

# Study The Electronic Transition Behavior of Divalent Transition Metal Cations Co (II), Ni(II) and Cu(II) in Aluminum Nitrate/Urea Room Temperature Ionic Liquid (1:1.2)

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**Abstract:** Divalent transition metal cations of Co(II), Ni(II) and Cu(II), were investigated in new ionic liquid of 1:1.2 mole ratio of  $Al(NO_3)_3 \cdot 9H_2O$ /urea and found to be soluble and interact with weak coordination bond with ionic liquid species. This was observed when change the strength of the electronic spectra of these cations or the feature of these spectra behavior when compared to those in aqueous solution and their substitution upon addition of thiocyanate. Basic species of ionic liquid were proposed to have weak ionic strength.

**Keywords:** Transition metal, Ionic liquid, Electronic transition

## 1. Introduction

Ionic liquids are usually consisting of an organic cation and inorganic anion, which are liquids below 100°C, consist almost exclusively ions<sup>[1]</sup>. These new solvents are greener alternatives to conventional volatile organic solvents (VOS), which referred to as designer solvents that can be used in various fields<sup>[2]</sup>. The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on environment<sup>[3]</sup>. Ionic liquid possess unique characteristics that make them important in research in the field of chemistry, physics, engineering and clean technology<sup>[4]</sup>. For its ability to dissolve a variety of organic materials and inorganic, due to the particular properties as vapor pressure paucity detectable, high thermal stabilities, replacement of volatile organic solvents, potential to be recycled and reused and nonflammability. So ionic liquid are seen as a class of solvents and studied widely in various applications like chemical synthesis, electrochemistry, catalysis for organic and inorganic, electrolytes, reaction media, enzymatic catalysis separations and biotransformation<sup>[5]</sup>. The ionic bond in ionic liquid is usually stronger than the vander waals forces between molecules of ordinary liquids. For this reason, common salts tend to melt at higher temperatures than other solid molecules. The present work concentrated on investigation the interaction, coordination and reactivity of Co(II), Ni(II), and Cu(II) in the new ionic liquid synthesizing by mixing Alum- nitrate with urea. Electronic spectroscopy was used to follow their coordination with ionic liquid ionic species and their substitution upon addition of thiocyanate to investigate their stability in Alum- nitrate / urea ionic liquid.

## 2. Experimental

Aluminum nitrate nonahydrate, Cobalt nitrate hexahydrate, Nickel nitrate hexahydrate, Copper nitrate trihydrate, of

BDH of not less than 99% and thiocyanate and urea of Thomas Baker were used without further purification.

Aluminum nitrate  $Al(NO_3)_3 \cdot 9H_2O$  and urea  $N_2H_4CO$  in mole ratio (1:1.2) were milled, mixed and heated gradually to 80°C with continuous gently stirring until both melted together producing colorless liquid. The resulted melt was gradually cooled to room temperature and remained liquid and stored in sealed container.

The electronic spectra of complex solution were obtained by using CECEL CE7200, Uv-Vis ultraviolet visible spectrophotometer at room temperature using quartz cell of 1.0cm path length and water reference in the range of wave length 190- 1100 nm. The low absorbance band at 300nm in the ultraviolet region was observed and related to the ionic liquid.

## 3. Results and Discussion

Cobalt (II) nitrate hexahydrate in ionic liquid cobalt cation (II) dissolved in Alum- nitrate/ urea ionic liquid with continuous magnetic stirring after 10 minutes, the mixing solution of (0.1M) were pink in color. This solubility was found to be much simpler than those reported for the same compound in other ionic liquid or molten salts<sup>[6-9]</sup>. For example the salt was found to be much better than that was found soluble 0.1M after 72hr in choline chloride/urea at R.T<sup>[6]</sup> in  $Ca(NO_3)_2 \cdot 4H_2O/CaCl_2$  at 40-70°C<sup>[7]</sup>, or acetamide/ $Ca(NO_3)_2 \cdot 4H_2O$  was soluble at 40-90°C<sup>[8]</sup>.

In molten salt Co(II) ions melt at 447-480°C in LiCl/KCl but in hydrated ammonium aluminum sulfate/urea ionic liquid was found to be the same solubility of Co(II) ion compared with ionic liquid in this work. This may show that ionic liquid is a good solvent than those reported with better interaction between the solvent and ionic species of this metal.

