IMIDAZOLIUM BASED PHYSIOCHEMICAL PROPERTIES OF IONIC LIQUIDES

M.DEEPA[1],C.UMA[2],M.ARIVUMATHI[3],M.MAHALAKSHMI[4]

ABSTRACT

The prepared complexes $[EtMeim]_2[NiCl_4]$, $[BenzMeim]_2[CoCl_4]$, assigned to (C-H) and (C=N) appeared at aromatic and aliphaticrespectively 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 $[EtMeim]_2Cl$ and metal complexes Ni and Co were found to play a role as a heterogenous catalyst for (C=C) (C=N) and formation.

The catalytic potential has increased donor ligands(O,S,N,P,etc….), in different organic transformation.[1] The donor ligands of type N are particularly interesting..They display a hard donor (N) and soft donor (S) that can coordinate to a wide range of metal ions .They can bind to the same metal in particular coordination state providing a different bond strength and liability for each donor atom. There is also a current interest in the incorporation of these N, S donor atoms (usually the ligands contain combination of imidazole groups or pyrazolyle or thiolato or thioether functional groups)inmacrocycles and in polydentate ligands in order to probe the biologically relevant coordination's chemistry, the supramolecular chemistry ,or the electrical conduction or catalytic reaction of differentmetals

imidazolium or benzimidazol rings for forming compounds containing spacer CH_2CH_2 or CH_2CH_2 CH_2CH .The scientific has presented various studies about ionic liquids in green preparation during recent year's .In addition, ionic liquids are attracting considerable attention as versatile media and materials due to their peculiar physicochemical properties, thermal stability, and easy recycling

Nowadays, organic salts, ionic salts and complexes have been used in the removal of sulfur compounds from diesel fuel for use of its specific physical and chemical properties .Such as its thermal stability, and its solubility for a large number of inorganic and organic compounds**IonicLiquid FUNCTIONS**

. IL 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.

EXPERIMENTAL METHODS

Molar ConductivityMeasurements

The molar conductivity of complexes has been measured by using (DMSO) as solvent with the concentration of 10^{-3} M at 25 °C

IRSpectrum

During the complexes formation anew coordination bond is formed between the ligand and the central metal atom resulting in the change of the electronic structure which has an effect on the energy level and the symmetry of the compound .All these factors have effects on the stretching vibration are the physical states of the samples, the degree of hydrogen bonding, the substitution pattern, the nature of the substituent and the polarity of the solvents

We have successfully prepared sample of a selection of the proposed ionic liquids, and we have shown that at least one of them. This is especially encouraging as this particular molecule has the aldehyde function in close proximity to the imidazolium positive charge .The deportation is an acid – catalyzed reaction and the positive imidazolium center is expected to discourage the approach of protons. Infrared spectrum has been recorded in range (200-4000 cm^{-1}) of the FTIR (ATR) Spectrophotometer and has been used in order to identify the prepared ligands and complexes. The values and positions of the spectra bands for ligands and their complexes are tabulated in Tables (12) exhibited following major bands.

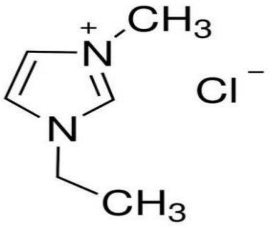
^{1}H NMR: Nuclear Magnetic Resonance Spectrum ($^{1}H.^{13}C$) NMRfor Complexes

The proton nuclear magnetic resonance spectrum $^{1}H.^{13}C$ (NMR) of $[EtMeim]_2[MCl_2Br_2]$ 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. ^{1}H NMR of the ligands were recorded using Bruker 300 MHz Avance –II FT-NMR Spectrometer with DMSO-d_6 as the solvent and TMS

Preparation of $[EtMeim]_2[NiCl_4]$complexes and $[BenzMeim]_2[CoCl_4]$ complexes

PROCEDURE:

(1)The metal of $NiCl_2.6H2O$, (0.01mol, 2.38gm) was dissolved in (10ml) ethanol, added to (0.02mol, 2.92g) of ligand [EtMeim]Cl. The resultant solution was stirred under refluxing for 2hrs .The resulting solution was filtered and the green product were washed with ethanol and diethyl ether and stored refrigerator at 5°C. all the complexes was prepared by the same methods as shown in Table (4):



