Synthesis, Characterization of Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ Complex Salts with Quinolinium and Isoquinolinium Halides Derivative Salts

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Abstract: The organic salts of type [S][Br](S = quinolinium-N-ethyl bromide and 3-methyl-N-benzyl bromide) were prepared by N-alkylation in acetonitrile solution. The series of new complex salts of type [S]$_2$[MCl$_2$Br$_2$] were synthesized by a slow addition of ethanolic solution of metal ions Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ to a solution of organic salts. Followed by reflux for 3 hr, then the solid product was isolated by filtration, washed and dried. These complex salts have been characterized by elemental analysis, IR, UV-vis.-spectroscopy, magnetic susceptibility and molar conductivity.

Keywords: Ionic liquids, Complex salts, Ionic complex, Quinolinium halides Salts, Green chemistry.

Introduction:

Ionic liquids (ILS) have recently emerged as "green" and environmental friendly solvents for their use in the industrial manufacture of chemicals, catalysis, electrochemical devisers and solvent extraction [1 – 4].

Another interesting and potentially very useful subclass of (ILS), metal containing ionic liquids (MILS) [5]. This is somewhat surprising because the presence of a metal ion furnishes the (ILS) with additional magnetic, optical, catalytic or electrochemical properties that are not accessible otherwise [1, 6 - 8].

The preparation and properties of transition metal tetrahalometallates with different cations such as pyridinium, imidazolium and pyrrolidinium, have been studied extensively over the past few decades; their spectroscopic as well as magnetic and crystal structure have been investigated by many groups [9 – 11]. The single crystal structure of the salt, 1-phenylpiprizine-1,4-diiiumtetrachlorocobalt(II) [C$_{10}$H$_{16}$N$_{2}$][CoCl$_4$] has studied; in tetrachlorocobaltate (II), dianion; the Co-Cl bond lengths for chloride ions not accepting hydrogen bonds are significantly shorter than those for the chloride ions accepting such bonds. In the crystal, the components are linked by N-H-Cl hydrogen bond generating a chains [12]. Also the salt [C$_5$H$_6$ClN$_2$]$_2$[ZnCl$_4$], containing two 2-amino-5-chloropyridinium cation and one [ZnCl$_4$]$^{2-}$ dianion which are held together by N-H-Cl and C-H-Cl hydrogen bonds. The [ZnCl$_4$]$^{2-}$...
anions have distorted tetrahedral geometry; weak intermolecular \( \pi-\pi \) stacking interactions exist between aromatic rings of the cation [13].

The current article describes the synthesis of some new complex salts based on quinolinium; isquinolinium and alkyl halides derivatives as cation and \([\text{MCl}_2\text{Br}_2]^2-\) as anion (Schem 1).

![Chemical structure of N-ethylquinolinium complex salt [S1]2[\text{MCl}_2\text{Br}_2] (a) and 3-methyl-N-Benzylisoquinolinium complex salt [S2]2[\text{MCl}_2\text{Br}_2]^2- (b)](image)

Schem 1: Chemical structure of N-ethylquinolinium complex salt \([\text{S}1]_2[\text{MCl}_2\text{Br}_2]\) (a) and 3-methyl-N-Benzylisoquinolinium complex salt \([\text{S}2]_2[\text{MCl}_2\text{Br}_2]^2-\) (b)

**Experimental**

These complex salts and ligands were analyzed for carbon, hydrogen and nitrogen using an 1106 (Carloforba) micro analyzer. IR spectra were recorded on pye-unicam Sp 1100 spectrophotometer using KBr and CsI pellets within the range 400-4000 cm\(^{-1}\) and 200-4000 cm\(^{-1}\) respectively. The electronic spectra in 10\(^{-3}\) M DMF solution were obtained on shimadzu uv-160 spectrophotometer at 25 °C. Magnetic susceptibilities were determined by Gouy method on sherwood scientific magnetic susceptibility balance (Model MKI) at room temperature using Hg[Co(SCN)\(_4\)] as calibrate, diamagnetic correction were calculated from pascal's constants. Molar conductance of ligands and complexes were determined for 10\(^{-3}\) M DMF solution using an electric conductivity measuring device model LF-42 at 25°C, metal analysis were carried out by using an AA240FS VARIAN instrument for atomic absorption.

