*Republic of Iraq*
*Ministry of Higher Education*
*And Scientific Research*
*Al-Nahrain University*
*College of Science*
*Department of Chemistry*

# ULTRAVIOLET VISIBLE INVESTIGATION OF SOME TRANSITION METAL COMPOUNDS IN ROOM TEMPERATURE IONIC LIQUIDS MOLTEN SALTS

A THESIS
SUBMITTED TO THE COLLEGE OF SCIENCE
AL-NAHRAIN UNIVERSITY
IN PARTIAL FULFILLMENT OF REQUIREMENTS
FOR THE DEGREE OF MASTER IN
CHEMISTRY

BY
MARIAM ALI SAEED
B.SC. (AL-NAHRAIN UNIVERSITY 2005)

Supervised By
DR. HADI M.A. ABOOD

May 2008 Rabeea Al-thani 1429

# SUPERVISOR CERTIFICATION

I certify that this thesis was prepared under my Supervision in the Department of Chemistry, College of Science, and Al-Nahrain University as a partial requirement for the degree of Master of Science in chemistry.

***Signature:***
***Name: Dr. Hadi M.A. Abood***
***Date:***

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

***Signature:***
***Name: Assistant Professor. Dr. Salman A. Ahmed***
***Head of Chemistry Department***
***College of Science***
***AL-Nahrain Univercity***

# Examining Committee's Certification

We the examining committees, certify that we read this thesis and examined the student ***Mariam Ali Saeed*** in its contents and that, according to our opinion, is accepted as a thesis for the degree of master, in chemistry.

***Signature:***
***Name:***
***(Chairman)***

***Signature:***
***Name:***
***(Member)***

***Signature:***
***Name:***
***(Member)***

***Signature:***
***Name:***
***(Member\advisor)***

Approved for the council of the College of Science, and for the College of Graduate Studies.

***Assistant Professor***
***Dr. Laith Abdul aziz Al-Ani***
***Dean of College of Science***
***Al-Nahrain University***

# Acknowledgement

First of all, thanks are due to God for his blesses. Then I would like to express my deepest gratitude and great appreciate to my respected supervisors, Dr.Hadi M.A. Abood for suggesting this project, and his valuable guidance, advice, support, and continuous encouragement through my study.

Sincere thanks to the chemistry department, Al-Nahrain University and to the staff of the department, specially the head of the department Dr. Salman A. Ahmed.

My deepest thanks and appreciations to our Professor Dr. Ayad H. Jassim (God bless his soul) for his help and support through all the years of my study.

My deepest thanks and appreciations to my lovely family, specially my mother & father (May God bless them) for their patient with me, and to all those who helped and support me through my work, I dedicate this work for them.

Finally, sincere thanks and deep respect goes to all my teachers, and friends for their help and support.

Mariam A. Saeed

2008

# LIST OF CONTENTS

# LIST OF FIGURES

## **Chapter Two: -Experimental Part.**

## **Chapter Three: -Results and Discussion.**

# LIST OF TABLES

# LIST OF ABBREVIATIONS

| *Abbreviation* | *Name* |
|---|---|
| *UV-Vis* | *Ultraviolet-Visible* |
| *Oh* | *Octahedral* |
| *Td* | *Tetrahedral* |
| $\grave{B}$ | *Racah parameter* |
| $\beta$ | *Nephelauxetic factor* |
| *nm* | *Nanometre* |
| *RTILs* | *Room temperature ionic liquids* |
| *TFA* | *Trifluoroacetate* |
| $Tf_2N$ | Bis(trifluoromethylsulfonyl) imide |
| $PF_6$ | *hexafluorophosphate* |
| *EEIm* | *1,3-Diethylimidazolium* |
| *BMIm* | *1-Butyl-3-methylimidazolium* |
| *EMIm* | *1-Ethyl-3-methylimidazolium* |
| $BF_4$ | *tetrafluoroborate* |
| $[BMMIm]Tf_2N$ | *1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl) imide* |
| *Acac* | *Acetylacetonate* |
| *phen* | *1,10-Phenanthroline* |
| *en* | *Ethylenediamine* |
| *bipy* | *2,2-Bipyridine* |
| $PPh_3$ | *Triphenylphosphine* |
| *Dppe* | *1,2-Bis(diphenylphosphino) ethane* |
| *VOC* | *Volatile Organic Compounds* |

| | |
|---|---|
| *DMSO* | *Dimethylsalfoxide* |
| *BEIm* | *1-butyl,3-ethylimidazolium* |
| $(CF_3SO_2)_2N^-$ | *Bis(trifluoromethyl)sulphomide anion* |
| *M* | *Concentration in unit of (mol/l) 'Molarity'* |
| *m* | *Concentration in unit of (mol/Kg) 'molality'* |
| *BPC* | *1-n –butylpyridinium chloride* |
| *MEIC* | *1-methyl-3-ethylimidazolium chloride* |
| $[BMP]Tf_2N$ | *1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide* |
| $[(CH_3)_3N^+CH_2CH_2OH.2(NH_2)_2C_2O_4^{2-}.2(NH_2)_2CS$ | *(2-hydroxy-ethyl)trimethyl ammonium oxalate dithiourea* |
| $HOCH_2CH_2N^+(CH_3)_3F^-.(2NH_2)_2$ | *(2-hydroxy-ethyl)trimethyl ammonium fluoride diurea* |
| *CFT* | *Crystal field theory* |
| *MOT* | *Molecular orbital theory* |

# Abstract

Investigation of some transition metal complexes were carried out at room temperature in the new clan of room temperature ionic liquids of choline chloride based composition.

The Ultraviolet Visible Spectroscopic spectra of $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ indicated a complexes formation between the metal ions and the entities of these types of RTILs solvents namely choline chloride/ urea and choline chloride/ malonic acid which have freezing point at 12°C and 0°C respectively.

The complexes in choline chloride/ urea were found to be of Octahedral geometry for $Cr^{3+}$, $Ni^{2+}$ and $Cu^{2+}$, and Tetrahedral geometry for $Fe^{3+}$, $Co^{2+}$ metal ions. Their spectra were found to be assigned to normal transition state of corresponding $d^n$ configuration in both geometries of Octahedral and Tetrahedral.

Substitution of solvent coordinated to these metals by added nitrate ions were observed, suggested a weak bonding between solvent molecules and transition metal cations, although they showed some geometrical coordination of corresponding metal cations. All complexes were found to reach final state of coordination at 72 hours, except $Co^{2+}$ complexes when they showed instability when they were left at room temperature for 40 days.

In choline chloride/ malonic acid the geometrical coordination of $Ni^{2+}$ and $Cu^{2+}$ showed tetrahedral geometry rather than octahedral geometry in this RTIL, while the other cations have similar coordination geometry.

CFT splitting value (10Dq) have been determined for most of new formed complexes using appropriate $d^n$ Orgel and Tanabe-Sugano diagrams, and Jorgenson rule was used to asset the suggestion of the type of ligands coordinated to transition metal cations. The nature of the bonding between the

metal ions and the donor ligands were demonstrated through the Jorgenson rule and calculation of Racah parameters $\boldsymbol{\grave{B}}$ were obtained form appropriate $d^n$ Tanabe-Sugano diagrams together with the qualitative assistance of Orgel diagrams.

# CHAPTER ONE

# INTRODUCTION

# CHAPTER TWO

# EXPAREMANTAL

# Part

# (MATERALS & METHODS)

# CHAPTER THREE

# RESULTS & DISCUSSION

# REFFRENCES

# Chapter One

# Introduction

## 1.1. Introduction.

### What is Molten Salt?

Molten salts are evidently numerous and potentially most significant and useful class of nonaqueous solvents. While “salts” is widely used though imprecise term, this class can be broadly defined as the liquid state of those compounds which melt, usually above room temperature to give liquids displaying ionic properties, at least to some degree. While they are probably more numerous than other nonaqueous solvents, molten salts are currently the least-known and least appreciated of the nonaqueous solvents, certainly much less so than their practical importance demands.(1,3)

Molten Salt is a rather dreadful name for an otherwise useful category of materials and processes. The term "Molten Salt" is self-descriptive; it is melted salt(s). Another common name is Fused Salt(s).(2,4)

Salts are simple, usually ionic (that is the chemical bonds are a simple ionic type) and stable compounds. The most common example of molten salt is "table salt", or sodium chloride (NaCl). Both sodium and chlorine are reactive; sodium is one of the most electropositive substances (tends to lose an electron) and chlorine one of the most electronegative (tends to take an electron). These two opposite substances readily join to form stable sodium chloride via a strong ionic bond. The melting point of sodium chloride is 801° C. At which point it becomes a liquid, and thus a "molten salt". This liquid is stable, has a heat capacity similar to water (by volume) and flows much like water does. The major differences are the obvious higher temperatures attainable in the molten salt state and when the salt solidifies (freezes) it contracts versus expanding in water. Thus, molten salt freezing in a pipe would not burst the pipe as water would.(3)

Molten salts are of considerable interest, not only from the technological point of view, but also from the standpoint of satisfying a fundamental curiosity. Structural studies of molten salts (such as alkali halides) by x-ray and neutron diffraction have been undertaken as part of a general program to determine the properties of molten salts.(3)

Molten salts, or if they are liquid under ordinary conditions, ionic liquids, are interesting for the special properties unique to fluids of charged particles and for applications of ionic liquids as environmentally friendly solvents.(3)

## ***1.2. Room Temperature Ionic Liquids 'RTILs'.***

Ionic liquids are highly solvating, non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve. They are outstanding good solvents for a variety of compounds, and their lack of a measurable vapour pressure makes them a desirable substitute for VOCs. Ionic liquids are attractive solvents as they are non-volatile, non-flammable, have a high thermal stability and are relatively inexpensive to manufacture. They usually exist as liquids well below room temperature up to a temperature as high as 200$^o$C.(5,6)

An ionic liquid is a liquid that contains essentially only ions. Some ionic liquids, such as ethyl ammonium nitrate, are in a dynamic equilibrium where at any time more than 99.99% of the liquid is made up of ionic rather than molecular species. In the broad sense, the term includes all molten salts, for instance, sodium chloride at temperatures higher than 800 °C. Today, however, the term "ionic liquid" is commonly used for salts whose melting point is relatively low (below 100 °C). In particular, the salts that are liquid at room temperature are called room-temperature ionic liquids, or RTILs.(7,8)

## ***1.3. A short history of ionic liquids—from molten salts to neoteric solvents.***

Ionic liquid is a salt with a melting temperature below the boiling point of water. Most salts identified in the literature as ionic liquids are liquid at room temperature, and often to substantially lower temperatures.The history of ionic liquids may be viewed as a relatively recent one, or one extending back to the 19th century. Which history you choose depends on your definition of ‘ionic liquid’ and how deeply you look for progenitors of the present materials receiving so much interest for green chemistry applications.(9) Accordingly, this may be the birth of new and important industrial materials, or we are witnesses to a renaissance of molten salt chemistry. One fairly general feature of ionic liquids that is not part of the definition is that most have organic cations and inorganic anions. There are many synonyms used for ionic liquids that complicate a literature search.(10) ‘Molten salts’ is the most common and most broadly applied term for ionic compounds in the liquid state. Unfortunately the term ‘ionic liquids’ was also used to mean the same thing long before there was much literature on low melting salts. It may seem that the difference between ionic liquids and molten salts is just a matter of degree (literally), however the practical differences are sufficient to justify a separately identified niche for the salts that are liquid around room temperature.(11) Synonyms for materials that meet the working definition of ionic liquid are ‘room temperature molten salt,’ ‘low temperature molten salt’, ‘ambient temperature molten salt’, ‘ionic fluid’ and ‘liquid organic salt.’ The term ‘neoteric solvent’ has been used in recent years to mean new types of solvents, or older materials that are finding new applications as solvents. Supercritical fluids and ionic liquids are good examples of neoteric solvents that have been known for a long time, but are being considered as process solvents.(10)

The link between ionic liquids and green chemistry is clearly related to the solvent properties of ionic liquids. Liquids range is the span of temperatures between the freezing point and boiling point of a liquid. The consequence for green chemistry is that ionic liquids are the ultimate non-volatile organic solvent, with emphasis on the ‘non-‘.(12) No molecular solvent (other than molten polymers) comes even close to the low volatility of ionic liquids. Ionic liquids have many of the advantages of molten salts, and they avoid the worst disadvantages caused by high temperature. In fact they are better viewed as a new type of non-aqueous solvent, which is a neoteric solvent.(13,14)

The early history of ionic liquids began in 1914 when the first report of a room temperature molten salt was reported by *Walden*. He reported the physical properties of ethyl ammonium nitrate, $[C_2H_5NH_3]\ NO_3$, which has a melting point of 12°C, formed by the reaction of ethylamine with concentrated nitric acid. Then, *Hurley* and *Weir* stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride(14). In 1970s and 1980s, *Osteryoung et al*(19). and *Hussey et al.*(20) respectively carried out extensive research on organic chloride–aluminum chloride ambient temperature ionic liquids and the first major review of room temperature ionic liquids was written by *Hussey*.(20) It was about in the middle of the 1990s when it was decided in the community to replace the term ‘‘room temperature molten salt’’ by ‘‘ionic liquid’’, and an ionic liquid is defined today as a liquid consisting solely of cations and anions with a melting point of 100°C and below. Although any high temperature molten salt is an ionic liquid, too, this novel term for the room temperature liquids clearly made a distinction.(15,16)

The ionic liquids based on $AlCl_3$ can be regarded as the first generation of ionic liquids. The hygroscopic nature of $AlCl_3$ based ionic liquids has delayed the progress in their use in many applications since they must be prepared and handled under inert gas atmosphere. Thus, the synthesis of air and water stable ionic liquids, which are considered as the second generation of ionic liquids, attracted further interest in the use of ionic liquids in various fields. (17) Generally, these ionic liquids are water insensitive; however, the exposure to moisture for a long time can cause some changes in their physical and chemical properties.(19) In 1992, *Wilkes* reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cation with either tetrafluoroborate or hexafluorophosphate as anions. Unlike the chloroaluminate ionic liquids, these ionic liquids could be prepared and safely stored outside of an inert atmosphere (18).

## 1.4. Green chemistry and green solvents.

Green chemistry involves the development of chemical products and synthetic procedures, which are environmentally friendly and have reduced health risks with the search for more efficient methods to do chemistry. Its roots stem back some years from a simple idea to a prominent concept which permeates all areas of modern chemistry.(20) Green solvents are environmentally friendly solvents or biosolvents, which are derived from the processing of agricultural crops. The uses of petrochemical solvents are the key to the majority of chemical processes but not without severe implications on the environment. The Montreal Protocol identified the need to re-evaluate chemical processes with regard to their use of volatile organic compounds (VOCs) and the impact theses VOCs has on the environment. Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents, Ethyl lactate, for example is a green solvent derived from processing corn. Lactate esters solvents are commonly used solvents in the paints and coatings industry and have numerous attractive advantages including being 100% biodegradable, easy to recycle, non-corrosive, non-carcinogenic and non-ozone depleting.(21,22)

Room temperature ionic liquids which melt below 100°C can be achieved by for example incorporating a bulky asymmetric cation into the structure to stop the ions packing easily. Since the melting points are low, ionic liquids can act as solvents in which reaction can be preformed, and because the liquid is made of ions rather than molecules, such reactions often give distinct selectivity and reactivity when compared with conventional organic solvents. Room temperature ionic have been utilized as clean solvents and catalysts for green chemistry and as electrolytes for batteries, photochemistry and electro-synthesis.(23)

These stemmed significantly as ionic liquids have no significant vapor pressure and thus create no volatile organic components. They also allow for easy separation of organic molecules by direct distillation without loss of the ionic liquid. Their liquid range can be as large as 300° C allowing for large reaction kinetic control, which, coupled with their good solvent properties, allows small reactor volumes to be utilized. Salt based upon poor nucleophilic anions such as $[CF_4]^-$, $[PF_3]^-$, $[CF_3CO_2]^-$,$[CF_3SO_3]^-$, etc, are water and air insensitive and possess remarkably high thermal stability.(22,24)

## 1.5. General characterization of ionic liquids.

Ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point. Ionic liquids come in two main categories, namely simple salts (made of a single anion and cation) and binary ionic liquids (salts where equilibrium is involved).(24) For example, $[EtNH_3][NO_3]$ is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of the aluminum(III) chloride and 1,3-dialkylimidazolium chloride present. Examples of ionic liquids consisting of a simple salt are given in Figure (1-1) and Figure (1-2) and these show simple melting behavior. For the binary systems, the melting point depends upon composition, and this complex behavior has been studied extensively for the archetypal system, $[emim]Cl\text{-}AlCl_3$ ($[emim]^+$ = 1-ethyl-3-methylimidazolium).(25,26)

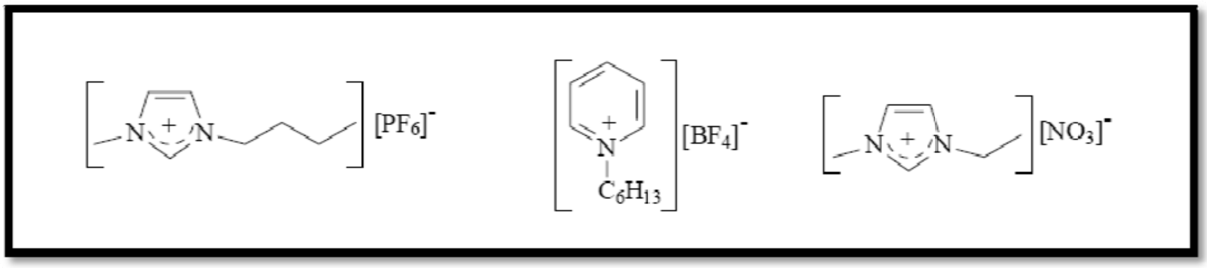

**Fig.(1-1):- Examples of simple room-temperature ionic liquids.(25)**

**Fig.(1-2):- Examples of room temperature molten salts.**(25,26)

With many chemical transformations taking place in solution, the role of solvents in chemistry is vital. Although, any liquid could be employed as a solvent, polar organic solvents have been extensively used for both synthetic chemistry and extraction technologies and have largely superseded water, which was widely employed historically. However, the ever-increasing awareness of the detrimental health and environmental effects of some organic solvents has given chemists the impetus to search for ‘green’ technologies Ionic liquids, especially those based on the 1,3-dialkylimidazolium cation, with a large range of liquid phase, negligible vapour pressure, low viscosity and high thermal and chemical stability are emerged as a new class of ‘green’ solvents for extraction and separation processes, organic synthesis and catalysis. The main milestones reached in the last two years, on the use of ionic liquids in green technologies.(27) The obviously ideal situation for a chemical process, from an ecological point of view, involves no solvent. Although many reactions can be performed without solvent, chemistry remains dominated by processes taking place in solution. Note that most of solvents have a significant solubility in the water phase, and therefore must be stripped from the water before it leaves the process, both for economic and environmental reasons.(26,29)

Room temperature molten salts (ionic liquids) are emerging as an attractive, alternative, ‘green’ technology in both organic and organometallic chemistry. Ionic liquids can also be described as liquid compounds that display ionic-covalent crystalline structures. This definition involves pure inorganic compounds (sodium chloride, mp=801$^o$C), organic compounds (tetrabutylphosphonium chloride, mp=80$^o$ C) or even eutectic mixtures of inorganic salts (such as lithium chloride/potassium chloride, 6/4, mp=352$^o$ C) (28) or organo-mineral combinations (triethylammonium chloride/cooper chloride, 1/1, mp=25° C). Organo-chloroaluminate ionic liquids, especially those resulting from the combination of N-alkylpyridinium chloride or 1,3-dialkylimidazolium chloride and aluminium chloride (Figure 1-1 and 1-2), have a broad range of liquid phase down to –88 °C.

These liquids have been widely used in electrochemical technologies as solvents for highly charged complex ions and electronic absorption spectra, for organic synthesis and for catalysis. The advent of air and water stable ionic liquids, in particular 1-*n*-butyl-3-methylimidazolium tetrafluoroborate and hexafluoro-phosphate ($BMI.BF_4$, liquid down to –81° C) and ($BMI.PF_6$) respectively, has led to a broader spectrum of applications involving these liquids (Figure 1-3).(29,30)

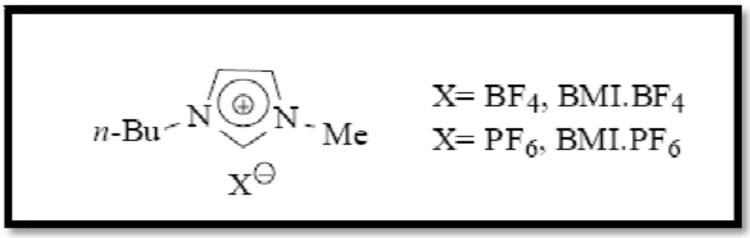

**Fig.(1-3):- Air and water stable molten salts.(28)**

Ionic liquids are the salts having very low melting temperature. Ionic liquids have received great interests recently because of their unusual properties as liquids. These unique properties of ionic liquids have already been mentioned in some books, these are entirely different properties from those of ordinary molecular liquids. The most important properties of electrolyte solutions are non-volatility and high ion conductivity.(31,32)

## 1.6. Advantageous characterizations of RTILs.

RTILs possess a unique array of physicochemical properties that make them suitable in numerous task-specific applications in which conventional solvents are non applicable or insufficiently effective. Such properties include:

1. Low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment.(33)

2. Very good solvents 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.(34)

3. Stability.

In most of these applications, the stability of ionic liquids, at least at a certain extent, is crucial for optimum process performance. Several studies have indicated that, although not 100% inert, certain ionic liquids incorporating 1,3-dialkyl imidazolium cations are generally more resistant than traditional solvents under certain harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes.(36)

4. Color.

High quality ionic liquids incorporating $[bmim]^+$ cation and a variety of anions, such as $[PF_6]^-$, $[BF_4]^-$, $[CF_3SO_3]^-$, $[CF_3CO_2]^-$ and $[(CF_3SO_2)_2N]^-$ have been reported to be colorless, even though they are not 100% pure. The color of less pure ionic liquids generally ranges from yellowish to orange. The formation of the color has been attributed to the use of raw materials with color or excessive heating during the synthesis of imidazolium salt.(35,36)

5. Hygroscopicity.

The water content has an influence on the viscosity of the ionic liquids. Viscosity measurements indicate that ionic liquids became less viscous with increasing water content. Hydrolysis problems can also occur. Most of the ionic liquids have extremely low vapour pressures, which allows removing water by simple heating under vacuum. Water contents below 1 ppm are quite easy to achieve with most of the liquids.

6. Hydrophopicity.

The degree of polarity can be varied by adapting the length of the 1-alkyl chain (in 1,3-substituted imidazolium cations). The anion chemistry has a large influence on the properties of IL, though little variation in properties might be expected between same-cation salts of these species, the actual differences can be dramatic:

for example, [bmim]$PF_6^-$ is immiscible with water, whereas [bmim]$BF_4^-$ is water-soluble.(36)

7. Conductivity.

Ionic liquids have reasonably good ionic conductivities compared with those of organic solvents/electrolyte systems (up to~10 mS $cm^{-1}$). However, at room temperature their conductivities are usually lower than those of concentrated aqueous electrolytes. Based on the fact that ionic liquids are composed solely of ions, it would be expected that ionic liquids have high conductivities. This is not the case since the conductivity of any solution depends not only on the number of charge carriers but also on their mobility(38). The large constituent ions of ionic liquids reduce the ion mobility which, in turn, leads to lower conductivities. The conductivity of ionic liquids is inversely linked to their viscosity. Hence, ionic liquids of higher viscosity exhibit lower conductivity. Increasing the temperature increases conductivity and lowers viscosity.(37,39)

8. Viscosity.

Generally, ionic liquids are more viscous than common molecular solvents and their viscosities are ranging from 10 mPa s to about 500 mPa s at room temperature. The viscosity of ionic liquids is determined by van der Waals forces and hydrogen bonding(40). Electrostatic forces may also play an important role. Alkyl chain lengthening in the cation leads to an increase in viscosity. This is due to stronger van der Waals forces between cations leading to increase in the energy required for molecular motion. Also, the ability of anions to form hydrogen bonding has a pronounced effect on viscosity. The fluorinated anions such as $BF_4^-$ and $PF_6^-$form viscous ionic liquids due to the formation of hydrogen bonding, in general, all ionic liquids show a significant decrease in viscosity as the temperature increases.(41)

9. Density.

Ionic liquids in general are denser than water with values ranging from 1 to 1.6 g $cm^{-3}$ and their densities decrease with increase in the length of the alkyl chain in the cation. For example, in ionic liquids composed of substituted imidazolium cations and $CF_3SO_3^-$ anion the density decreases from 1.39 g $cm^{-3}$ for $[EMIm]^+$ to 1.33 g $cm^{-3}$ for $[EEIm]^+$, to 1.29 g $cm^{-3}$ for $[BMIm]^+$ and to 1.27 g $cm^{-3}$ for $[BEIm]^+$. The densities of ionic liquids are also affected by the identity of anions. For example, the densities of 1-butyl-3 methylimidazolium type ionic liquids with different anions, such as $BF_4^-$, $PF_6^-$, $TFA^-$ and $Tf_2N^-$ are 1.12 g $cm^{-3}$, 1.21 g $cm^{-3}$, 1.36 g $cm^{-3}$ and 1.43 g $cm^{-3}$, respectively.(42-44)

10. Melting point.

As a class, ionic liquids have been defined to have melting points below 100 °C and most of them are liquid at room temperature. Both cations and anions contribute to the low meting points of ionic liquids(43). The increase in anion size leads to a decrease in melting point. For example, the melting points of 1-ethyl-3-methylimidazolium type ionic liquids with different anions, such as $[BF_4]^-$ and $[Tf_2N]^-$ are 15° C and -3° C, respectively. Cations size and symmetry make an important impact on the melting points of ionic liquids. Large cations and increased asymmetric substitution results in a melting point reduction.(45)

11. Thermal stability.

Ionic liquids can be thermally stable up to temperatures of 450° C. The thermal stability of ionic liquids is limited by the strength of their heteroatom–carbon and their heteroatom– hydrogen bonds, respectively. High temperatures are only tolerated by most liquids for a short time. Long time exposure to such high temperatures inevitably leads to decomposition.(46)

12. Electrochemical window.

The electrochemical window is an important property and plays a key role in using ionic liquids in electrodeposition of metals and semiconductors. By definition, the electrochemical window is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. This value determines the electrochemical stability of solvents(47). As known in aqueous solution, the electro-deposition of elements and compounds is limited by the low electrochemical window of water (about 1.2 V). On the contrary, ionic liquids have significantly larger electrochemical windows, e.g., 4.15 V for [BMIm] $PF_6$ at a platinum electrode, 4.10 V for [BMIm]$BF_4$ and 5.5 V for [BMP]$Tf_2N$ at a glassy carbon electrode. In general, the wide electrochemical windows of ionic liquids have opened the door to electrodeposit metals and semiconductors at room temperature which were formerly obtained only from high temperature molten salts. For example, Al, Mg, Si, Ge, and rare earth elements can be obtained from room temperature ionic liquids.(48)

## 1.7. ***Applications of Ionic liquids.***

1. Homogeneous and heterogeneous catalyst.

For some applications, ionic liquids offer the advantage of both homogeneous and heterogeneous catalysts. This is because selected ionic liquids can be immiscible with the reactants and products but dissolve the catalysts. This has the advantages of a solid for immobilizing the catalyst, with the advantages of a liquid for allowing the catalyst to move freely.(49)

2. Biological reactions media; Enzymes are also stable in ionic liquids, opening the possibility for ionic liquids to be used in biological reactions, such as the synthesis of pharmaceuticals.(49,50)
3. Treatment of high-level nuclear waste; Ionizing radiation does not affect ionic liquids, so they could even be used to treat high-level nuclear waste.(49)
4. Removing of metal ions; Researchers have designed and synthetized several new ionic liquids to remove cadmium and mercury from contaminated water. When these water-insoluble ionic liquids come in contact with contaminated water, they snatch the metal ions out of water and sequester them in the ionic liquid.(51)
5. Purification of gases, Ionic liquids can selectively dissolve and remove gases and could be used for air purification on submarines and spaceships.(51)
6. As solvent for synthetic and catalytic purposes, for example Diels-Alder cycloaddition reactions, Friedel-Craft acylation and alkylation, hydrogenation and oxidation reactions and Heck reactions.(52,55)
7. As biphasic system in combination with an organic solvent or water in extraction and separation technologies. (52)

8. As catalyst immobilization without need of special functionalization for the easy recycling of homogeneous catalysts. (52)
9. As electrolytes in electrochemistry. (52)

## 1.8. Room-Temperature Molten Salts Based on the Quaternary Ammonium Ion.

The number of families of molten salts exhibiting room temperature liquid behavior is quite limited. Excluding the hydrate salts, few purely inorganic systems form stable molten salts at room temperature. Molten organic salts, such as the quaternary ammonium and imidazolium salts, have been investigated for several reasons. They have been used as an effective tool in electrolyte solution chemistry and molten salt chemistry, as well as being excellent ionic media with negligible vapor pressure for organic reactions and instrumental analysis. In recent years, room-temperature molten salts have also been investigated as potential candidate electrolytes for use in batteries, photoelectrochemical cells, electroplating and capacitors. Molten salts have long been known in the family of quaternary ammonium salts, however, the melting point only approaches room temperature when the size of the cation and anion (Figure 1-4) is large. (53)

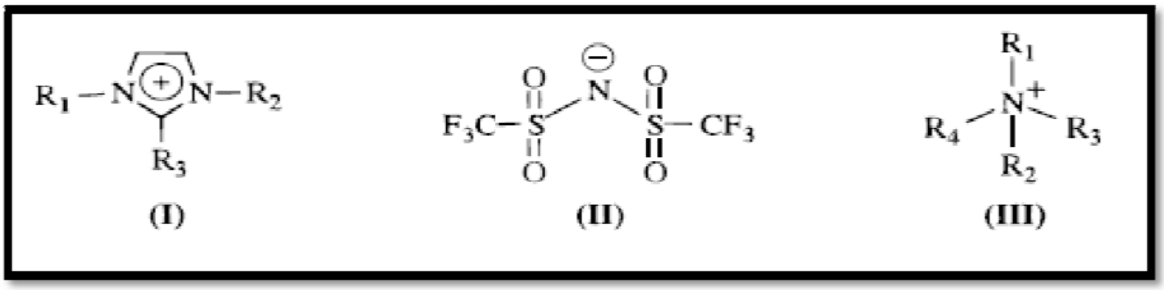

**Fig.(1-4):- Some types of room temperature ionic liquid.**

**(I) Molten Salts based on the imidazolium cation.**
**(II) Molten Salts based on the bis(trifluoromethylsulfonyl)imide ion anion.**
**(III) Molten Salts based on the quaternary ammonium cation.**

## 1.9. General properties of Choline Chloride.

Choline chloride [Ethanaminium, 2-hydroxy-N, N, N-trimethyl-, chloride], is a quaternary amine salt, with the chemical formula [$HOCH_2CH_2N$ $(CH_3)_3Cl$] it dissociates in water into the corresponding positively charged quaternary hydroxyl alkylammonium ion and the negatively charged chloride ion. Using different amounts of choline chloride showed that the lowest pH value of 4 was determined in a100 mg/L. Even if choline chloride of different specifications was used, choline chloride can be stated to be a weak acid. No data on dissociation constants are available for this compound. Choline chloride has neither explosive nor oxidizing properties due to its molecular structure (54). Choline is a dietary component and found in foods as free choline and as esterified forms such as phosphocholine, glycerol-phosphocholine, sphingomyeline, and phosphatidylcholine. Dietary choline is absorbed from the lumen of the small intestine. Additionally to dietary supply choline can be made available by enzymatic cleavage in the pancreas from other nutritional sources, before choline can be absorbed from the gut, some is metabolised by bacteria to form betaine and methylamines. Fasting plasma choline concentrations vary from 9 to 20 µmol/L. Choline chloride is a white crystalline solid but is marketed as an aqueous solution (70 – 75 % w/w in water) which is a colorless liquid with an amine-like odor. It has a measured water solubility of ca. 650 g/L and a calculated vapor pressure of $6.57\times10^{-10}$ Pa at 25°C.(55) Choline chloride or trimethyl (2-hydroxyethyl) ammonium chloride is an essential feed ingredient for optimum animal growth. Choline is classified as a vitamin and belongs to the group of water soluble B-vitamins. Choline has three essential metabolic functions :(56)

***i)*** It is a key constituent of phosphatidylcholine and phosphocholine and represents about 70 – 80 % of total phospholipids in the body.

***ii)*** It plays a vital role in fat transport and metabolism, thus preventing abnormal fat accumulation in the liver. It is also important in the establishment and maintenance of cell membrane structure.

***iii)*** Choline is a precursor to acetylcholine in impulse transmission of all nerves; Choline is a source of free methyl groups, essential for numerous biological functions. Animal studies with choline chloride show a low acute toxicity after oral uptake. No acute toxicity attributable to choline was observed in humans following oral doses of ≥3000 mg choline magnesium trisalicylate/day.

***iv)*** Choline chloride does not show a mutagenic, clastogenic or DNA damaging potential when tested *in vitro*; furthermore it has no structural alerts. There is therefore no indication of a genotoxic potential *in vivo*.

