

CHAPTER I

GENERAL INTRODUCTION

CHAPTER - I

SECTION A

Introduction “Research is creating new knowledge.” - Neil Armstrong

Interdisciplinary research integrating coordination chemistry and green chemistry concepts has led to the discovery of ionic liquid-supported Schiff base metal complexes. Ionic liquids have special qualities that make them excellent solvents and catalysts, as illustrated by groundbreaking work by Rogers and Seddon in the late 1990s. Later researchers investigated the integration of Schiff base ligands into metal complexes in these ionic liquid environments. Significant advancements in the discipline were made by researchers such as Dupont and others, who highlighted the applicability of these compounds in material science and catalysis. With time, these compounds' synthesis, characterization, and uses have become essential to the development of sustainable materials, catalysis, and chemistry [1-2]. Several literature reports highlight its applicability in biological science as well [16-23].

For a comprehensive understanding, we shall see transition metal complexes of ionic liquid-supported Schiff bases in four different parts comprising of Ionic Liquids (ILs), Schiff bases, Ionic Liquid-supported Schiff Bases, and Transition metal complexes of ionic liquid-supported Schiff bases.

1.1. Ionic Liquids (ILs)

Ionic liquids (ILs) are entirely ionized liquid salts at an ambient condition having a low vapor pressure and a wide liquid range which consists of two parts, viz. i) Cationic part and ii) Anionic part. The cationic part is mainly comprised of organic ions whereas the anionic part is mainly comprised of inorganic ions or polyatomic ions [3-5]. Fig.1.1 shows some of the common cations and anions used for the synthesis of ionic liquids.

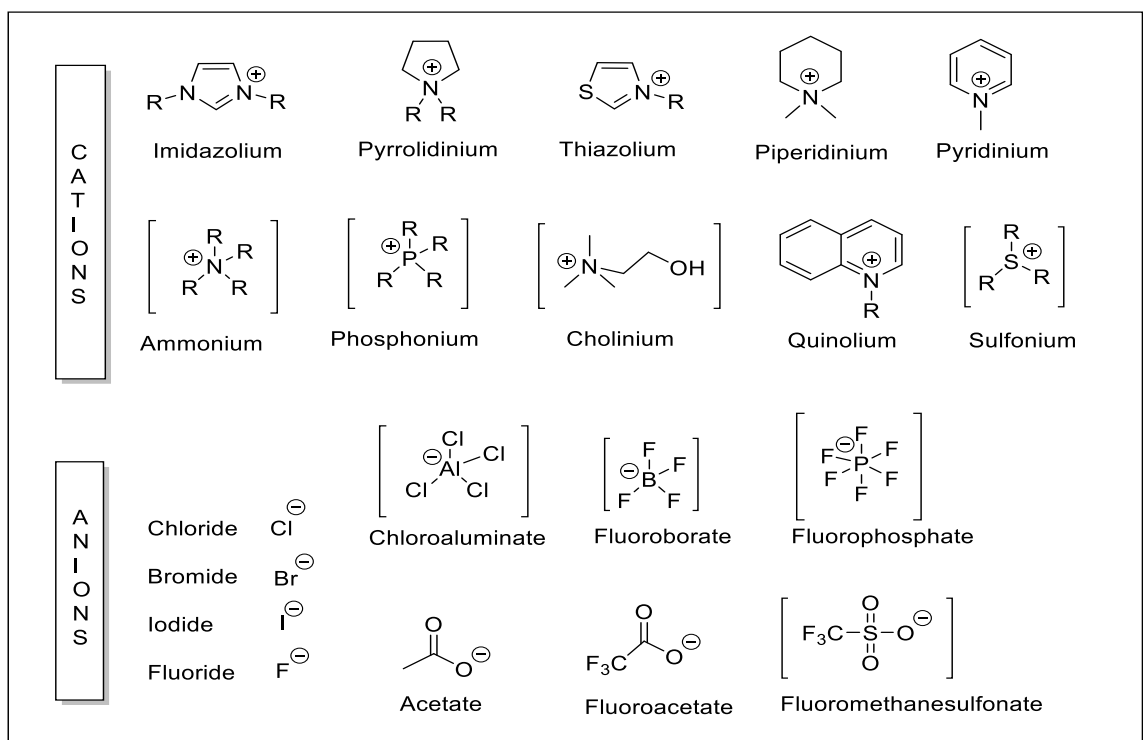


Fig.1.1 Some common cationic and anionic parts of ILs

Ionic liquids (ILs) have gained widespread attention only following Wilkes and Zaworotko's initial report on air and moisture stable room temperature liquid salts in 1992 [6], even though Paul Walden published the first ionic liquid, "Ethyl ammonium nitrate," in 1914 [7]. Since the initial report, the number of research papers published on ionic liquids has grown significantly, outpacing the annual growth rates of certain popular research fields. This suggests that a greater number of researchers are working on ionic liquids, with an abundance of results to show. Ionic liquids (ILs) are gaining attention in a variety of fields, including material science, chemical engineering, chemical synthesis, environmental science, and medicinal chemistry. They have many beneficial properties, including low vapor pressure, thermal stability, the ability to dissolve various substrates, high electrical conductivity, and more. One of the most notable aspects of ILs is the tenability of their physical and chemical properties through modification of the cation and anion combinations. Typically, large organic cations and smaller anions are designed to prepare useful ionic liquids. While most studies on ILs emphasize their use as reaction media in organic synthesis, these liquids are also gaining attention in the fields of inorganic, medicinal, and material chemistry [8-13]. While many reactions successfully employ these

ionic liquids as solvents and catalysts [14-15], a good number of research studies detail their biological activities, including cytotoxicity, antifungal, antibacterial, and antioxidant qualities [16-23]. Imidazolium, pyridinium, and pyrrolidinium moieties are found in certain common ionic liquids as their cationic component[24]. Although several pyridinium-containing ionic liquids have been documented in the literature, an in-depth analysis of the literature revealed that pyridinium moiety-containing ionic liquids can be investigated further. Some of the reported ionic liquids with pyridinium moiety are 1-(10-aminodecyl) pyridinium salt [25], polymeric 3-alkylpyridinium salts [26], 12-methacryloyloxy-dodecylpyridinium bromide [27], pyridinium-ceramide-bromide [28] which displays cytotoxicity activity against diverse cell types.

The synthesis of ILs involves essentially two steps. First, the synthesis of the desired cationic part, which is normally carried out through protonation by acid or by quaternization of amines with alkylating agents. It is then treated for anion exchange reaction in the next step. This involves the treatment of halide salts with Lewis acids to form Lewis acid-based ionic liquids or by anion metathesis. Fig.1.2 shows the schematic steps for the synthesis of ILs.