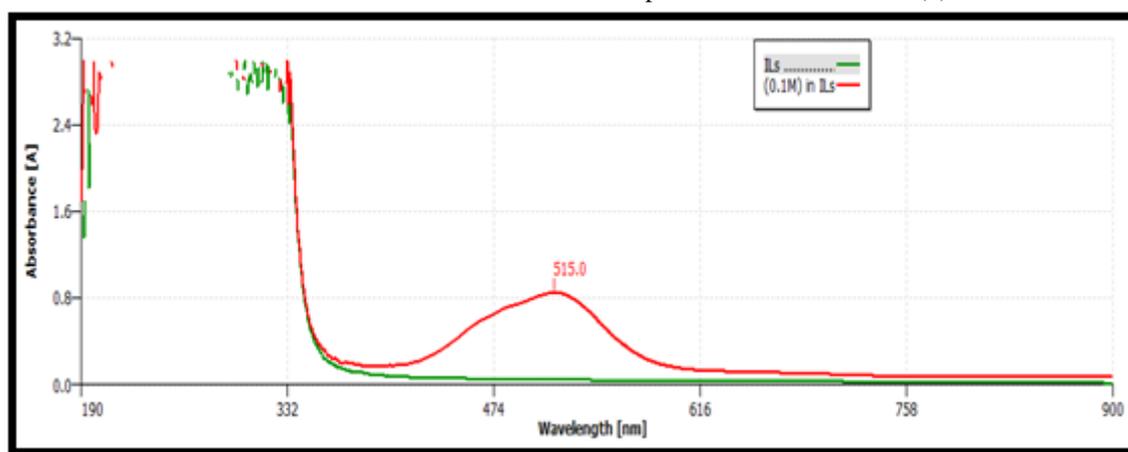
The electronic ultraviolet- visible , examine the pink solution was carried out to investigate the electronic behavior of the resulted coordinated Co(II) in the ionic liquid. Therefore the examine showed two absorption band in visible region at (890 and 515) nm and a shoulder band in UV-region at 334nm fig(1). It is known that electronic ground state  $^4F$  of  $d^7$  configuration of Co(II) would split in octahedral system into three electronic transition and thus the observed spectra were assigned to  $\nu_1 = ^4T_{1g} \rightarrow ^4T_{2g}$  and  $\nu_3 = ^4T_{1g} \rightarrow ^4T_{1g(p)}$  respectively, while the second transition  $\nu_2 = ^4T_{1g} \rightarrow ^4A_{2g}$  was calculated by using T.S.D and found to be have avalue 370.9nm. The absorption band at 334nm, almost in the same position of that of IL alone but with higher absorbance which covered that of the ionic liquid. The values of the nephelauxetic factor  $\beta$  and Racha parameter  $B'$ ,  $Dq$ ,  $10Dq$ ,  $Dq/B'$  were estimated by using  $d^7$  configuration from T.S.D. The ratio  $\nu_3/\nu_1 = 1.72$  fits the diagram at 1.31  $Dq/B'$ , therefore, from  $E_3/B' = 23$  and  $E_2/B' = 13.3$ ,  $B'$  will be  $844.5\text{cm}^{-1}$  and  $\beta = 0.86$  (taking  $B^\circ$  of free ion to be  $971\text{cm}^{-1}$ ), the value of  $10Dq = 11062\text{cm}^{-1}$ , and  $B'$  equal to 86% of free ion. In addition to these data the acidity and conductivity measurement for this complex is done and shown in table (1).

It was found that the band energies of coordinated Co(II) ion in Alum. Nitrate/urea were close to those reported in other ionic liquids, Table (1), such as Co(II) in hydrated ammonium alum sulfat/urea room temperature ionic liquid was observed at  $522\text{nm}^{[10]}$ , in  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}/\text{CaCl}_2$  two absorption bands maxima at 514 and 520 nm and the spectrum of acetamide, the band observed at 514.6nm. All these complexes which suggested to form octahedral coordination. So the present work an octahedral geometry with ionic species of IL was suggested. Yet the energy splitting of the electronic states is relatively at lower energy from those reported values in other media or solid alum reflecting the weaker field strength of ionic species of this IL.

Co(II) was also retested in aqueous medium by UV-Vis spectroscopy to establish whether the cations interacted solely with water molecules of the hydrated alum salt or with other species present in the IL such as, urea, nitrate or a complex ions arise from the formation of IL. Therefore, the electronic behavior of cobalt (II) in both ionic liquid and water are compared fig( 2 ).