## ***1.10. Deep eutectic solvents.***

Eutectic mixtures of salts have been utilized for a long time to decrease the temperature for molten salt applications. In the extreme, ambient temperature molten salts have been formed by mixing quaternary ammonium salts with metal salts. This type of ionic liquid can be viewed as a deep eutectic resulting from the formation of complex anions *e.g.* $Al_2Cl_7$ and $Zn_2Cl_5$ thus decreasing the lattice energy and decreasing the freezing point of the system (57, 58). Work in this area focused on chloroaluminate salts of imidazolium and pyridinium chloride. A variety of different anions are formed in solution the ratios of which vary with the changing aluminium chloride composition. The depression of freezing point at the eutectic composition is as much as 190 °C. These ideas have recently been extended to other chlorometallate salts including $ZnCl_2$, $SnCl_2$ and $FeCl_3$.(59,60)

### ***1.10.1. Eutectic mixtures of Urea and Choline chloride.***

Halide salts can also form complexes with hydrogen bond donors and previous work has shown that mixtures of urea with alkali metal halides form eutectics with melting points of < 150° C. While a few reports also exist for adducts of urea with other metal salts their use as solvents has been limited to high temperature applications. Substituted quaternary ammonium salts such as choline chloride with urea produce eutectics that are liquid at ambient temperature and have unusual solvent properties. Figure (1-5) shows the freezing point of mixture of choline chloride and urea, a eutectic occurs at a urea to choline chloride ratio of 2:1. The freezing point of the eutectic mixture is 12 °C, which is considerably lower than that of either of the constituents (m.p. choline chloride = 302 °C and urea = 133 °C) and allows the mixture to be used as an ambient temperature solvent. This significant depression of the freezing point must arise from an interaction between urea molecules and the chloride ion. This is consistent with the crystallographic data for the (mane) solid $[(CH_3)_3N^+CH_2CH_2OH^-]_2C_2O_4^{2-}$ $.2(NH_2)_2CS$ which shows extensive hydrogen bonding between the thiourea molecule and the oxalate anion. The existence of hydrogen bonding in these eutectic mixtures can be observed using NMR spectroscopy. An alternative approach to making large non-symmetric ions is to take a simple organic halide salt and complex the anion with something that will form a hydrogen bond. The complexing agent interacts with the anion, increasing its effective size. This in turn decreases the interaction with the cation and so decreases the freezing point of the mixture. The major advantage of this approach is that common, non-toxic components can be used and the properties of the liquid can be changed with each hydrogen bond formed and each halide salt. This approach has numerous possibilities. Therefore, many quaternary ammonium salts are available and the wide variety of amides, amines, carboxylic acids and alcohols which could be used to provide hydrogen bonds. These liquids are similar to the metal-containing ionic liquids, but to differentiate them from the wide range of ionic liquids that are available they have been given the name deep eutectic solvents. They are easy to make – simply take the two solids, mix them together with gentle heating, until they melt, and when they cool they remain liquid. Work to date has focused on choline (2-hydroxyethyl-trimethylammonium) chloride as the quaternary ammonium salt. This is vitamin B4 and is produced on the milirn tones per annum scale as an additive for chicken feed and a wide range of other applications. Thus choline chloride is not only cheap, but it is non-toxic and even biodegradable. Ionic liquids based on choline chloride have, therefore, the potential to be used on a large scale. One simple hydrogen bond 'donor' that has been used is urea

$((NH_2)_2C{=}O)$, which is a common fertiliser. Urea mixed with choline chloride in a 2:1 ratio produces a colorless liquid that freezes at ca 12°C as in (Figure 1-5),

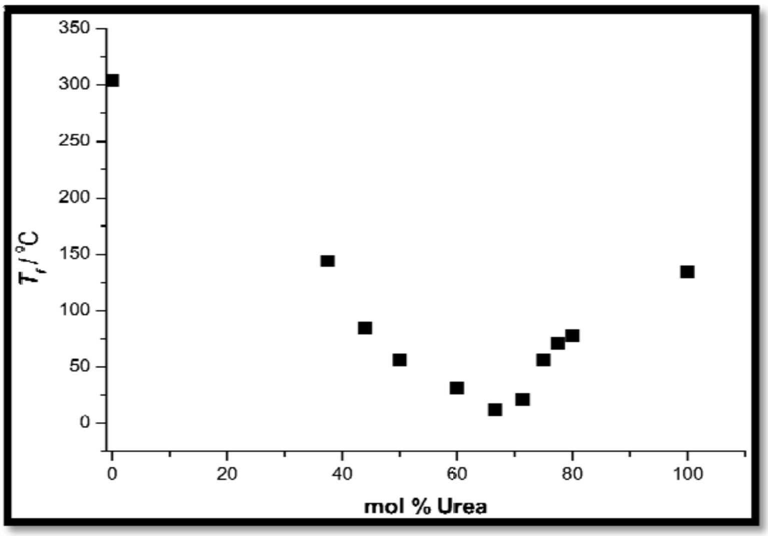

**Fig.(1-5):- Freezing point of Choline chloride/Urea Mixture as a function of composition.**(61)

This is remarkable given the melting points of the constituents (choline chloride melts at 303°C and urea at 134° C). The lowest melting point of these mixtures (termed the 'eutectic composition') reported to occur when the ratio of salt to hydrogen bond donor is 1:2. The depression of freezing point and the eutectic composition changes with the nature of the molecule providing the hydrogen bonds, e.g. oxalic acid (HOOCCOOH): choline chloride has a eutectic composition of 1:1 and a depression of freezing point of 212°C.(61) The depression of freezing point and the eutectic composition changes with the nature of the molecule providing the hydrogen bonds. With deep eutectic solvents, however, the magnitude of the freezing point depression is over 10 times greater than with ice and salt. It was reported that with addition of sliver nitrate to choline chloride/urea ionic liquid no precipitate was observed for sliver chloride, which indicated that the chloride is not as free ion in this ionic liquid and the formed ionic liquid is of molten salt nature.(59,76)

These deep eutectic solvents are highly conducting (*ca*. 1 mS $cm^{-1}$ at 30 $^oC$), confirming that the ionic species are dissociated in the liquid and can move independently; (Figure 1-6) shows that the conductivity increases significantly with temperature.

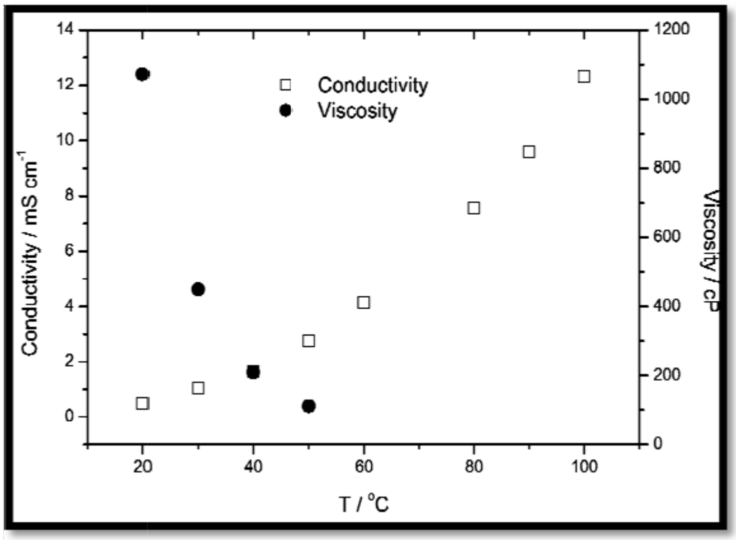

**Fig. (1-6):- Conductivity and viscosity of a 2 urea to 1 choline chloride mole ratio ionic liquid as a function of temperature.** (61)

The principle of creating an ionic fluid by complexing a halide salt can be applied to mixtures of quaternary ammonium salts with a range of amides. The charge delocalization is achieved through hydrogen bonding between the halide anion with the amide moiety. It was shown that a eutectic mixture of choline chloride with urea gave a liquid with a freezing point of 12 °C. This liquid was found to have interesting solvent properties that are similar to ambient temperature ionic liquids and a wide variety of solutes were found to exhibit high solubilities. While the depression of freezing point is less than analogous chlorometalate systems, there is a wide range of amides that can be used to form these eutectic mixtures. To differentiate these liquids from ionic liquids the term Deep Eutectic Solvents (DES) has been adopted. Unlike the room-temperature ionic liquids, these eutectic mixtures are easy to prepare in a pure state. They are nonreactive with water, many are biodegradable and the toxicological properties of the components are well characterized. The use of urea to form eutectics with alkali metal halides that have melting points of <150 °C has been known for a considerable time and a few reports also exist for adducts of urea with other metal salts.(61, 63)

### 1.10.2. Eutectic mixtures of Malonic acid and Choline chloride.(83)

Carboxylic acids can also form complexes with hydrogen bond donors and previous work has shown that mixtures of urea with quaternary ammonium salt (choline chloride) form eutectics with melting points of 12° C.

Another hydrogen bond 'donor' that has been used is malonic acid [$CH_2$ $(COOH)_2$], which is dicarboxylic acid. Malonic acid was mixed with choline chloride in mole ratio of 1:1 and was heated to $80^oC$, when a homogeneous colourless liquid was produced. The liquid was slowly cooled until it solidified at $0^oC$; freezing point was taken as the temperature at which the first solid began to form. The solidified melt turned into liquid state as temperature increased to room temperature which is considerably lower than that of either of the constituents (choline chloride melts at 303°C and malonic acid at 133° C). The bonding was suggesting being between the acid and chloride ion, or bridging acids between neighboring chloride ions. (62)

Phase Behaviour. Figure (1-7) shows the phase diagram for mixtures of choline chloride with phenylacetic and phenylpropionic acids as a function of composition. It is apparent that a eutectic is formed at a composition of 67 mol % acid which is similar to the eutectic recently reported for the choline chloride/urea system. It can be inferred that to form the eutectic two carboxylic acid molecules are required to complex each chloride ion. It is thought that the protons and carboxylate anions are extensively associated in the liquids.(62) (Figure 1-8) shows the phase diagrams for dicarboxylic acid (malonic acid). For these systems, the eutectic occurs at 50 mol % acid suggesting a 1:1 complex between the acid and chloride ion, or bridging acids between neighboring chloride ions, like malonic acid. These exhibit the rheology of gels and presumably have extensive bridging of the acids between neighboring chloride ions. The freezing point of the eutectic mixture of choline chloride and malonic acid mixture is $10^oC$, while the melting point of the pure acid is $135^oC$ and for choline chloride is $303^oC$.

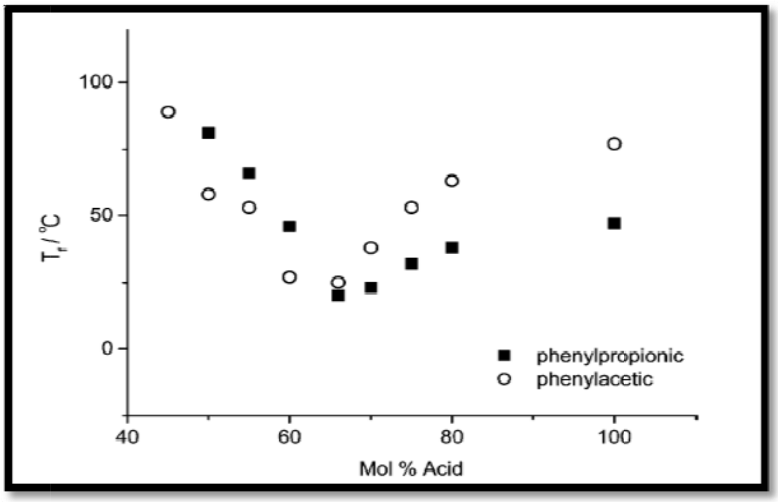

**Fig.(1-7):- Freezing points of Choline chloride with phenylpropionic and phenylacetic acids as a function of composition.(62)**

The triscarboxylic acids citric and tricarballylic acid have a eutectic composition in the region 30-35 mol % acid. These exhibit the rheology of gels and presumably have extensive bridging of the acids between neighbouring chloride ions. The lowest melting point of this eutectic occurs when the ratio of choline chloride to malonic acid is 1:1. The changing in freezing point depended on the nature on the molecule that donating the hydrogen bonding.(83)

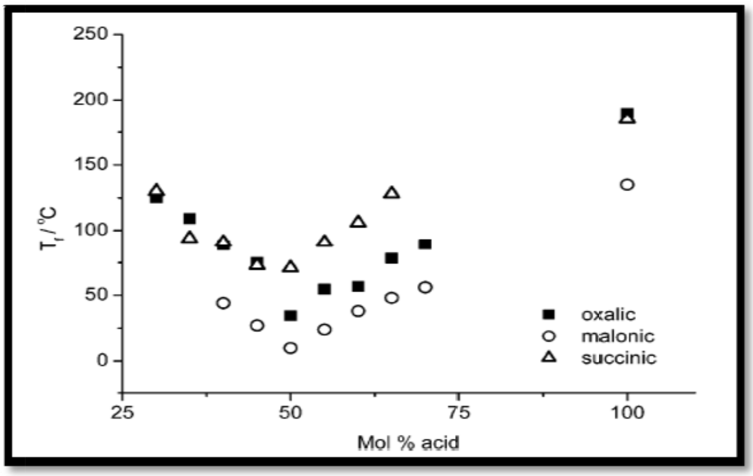

**Fig.(1-8):- Freezing points of Choline chloride with Oxalic, Malonic, and Succinic acids as a function of composition.(62)**

The resultant molten salts have the advantage that they are not water sensitive, although they are, in general, more viscous than their aluminum analogues. Mixtures of zinc chloride with substituted quaternary ammonium salts such as choline chloride have large depressions of freezing point (up to 270 °C). It has also recently been shown that these ideas can be extended to other metals by using hydrated salt mixtures. To circumvent the use of metals in ionic fluids a variety of closed shell anions have been synthesized and these have been the main focus of ionic liquids research over the past decade.

The viscosity of the DES of choline chloride/malonic acid changes significantly as a function of temperature, the hydrogen bond donor type and mixture composition as shown in (Figure 1-9). The viscosity values were found to cover the range 50 to 5000 cP, which is similar to those observed with ionic liquids.

The DES of choline chloride/malonic acid has conductivity of the range 0.1 to 10 mS $cm^{-1}$ changing with composition and temperature. These values are again similar to imidazolium based ionic liquids and similar to the choline chloride/urea DES. Approximately linear correlations are observed between $\sigma$ and $\eta^{-1}$ for this DES for all of the systems, although the slopes are markedly different.(62)

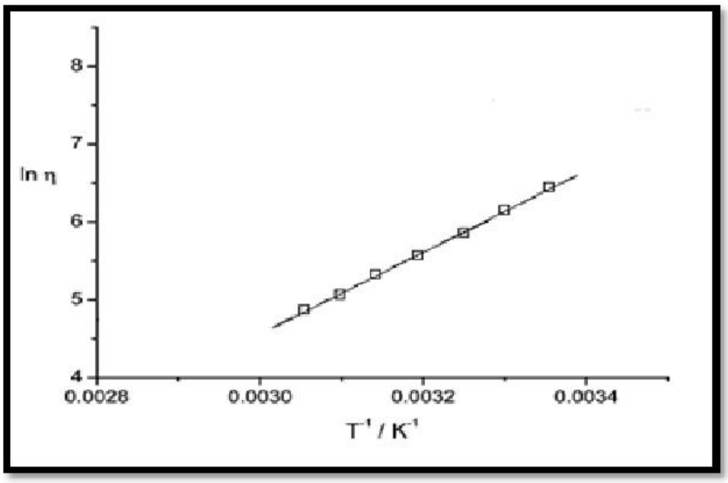

**Fig.(1-9):- Plot of log viscosity vs. reciprocal of temperature for the Choline chloride/Malonic acid ionic liquid.** (62)

## 1.11. Interaction of the ligands with the metal ions.

The tendency of metal ion to from a stable complex with ligands depend on many rules such as the hard and soft acids and bases (HSAB) rule of Pearson (58) which imply that metal ion tend to coordinate with certain functional groups of the ligand to from a stable complex. On the other hand, the tendency of transition metal ion of a special oxidation states is affected by the coordination to certain ligands. This phenomenon is called (symbiosis)**.**(64, 65)

Increasing the positive charge on the central transition metal ions strengthens the metal –ligands bond. The metal ion prefers to bind with atoms of high electron density such as $N^{3-}$, $O^{2-}$, $P^{3-}$, $S^{2-}$ and $C^{4-}$. The ligand should have certain characteristic properties to make it convenient to form stable complex with transition metal ions. The size, geometrical shape, number and geometrical arrangement of ligand and donor atoms play the important role in the stability of the resultant complex. Metal centers, being positively charged, are favored to bind to negative charged biomolecules, the constituents of proteins and nucleic acid offer excellent ligands for binding to metal ions (65). The Irving Williams series of stability for a given ligand shows a good criterian for the stability of complexes with dipositive metal ions which follows the order:

$$Ba^{2+}<Sr^{2+}<Ca^{2+}<Mg^{2+}<Mn^{2+}<Fe^{2+}<Co^{2+}<Ni^{2+}<Cu^{2+}>Zn^{2+}$$

This order arises in part from a decrease in size across the series and in part from ligand field effect. A second observation is that certain ligands form their most stable complexes with metal ions such as $Ag^{+}$, $Hg^{2+}$and $Pt^{2+}$, but other ligands seem to prefer ions such as $Al^{3+}$, $Ti^{4+}$, and $Co^{3+}$. Ligands and metal ions were classified as class (a) or (b) according to their preferential bonding. Class (a) metal ions includes those of alkali metals, alkaline earth metals, and lighter transition metals in higher oxidation states such as $Ti^{+4}$ ,$Cr^{+3}$ , $Fe^{+3}$ ,$Co^{+3}$ and the hydrogen ion, $H^{+}$. Class (b) metal ions include those of the heavier transition metals, and those in lower oxidation states such as $Cu^{+}$, $Ag^{+}$, $Hg^{+2}$, $Pd^{+2}$, and $Pt^{+2}$. According to their preference toward either class (a) or class (b) metal ions, ligands may be classified as type (a) or (b), respectively. Stability of these complexes may be summarized as follows **(65, 66)**; the ligand should have certain characteristic properties to make it convenient to form a stable complex with transition metal ions. The size, geometrical shape, number and geometrical arrangement of ligand donor atoms play the important role in stability of the resultant complex (65)**.**

| Tendency of ligands to complex with Class (a) metal ions | Tendency of ligands to complex with Class (b) metal ions |
|---|---|
| N>>P> As >Ab | N<<P< As >Sb |
| O>>S>Se>Te | O<<S<Se~Te |
| F>Cl>Br>I | F<Cl<Br<I |

One of the important aspects of CFT is that all ligands are not identical when it comes to a causing separation of the d-orbitals. For transition metal compounds, they were aware of the multitude of colors available for a given metal ion when the ligands or stereochemistry are varied. In octahedral complexes, this can be considered a reflection of the energy difference between the higher $dz^2$, $dx^2$-$y^2$ (eg subset) and the dxy, dyz, dxz ($t_2g$ subset).

It has been established that the ability of ligands to cause a large splitting of the energy between the orbitals is essentially independent of the metal ion and the spectrochemical series is a list of ligands ranked in order of their ability to cause large orbital separations.

A shortened list includes:

$I^- < Br^- < SCN^- \sim Cl^- < F^- < OH^- \sim ONO^- < C_2O_4{}^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 \sim pyr \sim en < bipy < phen < CN^- \sim CO$

When metal ions that have between 4 and 7 electrons in the d orbitals form octahedral compounds, two possible electron allocations can occur. These are referred to as both weak field (high spin) and strong field (low spin) configurations.

The MOT method has provided a quantitative measure of the d-splittings. The eg/$t_2g$ splitting (called the octahedral ligand field splitting $\Delta_0$= 10Dq) Follows the general trend. Point to consider about the $\Delta_0$ splitting:

1) charge on the metal:-

As charge increase, electrostatic attraction between M and L increases, M-L bond distance decreased and $S_{ML}$ increased. Also as charge increase, metal becomes more electronegative, decreasing $\Delta E_{ML}$. Both trends lead to greater field strength for the more highly charged ion.

2) The nature of the metal ion, radial extension of 2nd and 3rd row transition metals are greater, thus $S_{ML}$ larger, leading to the following trend in $\Delta_0$: 1st row transition metal << 2nd row transition metal ~ 3rd row transition metal.

3) Nature of ligand:-

Different ligands have different $S_{ML}$ for a given metal ion. Can assess by measuring $\Delta_0$ for different ligands about a given metal ion of given charge

$Cl^- < F^- < OH_2 < CN^-$ $Cl^- < OH_2 < NH_3 < CN^-$

From experiments such as these, may deduce a general ranking of ligands in terms of field strength… this ranking is called the spectrochemical series:

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < S^{2-} < F^- < O^{2-} < OH^- < H_2O < NH_3 < CN^- < CO < NO^+$

Weak field strength (small $\Delta_0$) strong field strength (large$\Delta_0$)
π-donors σ-only π-accepter

In the above series, the ligand type has been overlayed onto the spectrochemical series. As is readily apparent from the energetic disposition of $\Delta_0$, π-donors give weak ligand fields, σ-only ligands give intermediate fields and π-acceptors ligands give strong fields. (64, 65)

## 1.12. The Chemistry of the first Transition Metal Elements.

### 1.12.1. Chromium (III), ($d^3$).

Oxidation state (III) is by far the most stable and best known oxidation state of chromium there is literally thousands of chromium (III) complexes that with a few exceptions are all hexacoordinate. The principale characteristic of these complexes in aqueous solution is their relative kinetic inertness.(64)

Chromium (III) forms stable salt with all the common anions and it complexes with virtually any species capable of donating an electron-pair. These complexes may be anionic, cationic, or neutral and, with hardly any exceptions are octahedral. There is also a multitude of complexes with two or more different ligands such as pentammines $[Cr(NH_3)_5X]^{n+1}$ which have been extensively used in kinetic. These various complexes are notable for their kinetic inertness, which is compatible with the half-filled $t_2g$ level arising from an octahedral $d^3$ configuration, ligand displacement or rearrangement reaction of Cr (III) complexes are only about 10 times faster than those of Co(III), with half-times in the range of several hours. This is the reason why many thermodynamically unstable complexes of Cr $^{III}$ can be isolated as solid and that they persist for relatively long of time in solution, even under conditions of marked thermodynamic instability. (65)

$[CrX_6]^{3-}$ (X= halide, CN, SCN, $N_3$, $H_2O$, $NH_3$).

$[Cr(L\text{-}L)_3]$ (L-L= amino acid anions).

The hexaaqua ion $[Cr(H_2O)_6]^{3+}$, which is regular octahedral, occurs in aqueous solution and in numerous solid salts such as the violet $[Cr(H_2O)_6]Cl_3$. Chromium (III) is the archetypal $d^3$ ion and the electronic spectra and magnetic properties of its complexes have been exhaustively studied. The magnetic properties of the octahedral Cr(III) complexes are uncomplicated. All such complexes must have three unpaired electrons irrespective of the strength of the ligand field, and this has been confirmed for all known mononuclear complexes. The spectra of Cr(III) complexes are also well understood in their main features, in an octahedral field, the splitting of free ion ground $^4F$ term, along with the presence of the excited $^4P$

term of the same multiplicity, provides or indicating the possibility of three spin-allowed *d-d* transitions, and these have been observed in a considerable number of complexes, the spectrochemical series was originally established by Tsuchida using data for Cr(III) and Co(III) complexes. In the aqua ion the bands are found to be 17,400, 24,700, and 37,000 $cm^{-1}$. The frequencies of the spin-allowed bands of Cr(III) in ruby indicate that the Cr(III) ions are under considerable compression, since the value of $\Delta_o$ calculated is significantly higher than the $[Cr(H_2O)_6]^{3+}$ion or in other oxide lattice and glasses. Spin-forbidden transitions from the $^4A_2g$ ground state to the doublet states arising from $^2G$ state of the free ion are observed. The transitions to the $^2Eg$ and $^2T_1g$ states give rise to extremely sharp lines because the slope of the energy lines for these states is the same as that for the ground state. For $[Cr(H_2O)_6]^{3+}$, this has the simplifying effect that the crystal field splitting *10Dq*, is given directly by the energy of the lowest transition. The magnetic moment is expected to be very close value to the spin-only value for three unpaired electrons, and because of the absence of any orbital contribution, to be independent of temperature. (65)

In molten salts anhydrous Chromium (III) chloride dissolved only slowly forming pale green solutions after more than 15 h for $10^{-3}$ mol $dm^{-3}$ concentrations at 90°C in acetamide-potassium nitrate and 8 h at 140°C in butyramide-sodium nitrate melts. The spectrum for the acetamide eutectics (Figure 1-10, curve A) showed two absorption maxima, consistent with octahedral coordination. The band energies were close to those expected for 6 acetamide or 6 nitrate ligands, but the much higher extinction coefficients suggested mixed, lower symmetry, complexes, though probably with little or no coordination by chloride ligands. The coordination in the butyramide-sodium nitrate eutectic, spectrum in (Figure1-10, curve B), was probably rather similar.(67)

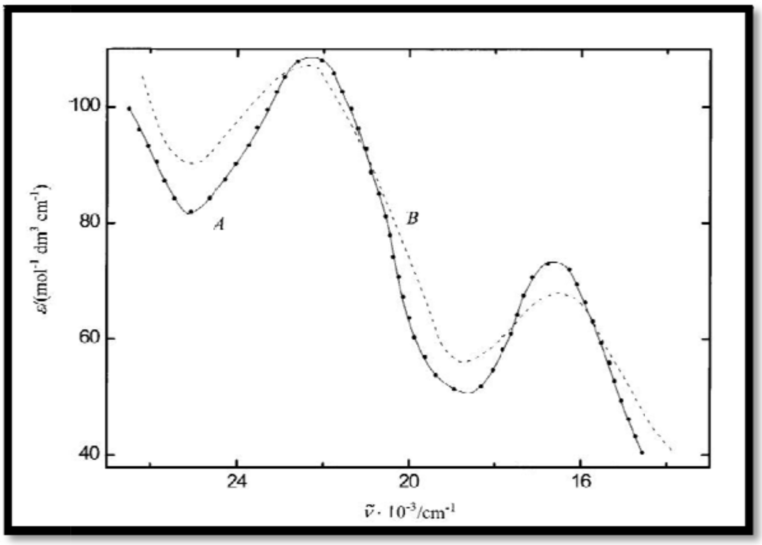

**Fig.(1-10):- Spectra of $CrCl_3$, curve A - c = 0.006 mol $dm^{-3}$ in acetamide-potassium nitrate at 90°C (•), curve B - c = 0.003 mol $dm^{-3}$ in butyramide-sodium nitrate at 140°C (- - -).(67)**

## 1.12.2. Iron (III), ($d^5$).

Iron (III) occurs in salts with most anions, except those that are incompatible with it because of their character as reducing agent. In aqueous solution Fe (III) one of the most conspicuous features of ferric iron in aqueous solution its tendency to hydrolyze and/ or form complexes. It has been establisned that the hydrolysis (equivalent in the first stage to acid dissociation of the aqua ion) is governed in its initial stage. The various hydroxo species, such as $[Fe(OH)(H_2O)_5]^{2+}$, are yellow because of charge transfer band in the ultraviolet region, which have tails coming into the visible region. Thus aqueous solutions of ferric salts even with noncomplexing anion are yellow unless strongly acid.(65)

The majority of Iron complexes are octahedral, but tetrahedral and square pyramidal ones are also important. The affinity of Iron (III) for amine ligands is very low. No simple ammine complex exists in aqueous solution, chelating amine like EDTA form some definite complexes. Iron (III) has its greatest affinity for ligands that coordinate by oxygen, viz., phosphate ions, polyphosphates, and polyols such as glycerol and sugars, with oxalate Iron (III) forms trisoxalate complex $[Fe(C_2O_4)_3]^{3-}$. Ferric ion forms complexes with halide ions and $SCN^-$, its affinity for $F^-$ is quite high. Iron (III) is isoelectronic with manganese (II), but much less is known of the details of $Fe^{III}$ spectra because of the much greater tendency of the trivalent ion to have charge transfer bands in the near-ultraviolet region with strong low-energy wings in the visible that obscure the very weak, spin-forbidden *d-d* band. Insofar as they are known, however, the spectral features of iron (III) in octahedral surroundings are in accord with theoretical expectations. Iron (III) is high spin in nearly all its complexes except those with the strongest ligands like $[Fe\ (CN)_6]^{3-}$, $[Fe\ (bipy)_3]^{3+}$, $[Fe\ (phen)_3]^{3+}$, and other tris compexes with imine nitrogen atoms as donor. The low-spin complexes with $t_2g^5$ configuration usually have considerable orbital contribution to their moments at about room temperature. There is evidence of very high covalence and electron delocalization in low-spin complexes such as $[Fe\ (phen)_3]^{3+}$ and $[Fe\ (bipy)_3]^{3+}$. Iron (III) may be high or low spin and even though an octahedral stereochemistry is the most common. A number of other geometries are also found. It has been suggested that $Fe^{III}$ species high spin and low spin are present in thermal equilibrium. The simplified Tanabe-Sugano diagram ($d^5$) shows how as the crystal field increases, it is designated as weak or strong (the configuration as high or low spin) depending on whether the ground term is a $^6A_1\ (t_2g^3eg^2)$ or $^2T_2\ (t_2g^5)$ term. Where CFT is close to this critical boundary value both terms are thermally accessible and the observed magnetic moment will depend on the precise distribution between them. As this distribution will be temperature dependent. (64, 66)

Iron (III) chloride was very soluble in the acetamide-potassium nitrate eutectic at 90°C giving initially a pale yellow solution which darkened rapidly to a strong brown color within 15 min. The pale yellow solution gave one absorption band at $\nu = 16900\ cm^{-1}$ ($\varepsilon = 35 mol^{-1}\ dm^3\ cm^{-1}$) close to an absorption edge at $\nu = 21000\ cm^{-1}$, while the dark brown solution showed only the absorption edge. The pale yellow solution may be due to a tetrahedral complex perhaps containing some chloride ($FeCl_4^-$ in $LiNO_3$-$KNO_3$ eutectic at 160°C, band at $\nu = 16000\ cm^{-1}$, $\varepsilon = 32 mol^{-1}\ dm^3\ cm^{-1}$) which was replaced over 15 min by more stable simple complexes containing acetamide and/or nitrate, or perhaps by more polymerized solvolyzed iron specie.(67)

### 1.12.3. Cobalt (II), ($d^7$).

There is a very marked contrast in this oxidation state between cobalt (II) on the one hand and the two heavier member of the group on the other hand, for cobalt (II) it is one of the two most stable oxidation state. Complexes of configuration comparable are stability with the $t_2g^6$ of Co (II), show a greater diversity of types and are more labile. The aqua ion $[Co\ (H_2O)_6]^{+2}$ is the simplest complex of cobalt (II). In aqueous solution containing no complexing agents, the oxidation to $Co^{III}$ is very unfavorable. Cobalt (II) forms numerous complexes, mostly either octahedral or tetrahedral but five-coordination and square species are also known. There are more tetrahedral complexes of Cobalt (II) than other transition metal ions. This is in accord with the fact that for a $d^7$ ion, ligand field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one to a smaller extent than for any other $d^n$ $(1 \leq n \leq 9)$ configuration. Because of the small stability difference between octahedral and tetrahedral $Co^{II}$ complexes, there are several cases in which the tow types with the same ligand are both known and may be in equilibrium. There is always some $[Co\ (H_2O)_4]^{2+}$ in equilibrium with $[Co(H_2O)_6]^{2+}$.(64) As already noted, Cobalt (II) occurs in a great variety of structural environments, because of this the electronic structures, hence the spectral and magnetic properties of the ion, are extremely varied. High-spin octahedral and tetrahedral complexes, in each case there is a quartet ground state $(^4F)$ and three spin-allowed electronic transitions to the excited quartet state $(^4P)$. As maybe inferred from the simple observation that octahedral complexes are typically pale red or purple and many common tetrahedral ones are an intense blue in each case the visible spectrum is dominated by the highest energy transition, $^4A_2 \rightarrow {}^4T_1(P)$ for tetrahedral and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ for octahedral complexes, however in the octahedral systems the $^4A_2g$ level is usually close to the $^4T_1g(P)$ level and the transition to these tow levels are close together. Since the $^4T_1g$ state is derived from a $t_2g^3eg^4$ electron configuration, and the $^4T_1g\ (F)$ ground state is derived mainly from a $t_2g^5eg^2$ configuration, the $^4T_1g(F) \rightarrow {}^4A_2g(F)$ *(shoulder)* transition is essentially a two-electron process. For octahedral complexes, there is one more spin-allowed transition *($^4T_1g$ (F) $\rightarrow ^4T_2g$)* which generally occurs in the near-infrared region. Tetrahedral complexes $[CoX_4]^{2-}$ are generally formed with monodentate anionic ligands such as $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $N_3^-$, and $OH^-$; with a combination of two such ligands and two neutral ones, tetrahedral complexes of the type $CoL_2X_2$ are formed. With ligands that are bidentate monoanions, tetrahedral complexes are formed. For tetrahedral complexes there is also a transition in the near-infrared region $[^4A_2 \rightarrow ^4T_1(F)]$ as well as one quite low energy ($^4A_2 \rightarrow ^4T_2$), which is observed because it is in region spectrum(1000-2000 nm)and it is orbitally forbidden. The visible transitions in both tetrahedral and octahedral cases, particularly in the tetrahedral case is more intense, because a number of transitions to doublet excited state occur in the same region, and these acquire some intensity by means of spin orbit coupling. Cobalt (II) is the only common $d^7$ ion, because of its stereochemical diversity its spectra have been widely studies. In the octahedral case the splitting is the same as the octahedral $d^2$ ion and the spectra can therefore be interpreted by using the same Tanabe-Sugano diagram as was used for $d^2$. Magnetic properties provide a complementary means of distinguishing stereochemistry the *T* ground term of octahedral ion is expected to give rise to a temperature dependent orbital contribution to the magnetic moment where as the *A* ground term of the tetrahedral ion is not, Low-spin octahedral complexes, a sufficiently strong ligand field ($\Delta_o \geq$ 15,000 $cm^{-1}$) can cause a $^2E$ state originating in the $^2G$ state of free ion to become the ground state. The electron configuration here is mainly $t_{2g}^6 eg$; thus a Jahn-teller distortion would be expected consequently perfectly octahedral low-spin Co (II) complexes must be rare.(64,65)

The dipositive 3d transition metal ions have been shown to occur as markedly different ionic species in the highly dissociated alkali chloride melts compared with the non dissociated aluminum chloride melt. From spectrophotometric measurements of Cobalt (II) chloride in calcium nitrate tetrahydrate melts containing variable amounts of calcium chloride (from 0 to 3.1 mol $dm^{-3}$) were reported at different temperatures from 40 $^oC$ to 70$^oC$. The solutions in pure calcium nitrate tetrahydrate showed octahedral coordination, the position of the absorption maximum being at 19420cm$^{-1}$ (512 nm). Addition of chloride caused a shift of the absorption maximum toward lower energies and a large increase of the absorption coefficient indicating a change from octahedral to tetrahedral or distorted octahedral coordination.$^{(68)}$

The absorption spectra of Cobalt (II) chloride complexes, containing variable concentrations of chloride ligand also reported, in a molten mixture of 80% acetmide-20% calcium nitrate tetrahydrate, in range of temperature 313 to 363 K, in the wavelength range 400-800 nm. The melt contained three ligands ($CH_3CONH_3$, $H_2O$, and $NO_3^-$) for competition with added chloride; addition of chloride caused a shift of the absorption maximum of octahedral Cobalt (II) nitrate towards lower energies and pronounced changes in shape of the initial spectrum of Cobalt (II) nitrate. The effect of temperature changes on the molar absorption of the Co (II) species was attributed to structural changes occurring in the Cobalt (II) species.$^{(69)}$