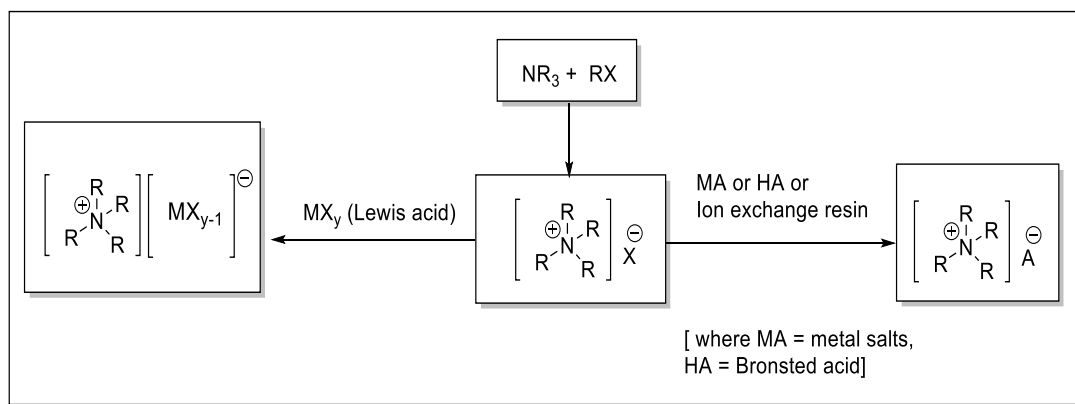


Fig.1.2 Schematic steps for the synthesis of ILs

1.2. Schiff bases

Schiff's bases are versatile pharmacophores with an azomethine linkage that are often created when primary amines condense with a carbonyl molecule. The azomethine group, which has the generic formula $\text{RHC}=\text{NR}'$ (where R and R' are alkyl, aryl, cycloalkyl, or heterocyclic groups), is the structural characteristic common to all Schiff's Bases. Schiff

bases, usually produced by the condensation of a primary amine with an aldehyde are one of the most abundant ligands in coordination chemistry. Because of the various ways that heteroatoms like nitrogen, oxygen, and sulfur can interact with transition metal ions, Schiff bases containing these elements are particularly interesting. Also, because of their wide range of uses in various areas as well as simple synthesis procedures, Schiff bases are referred to as "privileged" ligands [29]. These organic molecules are widely accessible, extremely versatile, and exhibit various denticities and functionalities depending on the properties of the precursors. A Schiff base's donor sites' features, number, and orientation about one another provide excellent control over the metallic center's geometry. Because of their structural diversity and ease of preparation, they are crucial to both synthetic and structural studies [30].

Ketones can also be employed, like aldehyde, in the synthesis of Schiff bases; though they do so less rapidly. Additionally, Schiff bases produced from aliphatic aldehydes are more prone to polymerization and are less stable [31]. An extensive conjugated aromatic aldehyde is found to produce a more stable Schiff base with an amine. When applied in conjugation with one or more donor atoms adjacent to the azomethine linkage, the lone pair of electrons on the sp^2 hybrid orbital of the nitrogen atom of the azomethine linkage exhibits remarkable chelating capability and has important chemical and biological importance [32]. The amine and carbonyl molecules used in the condensation reaction determine the coordination type of the Schiff bases. Depending on how many donor atoms or sites are in the specific structure, they may act as mono, bi-, tri-, tetra, or polydentate ligands. Fig.1.3 represents the general reaction scheme for the synthesis of Schiff bases.

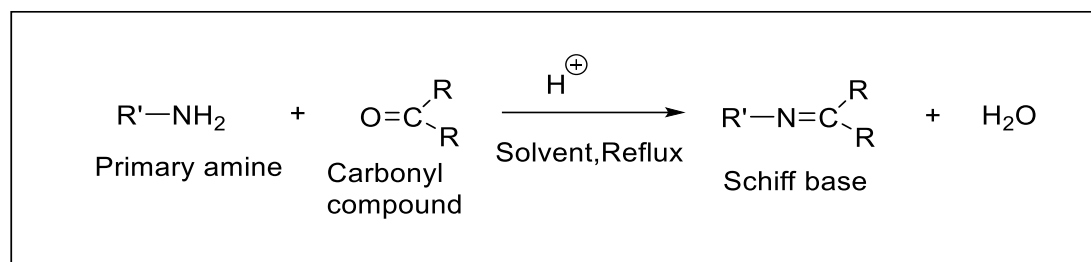


Fig.1.3 The general reaction for the synthesis of Schiff bases

1.3. IL-supported Schiff bases

According to literature studies, when ionic liquids are combined with Schiff bases, a modified Schiff base ligand system known as the Ionic Liquid-supported Schiff base Ligand System is formed. So it contains both the ionic liquid as well as Schiff base parts and exhibits properties different from its parent ionic liquids and Schiff bases. Such compounds have significant impact on inorganic and organic chemistry, environmental chemistry, material chemistry, and medicinal chemistry [33-37]. Fig.1.4 shows the synthesis of IL-supported Schiff bases.

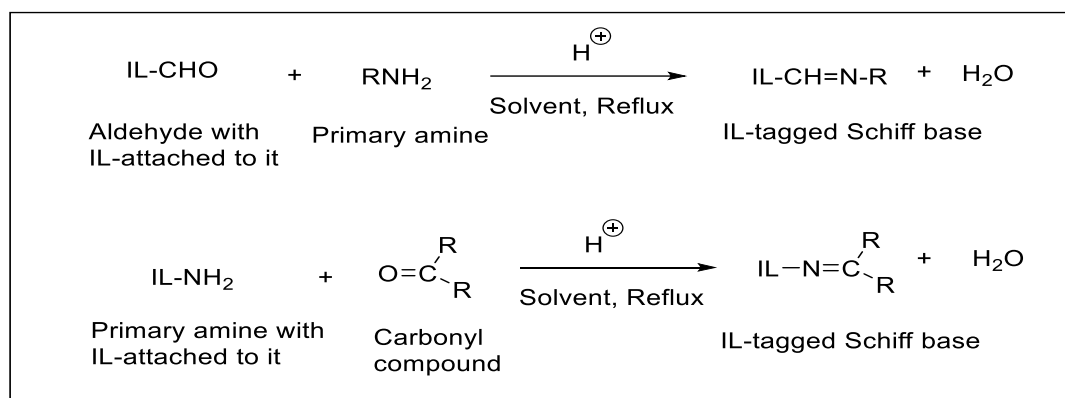


Fig.1.4 The synthesis of IL-supported Schiff bases

1.4. Transition metal complexes of IL-supported Schiff bases

Transition metal complexes of ILs-supported Schiff base ligand systems represent a fascinating fusion of coordination chemistry and other branches of Science, mainly material, catalysis, and biological sciences. These compounds, which are prepared by incorporating ILs during the synthesis of Schiff bases, exhibit enhanced thermal stability and unique structural adaptability. The synergy between Schiff bases and ILs results in multifaceted properties, making them promising candidates for catalysis, materials design, and medicinal applications. Their tunable solubility and reactivity contribute to their versatility, underscoring their potential to address contemporary challenges across diverse scientific disciplines. Ongoing research in this field is poised to uncover novel combinations, further expanding the utility of these innovative complexes. Focusing on the biological and catalytical activities only, several reports are found in the literature survey [38-45]. As found in the literature survey, transitional metal complexes of ILs-supported Schiff bases have several applications in different diverse fields but herein their application

is being restrict to studying their use in biological science and catalysis only. Hence, the literature review will focus on the synthesis of transitional metal complexes of ILs-supported Schiff bases and their application in biological and catalytical studies only. Fig.1.5 shows a schematic representation of the synthesis of transition metal complexes of ILs-supported Schiff base ligand system.