**Synthesis**

*Synthesis of N-ethylquinolinium bromide salt [S1]*

The salt was prepared by adding dropwise a solution of (0.01 mole, 0.129 gm) quinoline in (10 ml) in acetonitrile at 5 °C to (0.01 mole, 0.109 gm) of ethyl bromide with continuous stirring. The mixture was reflux for 48 hr. Then the solution was concentrated to half volume and cooled in an ice bath to obtain a lightly brown precipitate. Filtered off and washed several times by ethylacetate. The product was purified by crystallization was from ethanol, dried at 50 °C for 10 hr.

*Synthesis of N-benzyl-3-methylisoquinolinium bromide salt [S2]*

This organic salt was prepared as light brown precipitate by employing the above-described procedure using (10.01 mole, 0.143 gm) of 3-methylisoquinolinium and (0.01 mole, 0.171 gm) benzylbromide.

**Synthesis of \([\text{S}1]_2[\text{MCl}_2\text{Br}_2]\) complex salts (M= Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\)).**

These complex salts were synthesized by mixing 1:2 mole ratio of metal chloride and organic salt \([S1]\) in ethanol solvent. After refluxing 3 hr., the product solution concentrated to half volume and allowed to cool at room temperature. The precipitate complex was filtered off, washed with cold ethanol and diethylether. Dried in an oven for 3 hr. at 50 °C.

**Synthesis of \([\text{S}2]_2[\text{MCl}_2\text{Br}_2]\) complex salts (M= Mn\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\)).**

These complex salts were synthesized as solid product by mixing 1:2 mole ratio metal chloride and organic salts \([S2]\) followed by the same procedure described above.
Results and Discussion

In general, the reactions of organic salts with metal salts occurred at high rate with good yield. The complex salts are stable, non-hygroscopic, coloured solids. The melting points, colour, metal analysis and conductance measurements are listed in Table 1. The values of molar conductance in DMF for all complex salts are within (130-170) cm$^2$.ohm$^{-1}$.mol$^{-1}$ range of 1:2 electrolyte, nature, conforming the formula [S$_2$] [MCl$_2$Br$_2$] [14].

Table 1: Analytical and some physical properties of the complex salts.

| No. | Compound | Colour | Yield% | m.p $^\circ$C | Molar conductance cm$^2$.ohm$^{-1}$.mol$^{-1}$ | Calculated (Found)% |
|-----|----------|--------|--------|---------------|---------------------------------------------|---------------------|
|     |          |        |        |               | C  | H  | N  | M        |          |
| 1   | S$_1$    | Light brown | 70     | 96            | 44.16 | 4.27 | 5.16 | (43.72) | (3.93) | (5.01) |
| 2   | S$_2$    | Light brown | 80     | 139           | 43.83 | 4.8  | 4.64 | (42.49) | (4.01) | (4.30) | 7.10  |
| 3   | [S$_1$]_2[MnCl$_2$Br$_2$] | White | 67     | 184           | 43.77 | 4.79 | 4.61 | (43.22) | (4.23) | (3.95) | 9.20  |
| 4   | [S$_1$]$_2$[FeCl$_2$Br$_2$] | Brown | 59     | 122           | 43.52 | 4.77 | 4.61 | (42.81) | (4.37) | (4.52) | 9.71  |
| 5   | [S$_1$]$_2$[CoCl$_2$Br$_2$] | Blue  | 66     | 194           | 43.96 | 4.48 | 4.61 | (43.50) | (4.23) | (3.95) | 9.71  |
| 6   | [S$_1$]$_2$[NiCl$_2$Br$_2$] | Blue  | 79     | 229-231       | 43.52 | 4.77 | 4.61 | (42.81) | (4.37) | (4.52) | 9.71  |
| 7   | [S$_1$]$_2$[CuCl$_2$Br$_2$] | Brown | 71     | 149           | 43.52 | 4.77 | 4.61 | (42.81) | (4.37) | (4.52) | 9.71  |
| 8   | [S$_1$]$_2$[ZnCl$_2$Br$_2$] | White | 77     | 201           | 43.52 | 4.77 | 4.61 | (42.81) | (4.37) | (4.52) | 9.71  |
| 9   | [S$_2$]$_2$[MnCl$_2$Br$_2$] | White | 96     | 227           | 40.02 | 4.38 | 4.24 | (41.11) | (3.87) | (3.90) | 9.71  |
| 10  | [S$_2$]$_2$[MnCl$_2$Br$_2$] | White | 67     | 155           | 54.07 | 4.38 | 3.70 | (53.23) | (4.10) | (2.99) | 7.26  |
| 11  | [S$_2$]$_2$[FeCl$_2$Br$_2$] | Brown | 72     | 130           | 54.07 | 4.38 | 3.70 | (53.23) | (4.10) | (2.99) | 7.26  |
| 12  | [S$_2$]$_2$[CoCl$_2$Br$_2$] | Brown | 79     | 190-192       | 53.79 | 4.35 | 3.66 | (52.98) | (4.21) | (3.78) | 7.79  |
| 13  | [S$_2$]$_2$[NiCl$_2$Br$_2$] | Brown | 85     | 191           | 53.79 | 4.35 | 3.66 | (52.98) | (4.21) | (3.78) | 7.79  |
| 14  | [S$_2$]$_2$[CuCl$_2$Br$_2$] | Yellow| 90     | 160-162       | 53.79 | 4.35 | 3.66 | (52.98) | (4.21) | (3.78) | 7.79  |
| 15  | [S$_2$]$_2$[ZnCl$_2$Br$_2$] | Yellow| 55     | 199           | 53.79 | 4.35 | 3.66 | (52.98) | (4.21) | (3.78) | 7.79  |

