemistry and as novel electrochemical materials. Ionic liquids (ILs) are receiving increasing amounts of attention with regards to implementation as “green” alternatives to current laboratory solvent Ionic liquid have gained high popularity in various fields of chemistry, physics, and materials sciences. Nowadays, are used as

solvents for inorganic and organic or organometallic synthesis and catalysis, biocatalysis, chemical analysis, electrochemical devices and media for electrodeposition of metals. Various ionic liquids (ILs) have been used as extractants for the removal of sulfur compounds from the fuel because of their unique chemical and physical properties, such as negligible vapor pressure, high chemical and thermal stabilities and ability to dissolve a wide range of organic and inorganic compounds.

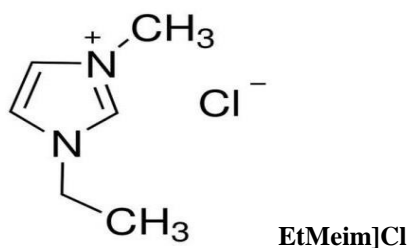
Along with the above interesting results we will synthesize some complexes with three ionic liquid ligands to prepare (15) transition metal. The higher conductivity of the imidazolium salts with the unsaturated side chains could be explained in terms of their molecular structures, the higher ionic conductivity shown by them is attributed to the lower viscosity that is rationalized by their relatively planar structures. Between the methyl substituent of the methyl group and imidazolium ring, resulting in a higher viscosity and lower conductivity.

RTILs possess a unique array of physico-chemical properties that make them suitable in numerous or insufficiently effective. Such properties include:

- high thermal stability,
- high electrical conductivity,
- large electrochemical window,
- low nucleophilicity and capability of providing weakly coordinating or non-coordinating environment,
- very good solvent properties for a wide variety of organic, inorganic and organometallic compounds: in some cases, the solubility of certain solutes in RTILs can be several orders of magnitude higher than that in traditional solvents.

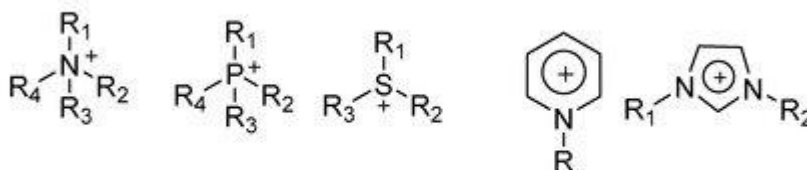
Moreover, by fine-tuning the structure, these properties can be tailor-designed to satisfy the specific application requirements. As a result, ionic liquids are very popular materials and they enjoy a plethora of applications in various domains of physical sciences.

EMIM]Cl was prepared by the reaction of equimolar amounts of 1-methylimidazole and 1-chlorobutane at 60°C using a rotary mantle and under reflux for 48 h and then cooled to room temperature. Then, the product was washed twice with ethyl acetate.



EtMeim Cl was prepared by the reaction of equimolar amounts of 1-methylimidazole and 1-chloroethane at 60°C using a rotary mantle and under reflux for 48 h and then cooled to room temperature. Then, the product was washed twice with ethyl acetate.

Cations



Anions

BF_4^- , PF_6^- , SbF_6^- , CF_3SO_3^- , $(\text{CF}_3\text{SO}_3)_2\text{N}^-$, ArSO_3^- , CF_3CO_2^- , CH_3CO_2^- , Al_2Cl_7^- , NO_3^-

The prepared complexes $[\text{EtMeim}]_2[\text{CuCl}_2\text{Br}_2]$, $[\text{EtMeim}]_2[\text{PdCl}_2\text{Br}_2]$ assigned to (C-H) and (C=N) appeared at aromatic and aliphatic respectively. This was supported by the appearance of new medium intensity band in the spectrum of the complexes which assigned to stretching frequency of (C=C) assigned to (M-Cl) for the complexes. These data indicate that the ligands is coordinated with the metal atom.

Imidazolium functionalised ionic liquids $[\text{EtMeim}]_2 \text{Cl}$ and metal complexes Pd and Cu were found to play a role as a heterogeneous catalyst for (C=C) (C=N) and formation.