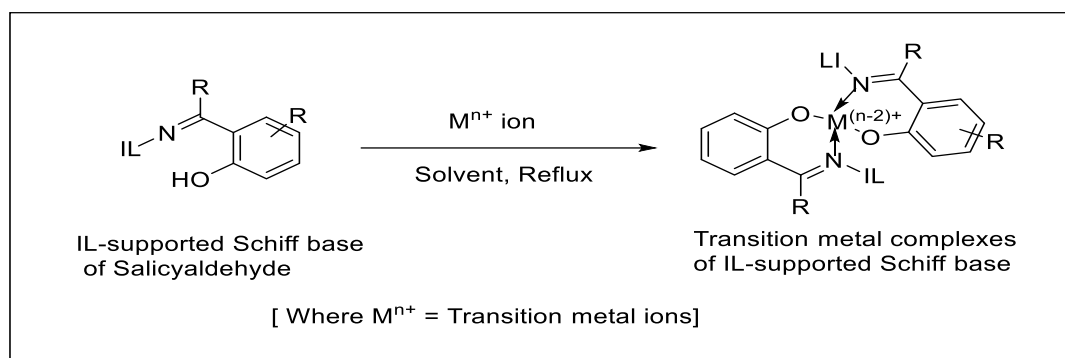


Fig.1.5 The synthesis of transition metal complexes of ILs-supported Schiff base

1.5. Literature review

Ionic liquids (ILs) emerged in the late 1800s and they have a long history. Their history began in 1914 with the synthesis of ethylammonium nitrate, the first IL, at room temperature by Paul Walden [46]. However, until developments in green chemistry in the late 20th century, interest in IL research had been declining. Their high melting points initially caused them to be disregarded, but with advancements in synthesis in the late 20th century, their usefulness was finally recognized. The introduction of ILs as environmentally acceptable solvents was made possible by the seminal work of Swatloski and Rogers in 2002 [82]. Due to their special qualities, such as their high solubility and low volatility, they were used in a variety of industries, including electrochemistry and catalysis. A boom of research in the 21st century revealed their versatility and eco-friendliness. Today, ionic liquids are essential to many industrial processes, signifying a paradigm change toward efficient and sustainable technologies and writing a revolutionary new chapter in the history of chemistry.

Synthesis of ethyl ammonium nitrate, the first ionic liquid, was first reported in 1914 by renowned scientist Walden and his colleagues [46]. To prepare and thus characterize ethylpyridinium bromotrichloroaluminate (III) $[\text{EtPy}][\text{AlBrCl}_3]$, Osteryoung and his team

first outlined the material's chemical and electrochemical characteristics [47]. In 1983, Hussey first mentioned the term “Ionic Liquids” to these unique salts [48]. Wilkes *et al.* pioneered the field of modern ILs research in 1992 when they outlined the synthesis of 1-ethyl-3-methylimidazolium acetate and tetrafluoroborate [49]. The synthesis of ILs 1-butyl-3-methylimidazolium hexafluorophosphate by Dupont and colleagues in 1996 was significant, since it exhibited hydrophobic properties and encouraged researchers to use it as a solvent in various kinds of chemical processes, particularly organic ones. Davis *et al.* in 1998 reported the synthesis of ILs by massive, asymmetric ions produced from the antifungal medication miconazole [50]. The study explained the possibilities for synthesizing salts that at low temperatures maintain their liquid state even when functional groups are introduced to the ion structure and promoted the development of the notion of task-specific ionic liquids (TSILs) [51]. Also starting with 1-(3-aminopropyl)imidazole, the same group reported on the synthesis of functionalized cations for task-specific ionic liquids (TSILs) and the applications of ILs containing functionalized ions [52-53]. Using the Michael reaction, Wasserscheid *et al.* developed a complementary technique for the synthesis of TSILs [54]. In solution phase combinatorial synthesis, Song *et al.* employed amine-functionalized ILs as an effective nucleophilic scavenger [55]. In Gu *et al.*'s work, SO₃H-functionalized ILs were synthesized and used as a dual function as a solvent and reusable catalyst for the oligomerization of a variety of olefins [56]. Also, the synthesis of functionalized ILs and their uses as recoverable catalysts for organic processes and metal scavengers were studied by Song *et al.* [57]. The same group also reported the synthesis and use of the Mn(III) complex of ILs-supported Schiff base as an efficient and recyclable catalyst for the epoxidation of chalcones [58]. X-ray crystal structure and the synthesis of a metal chelate prepared from imidazolium-based TSILs with ethylaminediacetic acid functioning as the chelating moiety were reported by Singer *et al.* [59]. According to their findings, the ligand and metal ion were in a 2:1 molar ratio. Several studies on the use of ILs as a catalyst and reaction media for favorable conversions have been reported by Ranu *et al.* [60]. In a biphasic condition using [bmim]PF₆ and hexane as the reaction medium, Nicasio and Perez group showed the synthesis of ILs-based Copper ion complexes and their application as a catalyst to transfer the CHCO₂Et unit in high yields from ethyl diazo acetate to several saturated and unsaturated substrates [61]. D. C. Forbes *et al.* reported on

