

3. METHODOLOGY

3.1. Methods

Solvent properties such as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent-solvent interactions. Conductance study is a very important tool in obtaining the information regarding the solvation and association behavior of ions in solutions [Dogonadze *et al.*, 1986]. Conductivities of electrolytes in various pure and mixed solvent systems are of much interest to chemists. The solvation behavior of ions in solutions can well understand in terms of ion-solvent, ion-ion and solvent-solvent interactions. Variation in the dielectric constant and viscosity in solvents due to mixing, leads to a better understanding of ion-ion and ion-solvent interactions. The use of mixed solvents in high energy batteries has also extended the horizon in the field of mixed solvent systems [Aurbach, 1999; Roy *et al.*, 2006]. The electrical conductivity of electrolytes in mixed solvent solutions mainly depends upon the concentration of the electrolyte and also upon the viscosity of the solvent. The electrical conductivities of the pure and mixed solvent solutions of the selected salts were measured at different temperatures. The limiting equivalent molar conductance (Λ_0), the association constant (K_A) of ion pair and limiting equivalent of triple ion (Λ_0^T) and triple ion formation (K_T) of the selected salts were calculated by using Shedlovsky [Shedlovsky, 1932], Fuoss [Fuoss, 1978] and Fuoss-Kraus method [Fuoss & Kraus, 1933]. The molar conductances (Λ) for all studied solution system have been calculated using following equation [El-Dossoki, 2010]

$$\Lambda = 1000\kappa/c \quad \dots(48)$$

A brief account on theories and equation used in our investigation are outlined below:

3.2. Evaluation of limiting molar conductance (Λ_0) and association Constant (K_A) of electrolytic salts by Shedlovsky technique.

The conductance data of the chosen simple and complex salts were analyzed by using Shedlovsky method [Shedlovsky, 1932].

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0^2}\right) \left(C\Lambda \int_{\pm}^2 S(z)\right) \quad \dots(49)$$

Where Λ is equivalent conductance at a concentration c (g.mol.dm^{-3}), Λ_0 is the limiting equivalent conductance and K_A is the observed association constant. The other symbols are given by [Shedlovsky and Kay, 1956]

$$S(z) = \left(\frac{z}{2} \sqrt{1 + \left(\frac{z}{2}\right)^2}\right)^2 ; \quad Z = \left[\frac{\alpha\Lambda_0 + \beta}{\Lambda_0^{s/z}}\right] (C\Lambda)^{1/2}$$

Applying the Debye-Huckel-Onsager conductance equation, α and β values were found as follows:

$$\begin{aligned} \Lambda &= \Lambda_0 - \left[\frac{29.15 \times 3\sqrt{3}}{(DT)^{1/2}} + \frac{9.90 \times 10^5}{(DT)^{3/2}} \Lambda_0 W \right] \sqrt{C(Z_+ + Z_-)} \\ &= \Lambda_0 - \beta + \alpha\Lambda_0 \sqrt{C} \end{aligned}$$

Therefore,

$$\beta = \frac{151.47}{(DT)^{1/2}\eta}, \quad \alpha = \frac{17.147 \times 10^5}{(DT)^{1/2}} W, \quad (\text{for 2:1 electrolytes})$$

$$\beta = \frac{82.501}{\eta(DT)^{3/2}}, \quad \alpha = \frac{0.8204 \times 10^6}{(DT)^{3/2}}, \quad (\text{for 1:1 electrolytes})$$

Where, $w = Z_+ Z_- \frac{2q}{1+q^{1/2}}$

$$q = \frac{Z_+ Z_-}{Z_+ + Z_-} \frac{\lambda_+ \lambda_-}{Z_+ \lambda_- + Z_- \lambda_+}$$

Z and λ are the valence and conductance of the ions respectively excluding their signs, D the dielectric constant of the medium, η the viscosity coefficient of the medium. The degree of dissociation (τ) is related to S(Z) by the equation.

$$-\log f_{\pm} = \frac{Az_+ z_- \mu^{1/2}}{1 + BR\mu^{1/2}} \quad \dots(50)$$

$$\text{Where, } A = \frac{1.8247 \times 10^6}{(DT)^{3/2}}; \quad B = \frac{0.5029 \times 10^{10}}{(DT)^{1/2}}; \quad \mu = \frac{1}{2} \sum_i (C_i \tau_i) z_i^2$$

