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Bis (N-methyl benzothiazolium-2-thio) ethane, pyridine or Bis (N-methyl benzoxazolium-2-thio) ethane diiodide and its Co(II), Ni(II), Cu(II) and Zn(II) ionic salts

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ABSTRACT

Three novel organic salts two of them based on 2-mercaptobenzothiazolium ion and the third based on 2-mercaptobenzoxazolium ion were synthesized by improved method. These organic salts were characterized by IR, conductivity and electronic spectra. New ionic salts bis (N-methyl benzothiazolium-2-thio) alkane (alkane=ethane (E) or pyridine (P) diiodo dichloro metalate and bis (N-methyl benzoxazolium-2-thio) ethane(E) diiododichlorometalate having the formula [NMBtE][MCl_2I_2], [NMBtP][MCl_2I_2] and [NMBoE][MCl_2I_2] (M= Co(II), Ni(II), Cu(II) and Zn(II) were obtained from the reaction of respective ionic liquid with metal chloride in 1:1 molar ratio. The prepared ionic salts were characterized using above method as well as magnetic measurement, metal content analysis. The conductance data indicate that the ionic salts are 1:1 electrolyte, while the electronic spectra and magnetic measurement indicate that the anions [MCl_2I_2] have a tetrahedral environment around the metal ions.

Keywords: Ionic liquids, Metal salts complexes.

INTRODUCTION

Ionic liquids have received considerable attention as substitutes for volatile organic solvents. Since they are nonflammable, non-volatile and recyclable, they are classified as green solvents. Due to their remarkable properties, such as outstanding solvating potential(1), thermal stability(2) and their tunable properties by suitable choices of cations and anions(3), they are considered favorable medium candidates for chemical syntheses(4).Also they have been widely used in electro deposition, electro synthesis, electro catalysis, electro chemical capacitor ,lubricants, plasticizers, solvent, lithium batteries(5) .Most of the ionic liquids are composed of organic cation and inorganic anions. In order to be liquid at room temperature, the cation should preferably be unsymmetrical; that is, the alkyl groups should be different. Polarity and hydrophilicity/hydrophobicity of ionic liquids can be tuned by suitable combination of cation and anion. It is this property of ionic liquids which has earned them the accolade “designer solvents.”(6).The most common hetero aromatic based ionic liquids include imidazolium, thiazolium, tetrazolium, pyridinium etc. However thiazolium and benzothiazolium based ionic liquids are very scarcely studie(7). Benzothiazoliums are also a part of many important dyes(8,9) . In medicine the benzothiazolium salts play an important role, for example Riluzole a benzothiazole-based drug is used to treat amyotrophic lateral sclerosis(10). While on the other hand the benzothiazolium salts have also been studied for their activity in different biological systems (11).By melting metal chlorides with dialkyl imidazolium chloride, many dialkyl imidazolium chloro metalate ionic liquids have been obtained in past few years (12-17). Recently, ionic liquid that contain a carboxylic group in the aliphatic side chain of imidazolium ring with bis (trifloromethysulfonyl) imide [TF_2N]$^-$ as a counter anion were found to be capable to solvate many metal oxides(18,19).The title compound 2,3-dimethylbenzoxazolium methosulfate is derived from 2-methylbenzoxazole reacting with a slight excess of dimethylsulfate, at room temperature. The reaction proceeds via an intrinsic exothermic reaction, and the benzoxazolium salt crystallized after a short time into a white crystalline form in 89% yield (20).

Metal containing ionic liquid crystals of N, N-dialkyl imidazolium salts of Pd(II) and Cu(II) [$(C_nH_{2n+1})_2$-im][MCl_4] n= 8,10,12,14,16 and 18 for M= Pd(II) and n=10,12,14,16 and 18 for M=Cu(II) were prepared crystal structures of two compound [$(C_{12}H_{25})_2$-im]$_2$[$PdCl_4$] and [$(C_{12}H_{25})_2$-im]$_2$[$CuCl_4$].H_2O has been characterized by single crystal X-ray diffraction. The cations of these two compounds adopt a U-shaped conformation and are packed in a highly interdigitated bilayer fashion. The square planer $PdCl_4^{2-}$ and distorted tetrahedral $CuCl_4^{2-}$ are sandwiched the cationic bilyares individually(21).