an imidazolium dirhodium (II) carboxylate complex that acts as an active catalyst for the styrene intermolecular cyclopropanation reaction using ethyl diazoacetate [62]. Li *et al.* described the synthesis of some ILs supported Schiff bases by condensation of certain aromatic aldehydes with the amine-functionalized ILs without the need for a solvent [63]. Although immobilization appears to be an effective approach because recovery tends to be quite difficult, the insoluble supports' low activity and accessibility to substrates may be a problem. The ILs attached to the chiral salen Mn(II) complex have been shown by Zhao and Peng *et al.* to improve the catalytic efficiency and the recovery of the in situ formed complex, which frequently displayed significant challenges [64-65]. For the enantioselective oxidation of methyl aryl sulphides, Yin and his colleagues developed a chiral oxovanadium (IV) ILs functionalized Schiff base complex. The synthesized complex was found to be an effective catalyst that was easily isolated by adding hexane and precipitating the mixture. It could be recycled multiple times without losing its activity or enantioselectivity [66]. Hydrophobic amino-functionalized ILs were synthesized by Shi *et al.*, and their extraction behavior for the Cu^{2+} ion, a model cation, has been reported. Because amino groups can chelate Cu^{2+} ions, ILs have been effectively used as standard reference materials for Cu^{2+} ion detection in environmental water [67]. The synthesis, structural analysis, characterization, and microbiocidal properties of ILs-supported Schiff bases have been reported by Kumar *et al.* [68-69]. As a scavenger, they also employed ILs-supported aldehydes to remove primary amines in the synthesis of secondary amines in the solution phase. The same group reported a Pd(II) complex of ILs-supported Schiff base that was water soluble and air-stable. In a water media, the complex was employed as an effective catalyst for the Suzuki-Heck cross-coupling reaction [70]. The design of a non-enzymatic biosensor for the electrochemical oxidation-based detection of glucose using an ILs-supported cobalt salophen metal complex adsorbed on electrochemically reduced graphene oxide (ERGO) [71]. Using both conventional and ultrasound-assisted syntheses, a unique series of task-specific fluorinated pyridinium ionic liquids (TSILs) supported with Schiff bases is put forward. Their toxicity, bioavailability, and pharmacokinetic properties are found to be good [72]. The zinc(II) complex supported with imidazolium ionic liquid was synthesized and thoroughly examined. The complex exhibited strong antifungal and antibacterial activity. It was found to possess strong DNA-cleaving potential. The

compound additionally showed strong catalytic activity towards a reaction of aromatic aldehydes and indoles to prepare bis(indolyl)methanes in water [73]. Using water as the solvent and under microwave irradiation, a nickel catalyst supported with imidazolium ions is employed for the C-S cross-coupling reaction between sulfonyl hydrazides and aryl halides [74]. A novel polymeric organometallic catalyst (PIL-SB-Mn(III)) has been synthesized for the first time, and characterized, and its potential applications were explored. These included the Biginelli reaction for producing various derivatives of 3,4-dihydropyrimidin-2(1H)-ones/thiones. The primary benefits of this approach are the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones with good to exceptional yields using polymeric ionic liquid Schiff base manganese complex, in solvent-free conditions at mild temperature (60 °C) in short time. Additionally, the catalyst could be recycled without significant loss in its activity for several runs [75]. Design of a New Poly Imidazolium-Supported Cobalt (II) Schiff Base Complex for Selective Oxidation of Alcohols and Sulfides in a Water Solvent [76]. A New Copper Supported Supported Ionic Liquid Phase Catalyst for Cu-catalyzed cycloaddition reactions of Azide and Alkyne in Water [77].

1.6. Objectives of this research work

The above literature review shows the importance of transition metal complexes of ionic liquids-supported Schiff bases because of their unique characteristic features and their application in catalysis and biological sciences with great outcomes. Also, their synthetic route is effortless. This encourages us to work on synthesizing and characterizing novel transition metal complexes of ionic liquids-supported Schiff base and their application in catalysis and biological sciences.

We find the Suzuki reaction most appealing because of its great importance in organic reaction. It involves the reaction between boron-containing substrates with halides or pseudohalides, catalyzed by palladium to form a C-C coupling product. Even though a large number of research articles have been published on the Suzuki reaction, it still possesses some drawbacks such as long reaction time, use of toxic solvents, non-recoverability, and recyclability of catalyst [15, 78-81]. Herein, we will try to address some of these drawbacks with our novel metal complexes.

It is reported that every year, kidney cancer claims the lives of about 131,000 people worldwide and is known to have a significant financial impact on society. However, not many projects have been done towards it [82]. ACHN is a human renal cell carcinoma and they are used by researchers to investigate medication responses, tumor biology, and possible treatments, which helps to advance the understanding of therapeutic approaches for kidney cancer. It is, therefore, the ACHN cell line will be opted for determining the potential of our synthesized compounds.

References

1. J. Dupont, Roberto F de Souza, Paulo A. Z. Suarez, *Chem Rev.*(2002); 102(10):3667-92
2. R. D. Rogers, *Nature* (2007); 447 (7147):917-8
3. Ehsan Kianfar, Sajjad Mafi, *Fine Chem. Eng.* (2020) 22–31
4. A. Marciniak, *Int. J. Mol. Sci.*, 11 (2010) 1973–1990
5. P. Kölle, R. Dronskowski, *Eur. J. Inorg. Chem.*(2004) 2313–2320
6. Wilkes, J. S.; Zaworotko, M. J., *J. Chem. Soc., Chem. Commun.* 1992, 965–967
7. N. V. Plechkova, K.R. Seddon, *Chem. Soc. Rev.* 37 (2008) 123–150
8. Z. Lei, B. Chen, Y.M. Koo, D.R. Macfarlane, *Chem. Rev.* 117 (2017) 6633–6635
9. R.D. Rogers, K.R. Seddon, *Science* (80) 302 (2003) 792–793
10. R.A. Sheldon, *Green Chem.* 7 (2005) 267–278
11. P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed* 39 (2000) 3772–3789
12. A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac, K.R. Seddon, *Org. Lett.* 1 (1999) 997–1000
13. B. Khungar, M.S. Rao, K. Pericherla, P. Nehra, N. Jain, J. Panwar, A. Kumar, *Comptes Rendus Chim.* 15 (2012) 669–674
14. R.A. Sheldon, *Green Chem.* 7 (2005) 267–278
15. P. Nehra, B. Khungar, K. Pericherla, S.C. Sivasubramanian, A. Kumar, *Green Chem.* 16 (2014) 4266–4271
16. S. Saha, D. Brahman, B. Sinha, *J. Serbian Chem. Soc.* 80 (2015) 35–43
17. A. Chhetri, S. Chettri, P. Rai, D.K. Mishra, B. Sinha, D. Brahman, *J. Mol. Struct.* 1225 (2021) 129230