R is the maximum centre to centre distance between the ions in the ion-pair. There exists at present no precise method [Hogman *et al.*, 1956] for determining the value of R'. In order to treat the data in our system, the R' value is assumed to be R' = a + d, where 'a' is the sum of crystallographic radii of the ions approximately equal to 5A⁰ and 'd' is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance d is given by [Fuoss and Onsager, 1955]

$$d = 1.183 \left(\frac{M}{\rho} \right)^{1/3} \text{ \AA} \quad \dots(51)$$

Where M is the molecular weight of the solvent and ρ is the density of the solution. For mixed solvent M is replaced by the mole fraction average molecular weight,

$$M_{\text{avg}} = \frac{M_1 M_2}{X_1 M_2 + X_2 M_1} \quad \dots(52)$$

X₁ is the mole fraction of methanol of molecular weight M₁ and X₂ that of water of molecular weight M₂. An initial value of Λ_0 was obtained by least square method (Λ and concentration C was introduced as input in a computer programmed). The mean activity

coefficient f_{\pm} was determined by equation (13) for the above chosen simple and complex salts [Akhadov, 1981]. From the linear plot of $1/\Lambda S(Z)$ versus $C \Lambda f_{\pm}^2 S(Z)$; Λ_0 and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope (K_A/Λ_0^2) respectively [Glasstone, 1942].

As per Shedlovsky method, an initial value of λ^0 was obtained from the intercept of the linear Onsager plot of Λ versus $c^{1/2}$, λ^0 is obtained from the literature at 25°C and at other temperatures it was obtained by using the following equation [Bag *et al.*, 2009]:

$$\lambda_t^0 = \lambda_{25}^0 [1 + \alpha'(t - 25)] \quad \dots(53)$$

α' is constant. Using these values of Λ_0 , λ^0 , λ^0_{+} , λ^0_{-} , z , $s(z)$ and r values were calculated. The mean activity coefficient f was determined by equation (20) for the above chosen complex salts. From the linear plot of $1/\Lambda S(Z)$ versus $C \Lambda f_{\pm}^2 S(Z)$; Λ_0 and K_A was evaluated from the intercept $1/\Lambda_0$ and the slope K_A/Λ_0^2 respectively [Nelson and Errington, 2005]. The procedure was repeated using these new values of Λ_0 and K_A .

3.3. Evaluation of limiting molar conductance (Λ_0) and association Constant (K_A) of electrolytic salts by Fuoss technique.

The conductance data in mixed solvents have been analyzed in terms of the limiting molar conductance (Λ_0) and the ion-association constant ($K_{A,c}$) of the electrolytes using Fuoss conductance-concentration equation, resolved by an iterative procedure programmed in a computer as suggested by Fuoss [Fuoss, 1978]. So with a given set of conductivity values ($c_j, \Lambda_j, j = 1, \dots, n$), three adjustable parameters, the limiting molar conductance (Λ_0), the association constant ($K_{A,c}$) and the distance of closest approach of ions (R) are derived from the Fuoss conductance equation. Since there is no precise method [Per, 1977] for determining the R -value and for the electrolytes studied no significant minima were observed obtained in the σ_{Λ} versus R - curves and thus in order to treat the data in our system, R -values were preset

at the centre-to centre distance of solvent separated ion-pairs, i.e., $R = a + d$; where $a = (r_+ + r_-)$ is the sum of the crystallographic radii of the cation (r_+) and anion (r_-) and d is the average distance corresponding to the side of a cell occupied by a solvent molecule.

The Fuoss conductance equation may be represented as follows:

$$\Lambda = P\Lambda_0[(1 + R_X) + E_L] \quad \dots(54)$$

$$P = 1 - \alpha(1 - \gamma) \quad \dots(55)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad \dots(56)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad \dots(57)$$

$$\beta = e^2 / (\epsilon_r k_B T) \quad \dots(58)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad \dots(59)$$

where R_X is the relaxation field effect, E_L is the electrophoretic counter current, k^{-1} is the radius of the ion atmosphere, ϵ_r is the relative permittivity of the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_A is the overall pairing constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance. The computations were performed using a program suggested by Fuoss.

The best value of a parameter is the one when equations is best fitted to the experimental data corresponding to minimum standard deviation δ for a sequence of predetermined R values, and standard deviation δ was calculated by the following equation

$$\delta^2 = \sum [\Lambda_j(\text{cal}) - \Lambda_j(\text{obs})]^2 / (n - m) \quad \dots(60)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two parameter fit (m = 2).

3.4. Evaluation of limiting molar conductance of triple ion (Λ_0^T) and triple ion formation constant (K_T) of electrolytic salts by Fuoss- Kraus technique.