The wavelength observed in aqueous solution were approximately the same with that observed in this new ionic liquid, this gives a support to the weaker nature of IL species coordination to Co(II) ions, thus water molecule presented in initial alum salt are not free in ionic liquid, otherwise it would coordinate to cobalt cations and give similar spectra to those shown in aqueous solution. An addition support to this conclusion is the higher molar absorptivity of this metal cation in IL ( $8.5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) than in aqueous solution ( $4.9 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) reflecting most probably the less symmetrical geometrical structure in ionic liquid where complex ionic species coordinated to metal cations than in aqueous solution where only water molecules are present.

In an attempt to study the possible substitution reaction of ionic liquid species by added anionic species, like thiocyanate to ionic liquid solution containing cobalt (II) nitrate (1:5) mole ratio. The original reddish pink solution of  $\text{Co}^{2+}$  in ionic liquid did not change the position of original spectrum of cobalt solution only the band for the transition  $\nu_3$  become broadness. The change was observed at last band that appeared at 417nm which may be referred to interaction with the compounds that which resulted from adding ( the ligand KSCN to IL) with the metal ion solution in present ionic liquid species and the distinctive higher absorbance band at 356.5 nm, followed by very high charge transfer transition, that indicated an interaction when added KSCN to  $\text{Co}(\text{NO}_3)_2$  in IL solution. In addition to that the molar absorptivity increase by approximately three time in presence of thiocyanate  $26.18 \text{ L. Mol}^{-1} \cdot \text{cm}^{-1}$  than in absence ligand  $8.5 \text{ L. Mol}^{-1} \cdot \text{cm}^{-1}$ , the addition supported a distorted octahedral geometry. The values of ligand field parameter and their absorptive are shown in Table (1).



**Figure 1:** UV-Visible electronic spectra of IL (green color) ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  0.1 M in aluminum nitrate nonahydrate /urea room temperature ionic liquid (red color)

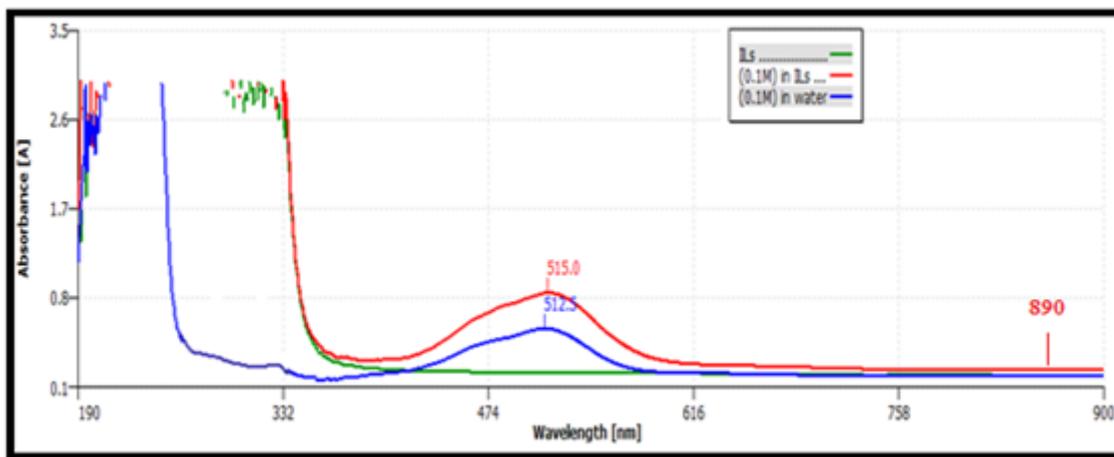


Figure 2: UV-Visible electronic spectra of IL (green),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  0.1 M in aluminum nitrate nonahydrate/urea room temperature ionic liquid (red) and, 0.1 M in aqueous solution (blue).

