

Synthesis and Characterization of New Complex Salts, of Some Transition and Non-Transition Metals with Isoquinolinium Derivative Salts

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Abstract - Two organic salts of type [S]_x, (S= 3-methyl – N-methyl isoquinolinium, 3-methyl-N-ethyl isoquinolinium, X=I or Br) were prepared by alkylation in ethanol solution, complex salts type[S]₂ [MCl₂X₂] of these organic salts were synthesized by addition of ethanolic solution of chloride ions (Mn⁺², Fe⁺², Co⁺², Ni⁺², Cu⁺², Zn⁺² and Cd⁺²) to the solution of organic salt in ethanol under reflux in (1:2) ratio, metal to ligand. The resulting product was found to be solid, which have been characterized using IR, UV-Vis. Spectroscopy. Elemental analysis have been performed using CHN and atomic absorption techniques, the magnetic susceptibility and molar conductivity have been measured.

Keywords - Ionic liquids, complex salt, 3-methylisoquinolinium salts, green chemistry.

I. INTRODUCTION

Ionic liquids (ILS) are ionic compounds with relatively low melting points. They are characterized by very low vapor pressures and consequently, are considered as environmentally benign solvents. In addition (ILS) possess interesting properties such as polarity, Lewis acidity, coordinating ability, and miscibility with various compounds [1-3]. Therefore, the (ILS) are an important area with regard to chemical synthesis and catalytic process [4]. The ammonium, phosphonium, pyridinium and imidazolium cations of (ILS) can coordinate to MX₄⁻² (M=Mn⁺², Fe⁺², Co⁺², Ni⁺², Cu⁺², Zn⁺², Cd⁺² and Pd⁺², X=Cl, I or Br) complex ions to form ionic liquid crystals [5-8]. Considerable interest has been shown over recent years in the transition metal halide complexes and among them tetrahalometalates with various organic counter cations have been subject of

theoretical structural, [9,11], magneto structural [12,13] and spectroscopic studies [14,15]. The crystal and molecular structure of [AMP]₂ [ZnCl₄], {[AMP]⁺=2-amino-6-methyl Pyridinium cation and [ZnCl₄]⁻² as anion}, which held together by N-H...Cl hydrogen bonds. bond length within (AMP) cation indicate that the imine tautomer make significant contribution to the structure. The molecules are associated by π-π interactions between identical antiparallel (AMP), with face to face distances of 3.627 and 3.342 (3) Å to form a one-dimensional chain [16]. Quinolinium quaternary family salts are widely used as a parent compound to make drugs (especially anti-malarial medicines) fungicides and antibacterial [17]. In our knowledge no complexes between metal (II) ions and quaternary quinolinium halides were reported yet. Hence, in this paper we synthesis some new complex salts of transition and non-transition metal (II) ions with isoquinolinium, which have improved by using the spectral and physico chemical techniques.

II. EXPERIMENTAL WORK

A. Materials and Methods

The transition and non-transition metal ions were used as supplied by Fluka. All reagents used chemically pure or analytical grade. Molar conductance were carried out for 10⁻³ M solution in diethyl formamide (DMF) using an electronic conductivity measuring device model LF-42 at 25 °C. Magnetic susceptibility measurements were performed on MSB-MKI (magnetic susceptibility balance) Sherwood scientific using Gouy Method.

The electronic spectra of complex salts were recorded on Shimadzu uv-1800 spectrophotometer at 25C° using a 1cm quartz cell. IR spectra were recorded on. Metal analysis was carried out by using an AA240FS Varian instrument for atomic absorption. The qualitative element of the sodium fusion solution of mixed halides, complex salts [19].

B. Preparation of 3-Methyl-N-methylisoquinolinium iodide salt

This salt was prepared by adding (0.01 mole, 1.43 g) of 3-methylisoquinoline dissolving in (10 cm³) of absolute ethanol to (0.01 mole, 1.42 g) of methyl iodide in an (50 cm³) round flask. The mixture was refluxed for 2h. Then it was allowed to cool in an ice bath, ethyl acetate (10 cm³) was added to obtain a yellow crystals. Filtered off and washed several times by ethyl acetate and diethyl ether, dried at 50 C° for 5h.

C. Preparation of 3-methyl-N-ethylisoquinolinium bromide [S₂][Br]

This organic salt was prepared by the same procedure in (B) by using (0.01 mole, 1.52g) of 3-methyl-N-ethylisoquinoline (0.01 mole, 0.95g) of methyl bromide to obtain light brown crystals .