In the LiC1-KC1 eutectic melt the absorption spectrum of Co (I1) is that of the tetrahedral $CoCl_4^{2-}$ species. The occurrence of the $CoCl_4^{2-}$ rather than the $CoCl_6^{4-}$ species in this highly ionic melt can be rationalized in terms of large (-30 kcal.) electrostatic repulsion energies favoring the four- over the six-coordinated form. In the covalent $A1C1_3$ melt $CoCl_2$ in an $A1C1_3$ melt with 35.5 mole % KC1, close to the composition $KA1_2C1_7$, is practically identical with the spectrum in pure $A1C1_3$, indicating that the postulated $Co(Al_2C1_7)_2$ complex is the only light-absorbing species present in the composition range 0-35.5 mole % KC1. Successive additions of KC1 to the 35.5 mole % KC1 melt resulted in only minor spectral changes until a composition of 42 mole % KC1 was reached. Upon further addition of KC1, the $Co(Al_2C1_7)_2$ spectrum characteristic of octahedral coordination gradually transformed into a new spectrum. Addition of KC1 to a melt containing 49.3 mole % KC1 resulted in partial precipitation of Co (I1) and the formation of a blue precipitate which chemical and X-ray analysis showed to be $CoCl_2$. Addition of KC1 to a melt whose KC1:$AlCl_3$ ratio was exactly equal to 1 caused the $CoCl_2$ precipitate to redissolve completely with only a few times more than the stoichiometric amount of KC1 needed to form $CoC1_4^{2-}$, as shown in (Figure 1-11).$^{(70)}$

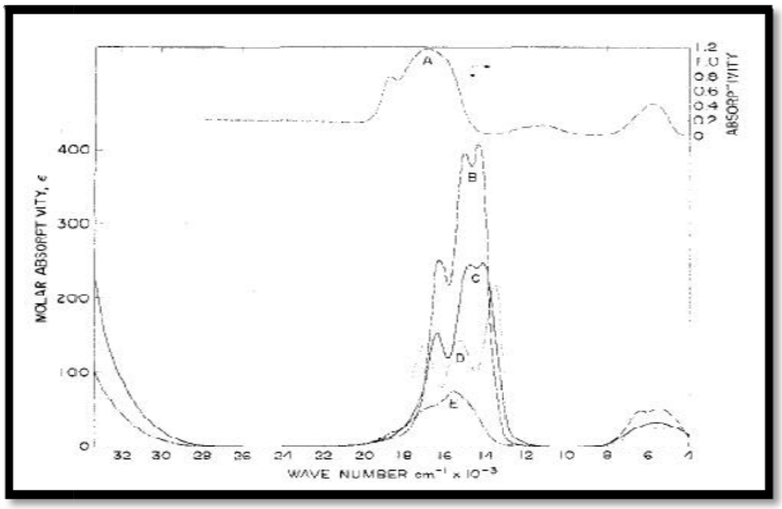

**Fig.(1-11):- Spectra of Co(II) in chloride surroundings: A, crystalline Co(AlC1$_4$)$_2$ at 25$^o$, B,50.3% KCl, 49.7%AlCl$_3$ (tetrahedral CoCl$_4^{2-}$), E, 50.3 mole % KC1, 49.7 mole % AlCl$_3$ at 300$^o$ (octahedral CoCl$_6^{4-}$ or Co(Al$_2$Cl$_7$)$_2$ ; C, 100.0 mole % KC1 at 800$^o$; D, 49.9 mole % KC1, 50.1 mole % MCl$_2$ at 300$^o$[Co(AlCl$_4$)$_2$] distorted octahedral; E, 35.5 mole % KCl, 64.5 mole % AlC13 at 300$^o$.** (70)

Absorption spectroscopy was used to study the coordination of Co (I1) ion in the room-temperature chloroaluminate melt system aluminum chloride-N-n-butylpyridinium chloride (AICI$_3$-BPC). Absorption spectroscopy indicated that Co (I1) was tetrahedrally coordinated as the CoCI$_4^{2-}$ ion in 0.8: 1 molar ratio AICI$_3$-BPC. Spectroscopic studies of Co (I1) in 2: 1 molar ratio A1CI$_3$-BPC melt suggested an octahedrally coordinated species, possibly Co (Al$_2$C I$_7$) $_m^{2-m}$ , with $m$ = 2, also suggested that two different Co(I1) species may exist in equilibrium close to the 1:l molar ratio composition region. As shown in (Figure1-12).(71)

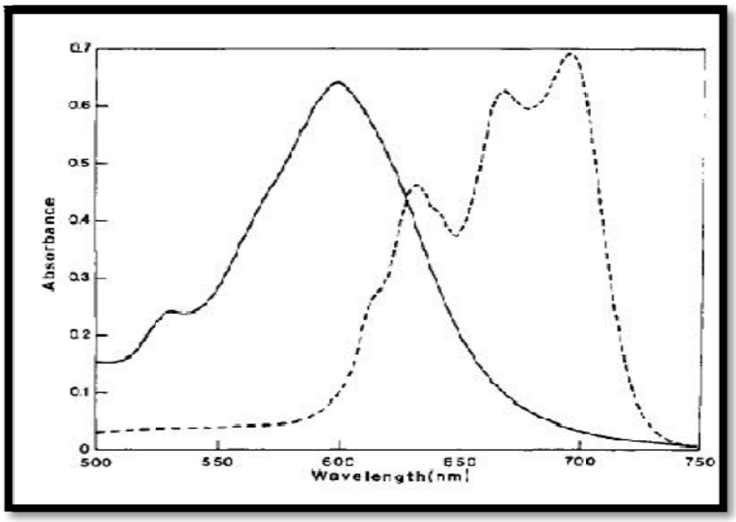

**Fig. (1-12):- Absorption spectra of Co (II) in AICI$_3$,-BPC melt at 40.0 $^O$C: (solid line) 2.04 ×10$^{-2}$ M Co (II) in 2:l AICI$_3$,-BPC melt (octahedral); (dotted line) 1.02 ×10$^{-3}$M Co(II) in 0.8:l AICI$_3$,-BPC melt (tetrahedral).**(71)

In another study anhydrous cobalt (II) chloride was found very soluble in both butyramide-sodium nitrate and acetamide-potassium nitrate, giving violet solutions. The visible- ultraviolet spectrum of the acetamide solution (Figure 1-13, curve A) showed two bands, with some splitting of the visible band, indicating octahedral coordination in each case. Calculations using Jorgensen's Rule of Average Environment suggest coordination by 4 acetamides and 2 chlorides in the acetamide-potassium nitrate eutectic. As the temperature of these solutions was gradually increased to 140°C, the absorption bands moved a little towards the red, while the band intensities increased considerably (Figure 1-13, curve B). This change was in accord with a shift to a lower symmetry environment, possibly some nitrates replacing acetamide or perhaps a shift from octahedral to a more tetrahedral coordination, as has frequently been found for cobalt (II) salts in many melts with increased temperature. The larger red shifts and even higher extinction coefficients found with butyramide-sodium nitrate (Figure 1-13, curve C) indicated an even lower symmetry coordination, possibly due at least in part to the steric strain imposed by the larger butyramide molecules.(67)

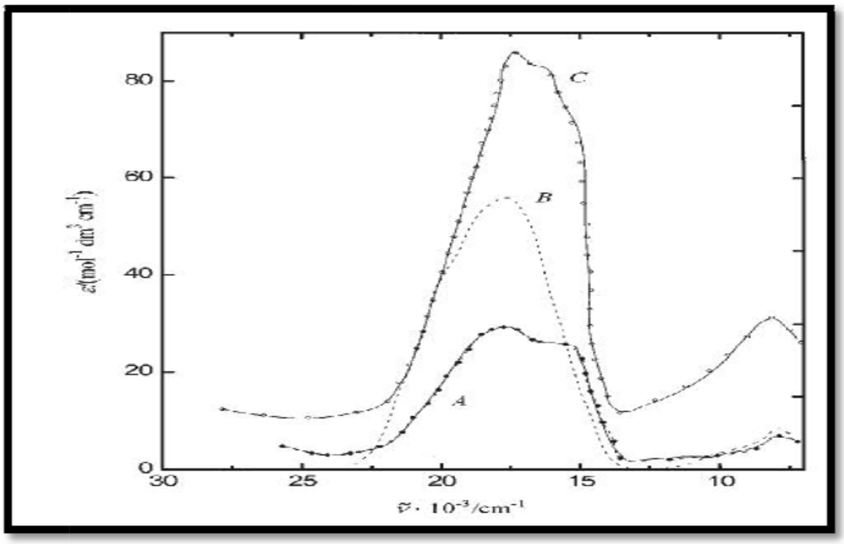

**Fig. (1-13):- Spectra of $CoCl_2$ (0.019 mol $dm^{-3}$) in acetamide-$KNO_3$ eutectic at different temperatures, curve A 90°C (•), curve B 140°C (- - -), and of butyramide-sodium nitrate at 140°C, curve C (o).(67)**

### 1.12.4. Nickel (II), ($d^8$).

This is undoubtedly the most prolific oxidation state for this group of elements. The stereochemistry of Ni (II) has been atopic of continuing interest, and kinetic and mechanistic studies on complexes of Ni (II). The absence of any other oxidation state of comparable stability for nickel implies compounds of Ni (II) are largely immune to normal redox reactions. Ni (II) forms salts with virtually every anion has extensive aqueous solutions chemistry based on the green hexaaaquanickel(II), $[Ni(H_2O)_6]^{2+}$ ion which is always present in the absence of strongly complexing ligands. The coordination number of Ni(II) rarely exceeds 6 and its principal stereochemistries are octahedral and square planer, tetrahedral (4-coordinate) with rather fewer examples of trigonal bipyramidal, square pyramidal (5-coordinate). Octahedral complexes of Ni (II) are obtained often from aqueous solution by replacement of coordinating water, especially with neutral N-donner ligands such as $NH_3$, en, bipy, and phen, but also with $NCS^-$, $NO_2^-$, and O-donner such as DMSO ($Me_2SO$). (64, 65)

Nickel (II) forms a large numbers of complexes encompassing coordination numbers 4, 5, and 6 in structural types of neutral ligands. It is characteristic of Ni(II)complexes that complicated equilibria, which are generally temperature dependent and sometimes concentration dependent. Nickel(II) is the only common $d^8$ and its spectroscopic and magnetic properties have accordingly been extensively studies in cubic field three spin-allowed transitions are expected, because of the splitting of the free ion ground $^3F$ term and the presence of the $^3P$ term, in an octahedral field the splitting is the same as for the octahedral $d^3$ ion and the same Tanaba-Sugano diagram, can be used to $[Ni(H_2O)_6]^{2+}$, the spectra can readily be interpreted by referring to the energy level diagram for $d^8$ ions. Three spin-allowed transitions are expected, and the three observed bands in each spectrum may thus be assigned. It is a characteristic feature of the spectra of octahedral nickel (II) complexes like $[Ni(H_2O)_6]^{2+}$, the molar absorbances of the bands are at low end of the range (1-100) for octahedral complexes of the first transition series in general, the splitting of the middle band in the $[Ni(H_2O)_6]^{2+}$ spectrum is due to spin-orbit coupling that mixes the $^3T_1g(F)$ and $^1Eg$ states, which are very close in energy at the $\Delta_o$ value given by 6 $H_2O$. The assigned bands are, $\nu_1$ $(^3A_2g\ (F) \rightarrow {}^3T_2g\ (F))$ is the 10Dq it is also evidence of weak spin-forbidden (spin triplet to singlet), $\nu_2$ $({}^3A_2g\ (F)\rightarrow{}^3T_1g(F))$ absorption has a strong shoulder on it. This has been a scribed to the influences of spin-orbit coupling ‘mixing’ (spin singlet $({}^1Eg)$ with the $({}^3T_1g)$ there by allowing the spin-forbidden transition to gain intensity from the spin-allowed transition, $\nu_3$ $({}^3A_2g(F)\rightarrow{}^3T_1g(P))$, it follows that they all should have tow unpaired electrons, and this is found always to be the case, for regular or nearly regular tetrahedral complexes there are characteristic spectral and magnetic properties, more irregular the geometry of a paramagnetic nickel (II) complex the less likely conform to these specification.(64,65)

Anhydrous Nickel (II) chloride was soluble in both eutectics, giving yellow solutions. The spectra (Figure 1-14, curves A and B) showed three absorption maxima indicating octahedral coordination of the Nickel (II) cations. The bands are shifted to slightly lower energies than those found in pure molten acetamide suggesting some coordination by chloride, or less likely by nitrate. Jorgensen's Rule suggested 4 acetamides and 2 chlorides could give the observed bands and the less symmetrical complexes resulting would explain the higher extinction coefficients found. There are no data on the band positions of butyramide complexes, but if its ligand field is similar to that of acetamide, then the calculated coordination would also be 4 amide and 2 chloride ligands.(67)

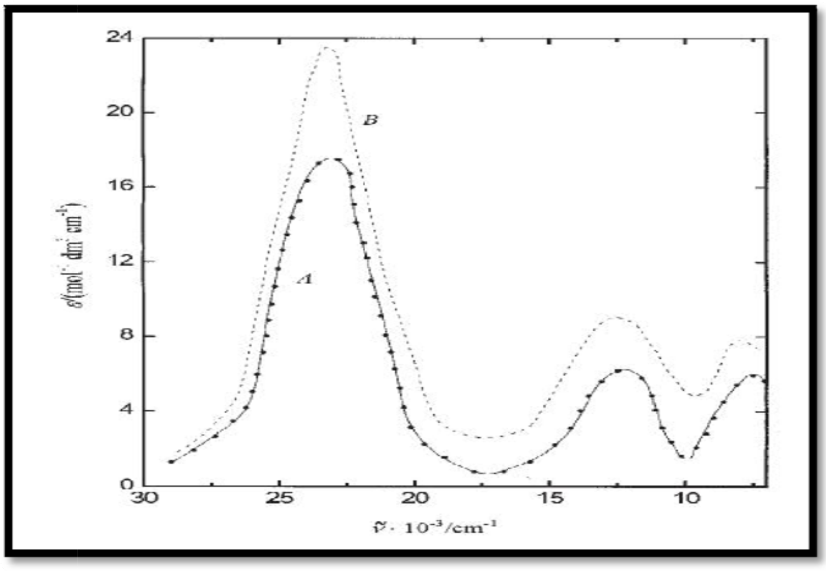

**Fig. (1-14):- Spectra of $NiCl_2$, curve A - c = 0.046 mol $dm^{-3}$ in acetamide-potassium nitrate at 90°C (•), curve B - c = 0.012 mol $dm^{-3}$ in butyramide-sodium nitrate at 140°C (- - -).(67)**

### 1.12.5. **Cupper (II), ($d^9$).**

The dispositive state is the most important one of Copper. In this oxidation state Copper which provide by for the most familiar and extensive chemistry. Simple salt are formed with most anions, except $CN^-$ and $I^-$. Which instead form covalent Cu(I) compounds which insoluble in water. Most Cu(I) compounds are fairly readily oxidized to Cu(II) compounds. there is a well-defined aqueous chemistry of $Cu^{2+}$, and large number of salts of various anions, many of which are water soluble, the blue color of their solution arising from the $[Cu(H_2O)_6]^{2+}$ion, and they frequently crystallize as hydrates. The aqueous solutions are prone to slight hydrolysis and, unless stabilized by a small amount of acid, are liable to deposit basic salts. The most common coordination numbers of Copper (II) are 4, 5, and 6, but regular geometries are rare and the distinction between square-planar and tetragonally distorted octahedral coordination is generally not easily made. The reason for this is ascribed to the Jahn-Teller effect arising from the unequal occupation of the *Eg* pair of orbitals ($dz^2$ *and* $dx^2$-$y^2$) when a $d^9$ ion is subjected to an octahedral crystal field. The $d^9$ configuration makes $Cu^{II}$ subject to Jahn-Teller distortion if placed in an environment of cubic (i.e. regular octahedral or tetrahedral) symmetry, and this has a profound effect on all its stereochemistry. The $d^9$ configuration can be thought of as an inversion of $d^1$, relatively simple spectra might be expected, and it is indeed true that the great majority of Cu (II) compounds are blue or green because of a single broad absorption band in the region 11000-16000 $cm^{1-}$, however as already noted, the $d^9$ion in characterized by large distortions from octahedral symmetry and the band is unsymmetrical, being the result of a number of transitions which are by no means easy to assign unambiguously. The free-ion ground $^2D$ term is expected to split in a crystal field in the same way as the $^5D$ term of the $d^4$ion, $(^2Eg \rightarrow {}^2T_2g)$.and a similar interpretation of spectra is like wise expected. Unfortunately this is now more difficult because of the greater overlapping of bands which occurs in the case of Cu (II). The *T* ground term of the tetrahedrally coordinated ion implies on orbital contribution to the magnetic moment, but the *E* ground term of the octahedrally coordinated ion because of ‘mixing’ of the excited *T* term into the *E* ground term with compounds whose geometry approaches octahedral having moments at the lower end, and those with geometries approaching tetrahedral having moments at the higher end, but their measurements can not be used diagnostically with safety unless supported by other evidence.(64,65)

Copper (I1) chloro complex formation was examined in basic melt by using absorption spectroscopy. Potentiometric titration experiments involving the Cu (II)/Cu (I) couple were attempted, but the resulting titration data were irreproducible and could not be analyzed in a meaningful way. The exact cause of this behavior could not be determined. Figure 16 shows absorption spectra for copper (I1) dissolved in 47.3 mol % $AlC1_3$,-MEIC melt and DMF containing either LiCl or MEIC as the chloride source. The spectrum for copper (I1) in DMF, containing high concentrations of LiCl, exhibits maxima at 295 and 411 nm. These absorption maxima have been reported for Copper (I1) in propylene carbonate and dimethyl sulfoxide, also. They are characteristic of the unsolvated $CuC1_4^{2-}$ ion. A spectrum of copper (I1) in 47.3 mol % $AlC1_3$,-MEIC exhibits maxima at 293 and 407 nm. The molar absorptivity for the 407-nm peak compares favorably with that for the 410-411nm peaks found in DMF and other solvents the peak at 293 nm, observed for copper(I1) in basic melt, seems distorted and exhibits a significantly higher absorbtivity than that observed for the 294-295-nm peaks in organic solvents containing LiCl. An absorption spectrum for Copper (I1) in DMF with MEIC as the source of chloride ion exhibits maxima at 282 and 408 nm and an ill-defined shoulder near 292 nm as in (Figure 1-15).(72)

Anhydrous Copper (II) sulfate dissolved readily in the acetamide-potassium nitrate eutectic to give blue-green solutions. Spectroscopy showed two bands at $\nu = 20700\ cm^{-1}$ ($\varepsilon = 43\ mol^{-1}\ dm^3\ cm^{-1}$) and $\nu = 14000\ cm^{-1}$ ($\varepsilon = 73 mol^{-1}\ dm^3\ cm^{-1}$) with a shoulder at $\nu = 11000\ cm^{-1}$. The copper cations appear to be in an octahedral coordination, though with a higher extinction coefficient, and thus probably a lower symmetry (perhaps $D_4h$), than those found for the regular octahedral complexes in aqueous solution (band maxima at $\nu = 12600\ cm^{-1}$, $\varepsilon = 12\ mol^{-1}\ dm^3\ cm^{-1}$), or in anhydrous alkali metal nitrate melts ($\nu = 13000\ cm^{-1}$, $\varepsilon = 14\ mol^{-1}\ dm^3\ cm^{-1}$), because in this binary eutectic coordination is by both acetamide and nitrate. The higher energy band is anomalous for a *$D_4h$* complex and may be due to small amounts of a square pyramidal *($C_4v$)* complex.(67)

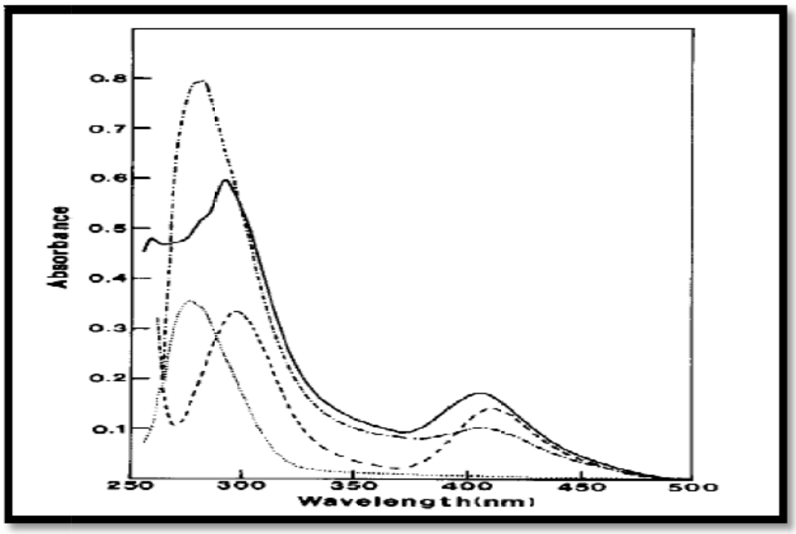

**Fig (1-15):- Copper (I1) absorption spectra in solvents containing chloride ion: —, 47.3 mol % $AlC1_3$-MEIC melt, 6.8 ×$10^{5-}$ M in Copper (I1); ---, DMF + 2.7 M LiC1, 5.4 ×$10^{5-}$ M inCopper(I1); -. -, DMF + 3.0 M MEIC, 5.0 M in Copper (I1); -, DMF + 0.4 M MEIC, no Copper (I1).(72)**

## *1.13*. ***The coordination chemistry of transition metal cations in chloride melts.***

The coordination chemistry of transition metal cations in chloride melts (LiCl/KCl) has been the subject of many studies which showed the deviation of oxidation state (II) and (III) cations of the first row transition elements from octahedral coordination by distortion and formation of tetrahedral geometries. Cr (III) in chloride melt at 400°C showed two bands as maxima absorption at $\nu_1$=18500 $cm^{-1}$, $\nu_2$=12500 $cm^{-1}$ indicating an octahedral coordination, Fe(II) in the same melt at 400°C showed one band at ν=5100 $cm^{-1}$ indicating tetrahedral coordination and at 1000°C showed one band at ν=6000 $cm^{-1}$ indicating distorted tetrahedral coordination, while Fe (III) in the same melt at temperature range of 370-450°C showed one absorption band at 25000 $cm^{-1}$ in a shoulder shape indicating probably tetrahedral coordination. Co(II) in chloride melt at temperature range of 447°C to 480°C showed three bands $\nu_1$=16700 $cm^{-1}$, $\nu_2$=15150 $cm^{-1}$, $\nu_3$=14700 $cm^{-1}$, also indicating tetrahedral coordination. In addition Ni(II) in LiCl/KCl melt showed the an absorption of three bands at ν=15300 $cm^{-1}$, ν= 14200

$cm^{-1}$, ν=8000 $cm^{-1}$ at 700-1000°C, indicating distorted tetrahedral coordination, and in CsCl melt at 864°C also showed three absorption bands at ν=15700 $cm^{-1}$, ν=14000 $cm^{-1}$, ν=7500 $cm^{-1}$ indicating similar tetrahedral coordination. Cu (II) in the chloride melt (LiCl/KCl) at 400°C showed one absorption band at ν=9500 $cm^{-1}$ indicating tetrahedral coordination.(1)

In the case of Ni(II) the three bands were initially assigned to a distorted tetrahedral coordination though in the light of more detailed measurements over a temperature range, the coordination ratio tetrahedral/octahedral centers was about to increases with potassium chloride concentration (in LiCl/KCl mixture) as well as with increasing temperature.(1)

## 1.14. Determination of spectra.

### 1.14.1. Orgel diagrams.

Orgel diagrams are useful for showing the number of spin-allowed absorption bands expected, and their *symmetry state designations*, for *Td* and weak field *Oh* -complexes ($d^5$ not included). The two diagrams (one for $d^{1, 4, 6, 9}$ the other for $d^{2, 3, 7, 8}$) pack a lot of information in very little space. Nevertheless, there are three major limitations to using Orgel diagrams:

(1) They are restricted to weak field/high spin conditions and offer no information for $d^{4, 5, 6, 7}$ strong fields/ low spin cases.

(2) They only show symmetry states of same highest spin multiplicity

(3) They are qualitative, and therefore energy values cannot be obtained or calculated from them.(74)

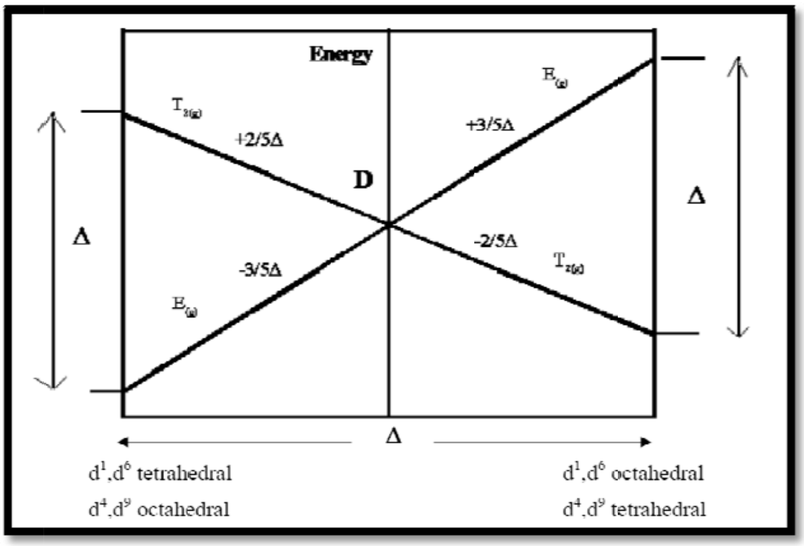

**Fig. (1-16):- The splitting of free-ion D terms in octahedral and tetrahedral fields.** (74)

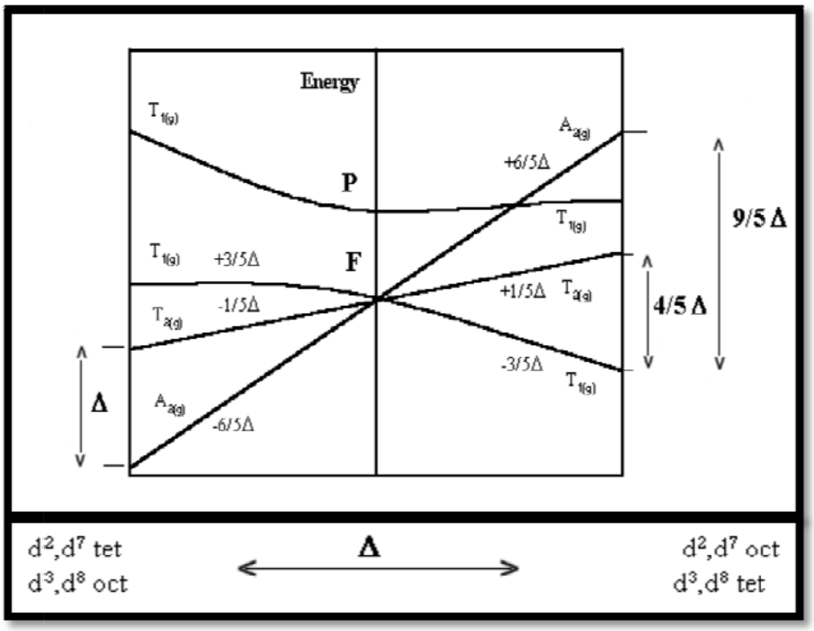

**Fig. (1-17):- The splitting of free-ion F and P term in octahedral and tetrahedral field.** (74)

### *1.14.2. Tanabe-Sugano diagrams.*

In contract to Orgel diagrams Tanabe-Sugano diagrams contain all terms arising from a configuration, not just terms of highest spin-multiplicity. They also differ from Orgel diagrams because they use the ground symmetry state as a straight-line horizontal base, whereas Orgel diagrams place the parent term in a central location and direct ground symmetry states below it. In addition the splitting of $d^4$, $d^5$, $d^6$, $d^7$, cases for both low and high spin symmetry states are included. Consequently, these diagrams appear to be discontinuous - having two parts separated by a vertical line. The left part pertains to the weak field /high spin condition and the right to strong field/ low spin condition.

First note why $d^1$ and $d^9$ cases have no T-S diagrams. A term description for an atom/ion is more informative than its electron configuration because terms account for e-e repulsion energies. However there is no e-e repulsion for one "d" electron so the $d^1$ configuration gives rise to a single term, $^2D$. In Oh and Td ligand fields this single term is split into $T_2g$, $Eg$, or $E$, $T_2$ symmetry states. Only one absorption band is expected and energy of the observed band gives the $\Delta_o$ or $\Delta_{Td}$ value directly. No calculations are necessary, so no T-S diagram for $d^1$ (and $d^9$).(74)

## *1.14. Aim of the present work.*

New class of room temperature ionic liquids (RTILs) based on choline chloride have been prepared.(59) These ionic liquids offered promising ease of handling and wide field of application as solvents and reacting media.(61) The behavior of some transition metal chlorides were investigated by ultraviolet visible spectroscopic measurements in two types of RTILs melts. The cationic metal are $Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ while the RTILs are choline chloride/ urea and choline chloride/ malonic acid mixtures which have freezing point of $12^{o}C$ and $10^{o}C$ respectively.

The solutions of these transition metals in ionic liquids will be studied by ultraviolet visible spectroscopy, infrared spectroscopy, conductivity and magnetic susceptibility, to determine their behavior and coordination in solution.

# Chapter Two

# Experimental Part

## 2.1. Chemicals and Instruments.

### 2.1.1. Chemicals.

All the chemicals used in this work were of highest purity available and without further purification. Table (2-1) shows the reagents, their purities and suppliers.

**Table (2-1):- The chemicals used in this work with their purities and suppliers.**

| Chemical compounds | Purity % | Company |
|---|---|---|
| Choline chloride | 99 | Merck |
| Urea | 99.5 | Merck |
| Malonic acid | 99 | Chem-Supply |
| Ammonium nitrate | 99.9 | Baker Analyzed Reagents |
| Chromium(III) chloride hexahydrate | 97 | Chem-Supply |
| Iron(III) chloride tetrahydrate | 99 | BDH |
| Cobalt(II) chloride hexahydrate | 98 | Chem-Supply |
| Nickel(II) chloride hexahydrate | 99 | BDH |
| Copper(II) chloride dihydrate | 95 | Fluka |
| Cobalt(II) nitrate hexahydrate | 98.5 | BDH |

### *2.1.2. Instruments.*

#### *2.1.2.1. Electronic absorption spectra measurements.*

The electronic spectra of complexes were obtained by using SHIMADZU (Japan), UV-Vis 1650 PC Ultraviolet Visible Spectrophotometer at room temperature using quartz cells of 1.0 cm length and ionic liquids as solvents in the range of wave length 190-1100 nm. The preparations of samples are described in section (2.5).

## *2.2. Setting of heating apparatus.*

The heating apparatus that was used in the preparation of the ionic liquid is consisted of: -

1- Hot plate.
2- Stand.
3- Clamp.
4- Thermometer.
5- Oil bath.
6- Reaction beaker.
7- Glass rod.

## *2.3. Drying method.*

The drying method was carried out by placing appropriate weight of samples in the oven under temperature range of 70 -75$^{o}$C; the dried compound was kept in sealed the desicator for further use.

## *2.4. Preparation of room temperature ionic liquid.*

### *2.4.1. Preparation of Choline chloride/Urea room temperature ionic liquid.*

Solid mixture of dry choline chloride and urea in mole ratio of 1:2 was milled, and well mixed and heated gradually to 75°C for a period of 20 min. using the apparatus described in (section 2.2) with continuous gentle stirring until both choline chloride and urea melted together producing colourless liquid, the mixture was gradually cooled down to room temperature, it was more viscose than water. Finally the prepared melt was kept in sealed dry desiccator for further use. (58, 61)

### *2.4.2. Preparation of Choline chloride/Malonic acid room temperature ionic liquid.*

Solid mixture of dry choline chloride and malonic acid in mole ratio of 1:1 was milled, and well mixed and heated gradually to 85°C for a period of 20 min. (62) using the apparatus described in (section 2.2) in the same way in (section 2.4.1).

## *2.5. Preparation of metal chloride ionic liquid mixtures.*

The fallowing general procedure was used for the preparation of the solution of metal chlorides salts to ionic liquids:-

A known weight of dry sold compound [Table (2-2)] was added to appropriate volume of ionic liquid at room temperature, the mixture was left to stand for 72 hours with occasional stirring to enhance dissolution of materials. The changes during this period were recorded such as colour changes and viscosities, however, no precipitation or gas evolution were noticed through out the entire experiments of this work.

In addition, during the investigation of coordination reaction, ammonium nitrate was added to above solution and any noticeable changes were recorded.

All prepared solutions of metal chloride in ionic liquids of chlorine chloride/ urea with and without the addition of ammonium nitrate and choline chloride/ malonic acid were investigated by Ultraviolet Visible Spectroscopy and the obtained spectra were analyzed.

**Table (2-2):- Concentration of metal chloride in aqueous solution and room temperature ionic liquid of choline chloride/urea and choline chloride/malonic acid.**

| Metal chloride | Weight (g.) | Concentration in aqueous solution (M) | Concentration in choline chloride/urea ionic liquid (m) | Concentration in choline chloride/malonic acid ionic liquid (m) |
|---|---|---|---|---|
| $CrCl_3.6H_2O$ | 0.3 g. | 0.1 M | $7.4\times10^{-2}$ m | $7.5\times10^{-2}$ m |
| $FeCl_3.4H_2O$ | 0.2 g. | 0.1 M | $6.6\times10^{-2}$ m | $6.9\times10^{-2}$ m |
| $CoCl_2.6H_2O$ | 0.25 g. | 0.1 M | $6.9\times10^{-2}$ m | $7.4\times10^{-2}$ m |
| $NiCl_2.6H_2O$ | 0.4 g. | 0.1 M | $1.1\times10^{-1}$ m | $1.2\times10^{-1}$ m |
| $CuCl_2.2H_2O$ | 0.2 g. | 0.1 M | $7.7\times10^{-2}$ m | $8.03\times10^{-2}$ m |

*M: - molarty, which is number of moles of solute per volume of solvent in L unit.*

*m: - molalty, which is number of moles of solute per weight of solvent in Kg. unit.*

## *2.6. Equations.*

The equations that have been used in the determination of spectra of each complex were different from metal to another according to the splitting of terms for $d^n$ configurations as shown in Figure (2-1) and in Table (2-3).