18. A. Chhetri, S. Chettri, P. Rai, B. Sinha, D. Brahman, *J. Mol. Struct.* 1224 (2021)
19. S. Sowmiah, J.M.S.S. Esperança, L.P.N. Rebelo, C.A.M. Afonso, *Org. Chem. Front.* 5 (2018) 453–493
20. V. Alptüzün, S. Parlar, H. Taşlı, E. Erciyas, *Molecules* 14 (2009) 5203–5215
21. S. Omid, V. Khojasteh, A. Kakanejadifard, M. Ghasemian, F. Azarbani, *J. Chem. Sci.* 130 (2018) 1–9
22. D. Hodyna, V. Kovalishyn, I. Semenyuta, S. Rogalsky, O. Trokhimenko, A. Gryniukova, L. Metelytsia, *Biointerface Res. Appl. Chem.* 12 (2022) 2905–2957
23. M. Musiał, A.B. Olejniczak, M. Denel-Bobrowska, E. Zorębski, M. Dzida, *ACS Sustain. Chem. Eng.* 9 (2021) 16459–16465
24. K.S. Egorova, E.G. Gordeev, V.P. Ananikov, *Chem. Rev.* 117 (2017) 7132–7189
25. V.R.R.K. Dasari, M.K.K. Muthyala, M.Y. Nikku, S.R.R. Donthireddy, *Microbiol. Res.* 167 (2012) 346–351
26. T. Turk, R. Frangež, K. Sepčić, Mar. *Drugs* 5 (2007) 157–167
27. Natalia S de Faria, Luana K B Moura *et al.*, *European journal of Oral Sciences* 2017:125(5):403-409
28. Donahoe, *Mol. Cell. Biochem.* 23 (2012) 1–7
29. P.G. Cozzi, *Chem. Soc. Rev.*, 33 (2004) 410
30. P. Espinet, M.A. Esteruelas, L.A. Ore, J. L. Sarrano, E. Sola., *Coord. Chem. Rev.*, 117 (1992) 215
31. P. M. Selvakumar, E. Suresh, P.S. Subramanian, *Polyhedron.*, 26 (2007) 749
32. D.M. Boghaei, S.S. Farvid, M. Gharagozlou, *Spectrochim. Acta., Part A* 66 (2007) 650
33. B. Khungar, M.S. Rao, K. Pericherla, P. Nehra, N. Jain, J. Panwar, A. Kumar, *Comptes Rendus Chim.* 15 (2012) 669–674
34. P. Nehra, B. Khungar, K. Pericherla, S.C. Sivasubramanian, A. Kumar, *Green Chem.* 16 (2014) 4266–4271
35. S. Saha, D. Brahman, B. Sinha, *J. Serbian Chem. Soc.* 80 (2015) 35–43
36. A. Chhetri, S. Chettri, P. Rai, D.K. Mishra, B. Sinha, D. Brahman, *J. Mol. Struct.* 1225 (2021) 129230
37. A. Chhetri, S. Chettri, P. Rai, B. Sinha, D. Brahman, *J. Mol. Struct.* 1224 (2021)

38. Mashhoori, M. S., Sandaroos, R. & Zeraatkar Moghaddam, ***Polycycl. Aromat. Compd.*** 0, 1–19 (2021)
39. Mashhoori, M. S., Sandaroos, R. & Zeraatkar Moghaddam, A., ***Res. Chem. Intermed.*** 46, 4939–4954 (2020)
40. Mashhoori, M., Sandaroos, R. & Zeraatkar, ***ChemistrySelect***, 5, 24, 7148–7154 (2020)
41. Nehra, P., Khungar, B., Pericherla, K. & Sivasubramanian, S. C., ***Green Chem.*** 16, 4266–4271 (2014)
42. Nehra, P. *et al.* ***Inorganica Chim. Acta*** 478, 260–267 (2018)
43. Khungar, B. *et al.* ***Comptes Rendus Chim.*** 15, 669–674 (2012)
44. Nehzat, F. & Grivani, G., ***J. Chem. Sci.***, 133(2), 56, (2020)
45. Rezki, N. *et al.* ***J. Mol. Liq.*** 264, 367–374 (2018)
46. P. Walden, ***Chem. Zentralbl.***, 85 (1914) 1800
47. H.L. Chum, V. R. Koch, L.L. Miller, R.A. Osteryoung, ***J. Am. Chem. Soc.*** 97 (1975) 3264
48. C. L. Hussey, ***Adv. Molten Salt Chem.***, 5 (1983) 185
49. J. S. Wilkes, M.J. Zaworotoko, ***J. Chem. Soc. Chem. Commun.***, (1992) 965
50. K.J. Forrester, T.L. Merrigan, J.H. Jr. Davis, ***Tetrahedron Lett.***, 39 (1998) 8955
51. A.E. Visser, R.P. Swatloski, W.M. Mayton, S. Sheff, A. Wierzbicki, J.H. Jr. Davis, R.D. Rogers, ***Chem. Commun.***, (2001) 135
52. J.H. Jr. Devis, ***ACS Symp. Ser.***, 818 (2002) 247
53. P. Wasserscheid, B. Driessen-Holscher, R. vanHal, H.C. Steffers, J. Zimmerman, ***Chem. Commun.***, (2003) 2038
54. G. Song, Y. Cai, and Y. Peng, ***J. Comb.***, 7 (2005) 561
55. Y. Gu, F. Shi, Y. Deng, ***Catalysis Commun.***, 47 (2003) 597
56. J. Li, Y. Peng, G. Song, ***Catal. Lett.***, 102 (2005) 159
57. Y. Peng, Y. Cai, G. Song, ***J. Chem. Synlett.***, 14 (2005) 2147
58. J. R. Harijani, T. Friscic, L.R. MacGillivray, R.D. Singer, ***Inorg. Chem.***, 45 (2006) 10025
59. B.C. Ranu, R. Jana, ***J. Org. Chem.***, 70 (2005) 8621
60. P. Rodríguez, A. Caballero, M.M. Díaz-Requejo, M.C. Nicasio, P.J. Perez, ***Org. Lett.***, 8 (2006) 557

61. D.C. Forbes, S.A. Patrawala, K.L.T. Tran, **Organometallics.**, 25 (2006) 2693
62. B. Li, Y.Q. Li, W.J. Zheng, M.Y. Zhou., **ARKIVOC.**, XI (2009) 165
63. L. Lou, Y. Peng, K. Yu, S. Liu, **Catal. Commun.**, 9 (2008) 1891
64. R. Tan, D. Yin, N. Yu, Y. Jin, H. Zhao, D. Yin., **J. Catal.**, 255 (2008) 287
65. R. Tan, C. Li, Z. Peng, D. Yin., **Catal Commun.** 12 (2011) 1488
66. Y. Fan, S. Zhang, F. Yang, H. Niu, J. Shi, **Microchimica Acta.**, 177 (2012) 237
67. M.K. Muthayala, A. Kumar., **ACS Comb. Sci.** 14 (2012) 5
68. B. khungar, M.S. Rao, K. Pericherla, P. Nehra, N. Jain, J. Panwar, A. Kumar., **C.R. Chimie.**, 15 (2012) 669
69. P. Nehra, B. Khungar, K. Pericherla, S.C. Sivasubramanian, A. Kumar, **Green Chem.** 16 (2014) 4266
70. N. Rezki, S.A. Al-Sodies, M. Messali, S.K. Bardaweel, P.K. Sahu, F.F. Al-belwi, P.K.Sahu, M.R. Aouad, **Journal of Molecular Liquids**, 284, 431-444(2017)
71. M. Benjamin, D. Manoj, K.T.P.R. Bhagat, D. Saravanakumar, and S. Senthilkumar **Biosensors and Bioelectronics** (2017), 91, 380-387
72. P. Nehra, B. Khungar, R.P. Singh, S.C. Sivasubramanian, P.N. Jha, V. Saini, **Inorganic Chim. Acta** (2018), 478, 260-267
73. V. Saini, and B.Khungar, **New J. Chem.**, 2018, 42, 12796
74. Mahboobeh-Sadat Mashhoori, R. Sandaroos, A.Z. Moghaddam, **Research on Chemical Intermedites** (2020), 46, 4939-4954
75. Mahboobeh-Sadat Mashhoori, R. Sandaroos, and A.Z. Moghaddam, **Polycyclic Aromatic Compounds** (2021), 42(8), 5067-5085
76. S.A. Sonawane, and D.M. Pore, **Catalysis Letters** 152(11), 3317-3331 (2022)
77. Pentsak, E. O. & Ananikov, V. P. , **European Journal of Organic Chemistry**, 26, 4239–4247 (2019)
78. Meng, G. & Szostak, **Org. Biomol. Chem.**, 2016, 14, 5690-5707
79. Srinivas Keesara and Saiprathima Parvathaneni, **New J. Chem.**, 2016, 40, 7596-7603
80. Martinez, E. E. *et al.* **Organometallics**, 40, 11, 1560-1564 (2021)
81. Safiri, S., Kolahi, AA., Mansournia, M.A. *et al.*, **Sci Rep** 10, 13862 (2020)
82. Swatloski, R.P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D., **J. Am. Chem. Soc.** 2002, 124, 4974-4975