In the cation of the title salt, $C_4H_8NO^+.C_{24}H_{20}B^-$, the C-N bond lengths are 1.272 (2), 1.4557 (19) and 1.4638 (19) A °, indicating double- and single-bond character, respectively. The C-O bond length of 1.3098 (19)A° shows that double bond character and charge delocalization occurs within the NCO plane of the cation. In the crystal, a C-H---π interaction is present between the methylene H atom of the cation and one phenyl ring of the tetraphenylborate ion. The latter forms an aromatic pocket in which the cation is embedded(22).

The new ionic liquids 3-cyanomethyl-1-methylimidazoliumtetrachlorocadmate(1) and 3-(4-cyanobutyl)-1-methylimidazoliumtetrachloro- cadmate (2) were obtained from the reaction of the respective alkyl imidazolium chlorides with cadmium chloride in 2:1 molar ratios. Structural characterization of (1) by single X-ray diffraction reveals the existence of $[CdCl_4]^{2-}$ tetrahedral and substantial C-H…Cl hydrogen bonding(23).

The presence of metal ions in ionic liquids provides many additional properties such as color, geometry and magnetism. These properties cannot be achieved easily by conventional ionic liquids. Whereas reports on the metal containing ionic liquids are relatively rare(24,25).

In view of these interesting results and as continuation of our study on transition metal complex salts with pyrrolium, pyridinium, indolium and benzimitrazolium organic salts(26-28) , we have prepared a new type of benzothiazolium and benzoxazolium derivative diiodide ionic liquids and their complex salts with Co(II), Ni(II), Cu(II) and Zn(II) .

EXPERIMENTAL

General

All reagent used were either analytical grade or chemically pure. Preparative work was carried out under dry nitrogen gas using standard schlenk techniques. Infrared spectra were recorded on a Brucker Tensor 27CO. FTIR spectrophotometer in the 200-4000 cm^{-1} range using CsI discs. The chloride was determined using the method in reference (29). Conductivity measurements were carried out on 10^{-3} M solution of the complexes in DMF using conductivity meter PCM3 Jenway at ambient temperature. The electronic spectra were recorded on a Shimadzu UV-visible spectrophotometer Uv-160 for 10^{-3}M solution of complexes in DMF at 25°C using 1 cm quartz cell. Magnetic measurement was carried out at 25°C on the solids by Faraday's method using Brucker BM6 instrument.

1-Preparation organic salts Bis-(N-methyl benzothiazolium-2-thio) ethane diiodide [NMBtE].2I

A solution of 1,2-bis(benzothiazozole-2-thio)ethane prepared in our laboratory(30) (3.60g,0.01 mol) in equivalent mixture of ethanol and tetrahydrofuran (10 cm^3) was added drop wise to a solution of methyl iodide (2.84g,0.02 mol) in ethanol . Addition was continued for ca. 30min. the reaction mixture was refluxed for 3h., then left to stand at room temperature. The brown solid thus formed was filtered off, washed twice with ethanol followed by diethylether then dried under vacuum for several hours. Bis-(N-methyl benzothiazolium-2-thio) pyridine diiodide and Bis-(N-methylbenzoxazolium-2-thio)ethanediiodide; [NMBtP].2I, [NMBoE].2I respectively, were prepared similarly as above.

2- Preparation of ionic salts [NMBtE][$CoCl_2I_2$]