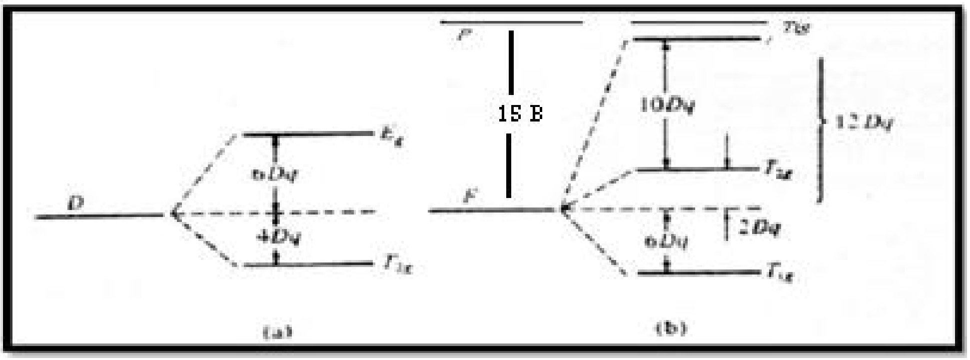

**Fig. (2-1):- Splitting of terms for $d^n$ configurations in to (a) and (b).(65)**

**Table (2-3):- Splitting of terms elected $d^n$ configuration.**[(65)]

| **Configuration of free-ion** | **Ground state of free-ion** | **Energy level diagram** | **Predicted in Figure (23)** |
|---|---|---|---|
| $d^3$ | $^4F$ | Inverted (b) | $\nu_1$=10 Dq<br>$\nu_2$=18Dq-x<br>$\nu_3$=12Dq+15B`+x |
| $d^5$ | $^6S$ | No splitting | |
| $d^7$ | $^4F$ | (b) | $\nu_1$=8Dq<br>$\nu_2$=18Dq<br>$\nu_3$=6Dq+15B` |
| $d^8$ | $^3F$ | Inverted (b) | $\nu_1$=10 Dq<br>$\nu_2$=18Dq-x<br>$\nu_3$=12Dq+15B`+x |
| $d^9$ | $^2D$ | Inverted (a) | $\nu_1$=10Dq |

Also Jorgenson rule have been used to measure the tendency of metal ion to form a complex, the *(g)* factors provide an estimate of the value of *10Dq* for an octahedral complex when combined with the *(f)* value for the appropriate ligands:(85)

$$10Dq = f_{\text{ligand}} \times g_{\text{ion}} \times 10^{3} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} \quad (2\text{-}1)$$

**Table (2-4):- Values of *g* and *f* factors for metal ions and various ligands.**

| Transition metal ion | Value of (*g)* factor | Various ligands | Value of(*f)* factor |
|---|---|---|---|
| Cr(III) | 17.4 | $Cl^-$ | 0.78 |
| Fe(III) | 14.0 | $CO(NH_2)_2$ | 0.92 |
| Co(II) | 9.00 | $H_2O$ | 1.00 |
| Ni(II) | 8.7 | $(CH_2COOH)_2$ | 0.96 |
| Cu(II) | 12.5 | $NO_3^-$ | 0.88 |

*In units of k K (=1000 $cm^{-1}$).*

If all three transitions are observed, it is a simple matter to assign a value to B`, since the following equation must hold; (B` is in $cm^{-1}$ units).

$15B` = \nu_3 + \nu_2 - 3\nu_1$ ________________________________________ (2-2)

The nephelauxetic ratio $\beta$ is given by:

$\beta = B`/B.$ ________________________________________ (2-3)

Where 'B' is Racah parameter.

And by using equation (2-4) to find the $\Delta_T$,

$10Dq_{Td} = 4/9\ (10Dq_{Oh})$ ________________________________________ (2-4)

## *2.7. Example of calculations.*

Consider an example application of a Tanabe-Sugano diagram for a $d^3$ case. The absorption spectrum of a $Cr^{3+}$ solution is shown below in Table (2-5). For example the mathematical determination of spectra of $CrCl_3.6H_2O$ in choline chloride/urea ionic liquid at room temperature was taken.

**Table (2-5):- Peaks positions of Chromium (III) ions in room temperature ionic liquid of Choline chloride/Urea solution.**

| Ion | $\nu_1$ cm$^{-1}$ | $\nu_2$ cm$^{-1}$ | $\nu_3$ cm$^{-1}$ | $\nu_2/\nu_1$ | $\nu_1/\nu_2$ | $\Delta/\grave{B}$ |
|---|---|---|---|---|---|---|
| $Cr^{+3}$ | 16447 | 22727 | ? | 1.38 | 0.724 | 26.00 |

Two bands are observed within the range of measurement. They have a maxima at about 16447 and 22727 cm$^{-1}$. These are spin-allowed LaPorte-forbidden d-d transitions. Chromium is in the 3+ oxidation state, so this is a $d^3$ system. Reference to an Orgel diagram informs that three d-d bands are expected and they can be assigned as:

$$\nu_1 = {}^4A_2g\ (F) \rightarrow {}^4T_2g\ (F)$$
$$\nu_2 = {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (F)$$
$$\nu_3 = {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (P)$$

$\Delta_o$ is taken to equal the absorption energy of 16447 cm$^{-1}$, and the intersect on the x-axis of Tanabe-Sugano diagram equal $\Delta_o/\grave{B}$ and by drawing a vertical line from this point will intersect with other allowed electronic states of Tanabe-Sugano diagram for $d^3$.

There are several “goals” sought in analyzing spectra using Tanabe-Sugano diagrams: (99)

*(1)* To make correct band assignments. The two bands observed could be the first and second, or the second and third. Their assignment cannot be made by inspection.

*(2)* To determine the magnitude of the Ligand Field splitting parameter, $\Delta_o$.

*(3)* To determine the magnitude of the e-e repulsion parameter (called a Racah $\grave{\boldsymbol{B}}$ parameter).

Assumes bands are the first and second (so third band is not observed). Compare the two results. Tanabe-Sugano diagrams are unit less graphs showing energy *ratios*. The abscissa shows values for the ratio $\Delta_o/\grave{B}$ (i.e., Ligand Field splitting parameter / e-e repulsion parameter) and the ordinate shows values for the ratio $(Ev/\grave{B})$ (i.e., absorption band energy / e-e repulsion parameter).(74,75)

<u>Step (1):</u> The calculated ratio of experimental band energies is: $E\,(v_2)\,/\,E\,(v_1)$, find chart lines for first and second symmetry states and record their values at each abscissa mark.

None of these chart ratios come close to the experimental ratio of (1.38).

<u>Step (2):</u> Find the specific value for $\Delta_o/\grave{B}$, having a chart value for $v_2/v_1$ that matches the experimental ratio of 1.38.

When $\Delta_o/\grave{B} = 30$, chart $v_2/v_1 = 1.40$, and at $\Delta_o/\grave{B} = 20$, chart $v_2/v_1 = 1.30$.

Verify (by extrapolation) that at a value of $\Delta o/\grave{B} = 26$, the chart ratio for $v_2/v_1 = 1.38$.

<u>Step (3):</u> Find the intersection of chart lines for $^4T_2g$ and $^4T_1g$ at $\Delta_o / \grave{B} = 26$,

And record their values on the ordinate $E\,(v_n)/\grave{B}$.

For $^4T\,2\,g$ at $\Delta_o / \grave{B} = 26$, then $E\,(v_1)\,/\,\grave{B} = 26$, and

For $^4T_1g$ at $\Delta_o$ / $\grave{B}$ = 26, then $E$ ($v_2$) / $\grave{B}$ = 37

<u>*Step (4):*</u> Use experimental values of $E$ ($v_1$) and $E$ ($v_2$) to obtain values for Racah $B$:

$\grave{B}$ [via $E$ ($v_1$)] = 16447 $cm^{-1}$ / 26 = 623.6 $cm^{-1}$

$\grave{B}$ [via $E$ ($v_2$)] = 22727 $cm^{-1}$ / 37 = 614.3 $cm^{-1}$

Then, $\grave{B}_{avr.}$ = 619 $cm^{-1}$.

The two determinations are in acceptable agreement. Furthermore, in free Cr (III) ion, Racah $\grave{B}$ = 918 $cm^{-1}$, a larger value. It is anticipated that e-e repulsion should be *reduced in compounds* because metal electron density becomes delocalized (as a result of bond formation to ligands) and metal e-e repulsions are decreased correspondingly.

<u>*Step (5):*</u> Use this value for Racah $\grave{B}$ to determine $\Delta_o$, the Ligand Field splitting parameter.

If $\Delta_o$ / $\grave{B}$ = 26, and $\grave{B}$ = 619 $cm^{-1}$, then $\Delta_o$ = 16447$cm^{-1}$.

All calculated values are reasonable. But what about the missing third band?

<u>*Step (6):*</u> Three bands are expected, but only two are observed. Fitting the first two absorption bands to the Tanabe-Sugano chart, according to the assignments produced good results. Information gained can be used to calculate the energy expected for the missing third transition:- $v_3$= $^4A_2g$ (F) → $^4T_1g$ (P)

At $\Delta_o$ / $\grave{B}$ = 26, the chart value for $E$($v_3$) / $\grave{B}$ = 56

Using the value already obtained for $B$ produces the result $E$ ($v_3$) calc'd = 56.00 × 618 $cm^{-1}$= 34608 $cm^{-1}$.

Is this reasonable?

*(1)* Refer to the diagram for the recorded spectrum and note that it only extends to 35,000 $cm^{-1}$. This is the upper energy limit of the instrument used to measure the spectrum.

*(2)* Notice that a small error in reading spectral band energies changes the experimental $v_2/v_1$ ratio which in-turn changes the matching $\Delta_o/\grave{B}$ ratio on the Tanabe-Sugano diagram.

This means a small change in $\Delta_o$ / $\grave{B}$ ratio will cause a large change in $Ev$ / $\grave{B}$ for $v_3$. Either or both of these factors could be responsible for third band not being observed. Observed at 16447 $cm^{-1}$, 22727 $cm^{-1}$ (third band not observed) Ligand Field parameters: $\Delta_o$ = 16447 $cm^{-1}$. Racah ($\grave{B}$) = 619 $cm^{-1}$ (free ion $B$ = 918 $cm^{-1}$).

And if the three expected bands were observed then by using the equations of splitting of term for $d^3$ in Table (2-3), we can determine the B\` and $\beta$ as following:

$\nu_1$=10 Dq.

16447 $cm^{-1}$= 10 Dq

Dq = 1644.7 $cm^{-1}$.

$\nu_2$=18Dq-x

22727 $cm^{-1}$ = 18(1644.7 $cm^{-1}$) – x

x = 6877.6 $cm^{-1}$.

$\nu_3$=12Dq+15B\`+x

34608 $cm^{-1}$ = 12 (1644.7 $cm^{-1}$) +15B\`+6877.6 $cm^{-1}$

B\`= 533 $cm^{-1}$

Or we can use the following equation to determine the B\`

15B\`= $\nu_3$+ $\nu_2$−3$\nu_1$

15B\`=34608 $cm^{-1}$+22727 $cm^{-1}$-3(16447 $cm^{-1}$)

B\`=533 $cm^{-1}$

To determine the nephelauxetic ratio $\beta$:

If $\beta$= B\`/B, Then $\beta$=533 $cm^{-1}$/619 $cm^{-1}$

And $\beta$=0.68.

# Chapter Three

# Results and Discussion

## *3.1. **Introduction.***

This project relates to ionic compounds and methods for their preparation. In particular the project relates to ionic compounds which are liquid at relatively low temperatures, generally below about 100°C, and preferably below about 60°C and more preferably which are liquid at or near to ambient temperature. In recent years, ionic compounds have been made which are liquid at relatively low temperatures, for example, trimethyl phenyl ammonium chloride with aluminium trichloride. The resulting ionic compound has a low freezing point (around -75°C), but suffers from the same water sensitivity, because of the presence of aluminium trichloride. There is much current interest in the field of ionic liquids. Such systems, which are examples of molten salts, have a number of interesting and useful chemical properties, and have utility, for example, as highly polar solvents for use in preparative chemistry, and as catalysts. They also have particular application in electrochemistry, for example in batteries, fuel cells, photovoltaic devices and electrodeposition processes, for example in baths for the electroplating of metals. Ionic liquids have very low vapour pressure and thus, in contrast to many conventional solvents, are very advantageous in that they produce virtually no hazardous vapours. They are therefore advantageous from a health, safety and environmental point of view.(63)

A new class of room temperature ionic liquid based on choline chloride have recently been prepared which have an advantageous over previous room temperature ionic liquid. The major advantageous are water insensitive which made them attractive RTIL for chemical and industrial applications. The potential of their advanced properties also arise from the availability, reasonable price and green characterization. The emerged RTILs have caught the attention of some researchers to establish their chemical, physical and industrial scope of understanding.

Therefore, it is not surprising, in addition to its own right, to study the characterization of some transition metal ions ($Cr^{3+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$ and $Cu^{2+}$) to determine their behaviour, particularly, coordination, interaction in such new clan of solvents.

## 3.2. Electronic absorption of transition metal chloride in room temperature ionic liquids.

Electronic absorption spectra of transition metal complexes are usually attributed to the partially filled d-orbital of the metal. The energy required for such transitions is that of the near ultraviolet and visible region. Charge transfer spectra are due to transitions between metal and ligand. Studies of electronic spectra of complexes help in the determination of structure of the complexes through the electronic interaction of the metal d-orbital and ligand orbital. (64, 65) In our work the spectra were investigated in the range (190-1100) nm, using two types of ionic liquids as solvent.

### 3.2.1.Spectroscopic investigation of Chromium (III) chloride solutions.

#### 3.2.1.1. Chromium (III) chloride in choline chloride/urea room temperature ionic liquids.

Chromium (III) chloride hexahydrate was found to be completely soluble in choline chloride/ urea room temperature ionic liquid after 72 hours in concentration of $7.4\times10^{-2}$m at room temperature see Table (3-1), producing a deep green colored solution. The viscosity of the choline chloride/urea ionic liquid before and after the dissolution of the salt seemed visually to have close viscosity.

The recorded ultraviolet visible spectrum of the solution showed two absorption bands at 16447 $cm^{-1}$(608 nm), at 22727 $cm^{-1}$ (440 nm) and a shoulder at 14502$cm^{-1}$ (689.56 nm). The U.V.-Vis. spectrum Figure (3-1) indicates that the Chromium (III) ion is consistent with octahedral coordination, as shown in Figure (3-1).

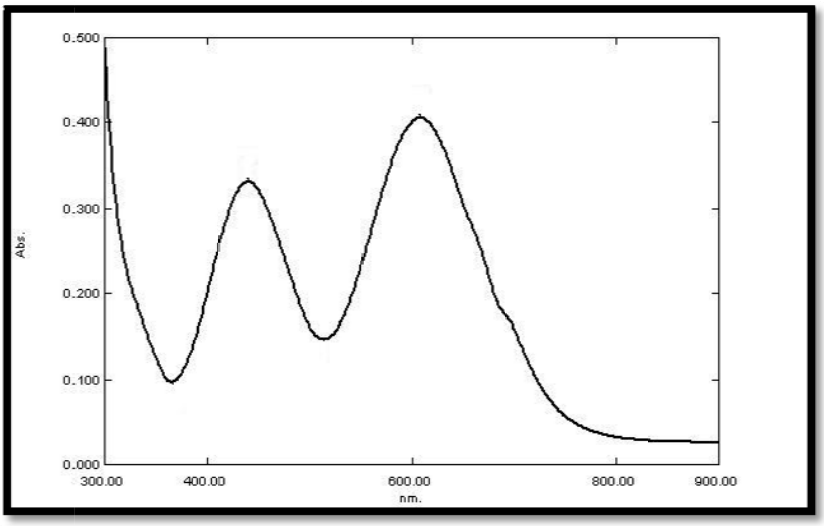

**Fig. (3-1):- The U.V.-Vis spectrum of Chromium (III) of ($7.4\times10^{-2}$m) in Choline chloride/Urea room temperature ionic liquid.**

The third band which normally occurred at the high charge transfer energy region was deduced by using Tanabe-Sugano diagram Figure (3-6) for $d^3$ electronic configuration and found to be 34733 $cm^{-1}$. The term symbol for the ground state of Cr (III) ion $^4F$ can split in octahedral crystal field and the bands may be assigned as illustrated in Figure (3-2) and according to Orgel diagram [Figure( 1-17)] as fallow :-

$$\nu_1 = {}^4A_2g\ (F) \rightarrow {}^4T_2g\ (F) = 10Dq$$

$$\nu_2 = {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (F)$$

$$\nu_3 = {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (P)$$

And the appeared shoulder on the first absorption peak was assigned to be of a spin forbidden transition from the ground state of $^4A_4g$ to the doublet state $^2G$.

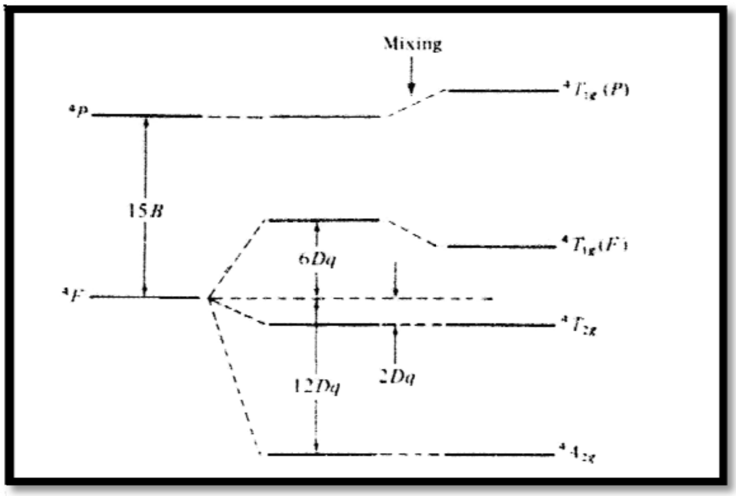

**Fig. (3-2):- Crystal field splitting of $^4F$ term of $d^3$ ion octahedral configuration.(64)**

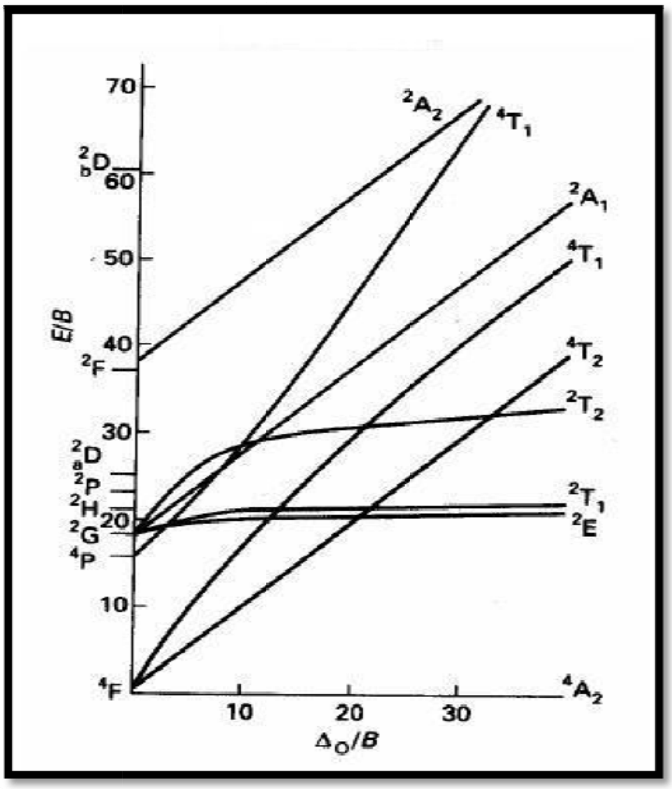

**Fig. (3-3):- Tanabe-Sugano diagram for d$^3$ ion configuration.**(73)

It was found that the observed band energies were close to those band energies for Chromium (III) ion in other ionic liquids. (67) The band energies of Chromium (III) ion in this eutectic were higher than in pure chloride melt like LiCl/KCl melt, of as 12500 cm$^{-1}$ and 18500 cm$^{-1}$, where the Chromium (III) ions were assigned to be octahedral coordinated with chloride ions.(1)[Table (3-1)] If so, then it is not surprising that the higher energy observed in this work explains the stronger nature of urea than chloride and it is in agreement with the spectrochemical series. However, the band energies were close to those found in acetamide-potassium nitrate (16760,22450 cm$^{-1}$) or butyramide-sodium nitrate (16600,22500 cm$^{-1}$) eutectics as in Table (3-1), where Chromium (III) ions assigned to have octahedraly coordinated with six acetamide or six nitrate ligands, as stated earlier in the introduction (section 1.12.1.).(67)

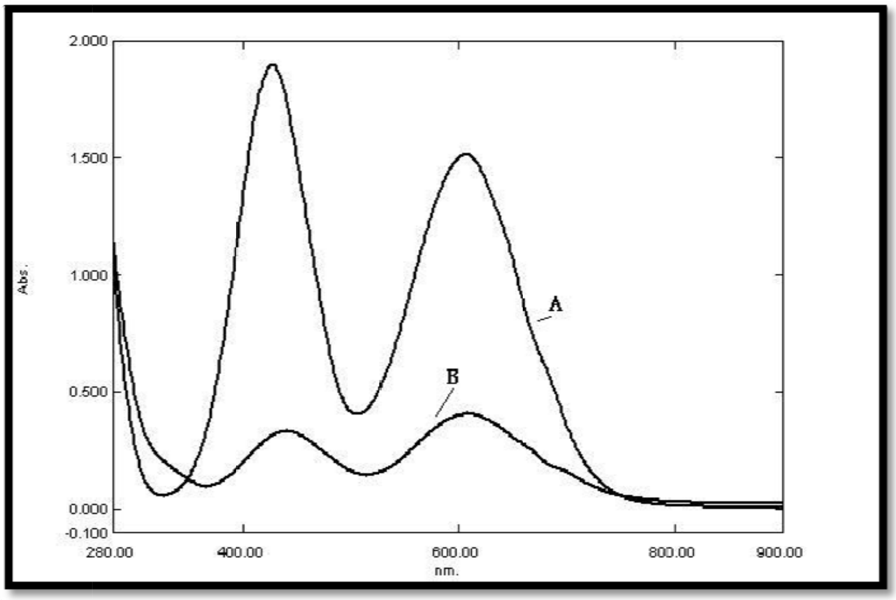

**Fig. (3-4):- The U.V.-Vis. Spectra of $CrCl_3.6H_2O$ (0.1 M) in aqueous solution (curve A), and in choline chloride/ urea eutectic solution ($7.4\times10^{-2}$m), (curve B) at room temperature.**

The band energies of chromium (III) ions in choline chloride/urea observed in this work were found to be shifted to lower energies than those obtained in aqueous solution Table (3-1). This might be due to water molecule which is stronger than urea molecule according to the spectrochemical series. In addition the absorbance and the molar absorptivity of Cr (III) in choline chloride/urea ionic liquid were found to be smaller than that observed in aqueous solution see Table (3-2). Figure (3-4) and Table (3-1) which show the difference in the illustrated behavior of Chromium (III) ion in aqueous solution and in choline chloride/urea eutectic.

Calculations using Jorgenson Rule of average environment suggested that Chromium (III) ions in this eutectic were octahedral coordinated with 6 ligands of urea molecules. This is expected in view of the stronger urea than chloride ions as the latter ion is at the lowest weak end of the spectrochemical series.

[$I^- < Br^- < S^{2-} < SCN^- \sim Cl^- < NO_3^- < N_3^- < F^- < CO(NH_2)_2 < OH^- \sim ONO^- < CH_2(COO)_2^{2-} \approx C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < EDTA^{4-} < NH_3 \approx$ pyr(pyridine) $\approx$ en (ethylenediamine) $<$ bipy (2,2'-bipyridine) $<$ phen (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- \approx$ CO].

The consistency of this interpretation can be checked and a value was obtained for the 'interelectronic repulsion parameter' **B̀**, by fitting the ratio of $\nu_1/\nu_2$ from the appropriate Tanabe-Sugano diagram, Figure (3-3). The obtained value of **B̀** equals to 632 $cm^{-1}$ as in [Table (3-1)], which is smaller than that for free ion 918$cm^{-1}$ or that of the metallic ion in the aqueous solution 918$cm^{-1}$. The low value of B̀ normally arises when the ligands have more expansion space for d-electron as in urea. And indicates coordination via covalent rather than ionic bonds where high value ought to be formed. The solution of Chromium (III) chloride hexahydrate in choline chloride/urea room temperature ionic liquid did not showed any observed changes in ultraviolet visible spectra when the solution was stored for 40 days, indicating that the solution already reached equilibrium and was stable over this period of storing time.

### *3.2.1.2. Substitution Reaction with Ammonium Nitrate.*

When ammonium nitrate ($NH_4NO_3$) was added to the chromium (III) chloride hexahydrate in choline chloride ionic liquid solution at room temperature, it showed no changes either in color or in the apparent viscosity of the solution. However, when the mixture was examined by ultraviolet visible spectrum of the Chromium (III) ion, the observed peaks shifted to higher energies than those obtained in pure melt and have the following values 16750 $cm^{-1}$ (597 nm) and 23529 $cm^{-1}$(425 nm) and a shoulder at 14502 $cm^{-1}$ (689.56 nm). The addition of nitrate also showed an increase in the maximum intensity of those bands in comparison with those obtained in choline chloride/urea alone as shown in Figure (3-5). The changes might indicate some interaction of the added nitrate with Chromium (III) ions. The third energy band was calculated from the Tanabe-Sugano diagram for $d^3$ ion configuration Figure (3-3) and it was found to be equal to 36551 $cm^{-1}$.

Calculation using Jorgenson Rule of average environment was found to be in agreement with replacement of two urea molecules by two nitrates in octahedral coordination; nitrate is considered to be stronger than urea as ligand according to the spectrochemical series, as showed in Figure (3-5). The increase absorbtivity indicates some distortion in symmetry due to the substitution reaction of two urea molecules with two nitrates see Table (3-2). This distortion might either be z-out or with in the plane of the geometry, as the formed bonds with the nitrates is more ionic the preferable one is the replacement that occurred on the z-axis to form more symmetrical complex, as shown in Figure (3-5).

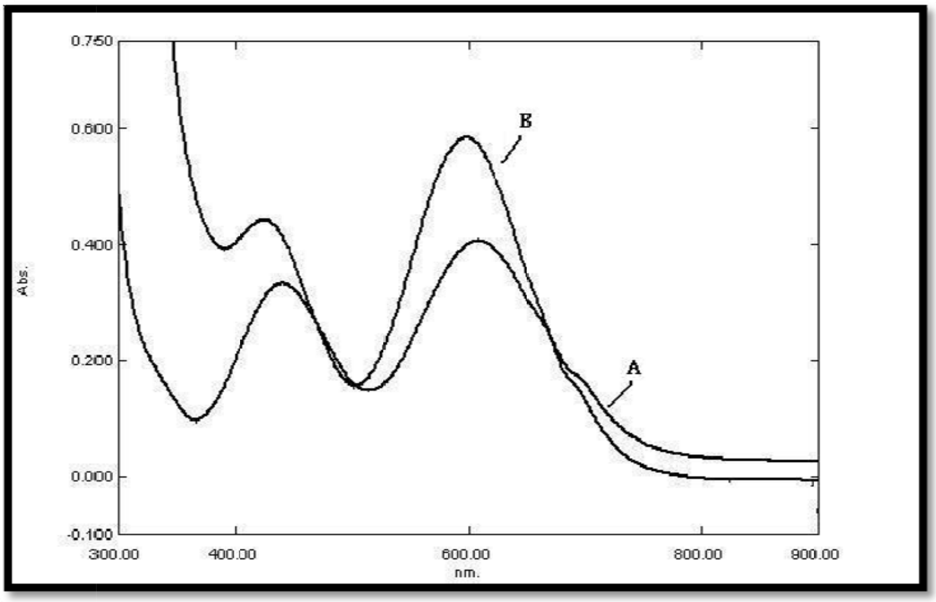

**Fig. (3-5):- The U.V.-Vis. Spectra of dissolved $CrCl_3.6H_2O$ ion in choline chloride/urea of ($7.4\times10^{-2}$m) (curve A), and in choline chloride/urea with addition of $NH_4NO_3$ salt (curve B) eutectics at room temperature.**

The Chromium (III) chloride solution in choline chloride/urea room temperature ionic liquid did not show any changes in ultraviolet visible spectra after 40 days indicating a stable complex over this period.

The Racah parameter $\grave{B}$ was calculated for the complex and was found to be equal to 664.56 $cm^{-1}$, this value is much smaller than that of free ion 918 $cm^{-1}$ or even the hydrated chromium (III) complex 713 $cm^{-1}$. However, it was higher than that value calculated for chromium (III) complex in choline chloride/urea ionic liquid alone 632 $cm^{-1}$, the higher value indicate that there is some kind of interaction with the added nitrates and the formed bonds were ionic which increase the value of $\grave{B}$**,** the higher value normally indicated a more repulsion in d-electron, due to more expansion of d-electron over a large cloud space.

### *3.2.1.3. Chromium (III) chloride in Choline chloride/Malonic acid room temperature ionic liquid solution.*

Chromium (III) chloride hexahydrate was found to be completely soluble in choline chloride/ malonic acid ionic liquid at room temperature after standing time of 72 hours in concentration of $7.5\times10^{-2}$m, producing a greenish grey solution without apparent chang in viscosity of the choline chloride/ malonic acid ionic liquid. The ultraviolet visible spectrum of the solution showed two absorption bands at 15576 $cm^{-1}$ (642 nm), 21141 $cm^{-1}$ (473 nm) and a shoulder at 14372 $cm^{-1}$(696 nm) Figure (3-6). The energies of these bands agree with those of octahedral coordination of Chromium (III) complexes.

The third spectra band of Chromium (III) complex which is expected to have higher energy than $\nu_1$ and $\nu_2$ was calculated with the used of Tanabe-Sugano diagram of $d^3$ ion configuration Figure (3-3) and found to equal to 33994 $cm^{-1}$ (294 nm) at the ultraviolet region. The bands were suggested to be due to the fallowing transition:-

$$\nu_1= {}^4A_2g\ (F) \rightarrow {}^4T_2g\ (F) =10Dq$$

$$\nu_2= {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (F)$$

$$\nu_3= {}^4A_2g\ (F) \rightarrow {}^4T_1g\ (P)$$

While the shoulder that appeared was assigned to be of a forbidden transition from ${}^4A_4g$ ground state to ${}^2G$ state.

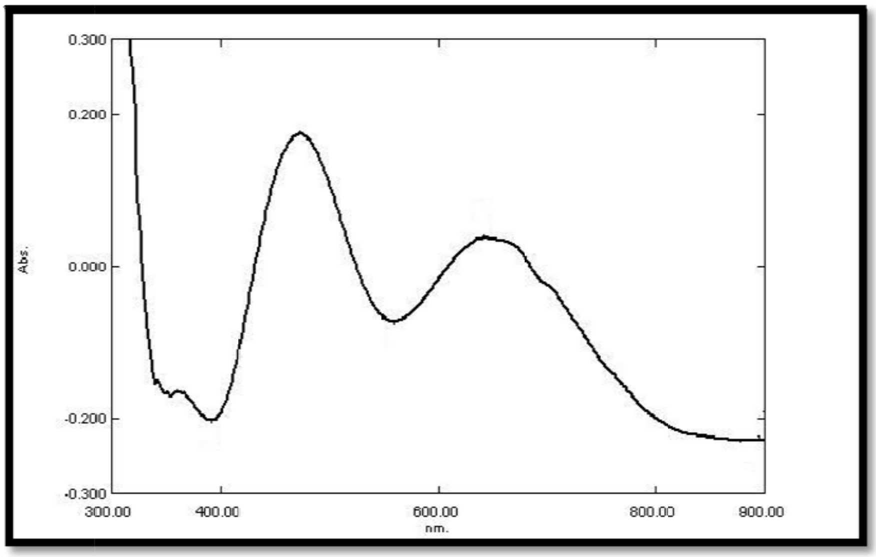

**Fig.(3-6):- The U.V.-Vis. Spectrum of $CrCl_3.6H_2O$ ion of ($7.5\times10^{-2}$m) in Choline chloride/ Malonic acid room temperature ionic liquid.**

Calculations using Jorgenson Rule of average environment for Cr (III) ions in choline chloride/malonic acid ionic liquid indicate that malonic acid replaced four of the six chloride ions in the octahedral coordination. Therefore, malonic acid is coordinated to Cr (III) ion as a bidentate ligand. The way of attached malonic acid ligand to the Cr (III) octahedral structure might occurred in different directions, the most suitable replacement of chloride ions might be occurred when two of the chlorides are on the z-axis and the other two are on the plane of x and y axis which made the formed complex more relaxed. As suggested in Figure (3-8).

The band energies are shifted to lower energy as compared with choline chloride/urea eutectic, this indicate that malonic acid has weak field than choline chloride/ urea ionic liquid. The absorbance was found to be less than in choline chloride/urea eutectic which indicates less distorted, as shown in Figure (3-7) and Table (3-2), that shows the deference between the spectra of Cr (III) in choline chloride/urea and choline chloride/malonic acid ionic liquids.

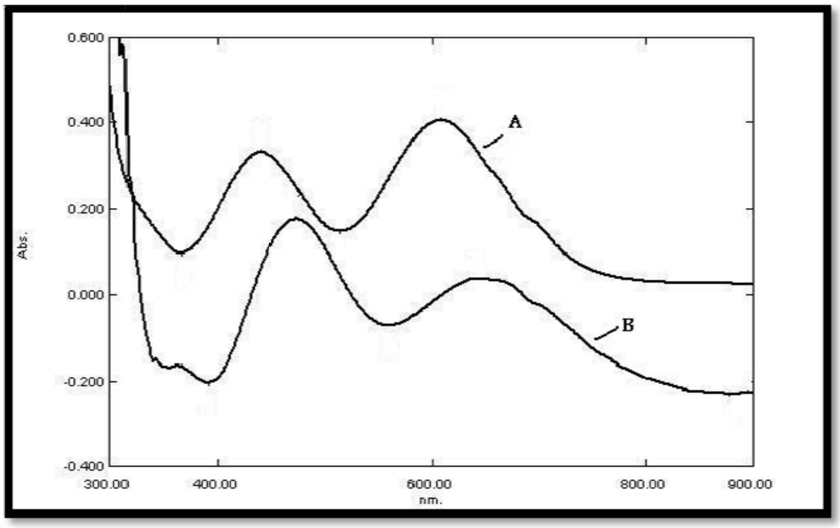

**Fig. (3-7):- The U.V.-Vis. Spectra of $CrCl_3.6H_2O$ ion in choline chloride/urea of ($7.4\times10^{-2}$m) (curve A), and in choline chloride/malonic acid of ($7.5\times10^{-2}$m) (curve B) eutectics at room temperature.**

The consistency of this interpretation can be calculated and a value was obtained for the interelectronic repulsion parameter or Racah parameter $\grave{B}$, by fitting the ratio of $\nu_1/\nu_2$ the appropriate Tanabe-Sugano diagram figure (3-6). It was found to be equal to 539.6 $cm^{-1}$, the value of $\grave{B}$ was less than that for free ion (918 $cm^{-1}$) and as well as less than that Cr (III) in choline chloride/urea solution (632 $cm^{-1}$), because of the more expansion of d-electron charge on complexation reduce the value of $\grave{B}$.