SECTION B

1.7. Chemicals and solvents

Table 1.1 List of chemicals and solvents used

Chemicals/Solvents	Mol.Weight (g/mol)	Source	CAS No.
Salicylaldehyde	122.12	SD	Fine 90-02-08
Methanol	32.04	chemicals	67-56-1
Dimethylsulfoxide	78.13	SD	Fine 67-68-5
Acetonitrile	41.05	chemicals	75-05-8
Ethanol	46.07	SD	Fine 64-17-5
Chloroform	119.38	chemicals	67-66-3
Diethyl ether	74.12	SD	Fine 60-29-7
O-vanillin	152.15	chemicals	148-53-8
3-aminopyridine	94.117	SD	Fine 462-08-8
3-carboxaldehyde pyridine	107.112	chemicals	500-22-1
Methyl Iodide	141.94	SD	Fine 74-88-4
2,4-dinitrophenyl hydrazine	198.14	chemicals	119-26-6
Iodobenzene	204.01	SD	Fine 591-50-4
3-iodotoluene	218.035	chemicals	625-95-6
4-iodoanisole	234.03	TCI chemicals	696-62-8
Bromobenzene	157.01	Sigma-Aldrich	108-86-1
3-chlorobromobenzene	191.253	Sigma-Aldrich	108-37-2
3-bromopyridine	157.998	SRL	626-55-1
Chlorobenzene	112.56	SRL	108-90-7
Phenyl boronic acid	121.93	Sigma-Aldrich	98-80-6
4-bromophenyl boronic acid	200.83	Sigma-Aldrich	5467-74-3
3-nitrophenyl boronic acid	166.93	Sigma-Aldrich	13331-27-6
4-methoxyphenyl boronic acid	151.96	Sigma-Aldrich	5720-07-0
4-iodophenyl boronic acid	247.83	Sigma-Aldrich	5122-99-6
Sodium bicarbonate	84.007	Sigma-Aldrich	144-55-8

Cesium carbonate	325.82	Sigma-Aldrich	534-17-8
Potassium carbonate	138.205	Sigma-Aldrich	584-08-7
Triethyl amine	101.191	Sigma-Aldrich	121-44-8
Zinc acetate	183.48	Sigma-Aldrich	5970-45-6
Cadmium acetate	266.53	Sigma-Aldrich	5743-04-4
Acetone	58.08	Sigma-Aldrich	67-64-1
Copper acetate	199.65	SRL	6046-93-1
Acetic acid (glacial)	60.052	Sigma-Aldrich	64-19-7
Ethyl acetate	88.11	SRL	141-78-6

1.8. Instruments used

The following instruments were used for weighing the mass and the characterization of the synthesized compounds.

1.8.1 Mass measurements

Digital electronic analytical balance (Mettler Toledo, ML204) were used to measure masses. Mass may be measured with extreme precision and accuracy using this digital balance within ± 0.1 mg accuracy.



Fig.1.6 Mettler Toledo, ML204, Digital Electronic Balance

1.8.2 Elemental Analysis

Perkin-Elmer(240C) analyzer were used for the elemental analysis of all the synthesized compounds. Atomic Absorption Spectrophotometer (Varian SpectraAA 50B) were used to determine the metal contents in the synthesized metal complexes by using the standard metal solutions obtained from Sigma-Aldrich, Germany.



Fig.1.7 Varian SpectrAA 50B, Atomic Absorption Spectrophotometer (AAS)

1.8.3 Magnetic Susceptibility Measurement

Magnetic susceptibility measures a material's response to an external magnetic field, indicating its degree of magnetization. Quantifying this property aids in understanding material characteristics, electronic structures, and applications like magnetic resonance imaging. It's crucial in various scientific. A magnetic susceptibility balance determines a substance's magnetic susceptibility by comparing its attraction in a magnetic field with a reference material. It gives us gram susceptibility of the material χ_g which on multiplying by the molecular mass of the material gives the molar susceptibility of the material χ_M . It is then corrected with the diamagnetic contribution to obtain the effective magnetic moment μ_{eff} as

$$\mu_{\text{eff}} = 2.83\sqrt{T \times \chi_A}$$

where χ_A is the corrected molar susceptibility.



Fig.1.8 Magway MSB Mk1, Magnetic Susceptibility Balance

1.8.4 Melting Point Apparatus

With the help of a melting point apparatus as shown below in Fig.1.9., the open capillary method was used to determine the compounds' melting points.



Fig.1.9 Melting point instrument

1.8.5 Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) is one of the techniques that may simultaneously define the precursor and the final product while offering a thorough qualitative presentation of their microstructural properties. A comprehensive understanding of the sample's chemical composition and crystalline structure can be obtained by PXRD, which is a potentially useful non-destructive characterization technique. PXRD can only assess the degree of crystallinity or the amorphization of the samples under examination by analyzing the overlap of diffraction peaks with identical d values.