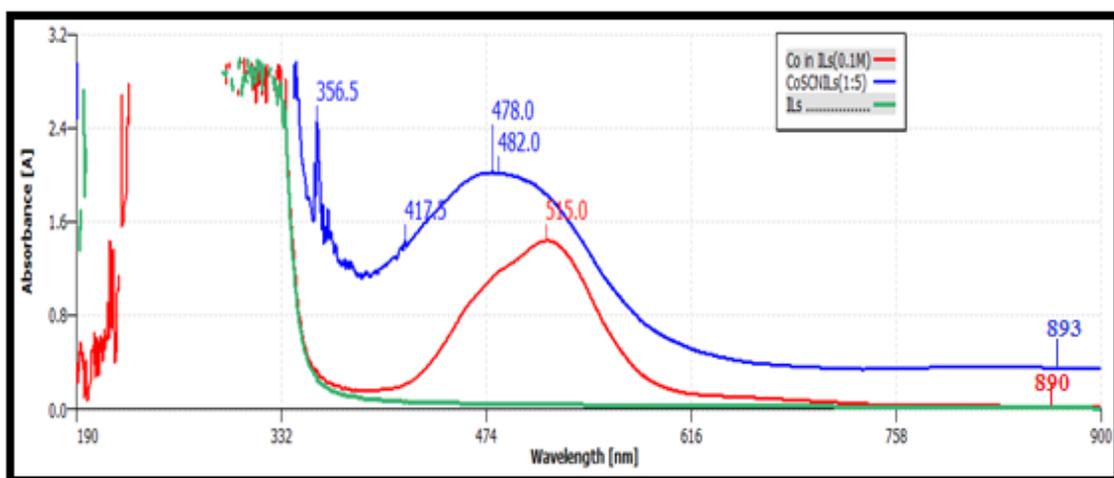


Figure 3: UV-Visible electronic spectra of IL (green),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  0.1 M in aluminum nitrate nonahydrate /urea room temperature ionic liquid (red) and, KSCN (blue).

Table 1: Electronic spectra for Co(II) in IL and various ligand

Cobalt (II) nitrate	Absorption Bands nm	Dq/B'	B' $\text{cm}^{-1}$	$\beta$	10Dq $\text{cm}^{-1}$	$\epsilon_{\text{L.mol}^{-1} \text{cm}^{-1}}$	cond. $\text{mS.cm}^{-1}$	pH	Suggested Structure
<b>Aqueous Solution</b>	$\nu_1 = 893$ $\nu_3 = 512.5$	-	-	-	-	4.9	-	-	Octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
<b>IL</b>	$\nu_1 = 890$ $\nu_2 = 370$ $\nu_3 = 515$	1.31	844.5	0.86	11062	8.5	3.89	1.0	Octahedral $[\text{Co}(\text{IL})_6]^{2+}$
<b>KSCN</b>	$\nu_1 = 893$ $\nu_2 = 403$ $\nu_3 = 480$	1.4	803	-	11242	20.18	-	-	Distortion Oh. $[\text{Co}(\text{IL})_4(\text{L})_2]$ or $[\text{Co}(\text{IL})_2(\text{L})_4]^{2-}$
<b><math>[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]/\text{UIL}</math></b>	$\nu_1 = 1309$ $\nu_2 = 522.5$ $\nu_3 = 276.5$	-	-	-	-	11 7.8	-	-	Octahedral $[\text{Co}(\text{IL})_6]^{2+}$
<b>ChCl/Urea IL</b>	$\nu_3 = 671$	-	1117	-	-	-	-	-	Tetrahedral $[\text{CoCl}_2(\text{U})_2]$

### Nickel nitrate hexahydrate in ionic liquid

Ni(II) nitrate hexahydrate dissolved in Alum/urea ionic liquid with continuous magnetic stirring after 15 minutes, the mixing solution of (0.1M) were pale green in colour. This solubility was found to be much easy than those reported for the same compound in other ionic liquid or molten salt<sup>[11,12]</sup>. The hydrated ammonium alumina sulfate/urea ionic liquid which give pale green complex which was achieved at 40°C

after 2hrs. similarly in choline chloride/urea ionic liquid nickel chloride dissolved with difficulty as it required 72hr at R.T. The chloride solubility was also reported in LiCl/KCl molten salt at (700-1000°C) and in CsCl melt at 864°C.

The electronic transition of the pale green solution of nickel nitrate ionic liquid was investigated by UV-Vis and revealed two bands. The split band at 721nm and 662 which referred to orbital coupling  ${}^3\text{A}_2\text{g} \rightarrow {}^1\text{E}_\text{g}$  and others assigned to

${}^3A_{2g} \rightarrow {}^3T_{1g_f} (v_2)$  other band at 394nm which revealed to  ${}^3A_{2g} \rightarrow {}^3T_{1g_p} (v_3)$ . These are known range for octahedral system, yet the first band was calculated from T.S.D for  $d^8$  configuration which equal (1292)nm and assigned to  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ , shown in Fig.(4).