Infrared spectral studies:

Infrared spectrum has been recorded in the range (400-4000 cm$^{-1}$) and 200-4000 cm$^{-1}$) using KBr or CsI pellets, then has been used to identify the prepared organic salts and complex salts. The values and positions of the spectra bands tabulated in Table 2.
The prepared organic salts (figs. 1, 2) and their complex salts (figs. 3, 4) showed adsorption band in (2391-2471 cm$^{-1}$) region due to the alkylation of aromatic nitrogen ring [15]. The organic salts and metal complexes exhibited a band at 1586-1642 cm$^{-1}$ and at 1514-1519 cm$^{-1}$ assigned to $\nu$(C=N) and $\nu$(C=C) respectively [16, 17].

The band between 3026-3105 cm$^{-1}$ belong to $\nu$(C-H) aromatic [18, 19]. A new band of prepared complex salts have been observed in the region 200-400 cm$^{-1}$ indicates the (M-X) stretching vibrations [20].

Table 2: Infrared data (cm$^{-1}$) of the ligand salts and their complexes.

| No. | $\nu$(N$^+$-R) | $\nu$(C=N) | $\nu$(C=C) | $\nu$(C-H) | $\nu$(M-Cl) | $\nu$(M-Br) |
|-----|----------------|-----------|-----------|----------|-----------|-----------|
| 1   | 2409           | 1631(s)   | 1514(s)   | 3074(s)  |           |           |
| 2   | 2391           | 1640(s)   | 1516(s)   | 3035     |           |           |
| 3   | 2432           | 1597      | 1515      | 3071     |           |           |
| 4   | 2437           | 1586(s)   | 1518(s)   | 3063(m)  | 295       | 235       |
| 5   | 2432           | 1630      | 1516      | 3072     |           |           |
| 6   | 2363           | 1624(vs)  | 1519(s)   | 3105(s)  |           |           |
| 7   | 2425(vw)       | 1628      | 1515      | 3082     | 310       | 242       |
| 8   | 2408 (vw)      | 1642(vs)  | 1516(s)   | 3046(m)  |           |           |
| 9   | 2413(vw)       | 1641(vs)  | 1517(s)   | 3030(m)  |           |           |
| 10  | 2452           | 1642      | 1517      | 3031     |           |           |
| 11  | 2408           | 1642(vs)  | 1516(s)   | 3046     |           |           |
| 12  | 2413(vw)       | 1641      | 1517(s)   | 3030(s)  | 370       | 252       |
| 13  | 2413           | 1647(vs)  | 1517      | 3037(s)  |           |           |
| 14  | 2448           | 1641      | 1516      | 3038     |           |           |
| 15  | 2471           | 1643      | 1517      | 3042(s)  | 320       | 245       |
| 16  | 2419           | 1641(vs)  | 1517      | 3037     |           |           |

vw = very weak, s = strong, m = medium
Fig. 1 Infrared spectra of N-ethyl quinolinium bromide salt \([S_1]\)

Fig. 2 Infrared spectra of 3-methyl-N-benzyl iso quinolinium bromid \([S_2]\)
Fig.3 Infrared spectra of Bis(N-ethylquinolinium) dibromodichloroIron(II) (complex4)

Fig.4 Infrared spectra of Bis(N-benzyl-3-methylisquinolinium) dibromo dichloro Cobaltate(II) (complex12)
Electronic spectra and magnetic measurements:

The electronic spectra for organic salts and complexes were recorded in the range 200-1100 nm using dimethylformamide (DMF) as a solvent.