The apparent value of $B$ in complexes is always smaller than that of the free ion. This phenomenon is known as nephelauxetic effect and is attributed to delocalization of the metal electrons over molecular orbitals that encompass not only the metal but the ligand as well. As a result of this delocalization or “cloud expanding” the average interelectronic repulsion is reduced and $\acute{B}$ (representing $\grave{B}$ in the complex) is smaller. (65)

The calculated values for Racah parameter could be put in the following sequence as ligand changes:

[Free ion > $H_2O$ > choline chloride/ urea with added nitrate >choline chloride/ urea > choline chloride/ malonic acid].

**Table (3-1):- Electronic spectra for complexes of Chromium (III) ions in aqueous solution and various ionic liquids.**

| Solution of Chromium (III) in: | Absorption band $cm^{-1}$ | B̀ ($cm^{-1}$) | calculated 15B´($cm^{-1}$) | calculated β | 10Dq | Suggested structure | Reference |
|---|---|---|---|---|---|---|---|
| Aqueous Solution<br>at room temperature | $\nu_1$=16474<br>$\nu_2$=23474<br>$\nu_{3cal.}$=37118 | 713.8 | 10707 | 1.043 | 16474 | Oh<br>(6 $H_2O$)<br>$[Cr(H_2O)_6]^{3+}$ | Present work |
| Choline chloride/Urea<br>at room temperature | $\nu_1$=16447<br>$\nu_2$=22727<br>$\nu_{3cal.}$=34733 | 632 | 9480 | 0.873 | 16447 | Oh<br>(6 urea)<br>$[Cr(urea)_6]^{3+}$ | Present work |
| Choline chloride/Urea<br>+ $NH_4NO_3$<br>at room temperature | $\nu_1$=16750<br>$\nu_2$=23529<br>$\nu_{3cal.}$=36551 | 664.56 | 9967.5 | 0.986 | 16750 | Oh<br>(4 urea, 2 $NO_3^-$)<br>$[Cr(urea)_4(NO_3)_2]^+$ | Present work |
| Choline chloride/ Malonic acid<br>at room temperature | $\nu_1$=15576<br>$\nu_2$=21141<br>$\nu_{3cal.}$=33994 | 539.6 | 8094 | 1.04 | 15576 | Oh<br>(2 malonic acid, 2 $Cl^-$)<br>$[Cr(malonic)_2Cl_2]^-$ | Present work |
| LiCl//KCl<br>at 400°C | $\nu_1$=12500<br>$\nu_2$=18500 | - | - | - | - | Oh<br>(6 $Cl^-$)<br>$[CrCl_6]^{3-}$ | 1 |
| Acetamide-$KNO_3$<br>at 90°C | $\nu_1$=16760<br>$\nu_2$=22450 | - | - | - | - | Oh<br>(6 acetamide) | 67 |
| Butyramide -$NaNO_3$<br>at 140°C | $\nu_1$=16600<br>$\nu_2$=22500 | - | - | - | - | Oh<br>(6 butyramide) | 67 |

From Table (3-1) we can see that Chromium (III) chloride hexahydrate in the ionic liquid of choline chloride/urea at room temperature was indicated in octahedral coordination complex with six urea molecule which is in agreement with the spectrochemical series where urea considered being in stronger ligand field than chloride. Addition of ammonium nitrate to the solution of Cr (III) in choline chloride/urea effected the coordination of Cr (III) with urea molecule where a replacement of two urea molecules with two $NO_3^-$ ions took place in spite of that $NO_3^-$ is in a weak ligand field than urea according to the spectrochemical series, as well as the concentrations of urea and chloride are much higher than $NO_3^-$ , but they were weaker than $NO_3^-$. This indicates that the ionic liquid has a molten salt properties defers in its coordination from its free ingredients in their coordination. And Chromium (III) chloride hexahydrate in ionic liquid of choline chloride/ malonic acid also at room temperature was indicated in octahedral coordination with two malonic acid molecules as bidentate and two chlorides. The most stable suggested structure for Cr (III) in both solvents is shown in Figure (3-8).

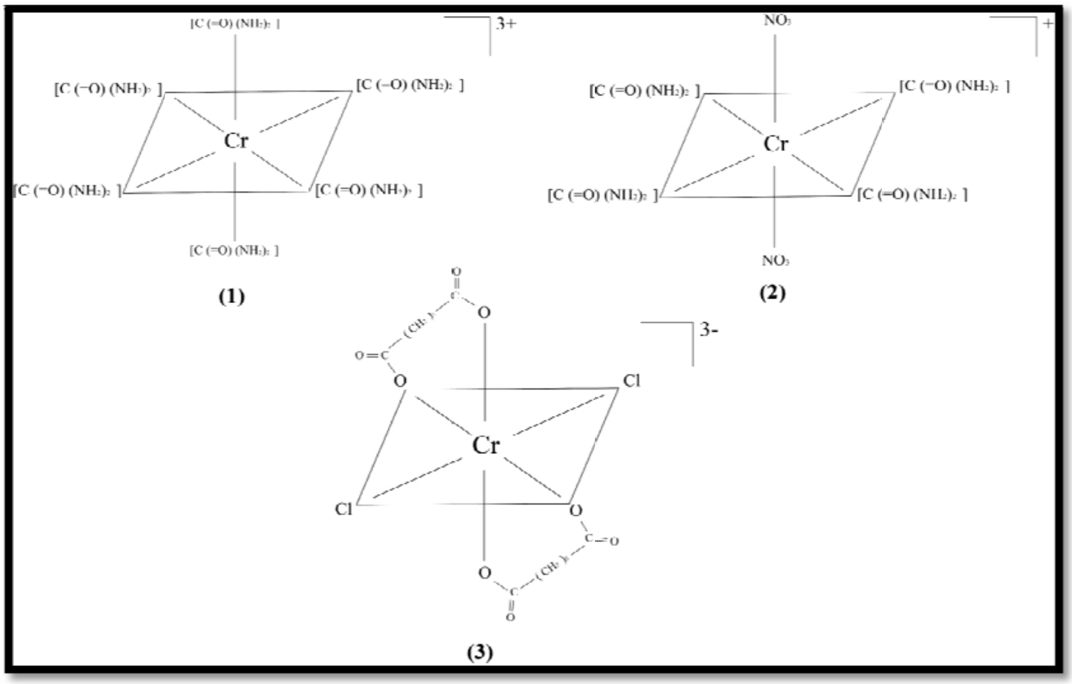

**Fig. (3-8):- Suggested structures for Chromium (III) in (1) choline chloride/urea ionic liquid, (2) choline chloride/urea ionic liquid with added salt $NH_4NO_3$ and (3) choline chloride/ malonic acid ionic liquid all formed at room temperature.**

**Table (3-2):- The molar absorptivity of Chromium (III) ions in ionic liquid based on choline chloride.**

| Ionic Liquids | Concentration (M) [mol/l] | Concentration (m) [mol/Kg] | Absorbance | Molar absoptivity (ε) [l $cm^{-1}mol^{-1}$] |
|---|---|---|---|---|
| Choline chloride/ Urea | 0.1 M | $7.4\times10^{-2}$ m | 0.406 | 4.06 |
| Choline chloride/ Urea + $NH_4NO_3$ | 0.1 M | $7.4\times10^{-2}$ m | 0.583 | 5.83 |
| Choline chloride/ Malonic acid | 0.1 M | $7.5\times10^{-2}$ m | 0.037 | 0.37 |

## 3.2.2. Spectroscopic investigation of Iron (III) chloride solutions.

Iron (III) is isoelectronic with Manganese (II), but much less is known of the greater tendency of the trivalent ion to have charge transfer bands in near ultraviolet region with strong low energy wings in the visible that obscure the very weak spin forbidden d-d bands. (64)

### 3.2.2.1. Iron (III) chloride in Choline chloride/Urea room temperature ionic liquid solution.

Iron (III) chloride tetrahydrate was found to be completely soluble in choline chloride/urea room temperature ionic liquid after 72 hours in concentration of $6.6\times10^{-2}$m, producing initially a pale yellow solution which darkened to brownish yellow color within the standing time of 72 hours. The pale yellow solution was examined by ultraviolet visible and showed one absorption band at 15748 $cm^{-1}$ (635.5 nm) and an absorption at the edge of ultraviolet absorption at 21881 $cm^{-1}$ (457 nm), as illustrated in Figure (3-9), bands can be assigned to the following spin forbidden transitions, the term symbol for the ground state of Fe (III) ion $^6S$ can split in tetrahedral crystal field as follows:- $\nu_1 = {}^6A_1 \rightarrow {}^4T_1$ and $\nu_2 = {}^6A_1 \rightarrow {}^4T_2$

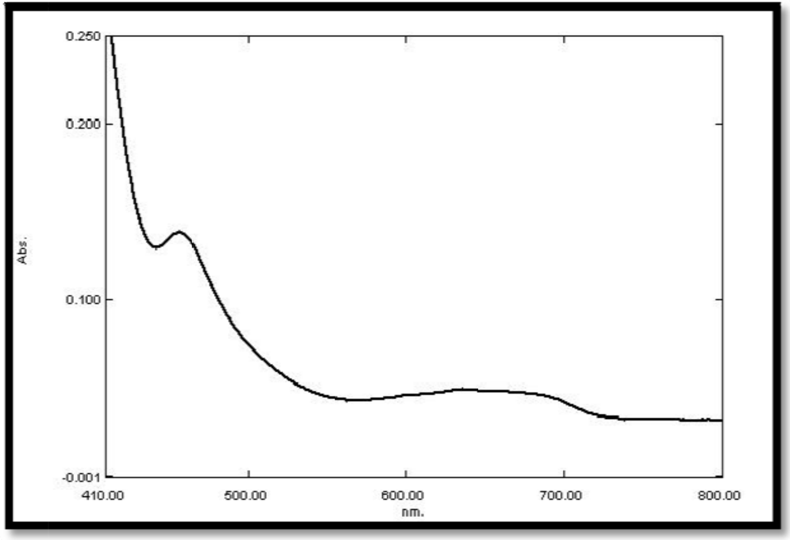

**Fig. (3-9):- The U.V.-Vis. spectrum of pale yellow solution of $FeCl_3.4H_2O$ of ($6.6\times10^{-2}$m) in Choline chloride/Urea ionic liquid at room temperature after 24 hours.**

The brownish yellow solution showed only the absorption on the edge of ultraviolet absorption at 21881 $cm^{-1}$ (457 nm), as shown in Figure (3-10).

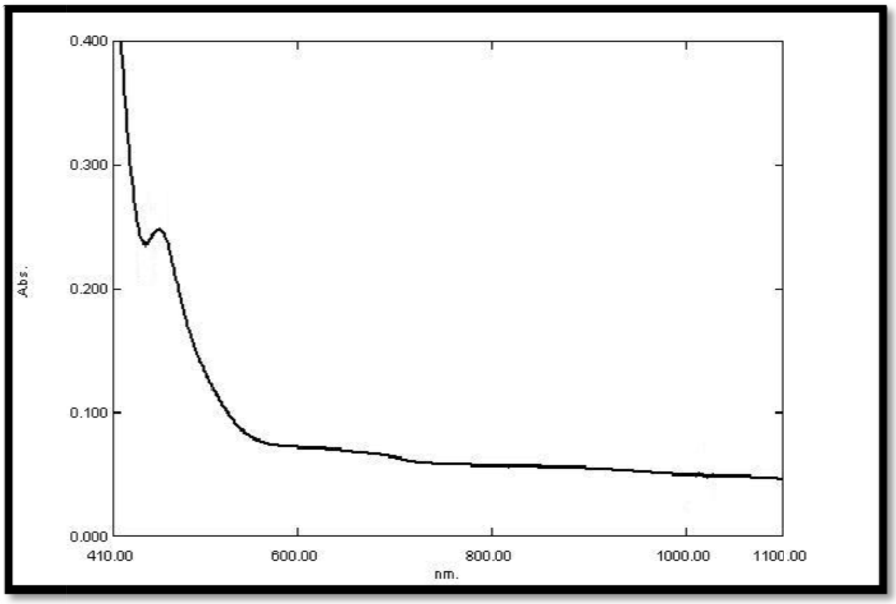

**Fig. (3-10):- The U.V.-Vis. spectrum of brownish yellow solution of $FeCl_3.4H_2O$ of ($6.6\times10^{-2}$m) in Choline chloride/Urea ionic liquid at room temperature after 72 hours.**

These absorptions were close to those for Iron (III) chloride in acetamide-potassium nitrate and Butyramide -sodium nitrate,$^{(67)}$ as showed in Table (3-3).

The pale yellow solution might be raised due to the formation of tetrahedral Fe (III) complex with chloride ions ($FeCl_4^-$) which might be replaced by more stable complexes containing urea, or perhaps by more polymerized solvolyzed Iron species. Because of that $Fe^{3+}$ is an oxidation state with half-filled d orbital in electronic configuration of $d^5$ with term symbol of $^6S$ that has no splitting. It could be suggested that the environment of the ligand for $Fe^{3+}$ are of mixed molecules of two urea and two chlorides in Td geometry. The prepared solution of Iron (III) chloride in choline chloride /urea room temperature ionic liquid was stable in the melt after 40 days as there were no changes in its spectra when examined by ultraviolet visible spectroscopy.

### *3.2.2.2. Substitution Reaction with Ammonium Nitrate.*

Addition of ammonium nitrate ($NH_4NO_3$) to the Iron (III) in choline chloride/urea solution at room temperature did not show visual changes in colour or in viscosity of the solution. However, it was examined by ultraviolet visible spectroscopy, and it indicated some changes in the ultraviolet visible spectrum of the solution, as showed in Figure (3-11). The edge band at 21881 $cm^{-1}$ (457 nm), was shifted to higher energy of the charge transfer region where the ultraviolet visible device could not detect it.

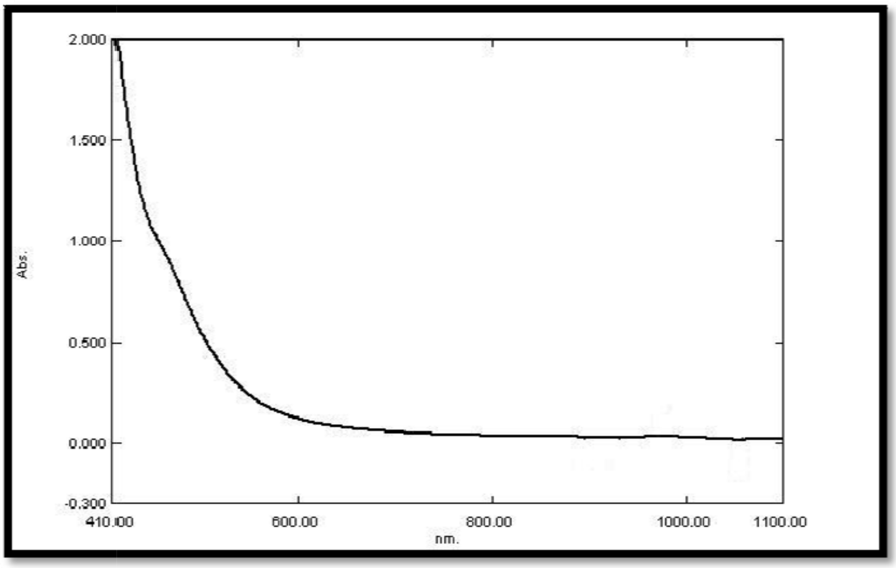

**Fig. (3-11):- The U.V.-Vis. spectrum of $FeCl_3.4H_2O$ of ($6.6\times10^{-2}$m) in Choline chloride/Urea with addition of $NH_4NO_3$ salt room temperature ionic liquid.**

This is not unexpected results as the $d^5$ configuration is normally stable and therefore no transitions are expected under the low ligand field as illustrated in

Tanabe-Sugano diagram Figure (3-13). Therefore it is not expected that the $NO_3^-$ and urea or chlorides are capable of inducing excitation to the Fe (III) ion to show absorption in the visible region. However, a raised from the ultraviolet absorption of the complex between Fe (III) and ligand as charge transfer spectra. $Fe^{3+}$ is an oxidation state with half-filled *d* orbital with term symbol of $^6S$ that has no splitting. It could be suggested that the environment of the ligand for $Fe^{3+}$ are of mixed molecules of two urea and two nitrates in tetrahedral geometry, when the two chlorides were replaced with two nitrates molecules that is more stronger ligand according to the spectrochemical series. The prepared solution of Iron (III) chloride in choline chloride /urea with added nitrate room temperature ionic liquid appeared to reach stable complex in the melt after 40 days, when it was examined with ultraviolet visible spectroscopy no changes were observed.

### 3.2.2.3. Iron (III) chloride in Choline chloride/Malonic acid room temperature ionic liquid solution.

Iron (III) chloride tetrahydrate was found to be completely soluble in choline chloride/ malonic acid room temperature ionic liquid after the standing time of 72 hours in concentration of $6.9\times10^{-2}$m, producing a pale yellow solution. The pale yellow solution was examined by ultraviolet visible spectroscopy and showed one absorption band at 11255 $cm^{-1}$ (888.5 nm) and an absorption close to an edge of ultraviolet region at 18762 $cm^{-1}$ (533 nm), and also showed another absorption at 14771 $cm^{-1}$ (677 nm), as showed in Figure (3-12),the bands can be assigned as shown below according to the term symbol for the ground state of Fe (III) ion $^6S$ for Td crystal field :- $\nu_1 = {}^6A_1 \rightarrow {}^4T_1$ , $\nu_2 = {}^6A_1 \rightarrow {}^4T_2$

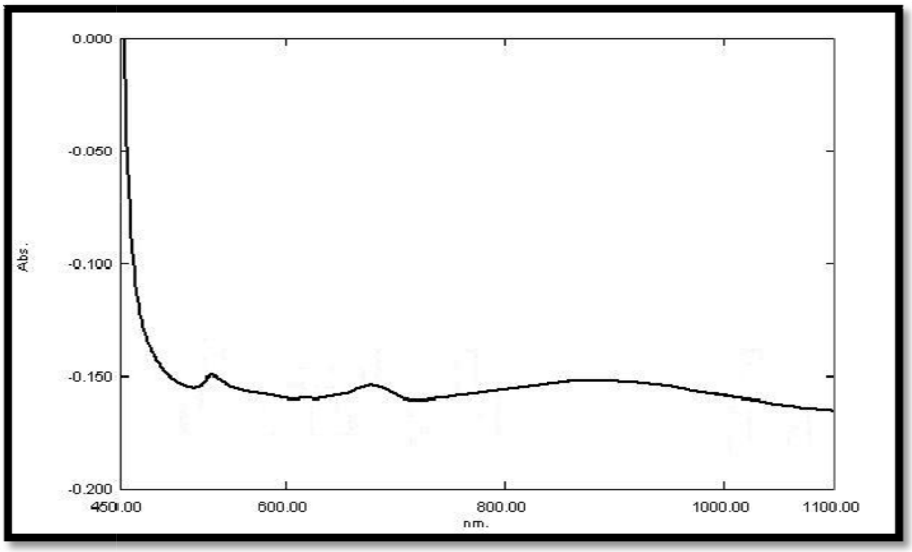

**Fig. (3-12):- The U.V.-Vis. spectrum of $FeCl_3.4H_2O$ of ($6.9\times10^{-2}$m) Choline chloride/Malonic acid ionic liquid at room temperature.**

The solution did not showed any change in color or in viscosity after the standing time of 72 hours, ultraviolet visible spectra of the solution indicates Td coordination of Fe (III) in this eutectic. Using Tanabe-Sugano diagram for $d^5$ Figure (3-13) the band that appeared between the assigned bands was found to be of a forbidden transition that probably a raised between $^6A_1g$ and $^4A_1g$, as it is the lowest energy.

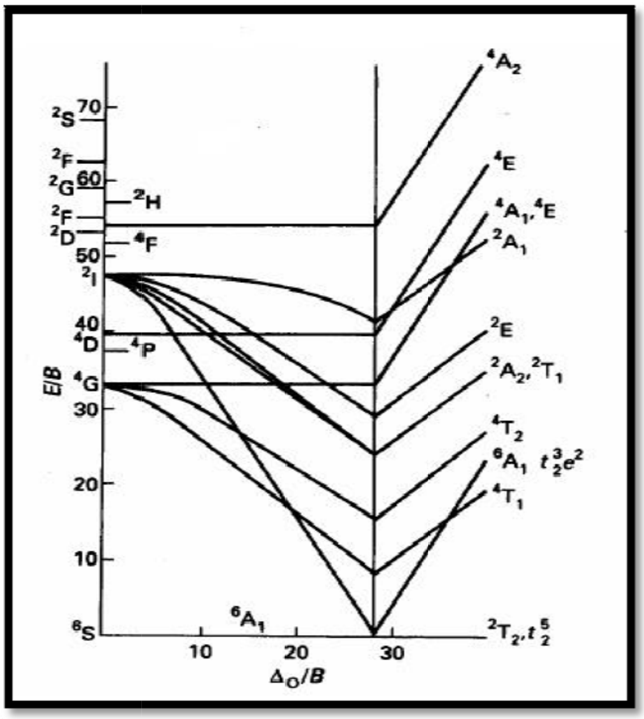

**Fig. (3-13):- Tanabe-Sugano diagram for Octahedral and Tetrahedral for $d^5$ ion configuration.(64)**

Because of $Fe^{3+}$ is in oxidation state with half-filled d orbital with term symbol of $^6S$ that has so splitting. It could be suggested that the environment of the ligand for $Fe^{3+}$ are of mixed molecules of one malonic acid molecule and two chlorides in tetrahedral geometry. The prepared solution of Iron (III) chloride in choline chloride /malonic acid room temperature ionic liquid was stable in the melt after 40 days as there were no changes in its spectra when examined by ultraviolet visible spectroscopy.

Iron (III) is the most stable oxidation state of the two oxidation states of Iron ($Fe^{II}$-$Fe^{III}$). Iron (III) in choline chloride/urea eutectic was found to be tetrahedraly coordinated with chloride ions producing the pale yellow solution as $FeCl_4^-$, where darken to brownish yellow because of the replacement of two chloride ions with two more stable urea molecules. And that's increased the absorbance of the visible light in the blue region of energy as charge transfer band. Addition of ammonium nitrate to the previous solution resulted in ligand substitution reaction between chlorides and nitrate ions.

As illustrated in Figures (3-10), (3-11) and (3-12). It had been noticed that $Fe^{3+}$ ions showed two absorption bands in choline chloride/ urea when examined after 24 hours (15748 $cm^{-1}$ - 21881 $cm^{-1}$) the first band disappeared leaving only the higher energy band at 21881 $cm^{-1}$ when examined after 72 hours. Further more, when nitrate was added to the observe solution, the remaining band at 21881 $cm^{-1}$ was also disappeared. This might be related to the slow reaction of Fe (III) with solvent molecules in the first case attending equilibrium after 72 hours producing more symmetrical coordination Iron (III) complex, the addition of nitrate ions afford more stable $d^5$ configuration producing no transition in the visible region, and the absorptivities of the solutions were listed in Table (3-4).

In Table (3-3), Ultraviolet visible spectrum of Iron (III) in choline chloride/urea eutectic showed two absorption bands initially, and only the edge band appeared after 72 hours when the solution darkened. Addition of nitrate to the solution shifted the edge absorbance band to higher energy charge transfer region where the device showed it as a shoulder near the ultraviolet region. In choline chloride/ malonic acid eutectic the absorption bands were shifted to lower energies than that in observed in water, and the absorbance in choline chloride/malonic acid was even lower than in choline chloride/ urea eutectic Table (3-3). When malonic acid could acts as a bidentate producing more stable Iron (III) complex while in choline chloride/ urea eutectic the absorbance was higher because urea is monodentate ligand and the formed Iron (III) complex was less stable. Figure (3-14) below showed the suggested structures for Iron (III) in the prepared ionic liquids at room temperature.

**Table (3-3):- Electronic spectra of complexes of Iron (III) ions in various ionic liquids.**

| Ionic liquids | Absorption band (cm$^{-1}$) | Transitions | Temperature ($^{o}$C) | Suggested structure | Reference |
|---|---|---|---|---|---|
| Choline chloride/urea | $\nu$=15748 cm$^{-1}$<br>$\nu$ = 21881 cm$^{-1}$ | ($\nu_1$) $^6A_1 \rightarrow {}^4T_1$<br>($\nu_2$) $^6A_1 \rightarrow {}^4T_2$ | Room temperature | Td<br>$FeCl_4^-$ →[Fe $Cl_2$ $(urea)_2]^+$ | Present work |
| Choline chloride/urea + $NH_4NO_3$ | About 457nm | ($\nu_1$) $^6A_1 \rightarrow {}^4T_1$<br>($\nu_2$) $^6A_1 \rightarrow {}^4T_2$ | Room temperature | Td<br>$[Fe\ (NO_3)_2\ (urea)_2]^+$ | Present work |
| Choline chloride/ malonic acid | $\nu_1$ =11255 cm$^{-1}$<br>$\nu_2$=14771 cm$^{-1}$<br>$\nu_3$=18762 cm$^{-1}$ | ($\nu_1$) $^6A_1 \rightarrow {}^4T_1$<br>($\nu_2$) $^6A_1 \rightarrow {}^4A_1$<br>($\nu_3$) $^6A_1 \rightarrow {}^4T_2$ | Room temperature | Td<br>[Fe (malonic acid)$Cl_2]^-$ | present work |
| Acetamide-$KNO_3$ | $\nu$=16900 cm$^{-1}$<br>$\nu$ = 21000cm$^{-1}$ | ($\nu_1$) $^6A_1 \rightarrow {}^4T_1$<br>($\nu_2$) $^6A_1 \rightarrow {}^4T_2$ | 90$^{o}$C | Td<br>$[FeCl_4]^-$ | 67 |
| Butyramide-$NaNO_3$ | $\nu$=16900 cm$^{-1}$<br>$\nu$ =21000 cm$^{-1}$ | ($\nu_1$) $^6A_1 \rightarrow {}^4T_1$<br>($\nu_2$) $^6A_1 \rightarrow {}^4T_2$ | 90$^{o}$C | Td<br>$FeCl_4^-$ | 67 |
| LiCl/KCl | $\nu$=5100 cm$^{-1}$<br>6000 cm$^{-1}$ | ($\nu_1$) $^6A_1 \rightarrow {}^4T_1$<br>($\nu_2$) $^6A_1 \rightarrow {}^4T_2$ | 400$^{o}$C<br>1000$^{o}$C | Td or<br>Distorted Td | 1 |
| $LiNO_3/KNO_3$ | $\nu$=1600 cm$^{-1}$ | | 160$^{o}$C | Td<br>$[FeCl_4]^-$ | 1 |

**Table (3-4):- The molar absorptivity of Iron (III) ions in ionic liquid based on choline chloride.**

| Ionic Liquids | Concentration (M) [mol/l] | Concentration (m) [mol/Kg] | Absorbance | Molar absoptivity (ε) [l $cm^{-1}mol^{-1}$] |
|---|---|---|---|---|
| Choline chloride/ Urea | 0.1 M | $6.6\times10^{-2}$ m | 0.247 | 2.47 |
| Choline chloride/ Urea + $NH_4NO_3$ | 0.1 M | $6.6\times10^{-2}$ m | 0.78 | 7.8 |
| Choline chloride/ Malonic acid | 0.1 M | $6.9\times10^{-2}$ m | 0.17 | 1.7 |

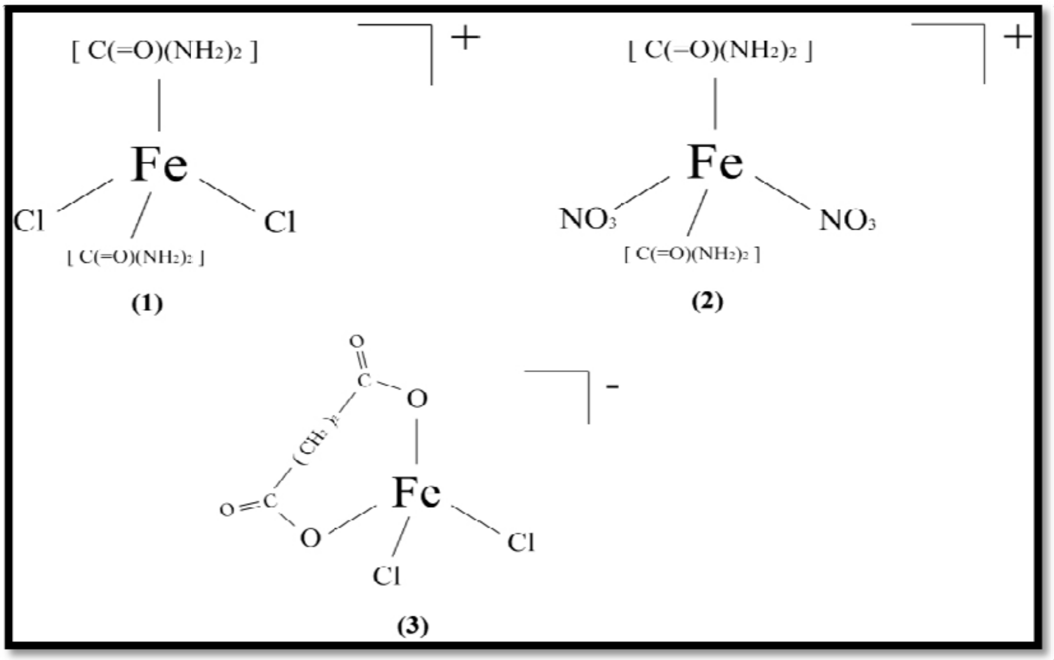

**Fig. (3-14):- Suggested structures of Iron (III) complexes in (1) choline chloride/ urea ionic liquid, (2) choline chloride/urea ionic liquid with added $NH_4NO_3$ salt, (3) choline chloride/malonic acid ionic liquids all formed at room temperature.**

### 3.2.3. Spectroscopic investigation of Cobalt (II) chloride solutions.

#### 3.2.3.1. Cobalt (II) chloride in Choline chloride/Urea room temperature ionic liquid solution.

Cobalt (II) chloride hexahydrate was found to be easily and completely soluble in choline chloride/ urea ionic liquid at room temperature after the standing time of 72 hours in concentration of ($6.9\times10^{-2}$m), producing a deep blue solution without visual changing in viscosity of the choline chloride/ urea ionic liquid after the dissolution of the salt.

The ultraviolet visible spectrum of the solution showed two absorption bands at 14903 $cm^{-1}$ (671 nm) and 15600 $cm^{-1}$ (641 nm), as shown in Figure (3-18). Cobalt (II) in choline chloride/ urea eutectic was consistent with tetrahedral coordination.

The absorbance of the solution was higher than expected and the solution considered to be saturated when the splitting of the observed peaks was not clear, so in order to make the splitting in the peaks more clearly the solution was diluted from $6.9\times10^{-2}$m to $3.45\times10^{-2}$m, and the positions of the observed peaks remained in the same values, as shown in Figure (3-15).

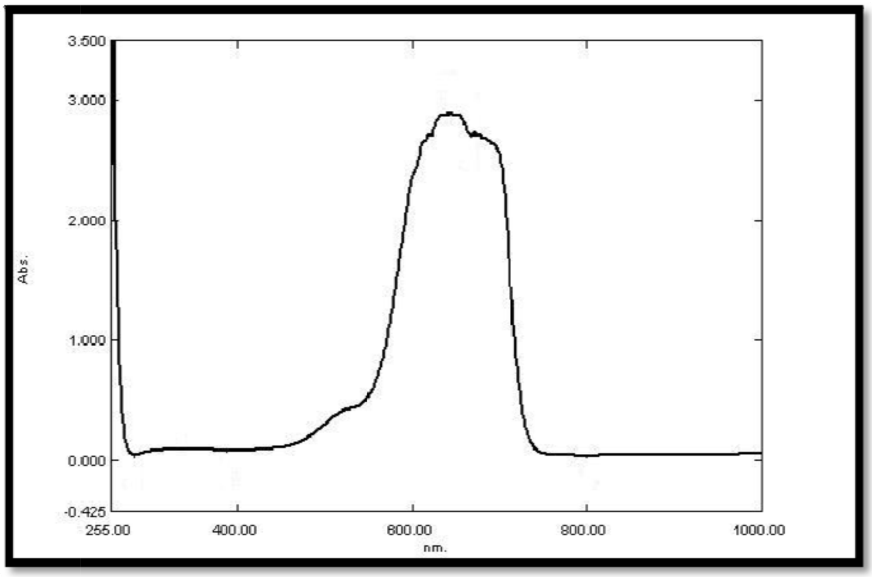

**Fig. (3-15):- The U.V.-Vis spectrum of $CoCl_2.6H_2O$ of ($6.9\times10^{-2}$m) Choline chloride/Urea room temperature ionic liquid.**

Cobalt (II) chloride showed a different behaviour in choline chloride/ urea non aqueous ionic liquid solvent than in aqueous solvent where it behaved as tetrahedral coordinated complex in the former room temperature ionic liquid and it coordenated as octahedral complex with 6 water molecules, $[Co(H_2O)_6]^{2+}$.