The conductance data have been analyzed by the classical Fuoss-Kraus theory of triple-ion formation [Fuoss-Kraus, 1933] in the form

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c \quad \dots(61)$$

where g(c) is a factor that lumps together all the intrinsic interaction terms and is defined by

$$g(c) = \frac{\exp \{-2.303\beta'(c\Lambda)^{0.5}/\Lambda_0^{0.5}\}}{\{1-S(c\Lambda)^{0.5}/\Lambda_0^{1.5}\}(1-\Lambda/\Lambda_0)^{0.5}} \quad \dots(62)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5} \quad \dots(63)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{0.5}} \quad \dots(64)$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution, Λ_0^T is the sum of the conductance value of the two triple-ions and $K_P \approx K_A$ and K_T are the ion-pair and triple-ion formation constants respectively and S is the limiting Onsager coefficient.

Furthermore, the ion-pair and triple-ion concentrations, C_P and C_T , respectively, have also been calculated using the following equations [Nandi *et al.*, 1993]

$$\alpha = 1/(K_P^{\frac{1}{2}} \cdot c^{\frac{1}{2}}) \quad \dots(65)$$

$$\alpha_T = (K_T/K_P^{1/2})c^{1/2} \quad \dots(66)$$

$$C_P = c(1 - \alpha - 3\alpha_T) \quad \dots(67)$$

$$C_T = (K_T/K_P^{1/2})c^{3/2} \quad \dots(68)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions present in the salt-solutions.

3.5. Evaluation of thermodynamic parameters

Thermodynamics properties for the association, viz., changes free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) for the ion-pair formation have been calculated from the values of association constants at different temperatures. The enthalpy change (ΔH_{ass}^0) is related to the changes in the number and strength of the bond in the process. The entropy change (ΔS_{ass}^0) is a measure of the change of randomness when comparing the association constant of some selected transition metals in pure and mixed solvents, one need a comparison of ΔG_{ass}^0 for the process. The ΔG_{ass}^0 can be calculated by using the Van't hoff isothermal correlation.

$$\Delta G^0 = \Delta H_{\text{ass}}^0 - T\Delta S_{\text{ass}}^0 \quad \dots(69)$$

Free energy of association process (ΔG_{ass}^0) was calculated from the equation

$$\Delta G^0 = -RT\ln K_A \quad \dots(70)$$

The entropy change of association (ΔH_{ass}^0) was obtained from the slope of $\log K_{\text{AVS}}$ $1/T$. the change of association entropy (ΔS_{ass}^0) was calculated from the Gibbs Helmholtz equation

$$\Delta S_{\text{ass}}^0 = \frac{\Delta H_{\text{ass}}^0 - \Delta G_{\text{ass}}^0}{T} \quad \dots(71)$$

3.6. Calculation of Walden product

The trend in Λ_0 and ion-association can be discussed through another characteristic function called the Walden product ($\Lambda_0\eta_0$) (product of the limiting molar conductance at infinite dilution and solvent viscosity) This is justified as the Walden product of an ion or solute is inversely proportional to the effective solvated radius (r_{eff}) of the ion or solute in a particular solvent/solvent mixtures [Bhat and Bindu, 1995].

$$\Lambda_0\eta_0 = \frac{1}{6\pi r_{\text{eff}}T} \quad \dots(72)$$

Therefore, variation of Walden product ($\Lambda_0\eta_0$) with the change in the composition of the solvent reflects the solvation of the ions [Conway *et al.*, 1965]. Another suggestion that has been made to explain this fact is that the ion in solution is so completely surrounded by solvent molecules [Conway, 1978] which move with it, it is so extensively ‘solvated’ that its motion through the medium is virtually the same as the movement of the solvent molecules past one another in viscous flow of the solvent. The starting point for most evaluations of ionic conductance is Stokes’ law which states that the limiting Walden product ($\lambda_0^\pm\eta_0$), (the limiting ionic conductance-solvent viscosity product) for any singly charged, spherical ion is a function only of the ionic radius and thus, under normal conditions, is a constant.

The λ_0^\pm values were in turn utilized for the calculation of Stokes’ radii (r_s) according to the classical expression [Robinson and Stokes, 1959]

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^\pm r_c} \quad \dots(73)$$

where, r_s is the Stokes’ radii, r_c is the crystallographic radii, N_A is the Avogadro’s no., λ_0^\pm is the limiting ionic conductance and F is the Faraday Constant.