EXPERIMENTAL METHODS

Instruments

The identification and physical properties of synthesized compounds were obtained by using the following instruments:

Melting or Decomposition Temperature Measurements

The measurements were carried out for ligands and complexes by using Melting point –MPD-100 pixel technology CO; limited.

Molar Conductivity Measurements

The molar conductivity of complexes has been measured by using (DMSO) as solvent with the concentration of 10^{-3} M at 25°C . this analysis was done by using Jenway conductivity meter 4200(093cell constant)

Nuclear Magnetic Resonance spectroscopy:

^1H NMR AND ^{13}C NMR:

The proton nuclear magnetic resonance spectrum ^1H . ^{13}C (NMR) of $[\text{EtMeim}]_2[\text{MCl}_2\text{Br}_2]$ complexes was measured by using DMSO-d_6 as solvent. The proton nuclear magnetic resonance spectrum ^1H . ^{13}C (NMR) of $[\text{EtMeim}]_2[\text{MCl}_2\text{Br}_2]$ complexes was measured by using DMSO-d_6 as solvent.

NMR for Complexes

The proton nuclear magnetic resonance spectrum ^1H . ^{13}C (NMR) of $[\text{EtMeim}]_2[\text{MCl}_2\text{Br}_2]$ complexes was measured by using DMSO-d_6 as solvent. Studying a molecule by NMR spectroscopy enables us to record differences in the magnetic properties of various magnetic nuclei present and to deduce the positions of this

nucleus within the molecule. One can deduce how many different kinds of environments there are in the molecule and also which atoms are present in neighboring groups. Usually, the number of atoms present in each of these environments is measured. Therefore, the diagnostic features of the NMR Spectra are the number of signals, position of signals, splitting pattern of signals and area of signals. ^1H NMR of the ligands were recorded using Bruker 300 MHz Avance –II FT-NMR Spectrometer with DMSO- d_6 as the solvent and TMS as internal standard

RESULT AND DISCUSSION

2.1 Preparation of ionic liquid complexes

2.1.1 Preparation of $[\text{EtMeim}]_2[\text{MBr}_2\text{Cl}_2]$ complexes

Preparation of $[\text{EtMeim}]_2[\text{CuCl}_2\text{Br}_2]$ complexes:

Chemical Requirements:

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O} = 1.70 \text{ g}, 0.02 \text{ mol}$

Ethanol = 20 ml

$[\text{EtMeim}]\text{Br} = 3.8214 \text{ g}, 0.02 \text{ mol}$

procedure:

The metal of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.70 g, 0.02 mol) was dissolved in (10 ml) ethanol. This solution as added to the mixture solution of $[\text{EtMeim}]\text{Br}$ (3.8214g, 0.02mol) in (10 ml) ethanol, Were heated under reflux for 2hrs, after the heating was stopped the solution was cooled to room temperature and a brown precipitate was removed by filtration and was washed with ethanol and diethyl ether ,all complexes was prepared by the same methods as shown in Table (1).

Complexes	$[\text{EtMeim}]\text{Cl}$ m.wt	Wt.of ligands (g)	Ethanol (ml)	Wt.ofmetal salts (g)	m.wt
$[\text{EtMeim}]_2\text{CuCl}_4$	146.62	2.932	10	1.70	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (170.4)
$[\text{EtMeim}]_2\text{PdCl}_4$	146.62	2.932	10	1.76	PdCl_2 (177.62)

2.1.1 Preparation of $[\text{BenzMeim}]_2[\text{MCl}_4]$ complexes

Preparation of $[\text{BenzMeim}]_2[\text{pdCl}_4]$ complexes

Chemical Requirements:

$\text{pdCl}_2 \cdot 6\text{H}_2\text{O} = 0.01 \text{ mol}, 2.38 \text{ g}$

Ethanol = 30 ml

[BenzMeim]Cl = 0.02 mol, 4.16g

procedure

The metal of (0.01mol, 2.38g) $\text{PdCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml ethanol were added to (0.02 mol, 4.16g) [BenzMeim]Cl were heated under reflux in 20 ml ethanol for 2hrs ,after the heating was stopped the solution was cooled to room temperature and a blue solution was removed by filtration ,after 3 weeks a blue products were washed with ethanol and di ethyl ether, all the complexes were prepared by the same methods as shown in Table(2)