EtMeim]Cl

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

(2)The metal of (0.01mol, 2.38g) $CoCl_2.6H_2O$ 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(5):

[BenzMeim]Clwas prepared by the reaction of equimolar amounts of 1-methylimidazole and 1-chloroBenzene at 60°C using rota mantle and under reflux for 48 h and then cooled to room temperature. Then, the product was washed twice with ethyl acetate.

preparation of $[EtMeim]_2[MCl_2Br_2]$ complexes:

Complexes	[EtMeim]Br M.wt	Wt. of ligand (g)	Ethanol (ml)	Wt of Metal salts(g).	M.wt of metals
$[EtMeim]_2CoCl_4$	146.62	2.932	10	2.38	$CoCl_2.6H_2O$ (237.92)

. preparation of [BenzMeim] Cl complexes:

Complexes	[BenzMeim]Cl (m.wt)	Wt of ligand(g)	Ethanol (ml)	Wt of metal salts (g)	m.wt of metal
$[BenzMeim]_2NiCl_4$	302.83	2.08	10	2.37	$NiCl_2.6H_2O$ (237.6)

Some physical properties of complexes

No.	Structure formula	Color	Melting point	% yield
1	$[EtMeim]_2[CoCl_4]$	Blue	119	72
2	$[BenzMeim]_2[NiCl_4]$	Green	_	63
3	$[BenzMeim]^2[CoCl_4]$	Blue	150	75

Molar Conductivity measurement values of (10^{-3}M) for prepared complexes ($ohm^{-1}.mol^{-1}.cm^2$) at (25^0C) by using DMSO as solvent:

Compound No.	Λ_m	Compound No.	Λ_m	Compound No.	Λ_m
$[EtMeim]_2[NiCl_2Br_2]$	61	$[EtMeim]_2[NiCl_4]$	43	$[BenzMeim]_2[NiCl_4]$	45
$[EtMeim]_2[CoCl_2Br_2]$	72	$[EtMeim]_2[CoCl_4]$	31	$[BenzMeim]_2[CoCl_4]$	52

Four types of electronic transitions are possible:

1. Ligand spectra: absorption bands ofligands are normallynoted in the ultraviolet. These bands may be shifted from their original positions.
2. Charge transfer spectra: these spectra arise from transitions between molecular orbitals that are principally those of the metal and orbital those are largely ligandorbitals.
3. Ligand field spectra: these arise from transition between d-d transition of the metal in a ligand field of thecomplex.

4 . Counter .ion spectra: a complex must be associated with a counter ion, knowledge of the spectrum due to the complexion.

Electronic spectra of prepared complexes:

Complexes	Band(1)ν(cm^{-1})	Band(2) ν(cm^{-1})	Band(3) ν(cm^{-1})
$[EtMeim]_2[CoCl_4]$	14927	16393	23809
$[BenzMeim]_2[CoCl_4]$	15151	16393	-------

Selected IR Spectra of Ligands (cm^{-1}):

No	Ligands	ν (CH)aromatic	ν (CH)aliphatic	ν (C=N)	ν (C=C)	ν (C-N)
1	[EtMeimBr]	3189	2998	1633.1	1698.1	1544.2
2	[EtMeimCl]	31296	2992	1675	1670	1498
3	[BenzMeimCl]	31205	29801	1603.1	1567.1	1492.2

Selected IR Spectra of prepared complexes (cm^{-1}):

No	Complex Symbol	ν (CH)aromatic	ν (CH)aliphatic	ν (C=N)	ν (C=C)	ν (C-N)	ν (M-Cl)
1	[EtMeim]$_2$[NiCl$_4$]	3118.90	3089.96	1649.14	1571.99	1562.34	264.0
2	[EtMeim]$_2$[CoCl$_4$]	3138.18	3088.03	1600.92	1560.41	1496.76	401.19
3	[BenzMeim]$_2$[NiCl$_4$]	3400.50	3080.32	1602.85	1571.99	1560.41	462.9
4	[BenzMeim]$_2$[CoCL$_4$]	3078.39	3061.03	1562.34	1454.33	1367.53	406.98