The significance of the term had since then been realized due to the development Debye-Hückel theory [Debye and Hückel, 1923] of inter-ionic attractions in 1923. The A-coefficient depends on the ion-ion interactions and can be calculated from interionic attraction theory and is given by the Falkenhagen and Vernon [Falkenhagen and Vernon,1983] equation:

$$A_{\text{Theo}} = \frac{0.2577\Lambda_0}{\eta_0(\epsilon T)^{0.5}\lambda_+^0\lambda_-^0} \left[1 - 0.6863\left(\frac{\lambda_+^0\lambda_-^0}{\Lambda_0}\right)^2\right] \quad \dots(74)$$

where the symbols have their usual significance. If A-coefficient is negative and very small, shows that the existence of the ion-ion interaction negligible, as compared to the ion-solvent interaction in the studied solvents.

3.7. Calculation of solvation number n_s

The number of solvent molecules that are involved in the solvation of the ion is called solvation number (n_s). Solvation region can be classified as primary and secondary solvation regions. Here we are concerned with the primary solvation region. The primary solvation number is defined as the number of solvent molecules which surrender their own translational freedom and remain with the ion, tightly bound, as it moves around, or the number of solvent molecules which are aligned in the force field of the ion as well as the ILs.

If the limiting conductance of the ions (λ_o^\pm) of charge Z_i is known, the effective radius of the solvated ion can be determined from Stokes' law and the volume of the solvation shell is given by the equation.

$$V_s = \left(\frac{4\pi}{3}\right) (r_s^3 - r_c^3) \quad \dots(75)$$

where r_c and r_s is the crystallographic and Stokes' radius of the ions. The solvation number n_s would then be obtained from

$$n_s = \frac{V_s}{V_0} \quad \dots(76)$$

Where V_0 is the volume of the solvent molecules.

3.8. Calculation of diffusion coefficient (D)

The diffusion coefficient (D) is obtained using the Stokes-Einstein Relation:

$$D = \frac{K_B T}{6\pi\eta_0 r_s} \quad \dots(77)$$

Where k_B is the Boltzmann's constant, T is the temperature, η_0 is the solvent viscosity and r_s is the Stoke's radius.

The ionic mobility was obtained using the following equation

$$i_{\pm} = \frac{z_{\pm} F}{R_g T} D \quad \dots(78)$$

where z_{\pm} , F, R_g , T and D is the ionic charge, Faraday constant, universal gas constant, temperature and diffusion co-efficient respectively.

3.9. Physical Measurements

3.9.1. Conductance Measurements: The electrical conductivities were measured by using EUTECH- PC-700 Conductivity Bench top meter with Epoxy 2 cell (K=1.0) digital conductivity bridge (accuracy $\pm 0.1\%$) with a dip type immersion conductivity cell.

3.9.2. Temperature Control

The temperature was control in the range of 10-40°C by using refrigerated Bath and Circulator - Cole-Palmer, Polystat R6L with the help of thermometer. The accuracy of the temperature measurement was $\pm 0.01^\circ\text{C}$.

3.9.3. Measurement of Weights

The measurement of weights was done accurately by using a METTER Balance, Model-Ae260, Delta Range.

3.9.4. Computations

The computations were performed using a program suggested by Shedlovsky, Fuoss and Fuoss-Kraus.

The complexes, Ionic Liquids were verified by comparing their IR spectrums obtained from NICOLET iS10 FT-IR spectrometer with the IR spectrums obtained from **Gaussian 09W.Gaussian 09W, Revision A.02**, program package (Gaussian Inc.) is a computational software with which **Gauss View 5.0.9** is used for graphical interface which is necessary for input and output analysis. In Gaussian calculation, the geometrical optimization and harmonic vibrational frequencies of the complexes are calculated under gas phase using the Density Functional Theory (DFT) with B3LYP three- parameter hybrid functional proposed by Becke [Becke, 1993]. The B3LYP functional comprises an exchange-correlation functional that mixes the nonlocal Fock exchange with the gradient-corrected form of Becke [Becke, 1988] and adds the correlation functional proposed by Lee et al. [Lee *et al.*, 1988]. Unrestricted calculations are needed for processes such as bond dissociation which requires the separation of an electron pair [Foresman *et al.*, 1996] and diffuse functions are necessary for describing the weak bond interaction. Therefore, for all calculation u6-311++G basis set is used. Gauss View 5.0.9 is a graphical user interface designed to help me prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. Gauss View 5.0.9 is not integrated with the computational module of Gaussian, but rather is a front-end/back-end processor to aid in the use of Gaussian. Gauss View 5.0.9 provides me three main benefits as Gaussian users (Gaussian.com, 2016).