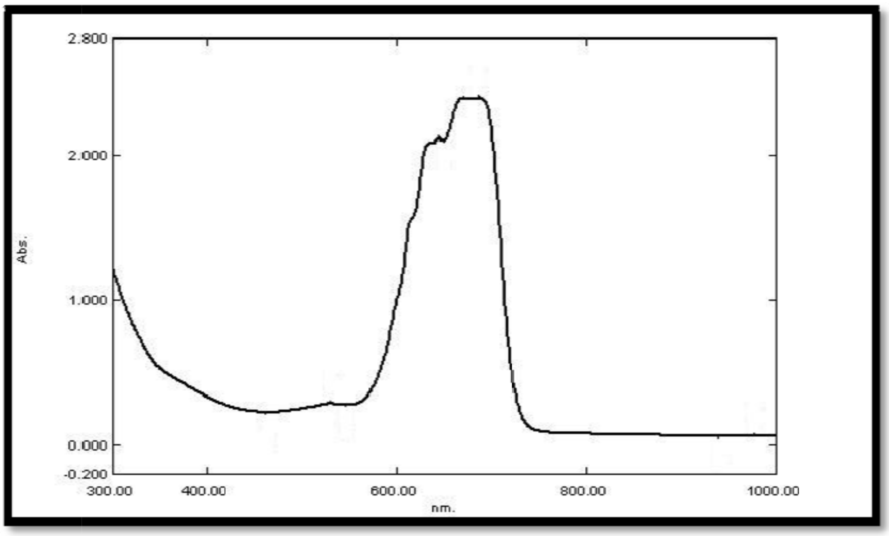

**Fig. (3-16):- The U.V.-Vis. spectrum of the diluted solution of $CoCl_2.6H_2O$ of ($3.45\times10^{-2}$m) in Choline chloride/Urea room temperature ionic liquid.**

Using Orgel diagram for the splitting of free-ion $^4F$ and $^4P$ term in octahedral and tetrahedral field Figure (1-17) and Figure (3-18) for the $d^7$ tetrahedral electronic configuration the appeared transition was assigned to be the third electronic transition of the tetrahedral complex of Co (II), where the first and second transitions were in the infrared spectra region. The splitting in the appeared band was due to the spin forbidden transition of the ground state $^4A_2$ to the doublet $^2G$ state.

$$\nu_1 = {}^4A_2 \rightarrow {}^4T_2\ (F),$$

$$\nu_2 = {}^4A_2 \rightarrow {}^4T_1\ (F)$$

$$\nu_3 = {}^4A_2 \rightarrow {}^4T_1\ (P)$$

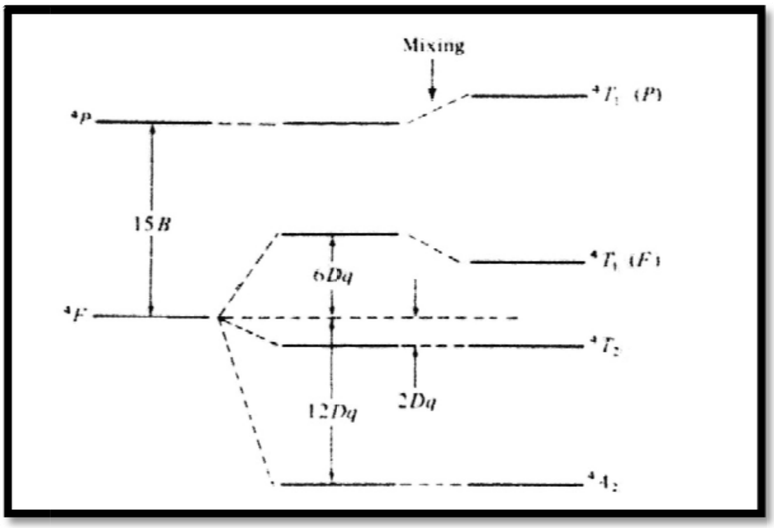

**Fig. (3-17):- Crystal field splitting of $^4$F term of d$^7$ ion Tetrahedral configuration.(64)**

It was obvious that changing the concentration of Cobalt (II) chloride in choline chloride/ urea eutectic did not affect the energy of the ultraviolet visible spectra of the solution, as it reported in other studies of Cobalt (II) chloride in other room temperature ionic liquids. In Calcium nitrate tetrahydrate melts containing variable amounts of calcium chloride where the solution in pure calcium nitrate tetrahydrate showed octahedral coordination with absorption maximum being at 19420 cm$^{-1}$ (512 nm) and with addition of chloride caused a shift of the absorption maximum toward lower energies and a large increase of the absorption coefficient indicating a change from octahedral to tetrahedral or distorted octahedral coordination.(68)

As well as in a molten mixture of 80% acetmide-20% calcium nitrate tetrahydrate, the absorption spectra of Cobalt (II) chloride complex, where addition of chloride shifted the absorption maximum of octahedral Cobalt (II) nitrate towards lower energies and pronounced changes in shape of the initial spectrum of Cobalt (II) nitrate was occurred.(69) The effect of temperature changes on the absorption of the Cobalt (II) species was attributed to structural changes occurring in the Cobalt (II) species, and also in many other studies where the geometry of Cobalt (II) formed complex(s) effected by changing the concentration of the solution, the temperatures or changing the mole ratio percent of the used ionic liquid components as listed in Table (3-5).

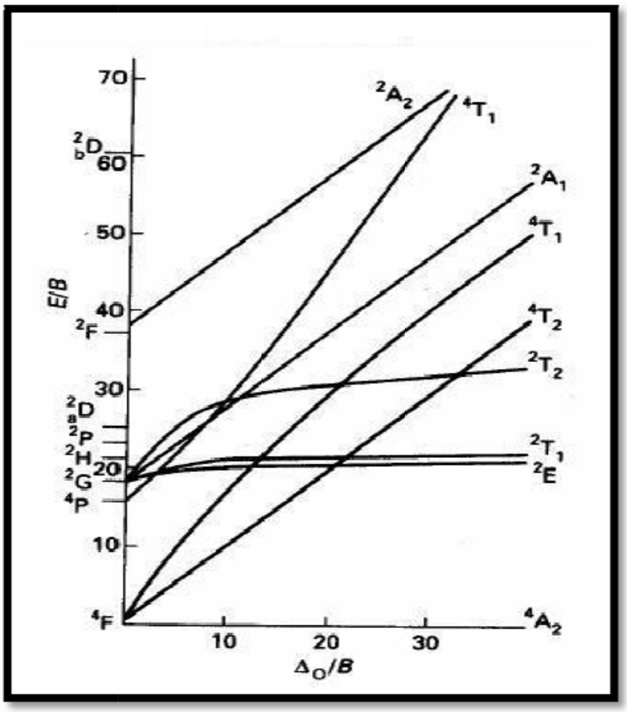

**Fig. (3-18):- Tanabe-Sugano diagram for $d^7$ Tetrahedral ionic configuration.(64)**

Suggestion for the average environment of Cobalt (II) in choline chloride/ urea ionic liquid suggested that Cobalt (II) were bonded with four chloride ions as ligand in tetrahedral coordination, as [$CoCl_4^{2-}$].

The absorbance of the solution was very large and the colour of the solution was intense when compared with the same concentration of the salt in aqueous solution which indicates qualitatively that the coordination of Cobalt (II) was either tetrahedral or distorted octahedral complex in choline chloride/ urea eutectic, as shown in Table (3-5) and the molar absorptivity of the solution listed in Table (3-6). The solution of Cobalt (II) chloride hexahydrate in choline chloride/ urea eutectic after 40 days from the first ultraviolet visible spectra measurements showed some changes in the shape of the peaks in the spectra of the concentrated solution ($6.9\times10^{-2}$m) as well as in diluted solution ($3.45\times10^{-2}$m) as showed in Figure (3-19), where the ultraviolet visible spectra of concentrated and diluted solution showed two absorption maxima at 15748 $cm^{-1}$ (635 nm) and at 18761 $cm^{-1}$ (533 nm).

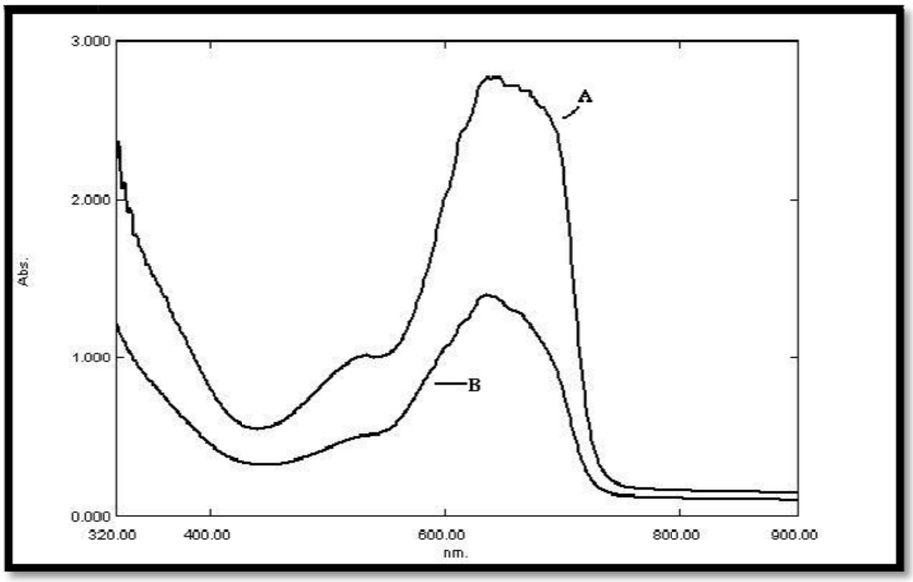

**Fig. (3-19):- The U.V.-Vis. spectra of Cobalt (II) in Choline chloride/Urea room temperature ionic liquid after 40 days, (curve A) concentrated solution ($6.9\times10^{-2}$m) and (curve B) diluted solution ($3.45\times10^{-2}$m).**

The ultraviolet visible spectra of the solution showed some differences its spectra after and before the standing time of 40 days where the absorbance and the molar absoptivity of the solution decreases after 40 days which means that the formed complex become more stable and more symmetrical. The molar absoptivity of the solution is listed in Table (3-7) showed the effect of the ligand attached to the Co (II) in this eutectic.

The changing in the ultraviolet visible spectrum of the solution indicates some substitution of the ligands that was attached to the Cobalt (II) ion in the eutectic, which decrease the energy of the formed complex of Co (II) and the peaks positions are shifted to higher energies. Calculations using Jorgenson rule of average environment suggested that Cobalt (II) ions in choline chloride/ urea eutectic after 40 days faced some replacements of chlorides by more stable urea molecules in Cobalt (II) a complex. This substitution took place between two chlorides with two urea molecules, which is preferable as urea is stronger ligand than chloride according to the electrochemical series. If so, it means that Cobalt (II) in choline chloride/ urea eutectic formed weak complex with chloride which substituted by the stronger urea molecule.

**Table (3-5):- Electronic spectra for complexes of Cobalt (II) chloride in various room temperature ionic liquids.**

| Ionic liquids | Percents of IL. Component. | Co (II) formed complexes | Absorption bands (cm$^{-1}$) | Temp. ($^o$ C). | Suggested structure. | References |
|---|---|---|---|---|---|---|
| $Ca(NO_3)_2.4H_2O$-$CaCl_2$ | Addition of $Cl^-$ | $[Co(NO_3)_4]^{2-}$<br>$[Co(NO_3)_2Cl_2]^{2-}$<br>$[CoCl_4]^{2-}$ | $\nu$=19420<br>Shifted to lower energy | 40-70 | Oh<br>Distorted Oh or Td | 68 |
| Acetamide-$Ca(NO_3)_2.4H_2O$ | 80%-20%<br>Addition of $Cl^-$ | $[Co(NO_3)_4]^{2-}$<br>$[Co(NO_3)_2Cl_2]^{2-}$<br>$[CoCl_4]^{2-}$ | $\nu$=19430<br>Shifted to lower energy | 40-90 | Oh<br>Distorted Oh or Td | 69 |
| KCl-$AlCl_3$ | (50.3-49.7)%<br>(50.3-49.7)%<br>(49.9-50.1)% | $[CoCl_4]^{2-}$<br>$[CoCl_6]^{4-}$ or $Co(Al_2Cl_7)_2$<br>$[Co(AlCl_4)_2]$ | _ | 25<br>300<br>300 | Td<br>Oh<br>Distorted Oh | 70 |
| $AICI_3$,-BPC | 2:1<br>0.8:1 | Co $(Al_2C\ I_7)_m^{2-m}$ *(m=2)*<br>$CoCI_4^{2-}$ | _<br>_ | 40<br>40 | Oh<br>Td | 71 |
| butyramide-Na $NO_3$ | (94.5-5.5)% | $[Co(butyramide)_4Cl_2]$ | $\nu$=1750<br>$\nu$=8200 | 140 | Oh | 67 |
| Acetamide-$KNO_3$ | | $[Co(acetamide)_4Cl_2]$ | $\nu$=1800<br>$\nu$=8200 | 90-140 | Oh | 67 |
| LiCl-KCl | | $[CoCl_4]^{2-}$ | $\nu$=(14700, 15150, 16700) | 447-480 | Td | 1 |

### *3.2.3.2. Substitution Reaction with Ammonium Nitrate.*

Addition of ammonium nitrate ($NH_4NO_3$) to the prepared solution at room temperature did not show noticeable changes neither in color nor in viscosity of the solution, but when it was examined by ultraviolet visible spectroscopy it showed some changes in the ultraviolet visible spectrum of the Cobalt (II) ions, where the shape and the position of the peaks changed as well as the absorbance, as shown in Figure (3-20).

The ultraviolet visible spectrum of the solution was taken to the diluted solution ($3.45\times10^{-2}$m) and not the concentrated solution ($6.9\times10^{-2}$m), because the concentrated solution showed unclear spectra with high absorbance even the device could not detect it. The ultraviolet visible spectrum showed three absorption bands with a clear splitting in the band, the absorption was at 15015 $cm^{-1}$ (666 nm), (15552, 15848 $cm^{-1}$), (643, 631 nm) and 18904 $cm^{-1}$ (529 nm), the changes in the absorption bands positions and the splitting in the band with small shift of the band to higher energy indicated that added nitrate made some interaction with the formed complex of Cobalt (II) in choline chloride/ urea melt.

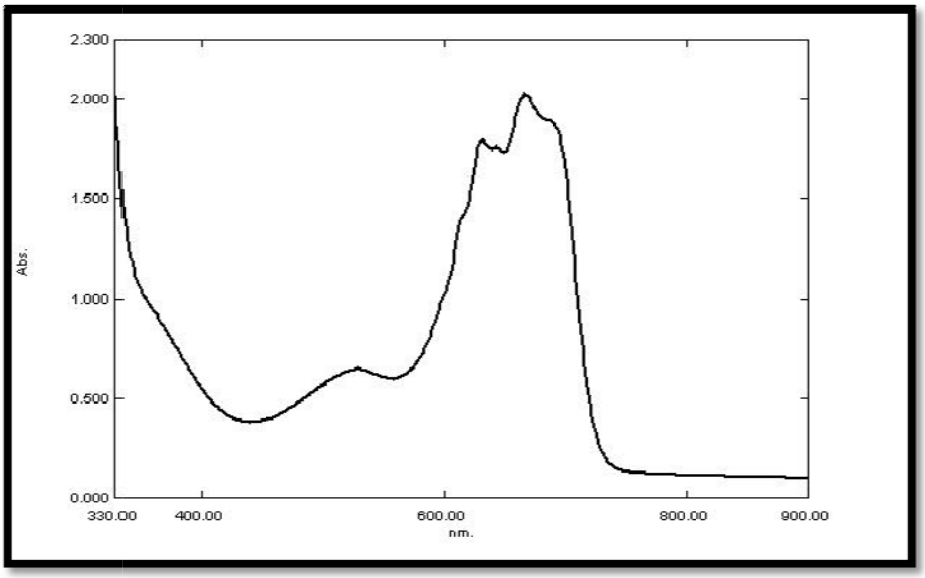

**Fig. (3-20):- The U.V.-Vis. spectrum of $CoCl_2.6H_2O$ of ($6.9\times10^{-2}$m) in Choline chloride/Urea room temperature with addition of $NH_4NO_3$.**

The appeared band was assigned to be of the third transition from $^4A_2$ (F) → $^4T_1$ (P) and the splitting in the band was due to forbidden transition from $^4A_2$ ground state to doublet $^2G$ state. While the second and first band were in the low energy range near infrared region.

Calculations using Jorgenson Rule for average environment suggested that a replacement reaction took place between added nitrates and chlorides bonded to Cobalt (II), no visual observed changes happened to the solution after time of 40 days, as that happened to the original solution of Cobalt (II) chloride in choline chloride/urea ionic liquid at room temperature. Figure (3-21) showed the changes that took place to the solution after addition of ammonium nitrate, as in table (3-6)

From Figure (3-21), it is obvious that after the replacement of two chlorides by two nitrates the complex became less symmetrical, as the absorbance of the solution as well as molar absorptivity increases; see Table (3-7), as the nitrate is stronger ligand than chloride according to the spectrochemical series.

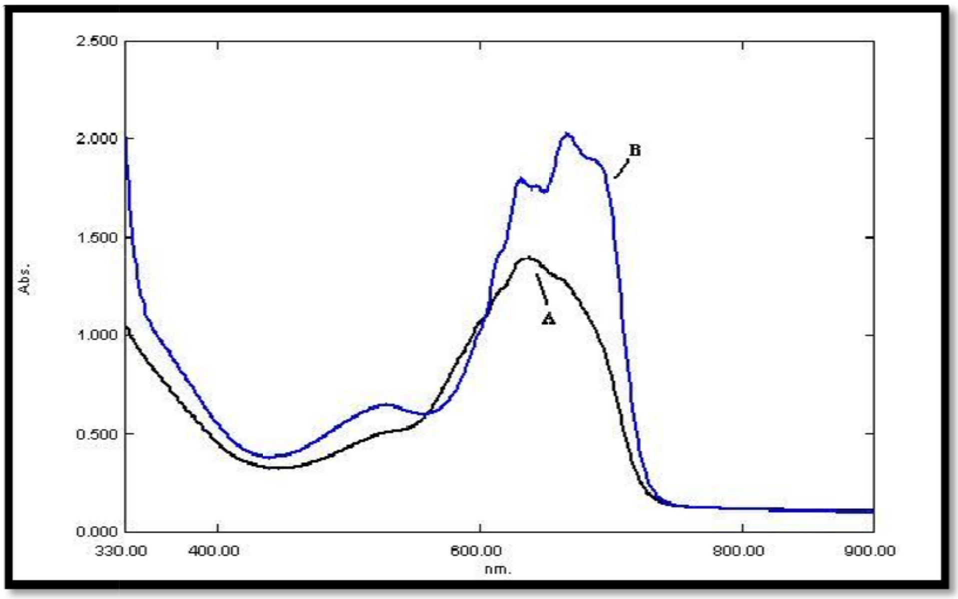

**Fig. (3-21):- The U.V.-Vis. spectra of $CoCl_2.6H_2O$ of ($3.45\times10^{-2}$m) in Choline chloride/Urea room temperature ionic liquid (curve A) and with addition of $NH_4NO_3$ (curve B).**

The consistency of this interpretation have a value obtained for the interelectronic repulsion Racah parameter $\grave{B}$, by fitting the ratio of $\nu_1/\nu_2$ the appropriate Tanabe-Sugano diagram, Figure (3-18), and it was found to be equal to 1117 $cm^{-1}$, the value of $\grave{B}$ was higher that for free ion (971 $cm^{-1}$) and higher than that for aqueous solution (920 $cm^{-1}$) in octahedral coordination , because of the more expansion of d-electron charge on complexation in tetrahedral as well as tetrahedral is less symmetrical than octahedral increases the value of $\grave{B}$.

### *3.2.3.3. Cobalt (II) chloride in Choline chloride/Malonic acid room temperature ionic liquid solution.*

Cobalt (II) chloride hexahydrate was found to be completely soluble in choline chloride/ malonic acid ionic liquid at room temperature after the standing time of 72 hours in concentration of $7.4\times10^{-2}$m, producing a blue colored solution without any visual changing in viscosity of the choline chloride/ malonic acid ionic liquid after the dissolution of the salt.

The ultraviolet visible spectrum of the solution showed three absorptions maxima bands at 14881 $cm^{-1}$ (672 nm), 15576 $cm^{-1}$ (642 nm) and 16155 $cm^{-1}$ (619 nm), that belong to the third transition band and the first and second transitions were in the infrared and near infrared region respectively. The third band showed a clear splitting and a spin forbidden transitions from $^4A_2$ ground state to doublet state with its splitting, indicating that Cobalt (II) chloride in choline chloride/ malonic acid ionic liquid at room temperature consist of Td coordination complex of Cobalt (II), as shown in Figure (3-22), the term symbol for the ground state of Co(II) ion $^4F$ can split in tetrahedral crystal field, Using appropriate Orgal diagram Figure (1-17), and Tanabe-Sugano diagram for the $d^7$ tetrahedral electronic configuration which is the same Tanabe-Sugano diagram for $d^3$ octahedral electronic configuration as in Figure (3-18), the transitions were assigned as below:-

$$\nu_1 = {}^4A_2\,(F) \rightarrow {}^4T_2\,(F) = 10Dq$$
$$\nu_2 = {}^4A_2\,(F) \rightarrow {}^4T_1\,(F)$$
$$\nu_3 = {}^4A_2\,(F) \rightarrow {}^4T_1\,(P)$$

The absorption bands of the solution were close to those of Cobalt (II) in choline chloride/ urea room temperature ionic liquid in its initial readings after 72 hours from the preparation, but Cobalt (II) showed changes in choline chloride/urea ionic liquid where it did not show any changes in choline chloride/ malonic acid ionic liquid, as showed in Table (3-6).

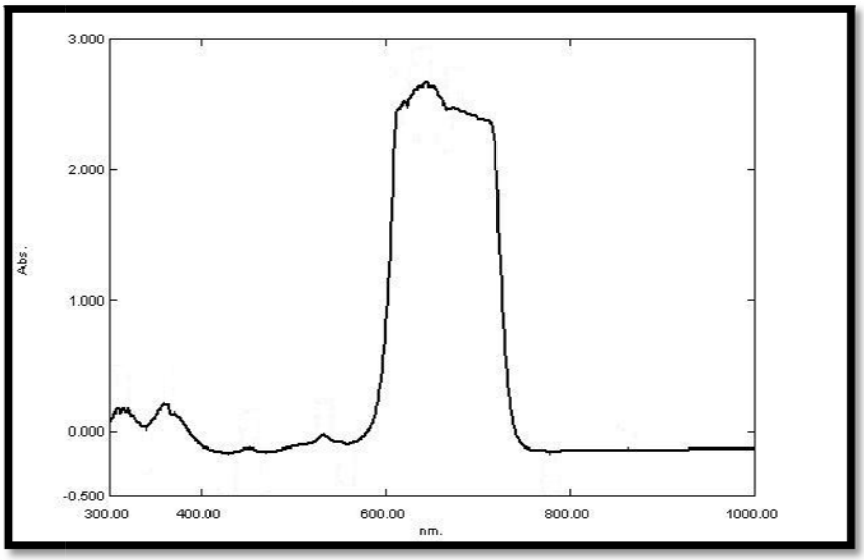

**Fig. (3-22):- The U.V.-Vis. spectrum of $CoCl_2.6H_2O$ of ($7.4\times10^{-2}$m) in Choline chloride/Malonic acid room temperature ionic liquid.**

Calculations using Jorgenson Rule for average environment suggested that Cobalt (II) in choline chloride/ malonic acid eutectic was bonded with chlorides as ligand in [$CoCl_4^{2-}$], and after standing time of 40 days the solution did not show any color change or viscosity change as well as absorption bands did not show shifts or changes, and the absorbance of the solution stayed the same which means that Cobalt (II) in choline chloride/ malonic acid eutectic formed stable complex, that the attached ligands would not be replaced by more stable molecule (malonic acid).

The consistency of this interpretation have a value obtained for the interelectronic repulsion parameter $\grave{B}$, by fitting the ratio of $\nu_1/\nu_2$ the appropriate Tanabe-Sugano diagram, Figure (3-18). And it was found to be equal to 1117 $cm^{-1}$, the value of $\grave{B}$ was higher that for free ion 971 $cm^{-1}$ and higher than that for aqueous solution 920 $cm^{-1}$ in octahedral coordination , because of the more expansion of d-electron charge on complexation in tetrahedral as well as tetrahedral is less symmetrical than octahedral increases the value of $\grave{B}$.

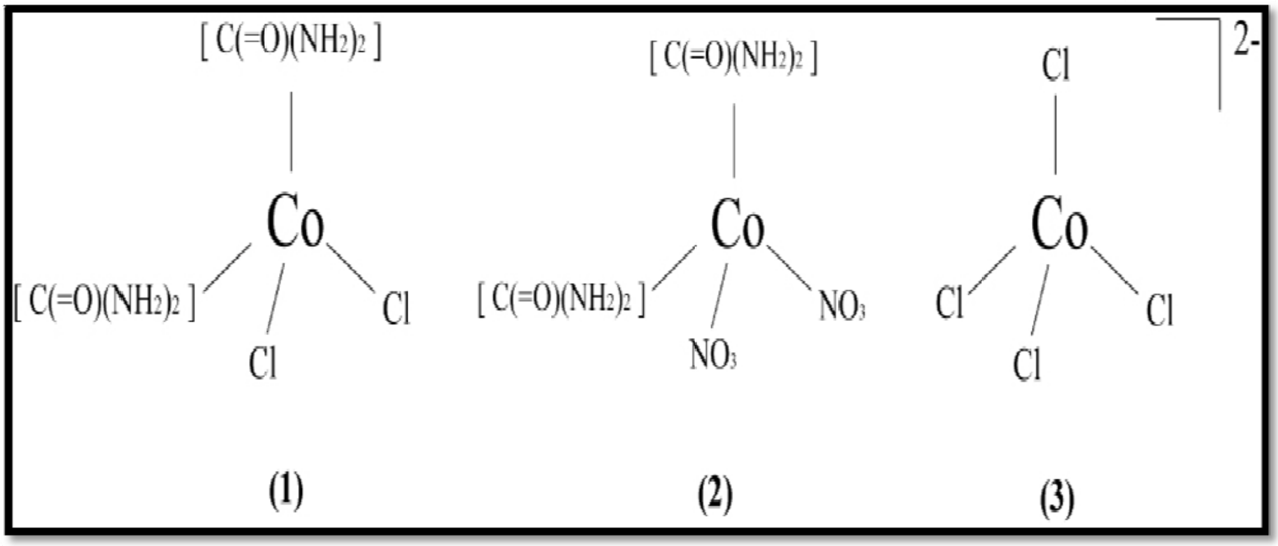

**Fig. (3-23):- Suggested structures for Cobalt (II) ions in (1) choline chloride/urea ionic liquid, (2) choline chloride/urea ionic liquid with added salt $NH_4NO_3$ and (3) choline chloride/malonic acid ionic liquid all formed at room temperature.**

**Table (3-6):- Electronic spectra of complexes of Cobalt (II) ions in aqueous and various ionic liquids.**

| Ionic liquid | Solution color | Transitions bands ($cm^{-1}$) | B ($cm^{-1}$) | 10Dq | suggested structure | Reference |
|---|---|---|---|---|---|---|
| Aqueous solution | Pink solution | $\nu_1$= 8100<br>$\nu_2$= 16000<br>$\nu_3$= 19400 | 920 | 8100 | Oh<br>$[Co(H_2O)_6]^{+2}$ | 64,65 |
| ➢ Choline chloride / urea | Deep blue | $\nu_1$= -<br>$\nu_2$= -<br>$\nu_3$ = (14903-15600) | 1117 | - | Td<br>$[CoCl_4]^{2-} \rightarrow [CoCl_2 (NH_2CONH_2)_2]$ | Present work |
| Choline chloride/ urea +$NH_4NO_3$ | Blue | $\nu_1$= -<br>$\nu_2$= -<br>$\nu_3$ = (15015-15848) | 1117 | - | Td<br>$[Co(NO_3)_2 (NH_2CONH_2)_2]$ | Present work |
| Choline chloride/ malonic acid | Blue | $\nu_1$ = -<br>$\nu_2$ = -<br>$\nu_3$ = (14881-16155) | 1117 | - | Td<br>$[CoCl_4]^{2-}$ | Present work |

- *The solution faced some changes after 40 days and the readings had shifted to higher energies.*

In the case of Cobalt (II) we saw that it behaved differently from other studies that have been done on Cobalt (II) in other ionic liquids at room temperature or with heating as showed in Table (3-5) and Table (3-6), where it was behaved in choline chloride/ urea and choline chloride/ malonic acid ionic liquids as tetrahedraly coordinated complex of [$CoCl_4^{2-}$], that in choline chloride/urea ionic liquid after a period of time up to 40 days, it faced some replacement of two chlorides with two urea molecules, while in choline chloride/ malonic acid Cobalt (II) did not faced any changes in its coordination with chlorides.

**Table (3-7):- The molar absorptivity of Cobalt (II) ions in ionic liquid based on choline chloride.**

| Ionic Liquids | Concentration (M) [mol/l] | Concentration (m) [mol/Kg] | Absorbance | Molar absorptivty (ε) [$l\ cm^{-1}mol^{-1}$] |
|---|---|---|---|---|
| Choline chloride/ Urea | 0.1 M | $6.9\times10^{-2}$ m | 2.737 | 27.37 |
| Choline chloride/ Urea + $NH_4NO_3$ | 0.1 M | $6.9\times10^{-2}$ m | 2.022 | 20.22 |
| Choline chloride/ Malonic acid | 0.1 M | $7.4\times10^{-2}$ m | 2.482 | 24.82 |

## *3.2.4. Spectroscopic investigation of Nickel (II) chloride solutions.*

### *3.2.4.1. Nickel (II) chloride in Choline chloride/Urea room temperature ionic liquid solution.*

Nickel (II) chloride hexahydrate was found to be easily and completely soluble in choline chloride/urea ionic liquid at room temperature after the standing time of 72 hours in $1.1\times10^{-1}$m, producing a pale green solution without visual changing in viscosity of the choline chloride/urea ionic liquid after the dissolution of the salt.

The ultraviolet visible spectrum of the solution showed three absorption maxima the first one at 9522 $cm^{-1}$(1050 nm), the second one at [13405 $cm^{-1}$ (746 nm)- 14948 $cm^{-1}$ (669 nm)] with clear splitting and the third one at 24390 $cm^{-1}$ (410 nm), as shown in Figure (3-24), indicating that Nickel (II) in consistent with octahedral coordination complex.

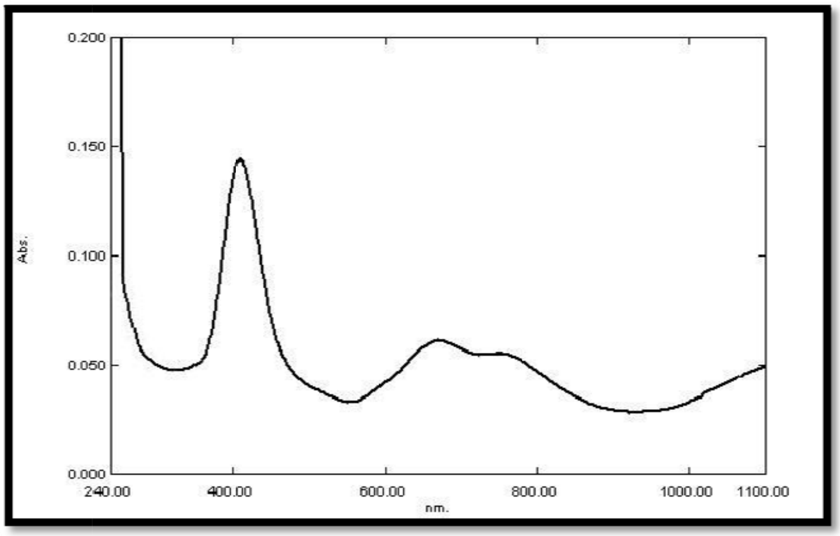

**Fig. (3-24):- The U.V.-Vis. spectrum of $NiCl_2.6H_2O$ of ($1.1\times10^{-1}$m) in choline chloride/ urea room temperature ionic liquid.**

Using appropriate Orgel diagram Figure (1-17) and Crystal field splitting of $^3F$ term of $d^8$ ion octahedral configuration Figure (3-25). The term symbol for the ground state of Ni (II) ion $^3F$ can split in octahedral crystal field as follows:-

$$\nu_1 = {}^3A_2g \rightarrow {}^3T_2g\ (F)$$

$$\nu_2 = {}^3A_2g \rightarrow {}^3T_1g\ (F)$$

$$\nu_3 = {}^3A_2g \rightarrow {}^3T_1g\ (P)$$

While the forbidden transition was due to spin-orbit coupling transition from the $^3A_2g$ ground state to the singlet state of $^1Eg$ which are very close in energy.

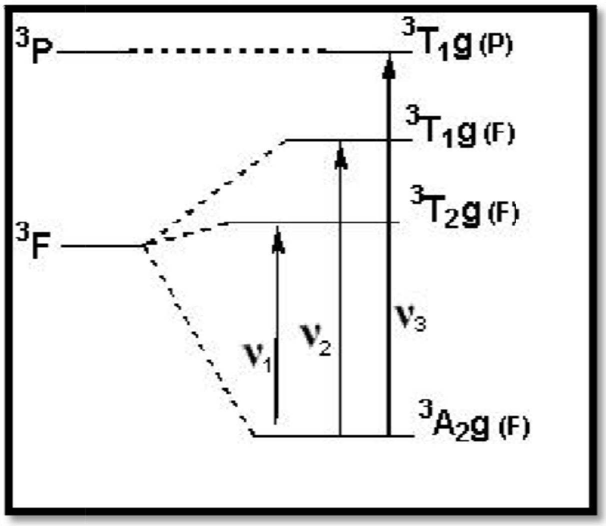

**Fig. (3-25):- Crystal field splitting of $^3F$ term of $d^8$ ion Octahedral configuration.**

Using Tanabe-Sugano diagram for $d^8$ electronic configuration Figure (3-26), the third transition was recalculated and it was found to be similar to the value of the experimental value, which is equal to 24390 $cm^{-1}$ (410 nm). The value of $\nu_1$ represent the crystal field splitting value (10 Dq) indicating ligand field effect, the different ligand field parameters have been calculated using Tanabe-Sugano diagram for $d^8$ electronic configuration.

The results of Nickel (II) in choline chloride/urea ionic liquid at room temperature were close to those taken in aqueous solution, but it was not so similar or close to those in other ionic liquid although Nickel (II) was found to have Oh coordination, Table (3-8) show the results of Nickel (II) taken in aqueous solution and some other ionic liquids at different temperatures.

**Table (3-8):- Electronic spectra of complexes of Nickel (II) ions in aqueous solution and ionic liquids.**

| **Ionic liquid** | **Ni (II) formed complexes** | **Absorption bands ($cm^{-1}$)** | **Temp. ($^o$ C).** | **Suggested structure.** | **References** |
|---|---|---|---|---|---|
| Aqueous solution | $[Ni(H_2O)_6]^{2+}$ | $\nu_1$= 8500<br>$\nu_2$= 13800<br>$\nu_3$= 25300 | Room temperature | Oh | 64,65,66 |
| LiCl/KCl | $[NiCl_4]^{2-}$ | $\nu_1$= 8000<br>$\nu_2$= 14200<br>$\nu_3$= 15300 | 700-1000 | Distorted Td | 1 |
| CsCl | $[NiCl_4]^{2-}$ | $\nu_1$= 7500<br>$\nu_2$= 14000<br>$\nu_3$= 15700 | 864 | Td | 1 |
| Acetamide-$KNO_3$ | $[Ni(acetamide)_4 Cl_2]$ | $\nu_1$= 7500<br>$\nu_2$= 12500<br>$\nu_3$= 23200 | 90 | Oh | 67 |
| Butyramide-$NaNO_3$ | $[Ni(butyramide)_4 Cl_2]$ | $\nu_1$= 8100<br>$\nu_2$= 12600<br>$\nu_3$= 23300 | 90-140 | Oh | 67 |

The consistency of this interpretation can be calculated and a value obtained for the interelectronic repulsion parameter ‘Racah’ parameter $\grave{B}$, by fitting the ratio of $\nu_1/\nu_2$ on the appropriate Tanabe-Sugano diagram, Figure (3-26). $\grave{B}$ value was found to be equal to 833 $cm^{-1}$, the value of $\grave{B}$ was lower than that for free ion 1042 $cm^{-1}$, because of the less expansion of d-electron charge on complexation reduce the value of $\grave{B}$.