Table(2)

Complexes	[BenzMeim]Cl (m.wt)	Wt of ligand(g)	Ethanol (ml)	Wt of metal salts (g)	m.wt of metal
[BenzMeim] ₂ CuCl ₄	307.68	2.08	10	1.70	CuCl ₂ ·2H ₂ O (170.48)
[BenzMeim] ₂ PdCl ₄	315.11	2.08	10	1.77	PdCl ₂ (146.62)
[EtMeim] ₂ [PdBr ₂ Cl ₂]	191.07	3.82	10	1.77	PdCl ₂ (176.4)

Some physical properties of complexes Table(3)

No.	Structure formula	Color	Melting point	% yield
	[EtMeim] ₂ [CuCl ₂ Br ₂]	Brown	–	65
2	[EtMeim] ₂ [PdCl ₂ Br ₂]	Dark brown	152*	74
3	[EtMeim] ₂ [CuCl ₄]	Brown	102	63
4	[BenzMeim] ₂ [CuCl ₄]	Brown	157	86
5	[BenzMeim] ₂ [PdCl ₄]	Dark brown	148*	76

EXPERIMENTAL DATA

The infrared spectra of the prepared complexes $[\text{EtMeim}]_2[\text{CuCl}_2\text{Br}_2]$, , $[\text{EtMeim}]_2[\text{PdCl}_2\text{Br}_2]$ show the strong bands at $(3095.6-3348.7)\text{cm}^{-1}$ assigned to (C-H) aromatic and at $(2908.9-3089.5)\text{cm}^{-1}$ assigned to (C-H) cm^{-1} aliphatic¹respectively and (C=N) appeared at $(1568-1637.56)\text{cm}^{-1}$. This was supported by the appearance of new medium intensity band at $(1456.1-1574.2)\text{cm}^{-1}$ in the spectrum of the complexes which assigned to stretching frequency of (C=C) and show the bands at $(1165.7-1455.8)\text{cm}^{-1}$ of (C-N) stretching vibration and the single peak at $(261.1-436.9)\text{cm}^{-1}$ assigned to (M-Cl) for the complexes. These data indicate that the ligands is coordinated with the metal atom .The frequencies of the main characterization band were listed in Table(4)

Table(4) Selected IR Spectra of prepared complexes (cm⁻¹):

No	Complex Symbol	N (CH)aromatic c	N (CH)aliphatic c	N (C=N)	v (C=C)	N (C-N)	v (M-Cl)
1	[EtMeim] ₂ [CuCl ₂ Br ₂]	3348.7	2933.1	1568.0	1456.1	1337.3	293.2
2	[EtMeim] ₂ [PdCl ₂ Br ₂]	3123.7	2992.2	1637.56	1560.41	1442.75	261.1
3	[BenzMeim] ₂ [CuCl ₄]	3076.46	3055.24	1649.14	1562.34	1452.40	468.70
4	[BenzMeim] ₂ [PdCl ₄]	3138.18	3084.18	1604.77	1560.41	1456.26	401.19

The infrared spectra of the prepared complexes [EtMeim]₂[CuCl₄], [EtMeim]₂[PdCl₄] were showed a strong bands at (3099.61-3138.18)cm⁻¹ for the assigned to the (C-H) aromatic and at (2974.23-3088.03)cm⁻¹ for the (C-H) aliphatic^[85] and the stretching vibration were observed at (1573.91-1649.14)cm⁻¹ for the (C=N) were shifted to lower or higher values which indicates that the ligands are coordinated to the metal ions and shows the band at (1458.18-1571.99)cm⁻¹ for (C=C)cm⁻¹ and the a band at (1342.46-1562.34)cm⁻¹ for (C-N) and at (222.7-464.5)cm⁻¹ for (M-Cl)

The infrared spectra for prepared complexes [BenzMeim]₂[CuCl₄], [BenzMeim]₂[PdCl₄] showed a strong bands at (3076.46-3400.5) cm⁻¹ assigned to the (C-H) aromatic and the stretching vibration were observed at (3055.24-3084.18)cm⁻¹ for the (C-H) aliphatic^[92]. and a band observed at (1562.34-1649.14)cm⁻¹ for (C=N) and at (1454.33-1571.99) for (C=C) and a band at (1367.53-1560.41) for (C-N) and at (401.19-468.70) cm⁻¹ for (M-CL)