First, through its advanced visualization facility, Gauss View 5.0.9 allows me to rapidly sketch in even very large molecules, then rotate, translate and zoom in on these molecules through simple mouse operations. It can also import standard molecule file formats such as PDB files.

Secondly, Gauss View 5.0.9 makes it easy to set up many types of Gaussian calculations. It makes preparing complex input easy for both routine job types and advanced methods like ONIOM, STQN transition structure optimizations, CASSCF calculations, periodic boundary conditions (PBC) calculations, and many more. Gauss View 5.0.9 can be used to launch jobs as well if Gaussian is installed on the same computer. Lastly, default can be define and named calculation templates, known as schemes, to speed up the job setup process. Finally, Gauss View 5.0.9 lets me examine the results of Gaussian calculations using a variety of graphical techniques. Gaussian results that can be viewed graphically include the following:

Optimized molecular structures.

Molecular orbitals.

Electron density surfaces from any computed density.

Electrostatic potential surfaces.

Surfaces for magnetic properties.

Surfaces can also be viewed as contours.

Atomic charges and dipole moments.

Animation of the normal modes corresponding to vibrational frequencies.

IR, Raman, NMR, VCD and other spectra.

Molecular stereochemistry information.

3.10. Materials

3.10.1. Ligands

The following ligands were selected for the preparation of the mixed ligand complexes

(i) Cystein

(ii) Serine

(iii) Histidine

(iv) Benzoyl isothiocyanate

(v) N-(benzyolamino)-thiozomethyl]-cystein

(vi) N-(benzyolamino)-thiozomethyl]-serine

(vii) N-(benzyolamino)-thiozomethyl]-histidine

(viii) The cystein, serine and histidine of analytical reagent grade were directly purchased from Merck Company and used as such. The ligands, N-(benzyolamino)-thiozomethyl]-cystein, N-(benzyolamino)-thiozomethyl]-histidine and N-(benzyolamino)-thiozomethyl]-serine were prepared for the following methods of A.T. Kabbani and co-workers [Kabanni *et al.*, 2005; El-Hammamy *et al.*, 2010].

i. Preparation of benzoyl isothiocyanate

A mixture of Benzoyl chloride (0.01mol) and ammonium thiocyanate (0.01mol) in 25ml acetone was refluxed with stirring for 1 hour, then filtered and the filtrate was used for further reaction.

ii. Preparation of N-(benzyolamino)-thiozomethyl]-cystein

0.01 mol of cystein from 25ml pure dry acetone were added rapidly onto the solution of benzoyl isothiocyanate and refluxed for 6 hrs, after which excess cracked ice was poured into the mixture with vigorous stirring. The resulting solid was collected, washed with water and then with acetone and recrystallized from ethanol. (m.p=176°C).

iii. Preparation of N-(benzyolamino)-thiozomethyl]-serine

0.01 mol of serine from 25ml pure dry acetone were added rapidly onto the solution of benzoyl isothiocyanate and refluxed for 6 hrs, after which excess cracked ice was poured

into the mixture with vigorous stirring. The resulting solid was collected, washed with water and then with acetone and recrystallized from ethanol. (m.p=210°C).

iv. Preparation of N-(benzyolamino)-thiozomethyl]-histidine

A 0.01 mol of histidine from 25ml pure dry acetone were added rapidly onto the solution of benzoyl isothiocyanate and refluxed for 6 hrs, after which excess cracked ice was poured into the mixture with vigorous stirring. The resulting solid was collected, washed with water and then with acetone and recrystallized from ethanol. (m.p=125°C).

3.10.2. Preparation of the compounds/ Complexes

i. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein manganese (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of manganese (II) chloride tetrahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

ii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein cobalt (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of cobalt (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

iii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein nickel (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of nickel (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

iv. Preparation of N-[(benzoyl-amino)-thioxomethyl]-cystein copper (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-cystein was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of copper (II) chloride dihydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

v. Preparation of N-[(benzoyl-amino)-thioxomethyl]-serine manganese (II) chloride

1.24mol of N-(benzyolamino)-thiozomethyl]-serine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of manganese (II) chloride tetrahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight

vi. Preparation of N-[(benzoyl-amino)-thioxomethyl]-serine nickel (II) chloride

1.24 mmol of N-(benzyolamino)-thiozomethyl]-serine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of nickel (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears

immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight

vii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-histidine manganese (II) chloride