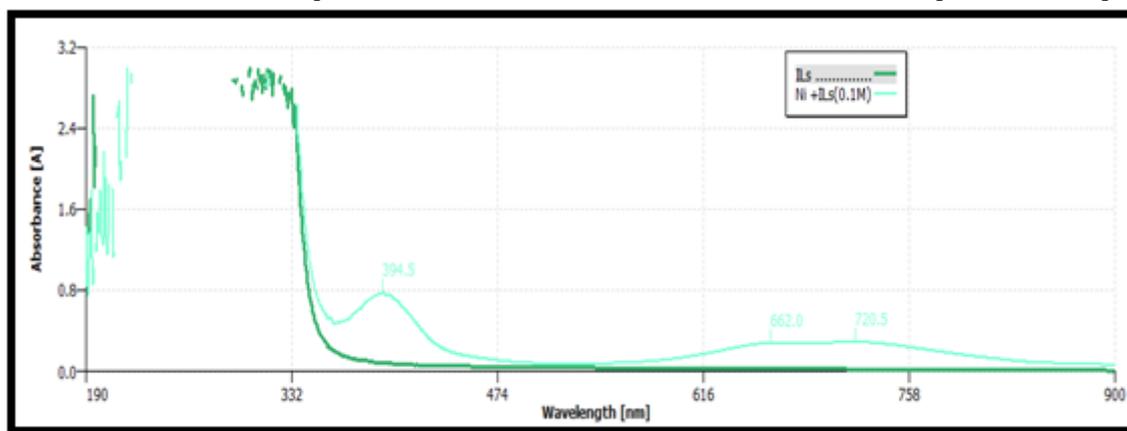
The ligand field parameter was illustrated in Table (2). The similarity in its behavior, nickel (II) nitrate hexahydrate, also showed octahedral configuration in aqueous solution, where its molar absorptivity less than of ionic liquid. The acidity and conductivity measurement also estimated and can be shown in Table (2). The same behavior observation as in Co(II) strongly suggest the free nature of originally present water, Fig.(5).

It was found that the band energies of coordinated Ni(II) ion in new ionic liquid were close to those reported in others ionic liquid, Table (2), such as in  $NH_4Al(SO_4)_2 \cdot 12H_2O$ /urea showed bands at 401, 670 and 1198nm at R.T ionic liquid<sup>[10]</sup>, in choline chloride/urea R.T ionic liquid showed bands at

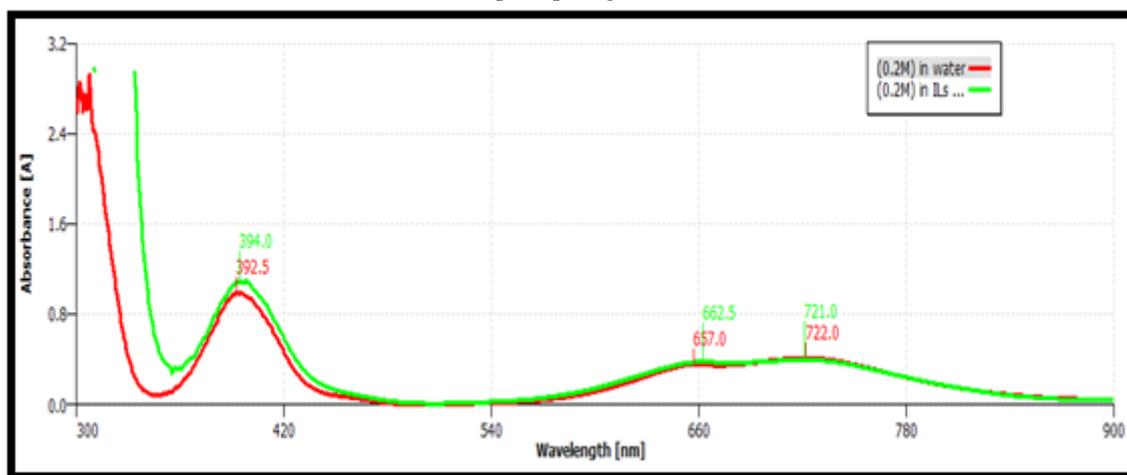
410, 669-746, 800 and 1333nm in butyramide/ $NaNO_3$ <sup>[13]</sup> which appeared three bands at 429, 793 and 1234nm all suggestion as Oh geometry.