2.2 Nuclear Magnetic Resonance Spectrum (¹H, ¹³C) NMR for Complexes

The proton nuclear magnetic resonance spectrum ¹H, ¹³C (NMR) of [EtMeim]₂[MCl₂Br₂] complexes was measured by using DMSO-d₆ as solvent. The bands observed are as follows The ¹H-NMR spectrum of complexes [EtMeim]₂[PdCl₂Br₂] exhibits that the singlet bands in (9.19 ppm) from this chemical shift, these bands belong to (1H)(N=CH-N), the triplet bands in (7.80-7.71 ppm) from (CH=CH) from the totomerzim for (CH=CH), the multiple bands in (4.22-4.17 ppm) from 2H (-CH₂Et) (3.86-3.85 ppm) from (CH₃-N=), the multiple bands in (1.44-1.39 ppm) from 3H (CH₃-CH₂) group The ¹H-NMR for [EtMeim]₂[CuCl₄], the singlet bands at (9.36 ppm) for (=N-CH-N) the doublet bands at (7.68-7.35 ppm) for (-CH=CH-), (4.29 ppm) for (2H)(CH₂-Et), (3.99 ppm) for (3H)(CH₃-N) and (1.56 ppm) for (3H)(-CH₃Et).

The ¹³C-NMR spectrum for [EtMeim]₂[CuCl₄], shows peaks at (131.99 ppm) for (N=CH-N) (131.18-131.11 ppm) for (N-CH-N) Totomerizm, (126.59-120.35 ppm) for (CH=CH), (51.86 ppm) for (CH₂-Et), (36.41 ppm) for (-N-CH₃) and (14.86 ppm) for (-CH₃Et) group.

No	Structure formula	CH ₃ Ethyl	DMSO	CH ₃ -N	- C ₅ H ₅	CH ₂ ethyl	CH=CH	N=C H-N
1	[EtMeim] ₂ [PdCl ₂ Br ₂]	1.44-1.39	2.50	3.86-3.85	----	4.22	7.80-7.71	9.19
2	[EtMeim] ₂ [CuCl ₄]	1.56	2.50	3.99	----	4.29	7.68-7.35	9.36
3	[EtMeim] ₂ [PdCl ₄]	1.42-1.38	2.50	4.23-4.18	----	4.23	7.82-7.73	9.29
4	[BenzMeim] ₂ [CuCl ₄]	-----	3.37	3.87-3.78	5.44	7.43	7.81-7.73	9.29

The ¹H-NMR spectrum of [EtMeim]₂[PdCl₄] , show the singlet bands at (9.29ppm) for (1H)(N=CH-N), the doublet bands at (7.82-7.73 ppm) for (2H)(CH=CH), the multiple bands at (4.23ppm) for (2H)(CH₂Et), the doublet bands at (4.23-4.18ppm) for (3H)(N-CH₃) and triplet bands at (1.42—1.38 ppm) for (3H)(CH₃Et).

The ¹³C-NMR spectra data of [EtMeim]₂[PdCl₄], shown peaks at (132.71 ppm) for (N=CH-N), the peaks at (119.96-118.38 ppm) for (CH=CH),(40.54 ppm) for (CH₂Et),(32.17 ppm) for (CH₃-N) and (11.61 ppm) for (CH₃Et).

The ¹H-NMR spectrum of [BenzMeim]₂[CuCl₄]: complexes show singlet band at (9.29 ppm) for (=N-CH-N), the doublet bands at (7.81-7.73 ppm) for (CH=CH), multiple band at (5.44 ppm) for (CH₂)aromatic, the singlet bands at (7.43ppm) for (-C₅H₅)aromatic ring, the doublet band at (3.87-3.78 ppm) for (CH₃- N=).

The ¹³C-NMR spectrum for [BenzMeim]₂[CuCl₄]: shows peaks at (136.65- 134.85 ppm) for two (N=CH-N) and at (128.95-128.28 ppm) for (-C₅H₅)(123.98 -122.31 ppm) for (-CH=CH) (51.83 ppm) for (CH₂-Et)and(35.89 ppm) for (CH₃-N).