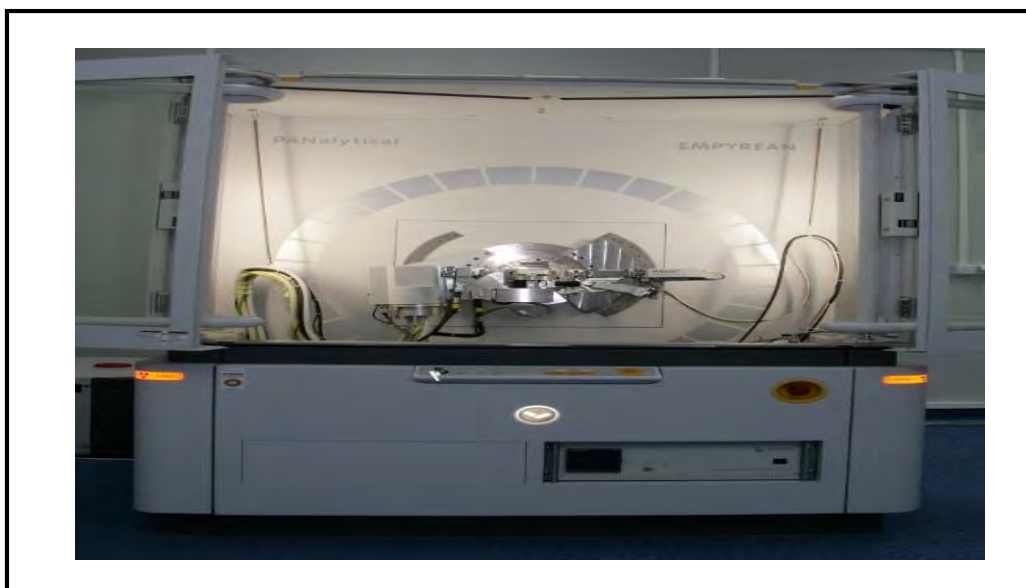


Fig.1.10 PANalytical X-ray diffractometer

1.8.6 FT-IR Spectrometer

Molecular vibrations are detected by infrared spectra, which provide distinct chemical fingerprints spectrum pattern. Such spectra are used in analytical chemistry in order to identify compounds by elucidating molecular structures through distinctive absorption patterns. Such spectral pattern can be recorded at room temperature (25°C) in the $4000\text{--}400\text{ cm}^{-1}$ range using a Perkin Elmer FT-IR spectrometer as shown below in Fig.1.11, with a resolution of 2 cm^{-1} .



Fig.1.11 Perkin Elmer FT-IR spectrometer

1.8.7 UV-VISIBLE Spectrometer

Electronic spectra display how light is absorbed or emitted by a molecule, providing information about its electronic structure. These spectra are useful in chemistry because they aid in the identification of bonding patterns, molecular configurations, and energy transitions, which leads to a better comprehension of the behavior and characteristics of molecules. Agilent 8453 UV-Visible spectrophotometer was used to record UV-Visible spectra, with a wavelength resolution uncertainty of ± 2 nm. An automated digital thermostat was used to maintain various temperatures during the measurements.



Fig.1.12 Agilent 8453 UV-Visible spectrophotometer

1.8.8 ^1H and ^{13}C NMR Spectrometer

Proton (^1H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR) spectra are indispensable tools in chemistry. They reveal unique signals corresponding to different environments in a molecule, enabling precise identification of compounds, elucidation of molecular structures, and insights into chemical environments and connectivity, fostering advances in chemical research. It relies on magnetic properties of atomic nuclei, detecting their response to a strong magnetic field and radiofrequency pulses for analysis. It was recorded in Bruker 400 spectrometer using DMSO- d_6 as the solvent for the samples.



Fig.1.13 Bruker 400 NMR Spectrometer

1.8.9 Mass Spectrometer

High-resolution mass spectrometry (HRMS) precisely measures mass, distinguishing subtle differences. It enables accurate identification and characterization of molecules in complex samples.



Fig.1.14 Bruker micro OTOF-Q11 spectrometer

Matrix-assisted laser desorption/ionization (MALDI) uses a matrix absorbing laser energy. Upon irradiation, the matrix transfers energy to analytes, producing ions for mass spectrometric analysis.

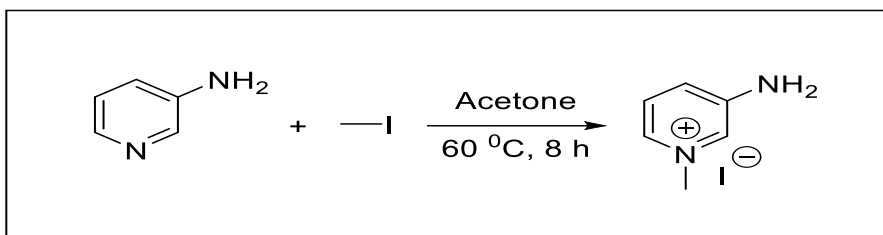


Fig.1.15 Bruker Daltonics auto flex TOF/TOF

1.8.10 Methods of Synthesis of compounds

1.8.10.1 Preparation of Ionic Liquid (IL)-I

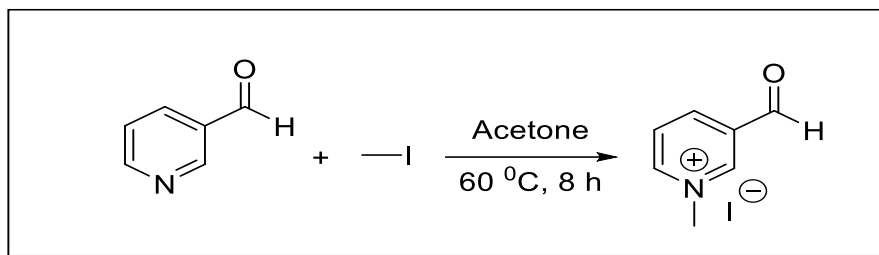
3-amino pyridine and methyl iodide in a 1:2 M ratio were dissolved in EtOAc and taken in a round bottom flask. It was then stirred at room temperature overnight. The pyridinium ILs thus obtained were filtered out, washed with dry ethyl ether, and dried in an oven. The final yield of the white salt was 90% [1].



Scheme 1.1 Synthesis of pyridinium ionic liquid (I) with amino group attached to it

1.8.10.2 Preparation of Ionic Liquid (IL)-II

3-formyl pyridine and methyl iodide in a 1:2 M ratio were dissolved in EtOAc and taken in a round bottom flask. It was then stirred at room temperature overnight. The pyridinium ILs thus obtained were filtered out, washed with dry ethyl ether, and dried in an oven. The final product was a creamy salt with 86 % yield [2].