Spectroscopic investigation of addition thiocyanate Fig(6) reveal an change in the transfer spectra which stated with very highly absorbance at ~345nm overshadow the ionic liquid transition. This might be taken as an indicate to interaction between thiocyanate with nickel ion. The electronic spectrum although give a broad band at maximum in 477 nm which may be referred to interaction with the compounds that which resulted from adding (the ligand KSCN to IL) with the metal ion solution in present ionic liquid (IL) species, so the solution of this metal ion leads to proposed the distorted Oh<sup>[14]</sup>.

Another indicate to the interacted thiocyanate with Ni(II) the molar absorptivity increased by three times on coordination of ligand to metal. This would revealed the less electrostatic nature of interaction of Ni(II) in present ionic liquid.



**Figure 4:** UV-Visible electronic spectrum of IL (green) and  $Ni(NO_3)_2 \cdot 6H_2O$  in aluminum nitrate nonahydrate/ urea ionic liquid (pale green).



**Figure 5:** UV-Visible electronic spectrum for  $Ni(NO_3)_2 \cdot 6H_2O$  in aluminum nitrate nonahydrate/ urea ionic liquid (green) and in aqueous solution (red)

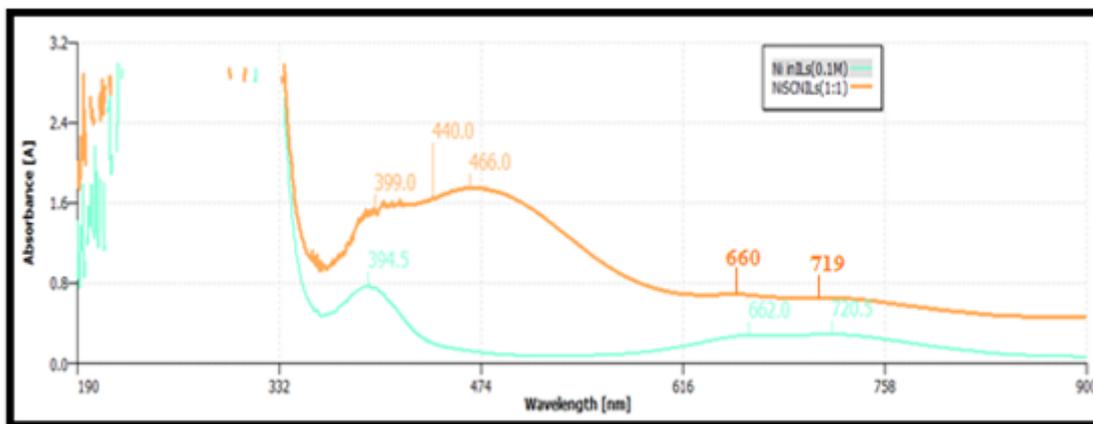


Figure 6: UV-Visible electronic spectrum for Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in aluminum nitrate nonahydrate/ urea ionic liquid (green) and in KSCN (brown ).

Table (2): Electronic spectra for Ni(II) in IL and various ligands

Ni (II) Nitrate	Absorption Bands nm	Dq/B'	B' cm <sup>-1</sup>	β	10Dq cm <sup>-1</sup>	ε L.mol <sup>-1</sup> .cm <sup>-1</sup>	cond. mS.cm <sup>-1</sup>	pH	Suggested structure
Aqueous solution	v <sub>2</sub> =656.5 v <sub>3</sub> =394.5	-	-	-	-	5.34	-	-	Oh. [Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>
IL	v <sub>1</sub> cal.=1292 v <sub>2</sub> =662 v <sub>3</sub> =394	0.85	963	0.92	8185.5	7.8	2.3	1.6	Oh. [Ni(IL) <sub>6</sub> ] <sup>2+</sup>
KSCN	v <sub>1</sub> cal = 1290. v <sub>2</sub> =660 v <sub>3</sub> =399	-	-	-	-	17.5	-	-	DistortionOh. [Ni(IL) <sub>4</sub> (L) <sub>2</sub> ] or [Ni(IL) <sub>2</sub> (L) <sub>4</sub> ] <sup>2-</sup>
[NH <sub>4</sub> Al (SO <sub>4</sub> ) <sub>2</sub> 12H <sub>2</sub> O]/UIL	v <sub>1</sub> cal.= 1198 v <sub>2</sub> = 670.5 v <sub>3</sub> = 401.5	-	927.2	0.9	-	4.1 9.1	-	-	Oh. [Ni(IL) <sub>6</sub> ] <sup>2+</sup>
ChCl/Urea IL	v <sub>1</sub> =1050 v <sub>1</sub> =746-669 v <sub>1</sub> =410	-	833	0.8	10000	-	-	-	Oh. [Ni(U) <sub>4</sub> Cl <sub>2</sub> ]