The uv-spectra of organic salts showed two absorption bands assigned to the transition $n\pi^*$ of the C=N group (36000, 76000 cm$^{-1}$) and $\pi \pi^*$ transition of aromatic ring [21, 22].

The electronic spectra of Mn(II) complex salts do not show any d-d transition spectra as expected [23] while their magnetic moment were found to be 5.8 and 5.8 B.M corresponding to a high spin tetrahedral geometry [24].

The electronic spectra of Fe(II) $[S_1]_2[FeCl_2Br_2]$ complex show a band observed in the visible region (10172 cm$^{-1}$), which caused by electronic transition $^5$ED $^5$T_2D (Lever, 1980; [25, 26]. The magnetic moment of this complex was found to be 4.478 B.M which with expected spin only values of tetrahedral geometry configuration [27, 28]. The complex $[S_1]_2[FeCl_2Br_2]$ shows d-d absorption bands in the near infrared and visible regions (15400, 24968 cm$^{-1}$) and are similar to reported spectra for square planar iron (II) complex [29]. Also the magnetic moment $\mu_{ef}$ (3.94 B.M) indicates a square planar stereochemistry of the complex [27].

The complex salts of Co(II) shows two bands at (12315, 13531 cm$^{-1}$) and (13698, 17960 cm$^{-1}$) attributed to $^4$A$_2 \rightarrow^4$T$_2$ (F$_1$(v$_2$)) and $^4$A$_2 \rightarrow^4$T$_1$ (P(v$_3$)) respectively [30, 31]. The magnetic moment for Co(II) complexes were found to be 4.4 and 4.32 B.M which within the expected spin only values of tetrahedral geometry [27, 30, 32].

The electronic spectra of Ni(II) complexes has revealed the electronic transition $^3$S$_1$($\Pi$) $^3$T$_1$($\Pi$) (v$_3$), at (11862, 11000 cm$^{-1}$) [30, 33, 34]. The higher values of magnetic moments of Ni(II) complexes (3.28, 3.94 B.M) may be due to the orbital contribution [24, 35].

Finally the electronic spectra of Cu(II) complex salts display bands at 14673 and 18726 cm$^{-1}$ (figs.5,6) which were attributed to the electronic transition $^2$T$_2$(D) $^2$E(D). This result confirmed the tetrahedral geometry around Cu(II) [31, 36].

The magnetic moments of Cu(II) complexes were found to be 1.9 and 1.93 B.M which lies within the expected value of one electron with orbital contribution [37, 38].

In general, the spectra of all complex salts show two intense peaks in the U.v region between (28400 - 37194) and (28052-42016 cm$^{-1}$) due to either charge or electronic transition of organic salts.
Table 3: The magnetic moments and uv-visible spectroscopy for complex salts.

| No. | $\mu_{\text{eff}}$ (B.M) | d-d transition cm$^{-1}$ | Charge transfer cm$^{-1}$ |
|-----|-----------------|------------------------|--------------------------|
| 1   | 28800, 36000    |                        |                          |
| 2   | 28400, 37600    |                        |                          |
| 3   | 5.8             | 10172                  | 37114, 42016             |
| 4   | 4.47            | 12315, 13698           | 29411, 35571             |
| 5   | 4.4             | 11862                  | 31948, 31250             |
| 6   | 1.92            | 14673                  | 31446, 40116             |
| 7   | Dia             |                        | 29585, 35714             |
| 8   | Dia             |                        | 28288, 313352            |
| 9   | 3.28            | 11862                  | 28288, 35352             |
| 10  | 5.8             | 15400, 24966           | 31298, 38910             |
| 11  | 3.82            | 11351, 12960           | 28409, 38910             |
| 12  | 4.3             | 10100                  | 28409, 34844             |
| 13  | 3.94            | 18726                  | 29496, 34844             |
| 14  | Dia             | 28571, 35714           |                          |
| 15  | Dia             | 29582, 35714           |                          |

Fig.5 The UV-Visible Spectra of Bis(N-ethylquinolinium) dibromodichloro cuprate(II) (Complex7)
Fig.6 The UV-Visible Spectra of Bis(3-methyl-N-benzylisoquinolinium) dibromodichloro cuprate(II) (Complex14)

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