This phenomenon is known as nephelauxetic effect and is attributed to delocalization of the metal electrons over molecular orbitals that encompass not only the metal well. As a result of this delocalization or “cloud expanding” the average interelectronic repulsion is reduced and $\grave{B}$ (representing $\grave{B}$ in the complex) is smaller (66), but in choline chloride/ urea eutectic the value of $\grave{B}$ was higher than in aqueous solution as well as for free ion although the nickel was found to be also Oh coordinated in both cases, as showed in Table (3-8).

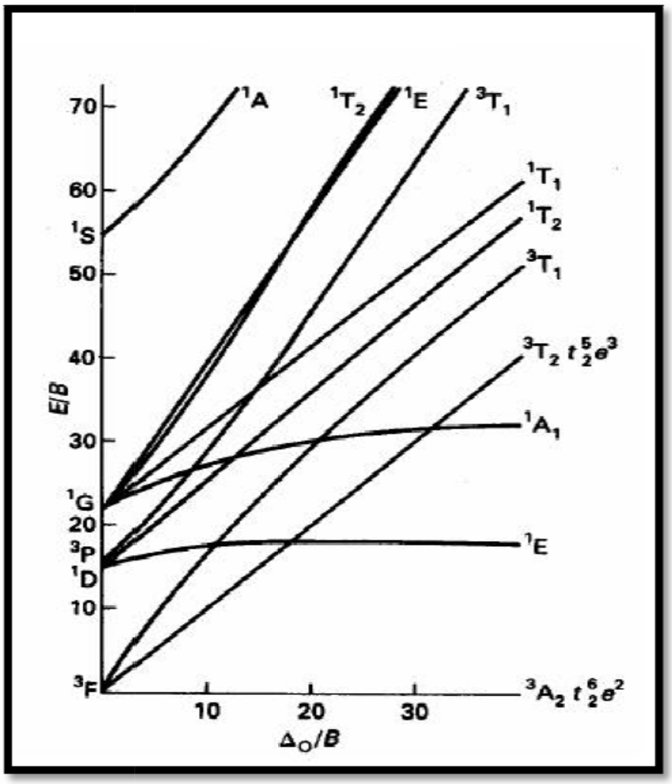

Fig. (3-26):- Tanabe-Sugano diagram for $d^8$ Octahedral electronic configuration.

Calculation using Jorgenson Rule for average environment suggested that Nickel (II) in choline chloride /urea eutectic is bonded with four urea molecules and two chlorides in octahedral coordination, where the chlorides were replaced with more stable urea molecule and according to the electrochemical series.

Nickel (II) in cholnie chloride/ urea was found to be more stable and symmetrical than in aqueous solution, as the absorbance in the choline chloride/ urea eutectic is smaller than in aqueous solution and the molar absoptivity is smaller see Table (3-10), from the absorbance we can suggest that the four urea molecules were bonded to Nickel (II) ions with in the plane of geometry and the chlorides were bonded with Nickel (II) with the z-axis, as in Figure (3-32).

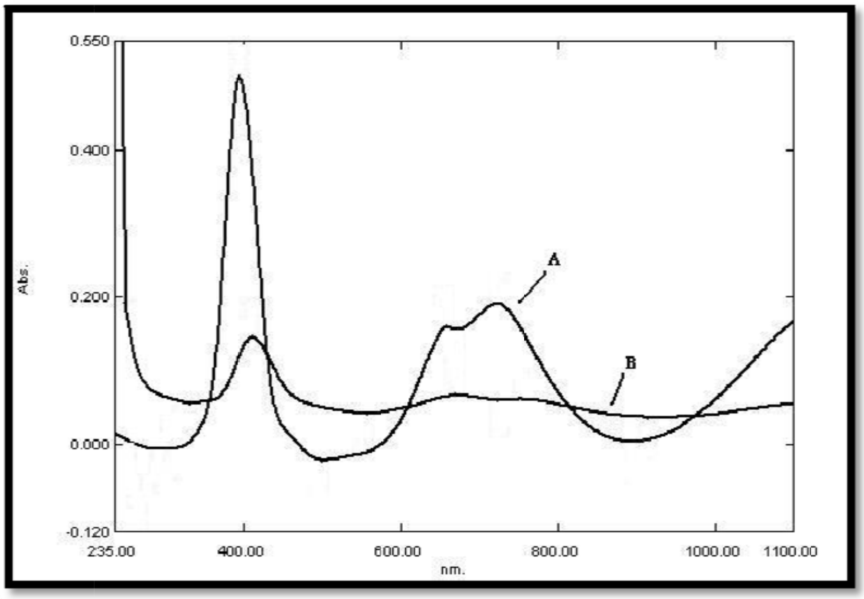

**Fig. (3-27):- The U.V.-Vis. spectra of $NiCl_2.6H_2O$ in aqueous solution of 0.1 M (curve A) and in choline chloride/ urea ionic liquid of ($1.1\times10^{-1}$m) at room temperature.**

### *3.2.4.2. Substitution Reaction with Ammonium Nitrate.*

Addition of ammonium nitrate ($NH_4NO_3$) to the solution of Nickel (II) chloride hexahydrate in choline chloride/ urea ionic liquid at room temperature did not showed visual changes neither in the color nor in the viscosity of the solution.

The ultraviolet visible spectrum of the Nickel (II) in this solution showed some changes in the shape and the position of the peaks and the absorbance as well as the molar absoptivity of the solution see Table (3-12), and the energies were shifted to lower energy bands and the appearance of new band between the second and third bands, as showed in Figure (3-28).

The ultraviolet visible spectrum of the solution showed four absorption bands, the first band at 9522 $cm^{-1}$ (1050 nm), second band at 13369 $cm^{-1}$ (748 nm)- 14771 $cm^{-1}$ (677 nm), the third at 18149 $cm^{-1}$ (551 nm) and the fourth 24390 $cm^{-1}$ (410 nm), indicating that the added nitrate to the solution made some interaction with Nickel (II) complex. The observed energy bands were shifted to lower energy bands.

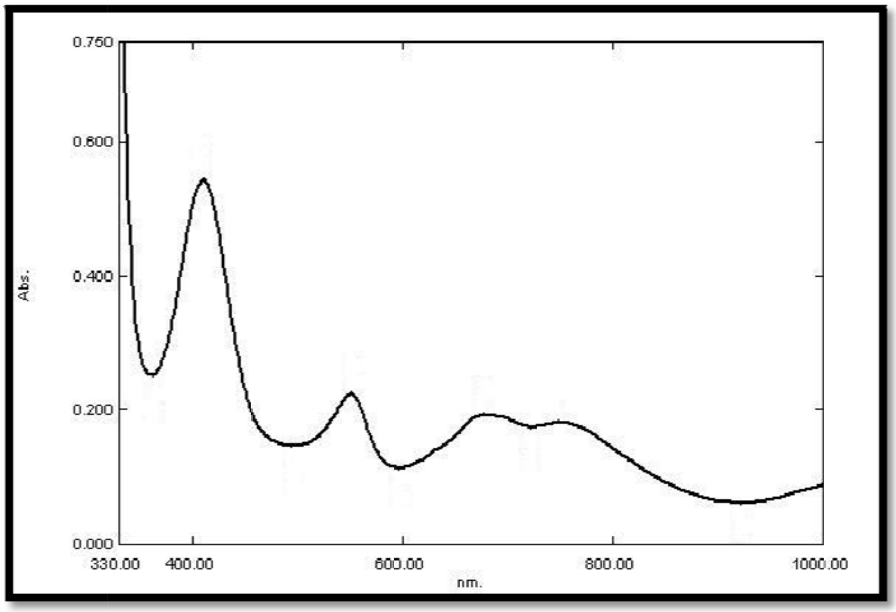

**Fig. (3-28):- The U.V.-Vis. spectrum of $NiCl_2.6H_2O$ in choline chloride/ urea with addition of $NH_4NO_3$ ionic liquid at room temperature.**

Using appropriate Orgel diagram Figure (1-17) the transition of Nickel in crystal field splitting were assigned as fallows, and showed in Figure (3-25).

$$^3A_2g\ (F) \rightarrow {}^3T_2g\ (F)\ (\nu_1) = 10Dq$$

$$^3A_2g\ (F) \rightarrow {}^3T_1g\ (F)\ (\nu_2)$$

$$^3A_2g\ (F) \rightarrow {}^3T_1g\ (P)\ (\nu_3)$$

While the forbidden transitions were from $^3A_2g$ ground state to singlet state of $^1Eg$, due to spin-orbital coupling that mixes the $^3T_1g$ (F) and $^1Eg$, and the second forbidden transition was from $^3A_2g$ to singlet $^1A_1g$ of the $^1G$ state.

Tanabe-Sugano diagram Figure (3-26) for $d^8$ electronic configuration was used to re-check the transitions and the value of ($\nu_1$) that refer to the crystal field splitting value (10 Dq).

Calculation using Jorgenson Rule for average environment suggested that Nickel (II) in choline chloride /urea eutectic with the addition of nitrate was bonded with four urea molecules and two nitrates in octahedral coordination, where the two chlorides were replaced with two nitrates, which according to the spectrochemical series this replacement is preferable because nitrates are stronger than chlorides but urea is more stable and stronger than nitrate. The absorbance of the solution of Ni (II) in choline chloride/ urea with addition of nitrate melt was higher than in pure melt. The solution of Nickel (II) in pure melt was less symmetrical as absorbance increased due to addition of $NO_3^-$ and the molar absorptivity of the Ni (II) in the pure melt was lower than in choline chloride/ urea with addition of $NH_4NO_3$ as in Table (3-10).

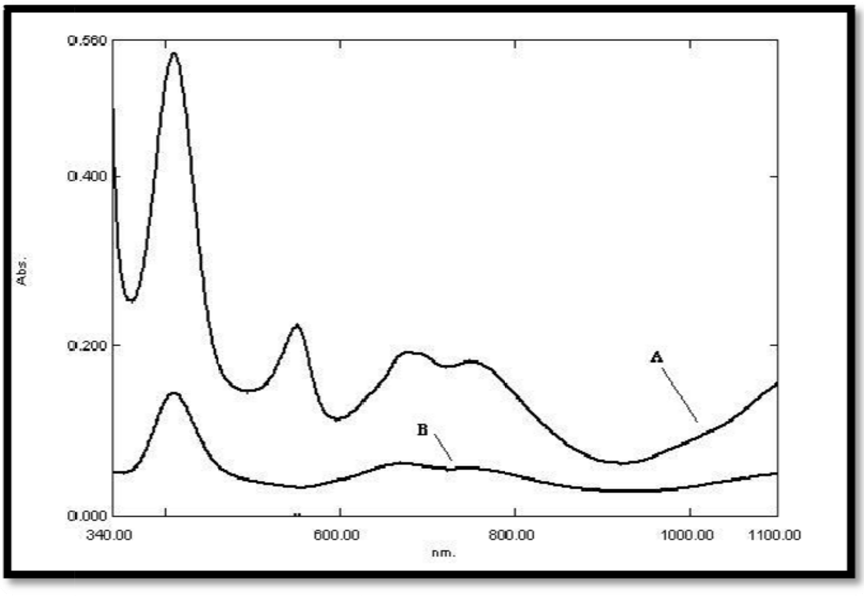

**Fig. (3-29):- The U.V.-Vis. spectra of $NiCl_2.6H_2O$ in choline chloride/urea with addition of $NH_4NO_3$ ionic liquid (curve A) and pure melt of choline chloride/ urea (curve B) at room temperature.**

A new transition band appeared in the ultraviolet visible spectra of the solution of Nickel (II) in choline chloride/ urea eutectic that pointed to the substitution reaction that took place between chlorides and added nitrates, as showed in Table

(3-9). This band was assigned to be in the value of 18149 cm$^{-1}$(551 nm), and had a probable a weak spin forbidden transition forbidden transition from triplet to singlet as [$^3A_2g$ ($^3P$) → $^1T_1g$ ($^1G$)], because it is the nearest forbidden transition before the third triplet to triplet allowed transition due to mixing of spin-orbital coupling.

The consistency of this interpretation can be calculated and a value obtained for the interelectronic repulsion parameter or Racah parameter $\grave{B}$, by fitting the ratio of $\nu_1/\nu_2$ on appropriate Tanabe-Sugano diagram, Figure (3-26). And it was found to be equal to 833 cm$^{-1}$, the value of $\grave{B}$ was lower than that for free ion 1042 cm$^{-1}$, and close to the value ***B*** obtained in the pure melt 1082 cm$^{-1}$, because of the less expansion of d-electron charge on complexation reduce the value of $\grave{B}$**.**

### 3.2.4.3. Nickel (II) chloride in Choline chloride/Malonic acid room temperature ionic liquid solution.

Nickel (II) chloride hexahydrate was found to be easily and completely soluble in choline chloride/ malonic acid ionic liquid at room temperature within the 72 hours in concentration of $1.2\times10^{-1}$m, producing a bluish green solution without visual changing in viscosity of the choline chloride/ malonic acid ionic liquid after the dissolution of the salt.

The ultraviolet visible spectrum of the solution showed two absorption maxima bands at 14184 cm$^{-1}$ (705 nm) and 15220 cm$^{-1}$ (657 nm) as show in Figure (3-30). The ultraviolet visible spectrum indicated that Nickel (II) in choline chloride/ malonic acid eutectic consisted of Td complex or distorted Oh complex of Nickel (II), but the Td complex is more preferable because it is closer to the value of absorbance bands in aqueous solution of Nickel (II) chloride with high concentration of chloride ions which indicates tetrahedral coordination as shown in Table (3-9).

The transitions of the Nickel (II) in choline chloride/ malonic acid melt were assigned as fallow:

$$^3T_1 \rightarrow {}^3T_2\ (F)\ (\nu_1)$$

$$^3T_1 \rightarrow {}^3A_2\ (F)\ (\nu_2)$$

$$^3T_1 \rightarrow {}^3T_1\ (P)\ (\nu_3)$$

And the appeared band in the spectra was assigned to be the third allowed transition that occurs in the visible region with a splitting due to the forbidden transition from $^3T_1$ ground state to singlet state of $^1D$. While the first and second transitions were in infrared and near infrared spectra region respectively.

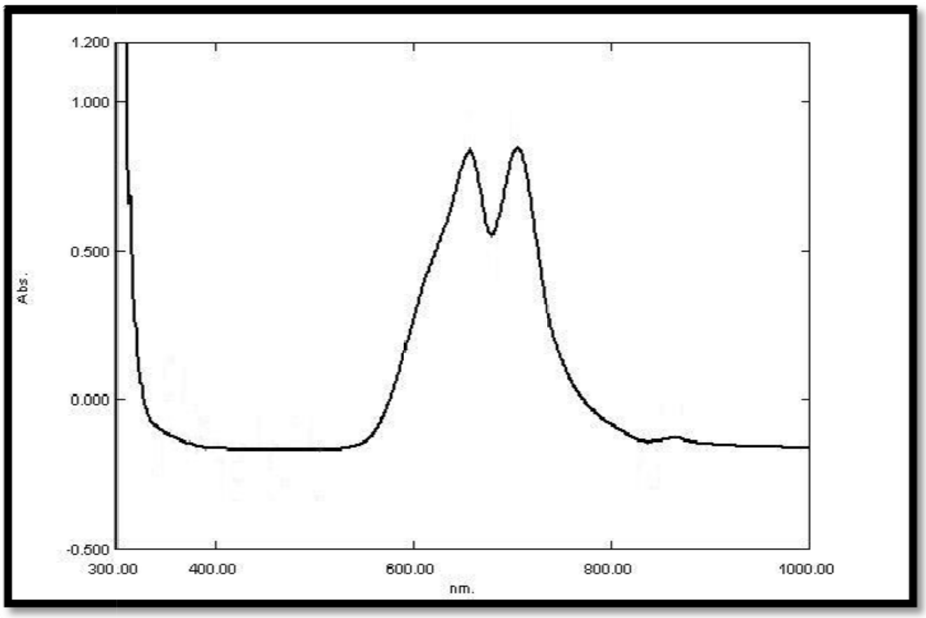

**Fig. (3-30):- The U.V.-Vis. Spectrum of $NiCl_2.6H_2O$ of ($1.2\times10^{-1}$m) in choline chloride/ malonic acid ionic liquid at room temperature.**

Nickel (II) formed Td complex in choline chloride/ malonic acid eutectic, and when referred to Tanabe-Sugano diagram of $d^2$ Oh electronic configuration, and Orgel diagram $d^8$ Td and $d^2$ Oh have the same transitions as in Figure (3-31), The most likely suggestion is that Nickel (II) formed a Tdcoordination complex in choline chloride/malonic acid eutectic.

Suggestion of the average environment of Nickel (II) in choline chloride/ malonic acid was based on the spectra of the solution, where Nickel (II) was bonded with one malonic acid molecule and two chlorides in Td coordination, where the two chlorides were replaced with malonic acid molecule, which according to the electrochemical series this replacement is preferable because malonic acid is stronger than chlorides. The observed bands are of the third transition with a split is similar to that resultant in aqueous solution of $NiCl_2.6H_2O$ containing high concentration of chloride ions as in Table (3-9).

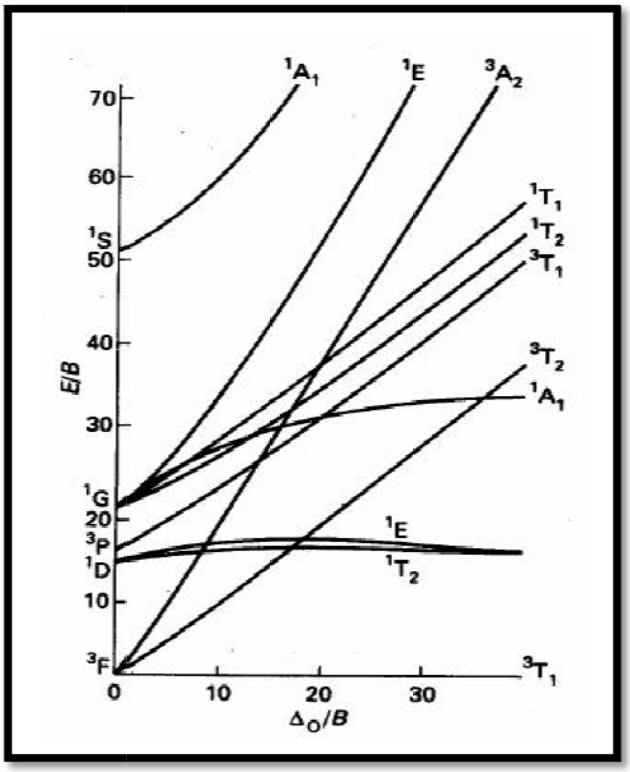

**Fig. (3-31):- Tanabe-Sugano diagram for $d^8$ tetrahedral electronic configuration.**

The absorbance of the solution is higher than the solution of Nickel (II) in choline chloride/urea eutectic before and after the addition of nitrate, which indicate that the Nickel (II) formed complexes in choline chloride/urea eutectic solutions more stable and more symmetrical and deferens in geometry than the complex formed in choline chloride/malonic acid eutectic, that considered to be less symmetrical and less stable complex. The absorbance and molar absoptivity were smaller in choline chloride/ urea melt than in choline chloride/ malonic acid melt. The tetrahedral complex of Nickel (II) $d^8$ gives a term symbol of ($^3F$), and the transitions assigned as fallows:-

$$(\nu_1) = {}^3T_1 \rightarrow {}^3T_2\ (F),\ (\nu_2) = {}^3T_1 \rightarrow {}^3A_2\ (F),\ (\nu_3) = {}^3T_1 \rightarrow {}^3T_1\ (P)$$

The consistency of this interpretation can be calculated and a value was obtained for the interelectronic repulsion parameter or Racah parameter $\grave{B}$, by fitting the ratio of $\nu_1/\nu_2$ from the appropriate Tanabe-Sugano diagram for $d^8$ tetrahedral configuration Figure (3-31), and it was found to be equal to 1030 $cm^{-1}$, the value of $\grave{B}$ was smaller than that for free ion (1042 $cm^{-1}$) and higher for that in choline chloride/ urea ionic liquid (833 $cm^{-1}$), because in tetrahedral complexes the expansion of d-electron charge is less than in octahedral complexes so the value of $\grave{B}$ was reduced. Table (3-9) shows the results of Nickel (II) in choline chloride/ urea and choline chloride/ malonic acid ionic liquids at room temperature together with those in aqueous solution.

As indicated in the Table (3-10), the absorption of Ni (II) ion had extended to higher energy in choline chloride/ urea ionic liquid solvent in compared with those observed in pure water. This is not unexpected, as urea is known to have stronger field than water molecules and they are available large concentration in the melt. However, when nitrate was added to Ni (II) solution in the previous melt solvent, the absorption shifted even to higher energy than in pure melt. This is contrast to the stronger field of urea than the nitrate as known in the spectrochemical series. Therefore, the coordination of urea in pure melt with the metal ion indicated that urea was already coordinated in the melt structure with other components, thereby offering a reduced strength when coordinated with metal ions. Chloride ions available in the melt compositions which are even weaker than urea and nitrate ions in free state would play a negligible role in such coordination.

$[I^- < Br^- < S^{2-} < SCN^- \sim Cl^- < NO_3^- < N_3^- < F^- < CO(NH_2)_2 < OH^- \sim ONO^- < CH_2(COO)_2^{2-} \approx C_2O_4^{2-} < H_2O < CN^- \approx CO]$.

Nickel (II) in the choline chloride/ urea and choline chloride/ malonic acid ionic liquids solutions did not show any visual changes neither in color nor in viscosity, and did not showed any spectral changes in the ultraviolet visible spectra of the solutions after 40 days, which indicates stable complexes of Nickel (II). Figure (3-32) showed the suggested structures for Nickel (II) in the prepared ionic liquids.

**Table (3-9):- Electronic spectra of complexes of Nickel (II) ion in aqueous solution and various ionic liquids solution.**

| Solution | Solution color | Transitions (cm$^{-1}$) | $\grave{B}$ (cm$^{-1}$) | 10 Dq (cm$^{-1}$) | Suggested Structure | References |
|---|---|---|---|---|---|---|
| Aqueous solution | Pale green | $\nu_1$= 8500<br>$\nu_2$= 13800<br>$\nu_3$= 25300 | 1042 | 8500 | Oh<br>$[Ni(H_2O)]^{2+}$ | 65 |
| Aqueous solution with high conc. of chloride ions | Yellow | $\nu_1$= -<br>$\nu_2$= 7549<br>$\nu_3$=(14250-15240) | 1030 | 4070 | Td<br>$[NiCl_4]^{2-}$ | 66 |
| Choline chloride/ Urea | Pale green | $\nu_1$= 9522<br>$\nu_2$= (13405-14948)<br>$\nu_3$= 24390 | 833 | 10000 | Oh<br>$[Ni(NH_2CONH_2)_4Cl_2]$ | Present work |
| Choline chloride/ Urea +$NH_4NO_3$ | Pale green | $\nu_1$= 9522<br>$\nu_2$= (13369-14771)<br>$\nu_3$= 24390 | 833 | 10000 | Oh<br>$[Ni(NH_2CONH_2)_4(NO_3)_2]$ | Present work |
| Choline chloride/Malonic acid | Bluish green | $\nu_1$= -<br>$\nu_2$= -<br>$\nu_{3cal.}$=(14184-15220) | 1030 | - | Td<br>$[Ni((CH_2COOH)_2)Cl_2]^{2-}$ | Present work |

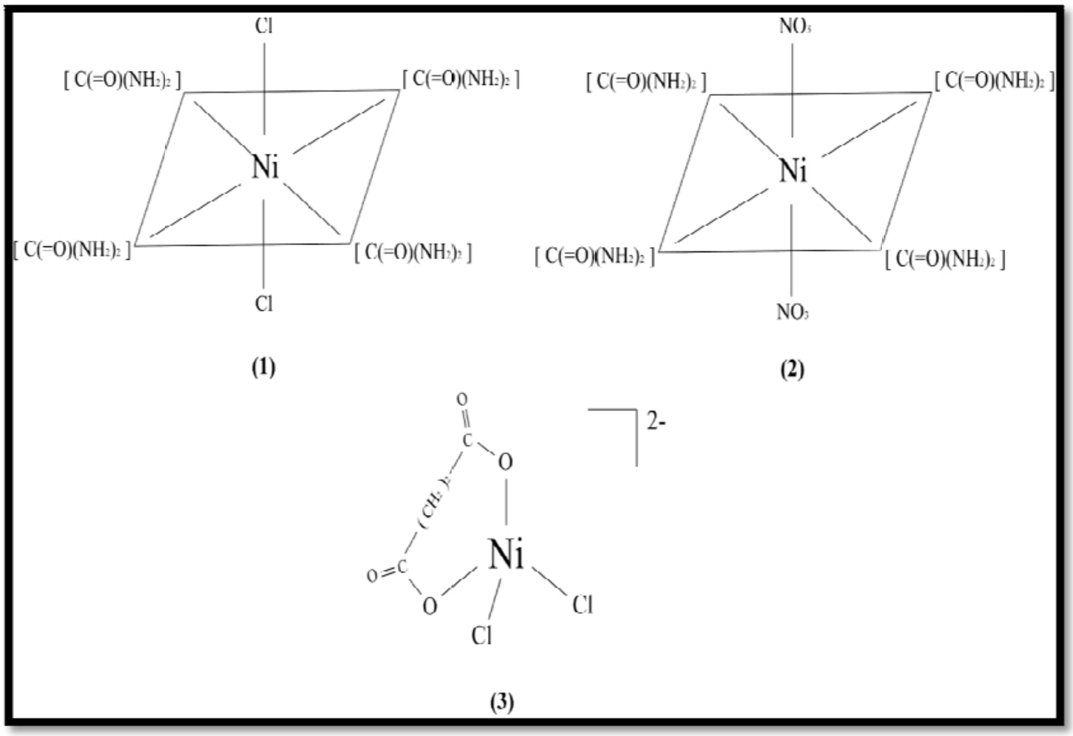

**Fig. (3-32):- Suggested structures for Nickel (II) ions in (1) choline chloride/ urea ionic liquid, (2) choline chloride/urea ionic liquid with added salt of $NH_4NO_3$ and (3) choline chloride/ malonic acid ionic liquid all formed at room temperature.**

**Table (3-10):- The molar absorptivity of Nickel (II) ions in ionic liquid based on choline chloride.**

| Ionic Liquids | Concentration (M) [mol/l] | Concentration (m) [mol/Kg] | Absorbance | Molar absoptivity (ε) [l $cm^{-1}mol^{-1}$] |
|---|---|---|---|---|
| Choline chloride/ Urea | 0.1 M | $1.1\times10^{-1}$ m | 0.054 | 0.54 |
| Choline chloride/ Urea + $NH_4NO_3$ | 0.1 M | $1.1\times10^{-1}$ m | 0.178 | 1.78 |
| Choline chloride/ Malonic acid | 0.1 M | $1.2\times10^{-1}$ m | 0.844 | 8.44 |

### 3.2.5. Spectroscopic investigation of Copper (II) chloride solutions.

Copper (II) compounds in general form blue or green colored solutions, raised from single broad absorption band in the region (11000 -16000) cm$^{-1}$. The d$^9$ ion is characterized by large distortion from octahedral symmetry and the bond is unsymmetrical, being the result of a number of transitions, which are by no means easy to assign unambiguously. The free ion ground $^2$D term is expected to split in a crystal field in the same way as the term$^5$D of the d$^4$ ion and a similar interpretation of the spectra is like wise expected(64) and according to the following Figure (3-33):-

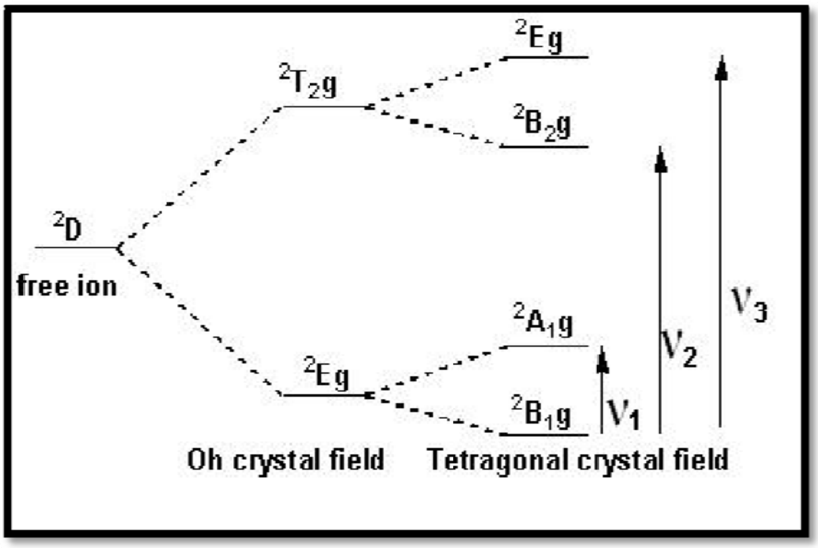

**Fig. (3-33):- Crystal field splitting for $^2$D configuration.**

#### 3.2.5.1. Copper (II) chloride in Choline chloride/Urea room temperature ionic liquid solution.

Copper (II) chloride dihydrate was found to be completely and easily soluble in choline chloride/ urea ionic liquid at room temperature after a standing time of 72 hours in a concentration of $7.7\times10^{-2}$m, producing a blue colored solution without visual changing in viscosity of the choline chloride/ urea ionic liquid after the dissolution of the salt.

The ultraviolet visible spectrum of the solution showed one broad absorption maxima for Cu (II) at 13055 $cm^{-1}$ (766 nm), as showed in Figure (3-34). The transition was assigned as in Figure (3-33) the only transition in $d^9$ of $^2D$ term symbol with abroad absorption band due to distortion of the Oh of Cu (II).

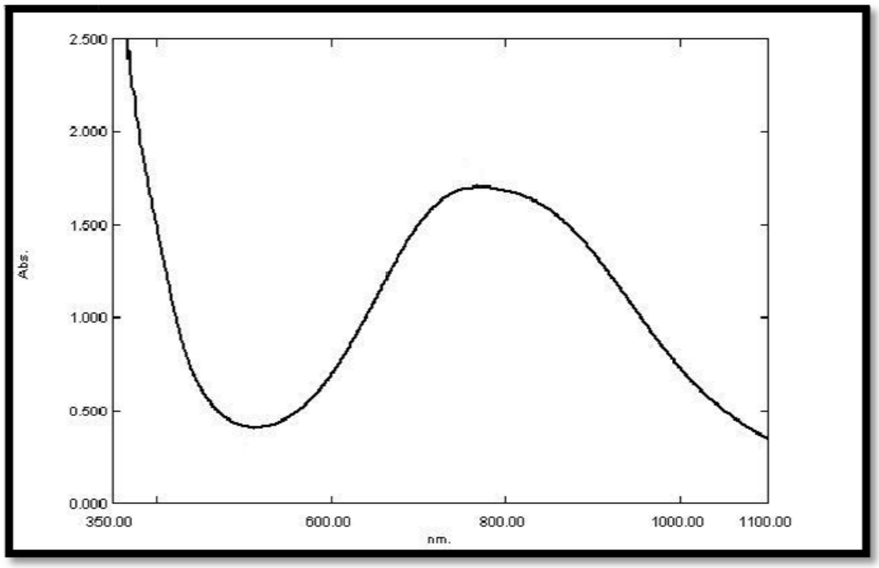

**Fig. (3-34):- The U.V.-Vis. Spectrum of $CuCl_2.2H_2O$ of ($7.7\times10^{-2}$m) in choline chloride/urea ionic liquid at room temperature.**

The color of the solution was similar to the color of the aqueous solution of the same used salt for Cu (II) which indicates an octahedral coordination of Copper (II). Because there was no Tanabe-Sugano diagram for the $d^9$ electronic transition, using Orgel diagram Figure (1-16) for $d^9$ octahedral electronic configuration to assign the value of 10 Dq, unfortunately, this is more difficult because of the overlap of bands. In the present work, the blue solution of Copper (II) complex showed a broad band at (13055 $cm^{-1}$) which can be assigned to $^2Eg\rightarrow^2T_2g$ transitions.

Previous studies of Copper (II) in ionic liquids and aqueous solution showed that Copper (II) behaved differently from one solution to other, Table (3-11) showed the results of Copper (II) in various solvents.

Copper (II) has $d^9$ electronic configuration, it was suggested that the environment of the ligands bonded with $Cu^{2+}$ are of mixed ligands molecules of four urea and two nitrates in Oh geometry.

**Table (3-11):- The ultraviolet visible spectroscopic behavior of Copper (II) in various solvents.**

| Solvents | Solution color | Absorption Band ($cm^{-1}$) | Transition | Suggested structure | References |
|---|---|---|---|---|---|
| Aqueous solution | Pale blue | ν = (11000-13000) | $^2Eg \rightarrow {}^2T_2g$ | Oh<br>$[Cu(H_2O)_6]^{2+}$ | 64,65 |
| LiCl/KCl | - | ν = 9500 | $^2B_1g \rightarrow {}^2B_2g$<br>$^2B_1g \rightarrow {}^2Eg$ | Distorted Oh or Td | 1 |
| $AlCl_3$- 1,methyl 3ethylimidazoluim chloride | - | ν =34139<br>ν =24570 | $^2B_1g \rightarrow {}^2B_2g$<br>$^2B_1g \rightarrow {}^2Eg$ | Td<br>$[CuCl_4]^{2-}$ | 72 |
| Acetamide-$KNO_3$ | Blue-green | $ν_1$ = 11000 (shoulder)<br>$ν_2$ = 14000<br>$ν_3$ = 20700 | $^2Eg \rightarrow {}^2T_2g$ | Oh | 67 |
| Choline chloride/ urea | Blue | $ν_1$ =13055 | $^2Eg \rightarrow {}^2T_2g$ | Oh<br>$[Cu(CO(NH_2)_2)_6]^{2+}$ | Present work |

The Cu (II) solution in choline chloride/ urea eutectic did not show any visual changes in color or viscosity as well as in the ultraviolet spectra after standing time 40 days, which means that Copper (II) already reached equilibrium and formed a stable complex with urea molecules, in octahedral coordination.