### Copper nitrate trihydrate ionic liquid

Copper(II) nitrate trihydrate showed a blue solution (0.1M) after 10 minutes, in alum/urea ionic liquid and easily achieved at lower temperature compare with others reported in different ionic liquid or molten salts. Copper(II) ions were found to be much soluble 0.1M after 72hr in choline chloride/urea at R.T<sup>[6]</sup>, while in Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O/CaCl<sub>2</sub> at 40-70°C<sup>[7]</sup> or in acetamide/Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O was soluble at 40-90°C<sup>[8]</sup> but in molten salt Cu(II) ions melt at 400°C in LiCl/KCl<sup>[9]</sup>. The Cu(bpp)[BF<sub>4</sub>] was prepared by the reaction of 1,3-bis (4-pyridyl) propan (bpp) and Cu(NO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O in [Cu mim][BF<sub>4</sub>] and heating at 140°C for three day<sup>[2]</sup>.

The electronic ultraviolet- visible spectroscopy examination of blue solution and showed one broad absorption with a maxima at 820nm with many bands over shadow the ionic liquid transition started around 345nm Fig(7). The term symbol for the ground state of Cu(II) ion in d<sup>9</sup> configuration in <sup>2</sup>D that split in octahedral crystal field with transition <sup>2</sup>E<sub>g</sub>→<sup>2</sup>T<sub>2g</sub>. Similarly coordination of Cu(II) in hydrated ammonium alumina sulphate/urea showed band at 802nm and attributed to form distorted octahedral geometry<sup>[15]</sup>, also Cu(II) in [EMIM]Cl shows one band and assigned as a distorted Oh coordination<sup>[16]</sup>. The same behavior

observation as in Cu(II) nitrate in aqueous solution which appeared a broad band at 807 nm also showed Oh configuration Table (3). The behavior of Cu(II) strongly suggest the non free nature of the originally present water, the molar absorptivity in IL increase by twice time from aqueous solution. The Cu(II) in new ionic liquid, also estimated the pH and conductivity measurement as illustrated in Table (3).

When added anionic species thiocyanate to ionic liquid solution containing Cu(II) nitrate a(1:1) mole ratio, the color changed the original blue solution to a pale blue which may be arise from the ligand to metal charge transfer. The transition lower absorbance band at 700 nm and 657nm was shifted to higher energy may be considered to the following spin allowed transition <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>1g</sub> (dx<sup>2</sup>-y<sup>2</sup>→dz<sup>2</sup>) and <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>B<sub>2g</sub> (dx<sup>2</sup>-y<sup>2</sup>→dxy) respectively<sup>[17]</sup> and others two new bands appeared at (460, and 402) nm related to adding SCN<sup>-</sup> anion which may be referred to interaction with the compounds that which resulted from adding (the ligand KSCN to IL) with the metal ion solution in present ionic liquid (IL) species, these d-d absorption with molar absorptivity of (3.98 and 3.96 L.mol<sup>-1</sup>.cm<sup>-1</sup>) which was lower than IL, then these bands followed by a very high charge transfer spectra Fig(8). This indicating less symmetrical coordination of ligand to metal ion.

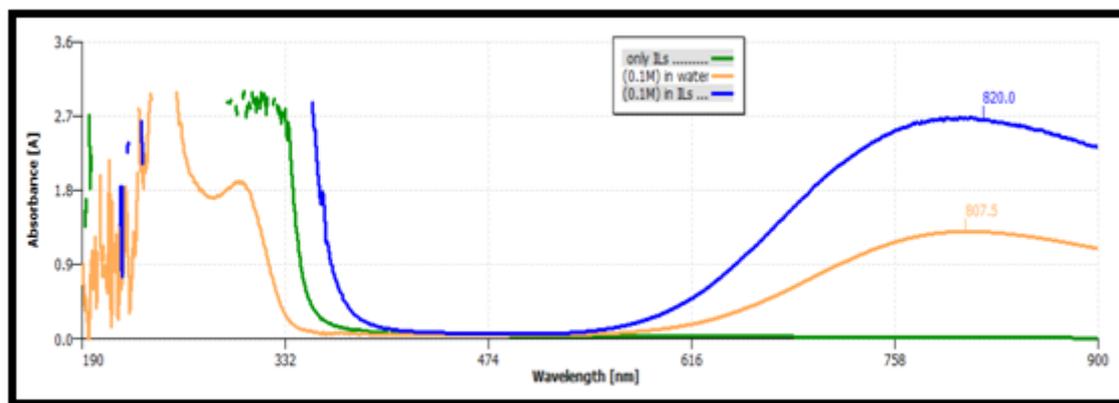


Figure 7: UV-Visible electronic spectrum for, IL green),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in aluminum nitrate nonahydrate/ urea ionic liquid (blue) and in aqueous solution (brown).