The ¹H-NMR spectrum of [BenzMeim]₂[PdCl₄] complexes show singlet band at(9.43 ppm) belong to (1H)(N=CH-N), the doublet band at (7.71-7.48 ppm) belong to (2H)(CH=CH) and, the doublet band at (5.40 ppm) belong to (2H) (- C₅H₅), the singlet bands in (3.92 ppm) belong to (3H)(CH₃-N), and singlet bands at(7.37 ppm) for (CH₂)aromatic ring.

The ¹³C-NMR spectrum for [BenzMeim]₂[PdCl₄] , complexes shows peaks (132.86 ppm) for (N=CH-N),(127.74-127-18 ppm) for (-C₅H₅)(122.80-121.16ppm) for (CH=CH),(51.90 ppm) for (CH₂-C₅H₅)and(36.65 ppm) for (CH₃) group.

The data of (¹³C-DEPT-135) spectra

The ¹³C-DEPT-135 spectral for[EtMeim]₂[PdCl₂Br₂] complexes appearance of one

5	[BenzMeim] ₂ [PdCl ₄]	-----	2.50	3.92	5.40	7.37	7.71-7.48	9.43
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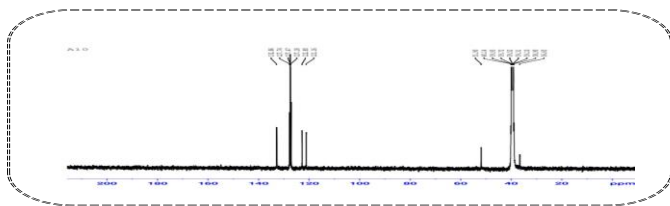
downward single for (N=CH-N) at (140.35 ppm), downward single for (CH=CH) at (127.68-126.10 ppm), the upward single at (48.26 ppm) for (CH₂Et), another downward single at (39.88 ppm) for (N-CH₃) and downward single for (CH₃Et) appeared at (19.28 ppm).

Nuclear Magnetic Resonance Spectrum (¹H-NMR) for prepared complexes

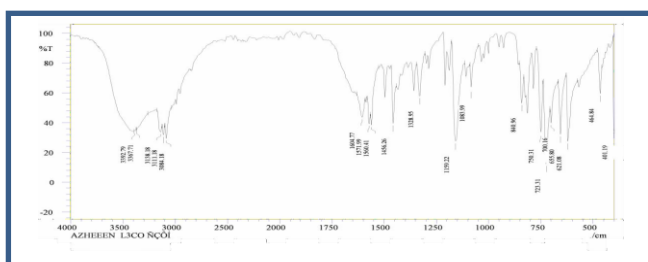
¹³C-NMR data for prepared complexes

No	Structure formula	-N-CH ₃	CH ₂ Et	CH=CH	-C ₅ H ₅	CH ₃ Et	N=CH-N
1	[EtMeim] ₂ [PdCl ₂ Br ₂]	35.73	44.12	123.53- 121.94	-----	15.12	136.20
2	[EtMeim] ₂ [CuCl ₄]	36.41	51.86	126.59- 120.35	-----	14.86	131.99
3	[EtMeim] ₂ [PdCl ₄]	32.17	40.54	119.96- 118.38	-----	11.61	132.71
4	[BenzMeim] ₂ [CuCl ₄]	35.89	51.83	123.98- 122.31	128.95- 128.28	-----	136.65- 134.85
5	[BenzMeim] ₂ [PdCl ₄]	36.65	51.90	122.80- 121.16	127.74- 127.18	-----	132.86

¹³C-NMR for [EtMeim]₂[PdBr₂Cl₂]



$^{13}\text{C-NMR}$ for $[\text{BenzMeim}]_2[\text{PdCl}_4]$



IR Spectra for $[\text{BenzMeim}]_2[\text{PdCl}_4]$

Conclusion.

The prepared complexes were characterized by elemental microanalysis, molar conductivity, IR, UV-visible spectra, magnetic measurements and the $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and atomic absorption analysis. The results exhibit that the complexes of Ni(II), Co(II), Cu(II) have tetrahedral geometry and Pd(II), Pt(II) complexes have square planar geometry, according to the molar conductivity data it has been suggested that all synthesis complexes are electrolyte types.

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