The infrared spectra of the prepared complexes [EtMeim]$_2$[NiCl$_4$], [EtMeim]$_2$[CoCL$_4$], 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 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)] and at (222.7-464.5)cm^{-1}for(M-Cl)

The infrared spectra for prepared complexes [BenzMeim]$_2$[NiCl$_4$], [BenzMeim]$_2$[CoCl$_4$], 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 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)$^{.}$

The ^{1}H-NMR of **[EtMeim]$_2$[CoCl$_4$]:,** shows peaks at (9.21 ppm) for (1H)(=N-CH-N) the duplet bands at (7.66-7.58 ppm) for (CH=CH),(4.08 ppm) for (2H)(CH$_2$-Et),(3.72-3.53 ppm) for (-N-CH$_3$) and the duplet bands at (1.37-1.26 ppm) for (3H)(CH$_3$Et).

The ^{13}C-NMR for of **[EtMeim]$_2$[CoCl$_4$],**complexes shows peaks at (132.16-132.14 ppm) for (N=CH-N) (121.45-119.80 ppm) for (CH=CH) (42.99 ppm) for (CH$_2$-Et) (35.53 ppm) for (CH$_3$-N) and (13.78 ppm) for (CH$_3$-Et).The ^{1}H-NMR spectrum of **[EtMeim]$_2$[PtCl$_4$],** shows the singlet bands at (9.27 ppm) for (1H)(=N-CH-N), the duplet bands at (7.82-7.73 ppm) for (CH=CH) the triplet bands at (4.22-4.19 ppm) for 2H (CH$_2$Et), and in (3.87-3.82ppm) for (-N- CH$_3$), the triplet bands at (1.44-1.38 ppm) for 3H (CH$_3$Et) groups.

4. The complexes of[BenzMeim]$_2$[MCl$_4$]:

The ^{1}H-NMR spectrum of **[BenzMeim]$_2$[CoCl$_4$]:** complexes was measured by using DMSO-d$_6$ as solvent. The singlet bands at (9.53 ppm) for (1H)(N=CH-N) group, the doublet bands at (7.72-7.65 ppm) for (2H)(CH=CH), the multiple bands at (7.39 ppm) for (5H)(-C$_5$H$_5$).

The singlet bands at (5.28 ppm) for (2H)(CH$_{2-}$C$_5$H$_5$), the singlet bands at (3.80

ppm) for (3H)(CH_3-N).

The ^{13}C-NMR spectrum for **[BenzMeim]$_2$[CoCl$_4$]:** shows peaks at (131.47 ppm) for (N=CH-N)(126.63-125.86 ppm) for (-C_5H_5),(122.00-120.13 ppm)for (CH=CH),(51.51 ppm) for (CH_2)aromatic (37.91 ppm) for (CH_3-N) group.

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

No	**Structure formula**	**CH_3 ethyl**	**DMSO**	**CH_3-N**	**-C_5H_5**	**CH_2 ethyl**	**CH=CH**	**N=CH-N**
1	[EtMeim]$_2$[CoCl$_4$]	1.37-1.26	2.50	3.72-3.53	----	4.08	7.66-7.58	9.21
2	[BenzMeim]$_2$[CoCl$_4$]	-----	2.52	3.80	7.39	5.28 arom.	7.72-7.65	9.53

^{13}C-NMR data for prepared complexes

No	**Structure formula**	**-N-CH_3**	**CH_2Et**	**CH=CH**	**-C_5H_5**	**CH_3Et**	**N=CH-N**
1	[EtMeim]$_2$[CoCl$_4$]	35.53	42.99	121.45-119.80	------	13.78	132.16-132.14
2	[BenzMeim]$_2$[CoCl$_4$]	37.91	51.51arom.	122-120.13	126.63-125.86	-----	131.47

The ^{13}C-DEPT-135 data for complexes:

Complexes	N=CH-N	CH=CH	CH_2Et	N-CH_3	CH_3Et
[EtMeim]$_2$[CoCl$_4$]	140.86	130.43-128.76	-52.06	44.70	22.88

According to conclusion we suggest following for future works:

1. Preparation of new ionic ligand complexes and using their applicationfor removal of sulfur compounds from dieselfuel.

2. Using the complexes of ionic liquid complexes for catalysis studies and forbasic electro-chemical studies of organic and inorganiccompounds.