### *3.2.5.2. Substitution Reaction with Ammonium Nitrate.*

Addition of ammonium nitrate ($NH_4NO_3$) to the solution of Cu (II) in choline chloride/ urea eutectic at room temperature did not show any visual changes neither in color nor in viscosity of the solution, but it showed some changes in the ultraviolet visible spectrum of the Copper (II) ions, as the absorbance and the position of the peak had changed. The band was shifted to lower energy band at average of 12903 $cm^{-1}$(775nm) and a new band appeared on the edge of high energy level near charge transfer at 25445.3 $cm^{-1}$ (393 nm) indicating the interaction between added nitrate and Cu (II) ion, as shown in Figure (3-35).

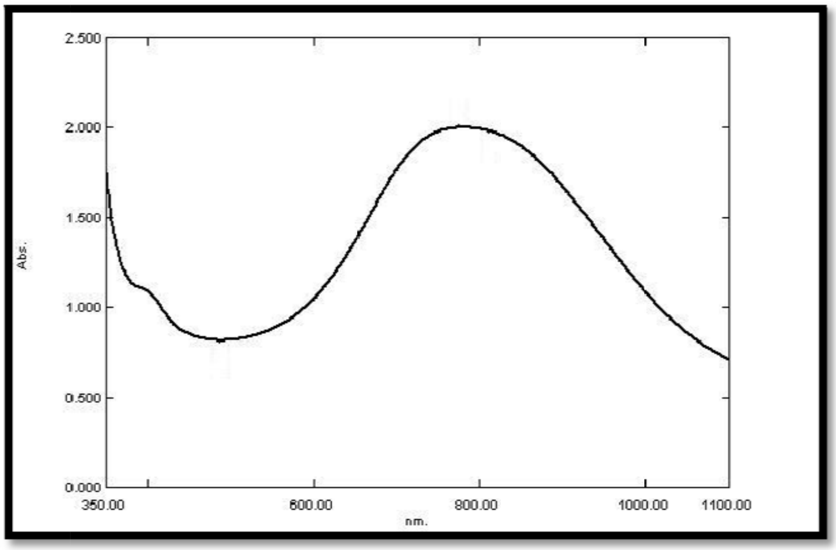

**Fig. (3-35):- The U.V.-Vis. spectrum of $CuCl_2.2H_2O$ in choline chloride/ urea ionic liquid with addition of $NH_4NO_3$ at room temperature.**

The absorbance of the solution when nitrate was added showed higher absorbance than in pure melt solution which indicates that the added nitrate had interacted Copper (II). The new absorption band near the edge of high charge transfer band. The $d^9$ configuration makes Cu (II) subject to Jahn-Teller distortion in placed in an environment of cubic (i.e. regular octahedral) symmetry, and this has a profound effect on all its stereochemistry. When six coordinate “octahedron” is severely distorted, the typical distortion is an elongation along one 4-fold axis, so that there is a planar array of four short Cu-L bonds and two trans long-ones.

Copper (II) is ionic state with $d^9$ electronic configuration, it could be suggested that the environment of the ligands bonded with $Cu^{2+}$ are of mixed ligands molecules of four urea and two nitrates in octahedral geometry. The prepared solution of Cu (II) chloride in choline chloride /urea room temperature ionic liquid was stable in the melt after 40 days as there were no changes in its spectra when examined by ultraviolet visible spectroscopy, which means that the complex reached equilibrium. The replacement took place between two urea molecules with two nitrates in octahedral coordination that tends to be distorted octahedral coordination. And as the absorbance and molar absorptivity increased in this solution from the pure melt solution see Table (3-13), the complex became less symmetrical and unstable, as shown in Figure (3-36), Table (3-12) showed the results of the Copper (II) in ionic liquids based on choline chloride.

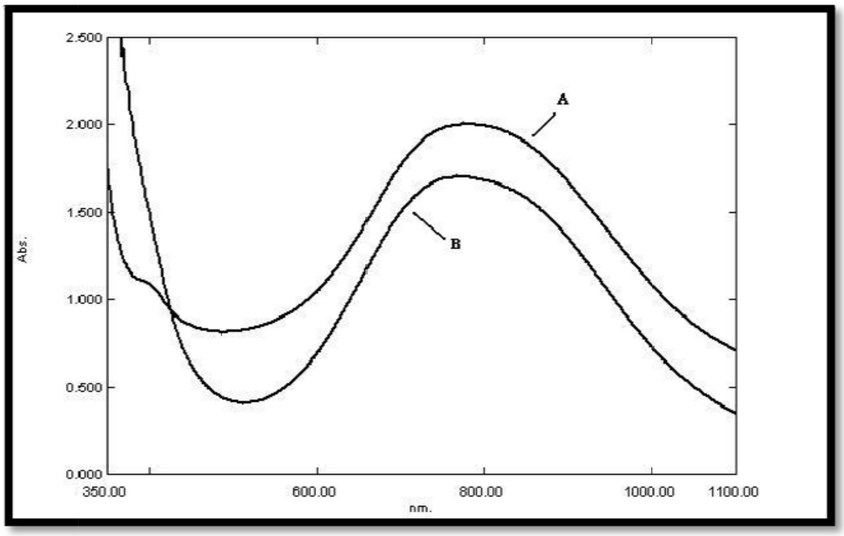

**Fig. (3-36):- The U.V.-Vis. spectra of $CuCl_2.6H_2O$ in choline chloride/ urea with addition of $NH_4NO_3$ ionic liquid at room temperature (curve A), and in pure melt (curve B).**

### *3.2.5.3. Copper (II) chloride in Choline chloride/Malonic acid room temperature ionic liquid solution.*

Copper (II) chloride dihydrate was found to be easily and completely soluble in choline chloride/ malonic acid ionic liquid at room temperature after standing time of 72 hours in concentration of $8.03\times10^{-2}$m, producing a deep yellow solution without visual changing in viscosity of pure choline chloride/ malonic acid ionic liquid.

The ultraviolet visible spectrum of the solution showed one absorption maxima broad band was shifted to lower energy at 9208 $cm^{-1}$ (1086 nm), as shown in Figure (3-37), The high absorbance of solution of Copper (II) in choline chloride/ malonic acid eutectic might indicate a large distortion in its geometry than in choline chloride/ urea alone or with added nitrate although the concentration of Cu (II) ions was the same in all solutions.

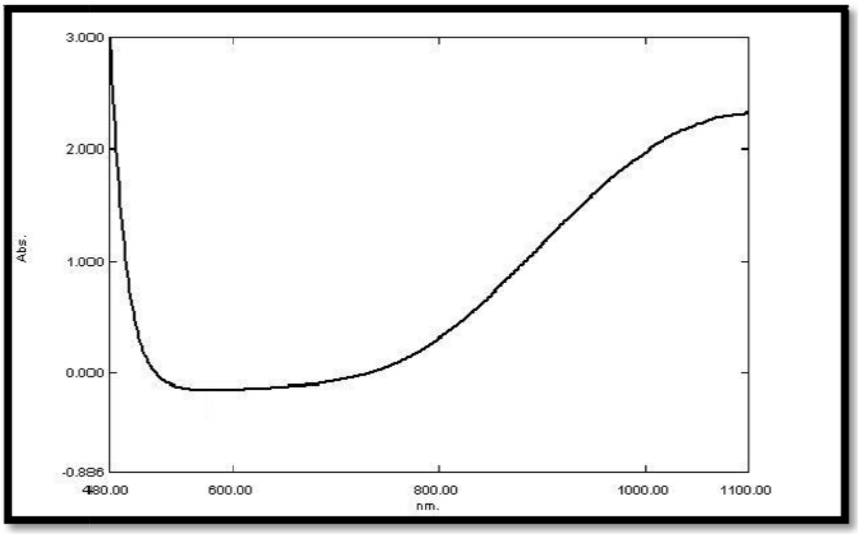

**Fig. (3-37):- The U.V.-Vis. spectrum of $CuCl_2.6H_2O$ of ($8.03\times10^{-2}$m) in choline chloride/ malonic acid ionic liquid at room temperature.**

The results of Copper (II) in choline chloride/ malonic acid eutectic is similar to those taken for Copper (II) in molten chloride of LiCl/KCl at 400°C which showed one absorption maxima at 9500 $cm^{-1}$, where Copper (II) prosed to be in distorted Oh to Td coordination. Table (3-12) showed all the results taken for Cu (II) in choline chloride based prepared ionic liquids.

Copper (II) is ionic state of $d^9$ electronic configuration, it could be suggested that the environment of the ligands bonded with $Cu^{2+}$ are of mixed ligands molecules of one malonic acid and two chlorides in distorted Oh or Td geometry.

Copper (II) in choline chloride/ malonic acid was bonded with two chlorides and one malonic acid molecule. This replacement of two chlorides with malonic acid molecule is preferable because according to the spectrochemical series malonic acid is stronger than chloride as ligand.

The solution of Copper (II) in choline chloride/ malonic acidionic liquid did not show any visual changes in the color or viscosity as well as in the electronic spectra after it stand for 40 days, which means that Copper (II) in choline chloride/ malonic acid eutectic formed stable complex.

**Table (3-12):- Electronic spectra of complexes of Copper (II) ions in choline based ionic liquids at room temperature.**

| Solution | Solution color | Absorption band ($cm^{-1}$) | Transitions | Suggested structure | References |
|---|---|---|---|---|---|
| Choline chloride/ urea | Blue | ν = 13055 | $^2Eg \rightarrow {}^2T_2g$ | Oh<br>$[Cu(CO(NH_2)_6]^{2+}$ | Present work |
| Choline chloride/ urea +$NH_4NO_3$ | Blue | ν =12903 | $^2Eg \rightarrow {}^2T_2g$ | Oh<br>$[Cu(CO(NH_2)_4(NO_3)_2]$ | Present work |
| Choline chloride/ malonic acid | Yellow | ν =9208 | $^2B_1 \rightarrow {}^2B_2$<br>$^2B_1 \rightarrow {}^2E$ | Distorted Oh or Td<br>$[Cu((CH_2COOH)_2)Cl_2]^{2-}$ | Present work |

**Table (3-13):- The molar absorptivity of Copper (II) ions in ionic liquid based on choline chloride.**

| Ionic Liquids | Concentration (M) [mol/l] | Concentration (m) [mol/Kg] | Absorbance | Molar absoptivity (ε) [$l\ cm^{-1}mol^{-1}$] |
|---|---|---|---|---|
| Choline chloride/ Urea | 0.1 M | $7.7\times10^{-2}$ m | 1.702 | 17.02 |
| Choline chloride/ Urea + $NH_4NO_3$ | 0.1 M | $7.7\times10^{-2}$ m | 2.005 | 20.02 |
| Choline chloride/ Malonic acid | 0.1 M | $8.03\times10^{-2}$ m | 2.312 | 23.12 |

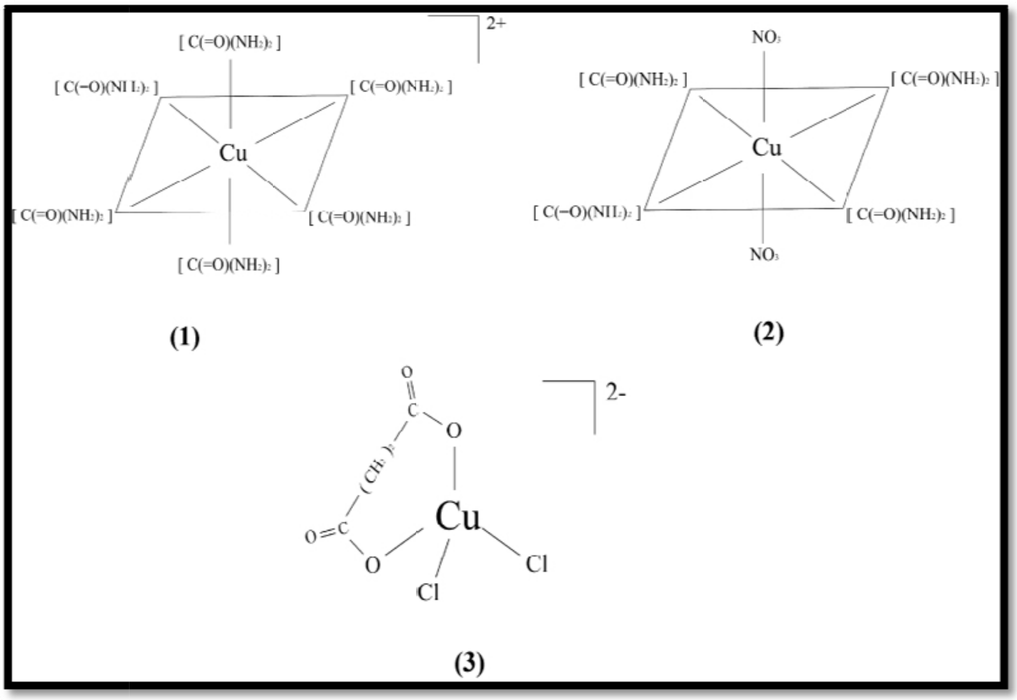

**Fig. (3-38):- Suggested structures for Copper (II) ions in (1) choline chloride/ urea ionic liquid, (2) choline chloride/urea ionic liquid with added salt of $NH_4NO_3$ and (3) choline chloride/malonic acid ionic liquid all formed at room temperature.**

## 3.3. Conclusion.

1) The prepared room temperature ionic liquids was based on quaternary ammonium salt (choline chloride) that was mixed with hydrogen bond donor molecules like urea $[CO(NH_2)_2]$ in mole ratio of 1:2, and malonic acid $[(CH_2COOH)_2]$ in mole ratio of 1:1. Showed different physical properties from other non aqueous solvent.
2) Those ionic liquids have been used as non-aqueous solvents to study the behavior of some first row transition metal compounds. The interaction that took place between transition metal ions and the possible ligands in each solution gave complexes comparable geometry.
3) All the prepared solutions of the transition metal ions were colored solution, while the prepared ionic liquids were colorless.
4) The new formed complexes solution of each transition metal ion in each ionic liquid was analyzed by ultraviolet visible spectroscopy, and the spectra of the solutions were studied.
5) The prepared ionic liquids showed different ligands field strength properties, because ionic liquids contents had molten properties.
6) The ligand field calculated showed different strength (according to the 10 Dq value), different Racah parameter ($\grave{B}$) and different electron- repulsion parameter ($\beta$), which refers to different ionic character between the metal and donor atoms of the ligands.
7) The infrared spectroscopy of the solutions of transition metals in ionic liquids was difficult to establish because the ionic liquids were insoluble in the solvents were used in the infrared spectroscopy instrument and it was soluble only in absolute ethanol, as well as it was not able to use the ionic liquids without dilution because the solution will be over saturated for the IR chart and the peaks will not be clear.

8) The conductivity of the transition metals in ionic liquids solutions was also difficult to determine because the ionic liquids solution is conductance himself, and it was hard to extract the formed complex of transition metal with ionic liquids from its solution with the known extraction method, to determine the conductivity of the formed complex.
9) The magnetic susceptibility of transition metal in ionic liquids solutions was difficult to calculate because the solutions were thick and hard to force into the magnetic susceptibility tubes with injection because of the formation of air bobble in the bottom on the tube that couldn't be gotten red of it by shaking or worming the tube.

## *3.4. Suggestion for future work.*

The following suggestions can be postulated to ensure completion of the study in this work.

1) Preparation of another set of transition metal complexes using other transition metal ions such as second or third rows of transition metal using the same prepared ionic liquids.
2) Preparation of another set of transition metal complexes using other reported room temperature ionic liquids or newly prepared ionic liquids.
3) Preparation of the same solutions with the same concentration of transition metal ions and by using the same analyzing instrument but in various temperature ranges.
4) Preparation of the same solutions of transition metal ions using different concentration of the used transition metal compounds.
5) To complete the measurements and identification of the new formed complexes of transition metal ions by using infrared spectroscopy, magnetic susceptibility measurements and x-ray diffraction.
6) Find a suitable method to isolate the prepared complexes of transition metal ions from their ionic liquid solution.

# References

1. J. J. Lagowski, *“The chemistry of non-aqueous solvents”*, vol. 5B**,** New York, **1978**.
2. J. E. Huheey, *“Inorganic Chemistry, Principles and reactivity”*, Harper, New York, **1972**.
3. Bruce N. Hoglund, *“What is Molten Salts and Its Technology”*, **1997**.
4. Alvin Martin Weinberg, *“The first Nuclear Era; the life and times of a technological fixer”*, page 198-200, **1994**.
5. H. G. Mac Pherson, “*The Molten Salts Adventure”*, vol. 90, page 374-380, **1985**.
6. Tames A. Lane, H.G. Mac Pherson and Frank Maslan, *“Fluid Fuel Reactor”*, **1958**.
7. R. C. Briant et al., *“Nuclear Science and Engineering”*, vol. 2, no. 6, page 795-853, **1957**.
8. Temma Vickery, *“Green chemistry”*, University of Bristol, **2001**.
9. Anastas P. T., Warner J. C., *“Green Chemistry Theory and Practice”*, **1999**.
10. Cann M.C. and Connelly M.E., *“Real world cases in green chemistry”*; American Chemical Society, **2000**.
11. G.P. Smith, A.S. Dworkin, R.M. Pabni, and S.P. Zingg; *J. Am. Chem. Soc.*, vol. 3, page 525, **1989**.
12. Di chio Donata, Fusco Marida, Halo Migen, *“Ionic liquids”*, University of Torino, **2004**.
13. Martyn J. Earle and Kenneth R. Seddon, *“Ionic liquid, Green solvents for the future.”*; Pure Appl. Chem., vol. 72 , no. 7, page 1391-1398 , **2000**.
14. M. Freemantle; Chem. Eng. News, vol. 76, (30th march) page 32-37, **1998**.
15. T. Welton; Chem. Rev., vol. 99, page 2071-2083, **1999**.
16. J. Holbrey and K.R. Seddon; Clean Prod. Proc., vol. 1, page 223- 236, **1999**.
17. K.R. Seddon; J. Chem. Tech. Biotech., vol. 68, page 351-356, **1997**.
18. H. L. Chem, V. R. Kock, L. L. Miller, R.A. Osteryoung; Jor. Am. Chem. Soc., vol. 97, page 3264- 3267, **1975**.

19. P. Walden; Bull. Acad. Imper; Sci., (St. Petersburg), page 1800, **1992**.
20. J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey; Inorg. Chem., vol. 21, page 1236- 1264, **1982**.
21. K.R. Seddon., *"In molten salt forum; proceedings of 5th international conference on molten salt chemistry and technology"*, vol. 5-6, H. Wendt ed., page 53- 62, **1998**.
22. C.L. Hussey, T.B. Scheffler, J.S. Wilker, A.A. Fannin; J. Electro-Chem. Soc., vol. 133, page 1389-1391, **1986**.
23. J.D. Holbrey and K.R. Seddon; J. Chem. Soc., Dalton Truns, page 2133-2139, **1999**.
24. C.M. Gordon, T.D. Hollrey, A.R. Kennedy, K.R. Seddon, J. Mater ; Chem., vol. 8, page 2627-2636, **1998**.
25. C. Hardacre, K.R. Seddon, J. McGrath, *"Room temperature Ionic liquids"*, Queens University Belfast, **2000**.
26. Hiroyuk; Ohno, *"Electro Chemical Aspects of Ionic liquids, chapter one: - Importance and possibility of Ionic liquids"*, John Wiley and Sons, Inc., 2005.
27. John S. Wilakes, "A short history of liquids– from molten salts to neoteric solvents"; Green Chemistry, The Royal Society of Chemistry, vol. 4, page 73-80, **2002**.
28. J.L. Copland, *"Transport properties in Ionic liquid"*, Gordon and Breach science publishers, New York, **1974**.
29. C. L. Hussey, "The Electro Chemistry of room-temperature haloaluminate molten salts", (ed.) G. Mamantov and A.I. Popov, *"Chemistry of non-aqueous solutions"*, VCH publisher Inc. New York, page 227- 276, **1994**.
30. R.T. Carlinand, J.S. Wlikes, *"Chemistry and speciotion in room-temperature chloroaluminate molten salts"*, (ed.) G. Mamantov and A.I. Popov, *"Chemistry of non-aqueous solutions"*, VCH publisher Inc., New York, page 277-307, **1994**.

31. R.T. Adams, Ger. Pat., 3347947, 1967; G.P. Hugen and D.T. Hung, Br. Pat. 2246788, 1992; E. Ceausescu, M. Corciovei, T. Sarbu, A. Schramm and D. Stadermann, Plaste Kautsch., vol. 35, page 378, **1988**.
32. Jairton Dupont, Crestina S. Consorti and John Spencer, *"Room Temperature Molten Salts: Neoteric "Green" Solvents for Chemical Reactions and Processes"*; J. Braz. Chem. Soc., vol. 2, no. 4, page 337- 344, **2000**.
33. Bolm C., Beckmann O., Dabard O. A. G.; Angew. Chem., vol. 3, page 957, **1999**; Angew. Chem. Int. ed., vol. 38, page 907, **1999**.
34. Metzger J.O.; Angew. Chem., vol.110, page 3141, **1998**; Angew. Chem. Int. ed., vol. 37, page 2975, **1998**.
35. Jessop, P.G. I. Kariya, T. Noyori R.; Chem. Rev., vol. 99, page 475, **1999**.
36. Walden, P. Bull, Acud. Imper. Sco. (St. Petersburg), page 405. C.A.1914, vol. 8, page 2291, **1914**.
37. C.L. Hussey, in *"Advances in molten salts chemistry"*; Mamantov G.; Mamantov C. (eds.); Elsevier , New York , vol. 3, page 185, **1983**.
38. Suarez, P. A. Z., Einloft S., Dullius, J.E.L., de Souza, R.F.; Dipont. J. Tor. Chem. phys., vol. 95, Page 1626, **1998**.
39. Frank Endres and Sherif Zien El Abedin, *"Air and water stable ionic liquid in physical chemistry"*; Phys. Chem. Chem. Phys., vol. 8, no. 18, Page 2101-2116, **2006**.
40. H.L. Chum, V.R. Koch, L.L. Miller and R.A. Osteryoung.; J. Am. Chem. Soc., vol. 97, Page 3264, **1975**.
41. J. Robinson and R.A. Osteryoung.; J. Am. Chem. Soc., vol. 101, Page 323, **1979**.
42. J.S. Wilkes, J.A. Levisky, R.A. Wilson and C.L. Hussey; Inorg. Chem., vol. 22, page 2099, **1983**.
43. T.B. Scheeffler, C.L. Hussey, K.R. Seddon, C.M. Kearad, P.D. Armitage; Inorg. Chem., vol. 22, Page 2099, **1983**.

44. D. Appleby, C.L. Hussey, K.R. Sedden and J.E. Trup; Nature, vol. 323, page 614, **1986**.
45. C. L. Hussey; *“Advanced Molten Salt Chemistry”*, vol. 5, page 185, **1983**.
46. P.C. Trulove and R.A. Mantez, *“In Ionic liquid in Synthesis”*, (ed.) P. Wasserscheid and T. Welton, Wiley –VCH, Weinheim, Page 103-126, **2003**.
47. R.A. Mantez and P.C. Trulove, *“In Ionic liquids, in synthesis”*, (ed.) P. Wasserscheid and T. Welton, Wiley –VCH, Weinheim, Page 56-68, **2003**.
48. J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker and R.D. Rogers; Green Chem., vol. 3, Page 156, **2001**.
49. P. Wasserscheid and W. Kiem; Angew Chem. Int. ed., vol. 39, Page 3772, **2000**.
50. J. Fuller, R.T. Carlin and R.A. Osteryoung; J. Electro Chem. Soc., vol. 144, Page 3881, **1997**.
51. J.D. Hlbrey and R.D. Rogers, *“In Ionic liquid in synthesis”*, (ed.) P. Wasserscheid and T. Welton, Wiley –VCH, Weinheim, Page 41-55, **2003**.
52. M.E. Van Valkenburg, R.L. Vaughn; Thermo Physical Properties, **2003**.
53. J. Sun, M. Forsyth and D.R. Mac Farlane, *“Room Temperature Molten Salts Based on the Quaternary Ammonium Ion.”*; J. Phys. Chem., B, vol. 102, Page 8858-8864, **1998**.
54. UNEP Publications, Foreword Introduction of Choline Chloride, Berlin, Germany, **2000**.
55. Heck, R.F., *“Organic Reaction”*; John Wiley and Sons, New York, vol. 27, Page 345, **1982**.
56. Chang Biying, Song Rong, Ding Yong Sheng and Liew Chee Yong, *“Determination of Choline chloride content”*, Asian Poultry Magazine, Aug. **2002**.
57. P. Wasserscheid and T. Welton, *“Ionic liquid in synthesis”*, Weinheim, Wily-VCH Verlag, **2003**.

58. Andrew P. Abbott, Glen Capper, David L. Davies, Raymond K. Rasheed and Vasuki Tambyrajah, *"Novel solvent properties of choline chloride/urea mixture"*; Chem. Commun., page 70-71, **2003**.

59. M.S. Sitze, E.R. Schreiter, E.V. Patterson and R.G. Freeman; Inorg. Chem., vol.40, page 2298, **2001**.

60. L.Z. Liu, Y.X. Tong and Q.Q. Yang; Rare Met, vol. 19, page 237, **2000**.

61. A.P. Abbott, G. Capper, D.L. Davies, H. Munro, R.K. Rasheed and V. Tambyrajah; Chem. Commun., page 2010-2011, **2002**.

62. Andrew P. Abbott, David Boothdy, Glen Capper, David L. Davis and Raymond K. Rasheed, *"Deep eutectic solvent formed between choline chloride and carboxylic acids"*; J. Am. Chem. Soc., vol. 126, no.29, page 9142-9147, **2004**.

63. Andrew P. Abbott, David Boothdy, Glen Capper, David L. Davis and Raymond K. Rasheed, *"Ionic Liquids and Their Use as Solvents"*, **2000**.

64. Frank Albert Cotton and Geoffrey Wilkinson; Advanced Inorganic chemistry, 4th edition, A Wiley intercince publication, **1980**.

65. James E. Huheey; Inorganic chemistry: principles of structure and reactivity, Harper international, S.I. edition, **1983**.

66. N.N. Greenwood and A. Earnshaw; Chemistry of the elements, A Wiley intercince publication, 3rd edition, **1986**.

67. E.I. Eweka and D.H. Kerridge, *"Solution chemistry of molten amide- nitrate eutectic"*; Chem. Papers, vol.53, no.1, page 11-15, **1999**.

68. Istvan J. Zsigrai, Slobodan B. Gadzuric and Ruzica Nikolic, *"Cobalt (II) chloride complexes in Calcium nitrate tetrahydrate melt"*, Institute of nuclear sciences 'Vinca', **2000**.

69. Jelena Savovié, Ruzica Nikolie, Agan Veselinovié, *"Cobalt (II) chloride complex formation in Acetamide- Calcium nitrate tetrahydrate melt"*; J. of solution chemistry, vol. 33, no. 3, page 287-300, March **2004**.

70. Harald A. Øye and Deiter M. Gruen, *“Cobalt (II) species in fused chloride solvents”*; Inorg. Chem., vol.4, no. 8, Aug. **1965**.

71. C.L. Hussey and T.M. Laher, *“Electrochemical and spectroscopic studies of Cobalt (II) in molten aluminium chloride N,n-butylpyridium chloride”*; Inorg. Chem., vol.20, no. 12, page 4201-4206, **1981**.

72. T.M. Laher and C.L. Hussey, *“Copper (I) and Copper (II) cholro complexes in the basic aluminium chloride 1-methyl, 3-ethylimidazolium chloride, ionic liquid”*; Inorg. Chem., vol.22, no. 22, page 3247-3251, **1983**.

73. R. J. Lancashire, Chemistry of the First Row Transition Metal Complexes, Inorganic Chemistry, September **2005**.

74. Calculations using Orgel Diagram and Tanabe-Sugano diagram, From Wikipedia, the free encyclopedia (www.wikipedia.org), **2005**.

75. CHEM 340, Lect-14, the using of Tanabe-Sugano diagram. (www. encyclopedia.org), **2004**.

*جمهورية العراق*
*وزارة التعليم العالي والبحث العلمي*
*جامعة النهرين*
*كلية العلوم*
*قسم الكيمياء*

# تشخيص طيفي لأملاح بعض العناصر الأنتقالية في منصهرات الأملاح بدرجة حرارة الغرفة

رسالة
مقدمة الى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل
***مريم علي سعيد***
بكالوريوس (جامعة النهرين) ٢٠٠٥

بأشراف
الدكتور هادي محمد علي عبود

ربيع الثاني ١٤٢٩ أيار ٢٠٠٨

بِسمِ اللهِ الرحمنِ الرحِيمِ

إذ قـال يوُسفَ لأبيهِ يـٰأبت إني رأيتُ أحدَ عشرَ كـوكبا و الشمسُ والقـمرُ لـي سـٰجدين۝قـال يـٰبني لا تقصص رُءياك على إخوتك فيكيدوا لـك كيدآ إن الشيطـٰن للأنـٰسن عدوٌ مُـبين۝و كذلك يجتبيك رُبك ويعلمكَ من تأويل الأحاديث ويتم نعمتهُ عليك وعلى آل يعقوب كما أتمها على أبويك من قبل إبراهيمَ و إسحـٰق إن ربك عليمٌ حكيمٌ۝

صدق اللهُ العظِيم

# الأهداء

فيا والديَ الذي أحببتُ
إن كنتُ أهديكم ذا الأثر
فأني أردُ الجميلَ جميلاً
بنور الضمير ونور البصر
فأن كان بحثي سماءاً بروحي
فأنتم شمسها و القمرُ

الى والدتي الغالية...والدي العزيز...اخي و أختي...أهلي و أصدقائي...وكل من له مكان في قلبي....

الى روح أستاذي العزيز الأستاذ الدكتور أياد حمزة جاسم الخفاجي...

اهدي عملي المتواضع.

مريم علي سعيد

# الخلاصة

في هذا البحث تم تحضير نوعين من الأملاح المنصهرة في درجة حرارة الغرفة للأستخدامها كمذيب لامائي في دراسة الهدف منها التعرف على السلوك الذي تسلكه هذه المركبات الأيونية السائلة تجاه أيونات العناصر الأنتقالية وهذه المركبات حُضرت من مزج ملح مشتق من جذر الأمونيم الرباعي و مواد لها قابلية على تكوين أواصر هيدروجينية مثل (اليوريا و حامض كاربوكسيلي ثنائي الكاربوكسيل) بنسب مولية ثابته.

تمت دراسة بعض معقدات العناصر الأنتقالية في نوع جديد من الأملاح المنصهرة في درجة حرارة الغرفة, حيث أن الأملاح المنصهرة تعتمد في تركيبها على كلوريد الكولين.

شُخصت المحاليل المحضرة التي تحتوي على المعقدات الجديدة تشخيصاً طيفياً بواسطة الأشعة الفوق البنفسجية-المرئية (UV-Vis). حيث لوحظ تكون معقدات بين الأيون الأنتقالي و مكونات الأملاح المنصهرة في درجة حرارة الغرفة. الأملاح المنصهرة سميت كولين كلورايد يوريا و كولين كلورايد و حامض المالونك و الذان يمتلكان درجة أنجماد في ١٠ و ٠ درجة مئوية على التوالي.

لوحظ أن الأيونات في محلول الكولين كلورايد يوريا كانت ذات أشكال ثمانية السطوح لكل من أيونات $Cr^{٣+}$, $Ni^{٢+}$, $Cu^{٢+}$ و أشكال رباعية السطوح لكل من أيونات $Fe^{٣+}$, $Co^{٢+}$. حيث أظهرت دراسة الطيف الأنتقالات المسموحة و الممنوعة لكل تركيب ألكتروني $d^n$ في كل من المعقدات ثمانية السطوح و رباعية السطوح.

تمت دراسة تفاعل أستبدال لليكندات المرتبطة بالأيون الأنتقالي في محلول الكولين كلورايد يوريا بأضافة أيون النترات على شكل نترات الأمونيوم, حيث أظهرت ضعف الأرتباط بين جزيئات المحلول و الأيون الأنتقالي الموجب في أشكال تناسقية. كل المعقدات المتكونة أظهرت حالات مستقرة في أشكال معقداتها خلال ٧٢ ساعة من تحضيرها, عدا في حالة أيون الكوبلت الثنائي حيث أظهر تغير في طيفه بعد ٤٠ يوم مما يدل على عدم وصول المعقد المتكون حالة الأستقرار.

أما في محلول الكولين كلورايد و حامض المالونك فأن أيوني $Ni^{٢+}$, $Cu^{٢+}$ أظهرا شكل رباعي السطوح أكثر من أشكال ثمانية السطوح.

تم أقتراح نوع الأرتباط بين الأيون الأنتقالي الموجب و الليكند بأستخدام قاعدة جورجنسن كما فُسرتْ طبيعة التآصر بين أيون الفلز والذرات المانحة في الليكند بمعامل راكاح و تم تحديد الأنتقالات بأستخدام مخطط أوريكل ومقاييس المجال الليكندي والتي تم أحتسابها بوساطة مخطط (تنابا- سوكانو) لجميع المعقدات المحضرة .

**بسم الله الرحمن الرحيم**

الأسم: مريم علي سعيد البياتي.

المواليد: 1984

عنوان السكن: بغداد - الدورة - م/ 836 , ز/ 49 , د/ 134

رقم الهاتف: 7713573

الأيميل: chemist_mas84@yahoo.com

التحصيل الدراسي: ماجستير علوم كيمياء.

سنة التخرج: بكالوريوس 2005 – كلية العلوم – جامعة النهرين.

أسم المشرف: دكتور هادي محمد علي.

تأريخ المناقشة: 2008/05/15

عنوان الأطروحة: تشخيص طيفي لأملاح بعض العناصر الأنتقالية في منصهرات الأملاح بدرجة حرارة الغرفة.

# Curriculum Vitae

Name: Mariam Ali Saeed Al-Bayatie.

Year of Birth: 1984.

Address: Iraq- Baghdad, Al-Dura, 836/49/134.

Phone Number: 0096417713573.

E-mail: chemist_mas84@yahoo.com

Academic Qualifications: Bs.c. in Chemistry (2005), Master degree in chemistry (2008), Al-Nahrian University, College of Science.

Supervisor: Dr. Hadi M.A. Abood.

Discussion Date: 15/5/2008.

Thesis title: Ultraviolet visible investigation of some transition metal compounds in room temperature ionic liquids, molten salts.