D. Synthesis of bis(3-methyl-N-methylisoquinolinium) dichlorodiodidemetalate (II), [S₁]₂[MCl₂I₂]

A solution of MnCl₂.4H₂O, FeCl₂.2H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, ZnCl₂, CdCl₂ (0.01 moles) each in absolute ethanol (10 cm³) was added to a solution of [S₁][I] (0.02 mole, 5.71g) in absolute ethanol (10 cm³). After heating under reflux for 1h, the product solution concentrated to half volume and allowed to cool at room temperature. The precipitate complexes were filtered off. Washed several times with cold ethanol and diethyl ether. dried in an oven for 3h at 50C.°

E. Synthesis of bis (3-methyl-N-ethyl isoquinolinium) dichlorodibromometalate (II) [S₂]₂[MCl₂Br₂]

These complexes were synthesized as solid products by employing the above described procedure using

(0.02 mole, 5.05g) 3-methyl-N-ethylisoquinolinium bromide instead of iodide salt.

III. RESULTS AND DISCUSSION

The physical properties, elemental analysis and molar conductivity of organic salts and their complexes are given in table (1) The ionic complexes were air stable at room temperature and coloured solid. All complex salts are new synthesized by the typical reaction of metal ions with 3-methyl-N-methylisoquinoliniumhalids (scheme1) .



M= Mn⁺², Fe⁺², Co⁺², Ni⁺², Cu⁺², Zn⁺² and Cd⁺², X=I or Br, R=CH₃,CH₂CH₃

The molar conductivity in DMF of organic salts and complexes were between (76 - 82) and (136-170) ohm⁻¹ cm² mole⁻¹, indicates as 1:1 and 1:2 electrolyte nature as expected for organic salts and their complexes respectively [20,21]. Also, The metal analysis and CHN analysis data are in a good agreement with the calculated values based on the mentioned formulas of complex salts.

A. Infrared Spectral Studies

The characteristic vibrations assignments of organic salts and their complexes by using CsI or KBr disc are described in table (2). The spectrum of 3-methyl-N-alkylisoquinolinium halides exhibited bands between (3018-3059) cm⁻¹ and (2370-2380)cm⁻¹ are attributed to ν(C-H) aromatic and ν(N+-CH₃) respectively [22-24]. While the bands between (1614-1651)cm⁻¹ and (1519-1593) cm⁻¹ which belongs to the vibration of ν(C=N) and ν(C=C) respectively [18,24,25]. The infrared spectra of the prepared complex salts exhibited ν(C=N)cm⁻¹ the range of (1638-1646) cm⁻¹. the other bands appeared in the range (2320-2416) cm⁻¹, (1486-1515) cm⁻¹ and (2982-3033)cm⁻¹ due to the vibration of ν(N+_CH₃), ν(C=C) and ν(C=H) respectively [24,26]. New bands appeared for the prepared complexes in the region 200-4000 cm⁻¹ indicates the (M-X) Stretching vibrations [25] .

Table I

physical properties , elemental analysis and molar conductivity of organic salts and their complexes

compo undNO ·	Compund	colour	Yield (%)	Molting Point(C)	Molar Conductivity $\text{ohm}^{-1} \cdot \text{mol}^{-1}$ $\cdot \text{cm}^2$	(%)C H N (Fond)calc.			%M (calc.)
						C	H	N	
1	S ₁	Pale yellow	84.6	221	76	46.28 (45.84)	5.07 (4.38)	4.90 (4.12)
2	S ₂	brown	70	191	82
3	[S ₁] ₂ [MnCl ₂ I ₂]	Pale yellow	67	211	136	37.93 (37.60)	4.15 (3.89)	4.02 (4.13)	7.88 (8.04)
4	[S ₁] ₂ [FeCl ₂ I ₂]	brown	71	202-204	169	8.10 (7.92)
5	[S ₁] ₂ [CoCl ₂ I ₂]	green	67	210	158	37.71 (37.02)	4.13 (4.22)	3.99 (3.89)
6	[S ₁] ₂ [NiCl ₂ I ₂]	Plae green	79	222-224	157	37.73 (38.62)	4.13 (3.67)	4.00 (3.82)	8.38 (9.02)
7	[S ₁] ₂ [CuCl ₂ I ₂]	darck red	66	171	136	37.47 (37.21)	4.10 (4.12)	3.97 (3.90)	9.00 (8.78)
8	[S ₁] ₂ [ZnCl ₂ I ₂]	white	70	261	169	36.97 (37.02)	4.09 (4.13)	3.96 (3.72)	9.20 (8.49)
9	[S ₁] ₂ [CdCl ₂ I ₂]	white	72	209	169	35.04 (35.96)	3.84 (4.11)	3.71 (3.42)
10	[S ₂] ₂ [MnCl ₂ Br ₂]	white	60	250	156	8.70 (8.13)
11	[S ₂] ₂ [FeCl ₂ Br ₂]	brown	64	171	171	9.28 (8.74)
12	[S ₂] ₂ [CoCl ₂ Br ₂]	blue	86	239	169	9.28 (8.74)
13	[S ₂] ₂ [NiCl ₂ Br ₂]	green	71	240	157	45.41 (44.23)	5.21 (4.91)	4.41 (3.72)	9.28 (7.93)
14	[S ₂] ₂ [CuCl ₂ Br ₂]	dark red	79	201	169	45.07 (44.87)	5.17 (4.73)	4.38 (4.18)	9.92 (8.90)
15	[S ₂] ₂ [ZnCl ₂ Br ₂]	white	67	241	134	44.94 (44.69)	5.15 (4.83)	4.36 (3.27)	10.18 (9.94)
16	[S ₂] ₂ [CdCl ₂ Br ₂]	white	67	231	169	41.8 (40.77)	4.80 (4.21)	4.06 (3.69)