3. Formation of metal nanostructures, analytical chemistry including sensors,bio-analytical chemistry and electro-chemicalbiosensors.

Referance

1)W.A.Chomitz and J.Arnold .,**J.Chem.Eur**.,15,2020-2030,(2009).

2) L.C.Liang ,**Coord.Chem.Rev**.,250,1152-1177,(2006).

3) F.A.Lewis ,and W.B.Tolman,**Chem.Rev**.,104,1047-1076(2004).

4) S.Q.Bai,L.L.Koh, and T.S.A.Hor,**Inorg.Chem**.,48,1207-1213,(2009).

5) J.A.Zhang.M.Pan.J.Y.Zhang and B.S.Kang .,**Polyhedron**.28,145-149,(2009)

6) 7) O.P.Melnyk.Ya.E. Filinchuk, **Chem**,627,287-293,(2001).

7) A.A.Ismail ,**M.Sc.Thesis**,University ofMosul,(1981).

8) R.L.He.F.J.Meng and J.W.Xu,**ActaCryst.**SectionE66,750-761,(2010).

9) A.Seeberger and A.Jess**,Green Chem**.,12,602-608,(2010).

10) L.F.R.Verduzco,E.T.Garcia,R.G.Quintana,V.P.Gonzalez and F.G.Murrieta,

Catal Today, 98,289-294,(2004).

11) F.E.Hahn andM.C.Jahnke.Angew.**Chem.Int.Ed**.47,3122-3172,(2008).

12) J.D.Holbrey,**Green Chemis.**,4,407-413,(2002).

13) K. Wang.F.Jian and R.Zhuang,J.Chil.**Chem.Soc**.,55(2),257-260,(2010).

14) G.H.Min,andTaeeun Yim,**Chem**.Soc.,27(6),847-851,(2006).

15) A.R.Katritzky,**Chem**.,12,4630-4641,(2006).

16) G.V.Ahsen and O.Bekaroglu.,**J.Chem.Soc.DaltonTrans**.,2283-2286,(1992).

17)R.J.Lewis and Thomas Welton.,**Polyhedron**.,12(16),2039-2044,(1993).

18)M.Blomenkemper,H.Schroder,T.Pape and F.E.Hahn, **Inorg.Chim.Acta**, 390,143-137,(2012).

19) I.J.B.Lin and C.S.Vasam,**J.Orgmet.Chem**.,690,3498-3512,(2005).

20) P.Wasserscheid and W.Schroer.,**J.Molec.liquids**.,192,3-8,(2014).

21) A.A.Shamsuri andD.K.Abdullah,**Physi.Scien.**.,21(1),15-28,(2010).

22) K.J.Fraser and DouglasR.Macfarlane.,**J.Chem**.,62,309-321,(2009).

23) T.Sonnleitner.D.A.Turton and R.Buchner.,J. **Molec.liquids**.,192,19-25,(2014).

24)A.K.AbdulSadaA.M.Greenway,P.B.Hitchcoch,T.J.Moohammed,K.R.Seddon, and,**J.Chem.Soc.Chem.Commun**.,1753-1760,(1986).

25) D.Castillo,P.Astudillo,J.Mares,F.J.Gonzalez,A.Vela and J.Tiburcio, **Org.Biomol.Chem**.,5,2252-2256,(2007).

26) B.Li.Yi-Q.Li,W.J.Zheng and M.Y.Zhou,**Arkivoc**.,Xl,165-171,(2009).

27) M.H.Ghorbani,**Acta Cryst**.,E68,o2605,(2012).

28) J.M.Suisse,S.B.Laponnaz,L.D.Aline and R.Welter.,**Elsevier**.,46,4303-4305,(2005).

29) S.Ch.Turmannova.,**poly**.,1,(9),585-593,(2007).