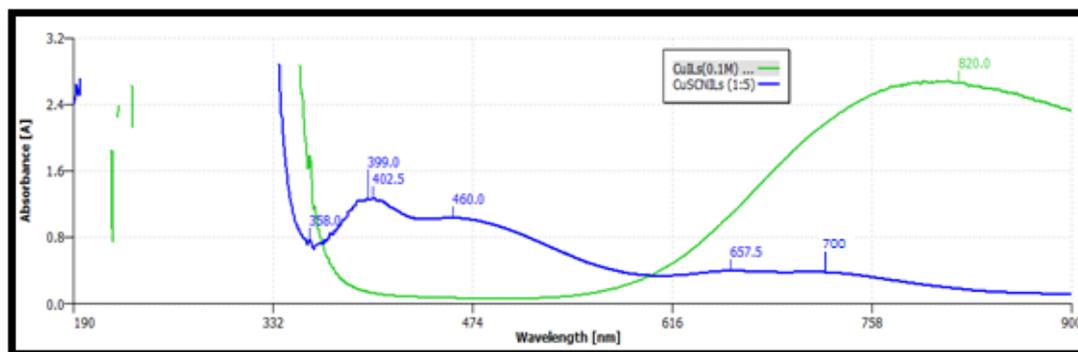


Figure 8: UV-Visible electronic spectrum for  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in aluminum nitrate nonahydrate/ urea ionic liquid (green) and in IL with KSCN(blue).

Table 3: Electronic spectra for Cu(II) in IL and various ligands

Cu (II) Nitrate	Absorption Bands nm	Transition	$\epsilon$ $\text{L.mol}^{-1} \text{cm}^{-1}$	cond. $\text{mS.cm}^{-1}$	pH	Suggested Structure
Aqueous solution	807.5	${}^2\text{E}_g \rightarrow {}^2\text{T}_2g$	13.03	-	-	Oh. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
IL	802	${}^2\text{E}_g \rightarrow {}^2\text{T}_2g$	26.66	3.5	1.6	Distorted Oh. $[\text{Cu}(\text{IL})_6]^{2+}$
KSCN	700 657	${}^2\text{B}_1g \rightarrow {}^2\text{A}_1g$ ( $dx^2-y^2 \rightarrow dz^2$ ) ${}^2\text{B}_1g \rightarrow {}^2\text{B}_2g$ ( $dx^2-y^2 \rightarrow dzy$ )	3.9 3.98	-	-	Distorted Oh. $[\text{Cu}(\text{IL})_4(\text{L})_2]$ or $[\text{Cu}(\text{IL})_2(\text{L})_4]^{2-}$
$[\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]/\text{UIL}$	802.5	${}^2\text{E}_g \rightarrow {}^2\text{T}_2g$	-	-	-	Distorted Oh
ChCl/Urea IL	766	${}^2\text{E}_g \rightarrow {}^2\text{T}_2g$	17.02	-	-	Oh. $[\text{Cu}(\text{urea})_6]^{2+}$

#### 4. Conclusions

In conclusion, it was found that hydrated divalent transition metals, cobalt(II) nitrate, nickel(II) nitrate and copper(II) nitrate simply soluble in new aluminum nitrate nonahydrate / Urea ionic liquid and their coordination with the ionic species of ionic liquid was weak refer to weak ionic strength of basic ionic liquid species. The water molecule presented in the initial aluminum salt are not free in ionic liquid other wise it would coordinate to metal cations and give similar spectra to those shown in aqueous solution. An additional support to this result is the higher molar absorptivity of metal cations in new ionic liquid than in aqueous solution, reflecting most probably the less symmetrical geometrical structure in ionic

liquid where complex ionic species coordinated to the metal cations than in aqueous solution where only water molecules are present. All metal cations showed high spin with distorted octahedral in this liquid.

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