Table II
Infrared data (cm^{-1}) of the organic salts of their complexes

Compound	$\nu(\text{C-H})$	$\nu(\text{N}^+-\text{CH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{M-Cl})$	$\nu(\text{M-Br})$	$\nu(\text{M-I})$
S1	3010 _s	2370 _m	16511 _w	1519 _s
S2	3059 _w	2380 _s	1614 _s	1593 _s
[S ₁] ₂ [MnCl ₂ I ₂]	3015 _w	2340 _s	1646 _w	1515 _m	285 _s	235 _m
[S ₁] ₂ [FeCl ₂ I ₂]	3011 _s	2412 _m	1643 _w	1514 _m
[S ₁] ₂ [CoCl ₂ I ₂]	2989 _w	2416 _m	1643 _s	1515 _m
[S ₁] ₂ [NiCl ₂ I ₂]	2982 _w	2416 _s	1643 _w	1515 _s	298 _s	240 _s
[S ₁] ₂ [CuCl ₂ I ₂]	3022 _m	2346 _s	1638 _s	1509 _s
[S ₁] ₂ [ZnCl ₂ I ₂]	3023 _m	2346 _s	1643 _m	1515 _s
[S ₁] ₂ [CdCl ₂ I ₂]	3030 _w	2366 _m	1645 _s	1513 _s
[S ₂] ₂ [MnCl ₂ Br ₂]	3032 _m	2320 _s	1643 _s	1486 _m
[S ₂] ₂ [FeCl ₂ Br ₂]	3031 _w	2344 _m	1642 _s	1488 _m	275 _m	252 _s
[S ₂] ₂ [CoCl ₂ Br ₂]	3031 _m	2343 _m	1643 _s	5111 _m
[S ₂] ₂ [NiCl ₂ Br ₂]	3033 _w	2302 _m	1640 _s	1515 _s
[S ₂] ₂ [CuCl ₂ Br ₂]	3023 _m	2372 _w	1642 _s	1487 _m	331 _w	262 _m
[S ₂] ₂ [ZnCl ₂ Br ₂]	3032 _m	2382 _w	1641 _s	1489 _m
[S ₂] ₂ [CdCl ₂ Br ₂]	3031 _m	3246 _m	1641 _s	1490 _s

B-Electronic spectra and magnetic moment

The electronic spectra and magnetic moment of metal complexes, are listed in table (3). The uv-vis spectrum of the ligands showed absorption bands at 28991 and 28511 cm⁻¹ assigned for $\pi \rightarrow \pi^*$ transitions of the aromatic quinoline rings. The bands observed at 35507 and 37314 cm⁻¹ would be due to the $n \rightarrow \pi^*$ transition of C=N group [27,28]. In all the reflectance spectra of the complex salts the bands appeared at 35567 cm⁻¹ due to the ligand absorptions or charge transfer. The reflectance spectrum of the Mn(II) complex salts showed a weak band at (25326 and 26178 cm⁻¹). This band is both laporte and spin forbidden [29,30]. The value of magnetic moment of high spin Mn(II), mostly equals to (5.94 BM). The μ_{eff} of prepared complex salts of Mn(II) are 5.3 and 5.8 (B.M), which agrees with tetrahedral geometry [31].

The electronic spectra of Iron(II) complex [S₁]₂[FeCl₂I₂] show absorption band in near infrared, visible and

ultraviolet regions and similar to reported spectra for square planar Iron (II) complexes [32]. Also, the magnetic moment (3.3 B.M) indicates as reported for square planar [33]. The electronic spectra of [S₂]₂[FeCl₂Br₂] complex show a band at 15600 cm⁻¹ which is caused by electronic transition $^5E_D \rightarrow ^5T_{2D}$ [29,34,35]. The magnetic moment for this complex was found to be 4.8 B.M which with the expected spin-only values of tetrahedral configuration [23,36].