1.24 mmol of N-(benzylamino)-thioxomethyl]-histidine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of manganese (II) chloride tetrahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitates appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

viii. Preparation of N-[(benzoyl-amino)-thioxomethyl]-histidine nickel (II) chloride

1.24 mmol of N-(benzylamino)-thioxomethyl]-histidine was dissolved in 25ml of pure methanol containing 1.25 mmol of NaOH. A solution of nickel (II) chloride hexahydrate (0.62mmol) in methanol was added dropwise over the mixture, and the precipitate appears immediately. After stirring the mixture at room temperature for 2 hours, the precipitate was collected by filtration, washed with methanol and dried under vacuum to constant weight.

ix. Preparation of Tetraammine Copper (II) sulfate.

The complex was synthesized as described by [Glemser and Sauer *et al.*, 1963]. 6 g of copper(II) sulphate pentahydrate dissolves in 15 mL of deionized water. The solution was then heated to the fume hood and adds conc NH₃ until the precipitate that initially forms has dissolved. Cool the deep blue solution in an ice bath. Cool 20 mL of 95% ethanol to ice bath temperature and then slowly add it to the solution. The blue, solid complex is then form and filtered in a filter paper, washed with two 5-mL portions of cold 95% ethanol and 5 mL of

acetone. The product was dried at room temperature. The amount of the product is 6g, corresponding to a yield of 96%.

x. Preparation of Tris(ethylenediamine) copper (II) sulphate pentahydrate:

The complex was synthesized as described by [Girolami *et al.*, 1999]. 6 g of copper(II) sulphate pentahydrate dissolve in 10 mL of warm deionized water. The solution cooled in an ice bath and slowly adds 10 mL ethylenediamine. The mixture cooled again in an ice bath. The cold 15 mL of 95% ethanol slowly add it to the solution. The mixture allows settling for complete precipitation. The precipitate filtered in a filter paper, washed with two 5-mL portions of cold 95% ethanol and 5 mL of acetone. The product was dried at room temperature. The amount of the product is 6g, corresponding to a yield of 95%.

xi. 1-butyl-4-methylpyridinium hexafluorophosphate [4MBPPF₆]

xii. 1-ethyl-3-methylimidazolium nitrate [EMIm]NO₃

xiii. 1-ethyl-3-methylimidazolium methanesulfonate [EMIm]CH₃SO₃

xiv. 1-ethyl-3-methylimidazolium tosylate [EMIm]Tos

xv. 1-butyl-3-methylimidazolium hexafluorophosphate [BMimPF₆]

xvi. 1-benzyl-3-methylimidazolium hexafluorophosphate [BZMimPF₆]

Also the above six ILs selected for the present work puriss grade was procured from Sigma-Aldrich, Germany and the mass fraction purity of the ILs was ≥ 0.95 .

3.11. Elemental analysis of few complexes

Table 1: Elemental analysis data of some N-[(benzoyl-amino)-thioxomethyl]-amino acids and their metal complexes.

Compound	Stoichiometry	% C		% H		% N	
		Calc.	(Found)	Calc.	(Found)	Calc.	(Found)
N-[(benzoyl-amino)-thioxomethyl]-cystein + MnCl ₂	MLCl	34.95	(34.40)	2.67	(2.42)	7.25	(7.20)
N-[(benzoyl-amino)-thioxomethyl]-cystein + CoCl ₂	MLCl	35.19	(34.39)	2.75	(2.41)	7.27	(7.19)
N-[(benzoyl-amino)-thioxomethyl]-cystein + NiCl ₂	MLCl	35.31	(34.44)	2.81	(2.43)	7.30	(7.18)
N-[(benzoyl-amino)-thioxomethyl]-cystein + CuCl ₂	MLCl	35.55	(34.43)	2.87	(2.48)	7.32	(7.21)
N-[(benzoyl-amino)-thioxomethyl]-serine + MnCl ₂	MLCl	33.98	(31.81)	2.61	(2.52)	7.21	(7.15)
N-[(benzoyl-amino)-thioxomethyl]-serine + NiCl ₂	MLCl	34.65	(33.52)	2.67	(2.57)	7.29	(7.20)
N-[(benzoyl-amino)-thioxomethyl]-histidine + MnCl ₂	MLCl	31.64	(29.89)	2.53	(2.46)	7.20	(7.17)
N-[(benzoyl-amino)-thioxomethyl]-histidine + NiCl ₂	MLCl	31.28	(29.87)	2.63	(2.49)	7.27	(7.21)