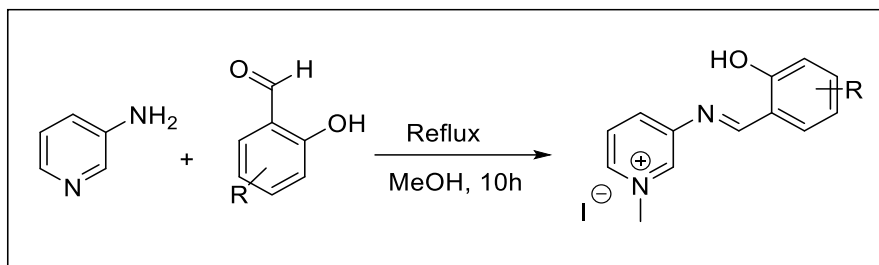


Scheme 1.2 Synthesis of pyridinium ionic liquid (II) with Carbonyl group attached to it

1.8.10.3 Preparation of IL(I)-supported Schiff base (Ligand A)

A conventional condensation method was used to synthesize pyridinium IL-supported Schiff base [3]. When the ILs and Salicylaldehyde (2) in a 1:1 M ratio were refluxed in MeOH for 10 h, a yellow solid was obtained on cooling it down. It was then filtered out,

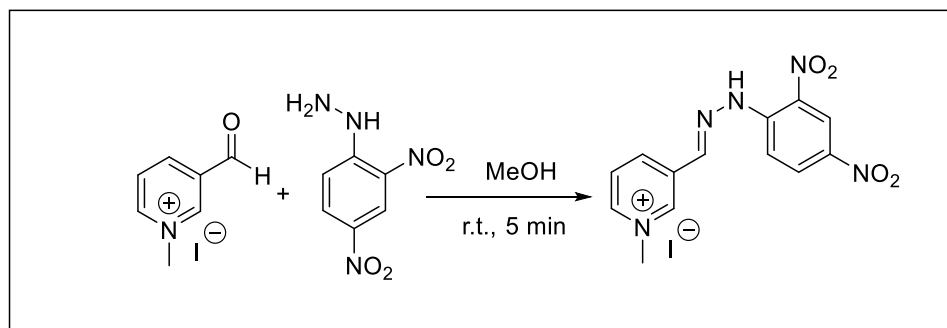
washed with cold MeOH, followed by dry diethyl ether, and dried in an oven. The yield of the product was 60-65 % .



Scheme 1.3 Synthesis of pyridinium iodide-supported Schiff base (Ligand A)

1.8.10.4 Preparation of IL(II)-supported Schiff base (Ligand B)

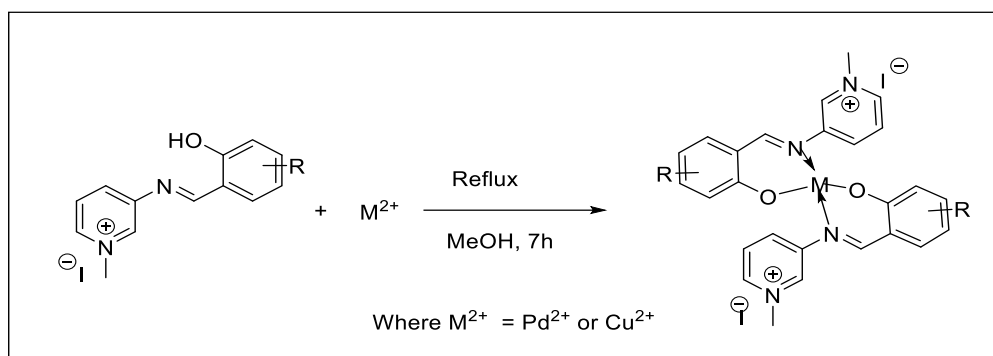
When a warm solution of ILs in methanol was slowly added to an acidified clear solution of 2,4-dinitrophenylhydrazine (4) (198mg, 1.0 mmol) in methanol. Within 5 minutes a yellowish precipitate was seen which was filtered out, washed with methanol, and dried in a hot air oven. The final yield of the product was 90% [4].



Scheme 1.4 Synthesis of pyridinium iodide-supported Schiff base (Ligand B)

1.8.10.5 Preparation of IL-supported Schiff base (Ligand A) metal complexes

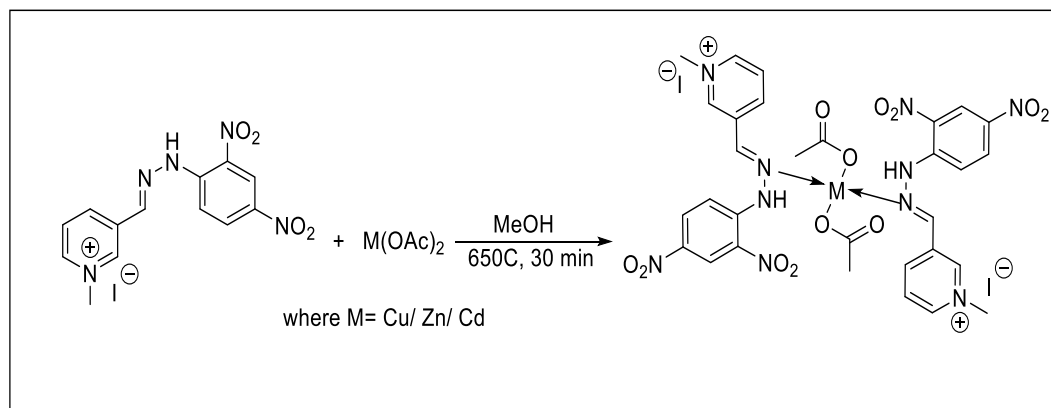
To a hot solution of pyridinium IL-supported Schiff base in MeOH, a warm solution of $M(\text{OAc})_2$ in MeOH was added slowly and set up the reaction for refluxing. The pyridinium IL-supported Schiff base and $M(\text{OAc})_2$ were taken in a 2:1 M ratio. After 7 h, the reaction was stopped and the precipitate formed was filtered out, washed with cold MeOH, followed by dry diethyl ether, and dried in the oven. 52 % was the final yield of the product [3].



Scheme 1.5 Synthesis of pyridinium iodide-supported Schiff base Pd/Cu complexes

1.8.10.6 Preparation of IL-supported Schiff base (ligand B) metal complexes

A reflux reaction in a 1:2 molar ratios for the metal salt and the ligand was set up by slowly adding a clear solution of metal salts to a clear solution of ligand in methanol at around 65 °C with constant stirring. The reaction continued for 30 minutes. The precipitate formed was filtered out, washed with cold methanol, and dried in a hot air oven at around 80 °C. The final product was a yellow powder with the yield of 50–55% [3].



Scheme 1.6 Synthesis of pyridinium iodide-supported Schiff base metal complexes

References

1. Egorova, K.S., Gordeev, E. G., Ananikov, V.P., *Chem. Rev.* 117, 7132-7189 (2017)
2. Hosseini, S. A., Moghimi, A., Iman, M., Ebrahimi, F., *Iran. J. Pharm. Res.* 16, 880-892 (2017)
3. Saha, S., Brahman, D., Sinha, B., *J. Serbian Chem. Soc.*, 80, 35-43 (2015)
4. Monfared, H. H., Pouralimardan, O., Janiak, C., *Zeitschrift Fur Naturforsch.-Sect. B J. Chem. Sci.*, 62, 717-720 (2007)