The electrical spectra of [S₁]₂[CoCl₂I₂] complex salt exhibit a strong band at 15882 cm⁻¹ which may be assigned to $2A_g \rightarrow 2E_g$ transition in square planar field for Co(II) complex [37,40]; value of magnetic moment was 1.7 B.M in agreement with reported values of low spin square planar [39,38]. The complex salt [S₂]₂[CoCl₂Br₂] exhibits prominent two transition bands at 12919 and 14662 cm⁻¹ corresponding to transition $^4A_{2(F)} \rightarrow ^4T_{1(F)}$ (V2), $^4A_{2(F)} \rightarrow ^4T_{1(P)}$ (V3) respectively.

Occurrence of these transition bands suggest a tetrahedral geometry proposed for the complex [41,42]. The magnetic moment value of complex was 4.8 B.M Support the tetrahedral geometry proposed for complex [43,44]. The electronic spectrum of [S1]₂[NiCl₂I₂] show a band at 23000 cm⁻¹ which is attributed to ²A_{1g} → ²B_{2(g)} transition [29,45]. This transition, as well as, the measured value of the magnetic moment (μ_{eff} B.M) suggests square planar stereochemistry of complex [45]. The complex salt [S₂]₂[NiCl₂Br₂] show a strong band at 15600 cm⁻¹ due to ³T_{1(F)} → ³T_{1(P)} (V 3) indicated a tetrahedral geometry [31]. This geometry is confirmed by a magnetic moment (2.8 BM) [46,47].

The electronic spectrum of [S1]₂[CuCl₂I₂] exhibit a band at 15800 cm⁻¹ which could be attributed to the ²A_{1g} → ²B_{2g} transition characterized Cu(II) in a square planar geometry [28,48]. The square planar geometry of Cu(II) ion in the complex salt is confirmed by the measured magnetic moment 1.7 B.M [28,29,46]. The complex [S₂]₂ [CuCl₂Br₂] exhibits a weak broad band in the visible region at 16200 cm⁻¹ assigned to transition ²T₂ → ²E₁ in tetrahedral field [39,49]. In which the magnetic moment value is close to a value for an unpaired at 1.93 B.M[50].

The Zn(II) and Cd(II) complex salts were expected diamagnetic with only charge transfer in the visible region [51].

Table III
Electronic spectra and magnetic moment

Compound	μ _{eff} (B.M)	π → π*, n → π* C.T. Cm ⁻¹	d → d TransitionCm ⁻¹
S1		28991, 35507	
S2		28511, 37313	
[S1] ₂ [MnCl ₂ I ₂]	5.38	28932, 35212	25326
[S1] ₂ [FeCl ₂ I ₂]	3.3	29412,35971	12886
[S1] ₂ [CoCl ₂ I ₂]	1.7	29411,35971	15882
[S1] ₂ [NiCl ₂ I ₂]	dia	29761 ,37037	23000
[S1] ₂ [CuCl ₂ I ₂]	1.7	28818 ,35460	15800
[S1] ₂ [ZnCl ₂ I ₂]	dia	28985,37313	
[S1] ₂ [CdCl ₂ I ₂]	dia	28921,35507	
[S1] ₂ [CdCl ₂ I ₂]	dia	28921,35507	
[S2] ₂ [MnCl ₂ Br ₂]	5.8	28901,35460	
[S2] ₂ [FeCl ₂ Br ₂]	4.8	28901,35211	15600
[S2] ₂ [CoCl ₂ Br ₂]	4.8	28901,35335	12919,14662
[S2] ₂ [NiCl ₂ Br ₂]	2.8	28735,35460	15600
[S2] ₂ [CuCl ₂ Br ₂]	1.93	27937,38314	16200
[S2] ₂ [ZnCl ₂ Br ₂]	dia	28511,35587	
[S2] ₂ [CdCl ₂ Br ₂]	dia	28570,37313	

IV. CONCLUS ION

In this study we have reported the synthesis of isoquinolinium N-methyl and ethyl halides organic

salts. The series of new complex salts of type $[S]_2[MCl_2X_2]$ were prepared (S= organic salts, X=I or Br, M=Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺). The physicochemical analysis such as IR, UV, spectroscopy, magnetic measurements, molar conductivity and elemental analysis were used to perform the geometry structure of these complex salts.

V. REFERENCES

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