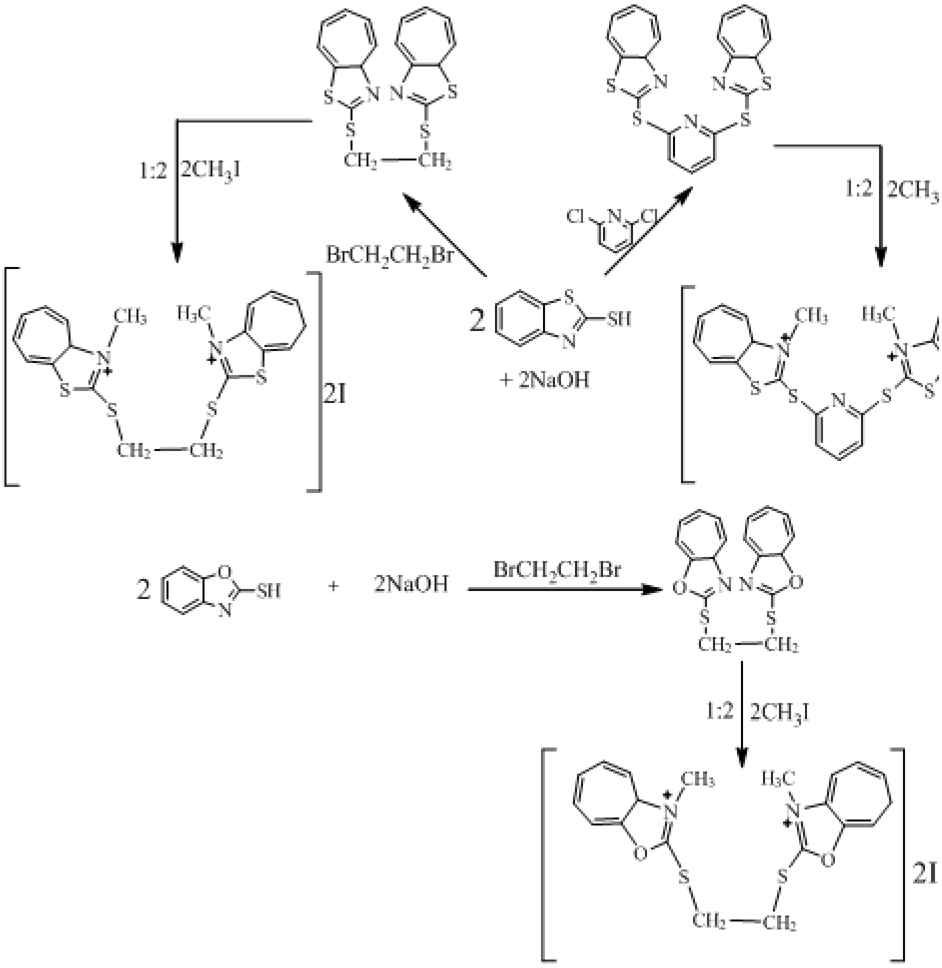
A solution of $CoCl_2.6H_2O$ (0.24 g,0.001mol) in ethanol (10cm^3) was added dropwise to a solution of Bis-(N-methylbenzothiazolium-2-thio) ethane (0.64g,0.001 mol) in chloroform (10 cm^3). The mixture was refluxed for 2h., and then the solution was allowed to cool to room temperature. The purple solid thus formed was filtered off, washed with ethanol followed by diethylether and then dried under vacuum for several hours. The rest of ionic salts were prepared in similar manner.

3- Preparation of [NMBtP][MCl_2I_2] and [NMBoE][MCl_2I_2]

The ionic salts [NMBtP][MCl_2I_2] and [NMBoE][MCl_2I_2] were prepared in the same method mentioned in the paragraph above.

RESULTS AND DISCUSSION

The synthetic route of the Bis-(N-methylbenzothiazolium-2-thio)ethane or pyridine diiodide or Bis-(N-methylbenzoxazolium-2-thio) ethane diiodide ionic organic salts are depicted in Scheme(1) Bis-(N-methylbenzothiazolium-2-thio) ethane or pyridine or Bis-(N-methylbenzoxazolium-2-thio) ethane were synthesized by the reaction of 2-mercaptobenzothiazole or 2-mercaptobenzoxazole and 1,2-dibromoethane or 2-mercaptobenzothiazole and 2,6-dichloropyridine with sodium hydroxide in (2:1:2) molar ratio. The products are further quarternized with methyl iodide in (1:2) molar ratio, as shown in (Scheme 1).



(Scheme 1): Synthesis of ionic liquid

The ionic salts with general formula of [NMBx(A)][MCl_2I_2] (A= ethane ,pyridine, Bx=2-mercaptobenzothiazole,2-mercaptobenzoxazole) were prepared by reacting metal chloride with the above organic di-iodide salts under refluxing conditions. The prepared ionic salts are stable for long time, non hydroscopic and colored solids. The melting point, conductance and magnetic measurements of organic and ionic salts are listed in (Table 1).

Conductance measurements were carried out to ascertain the electrolytic/non electrolytic nature of metal complexes, molar conductance values of complexes in 10-3M DMF solution at room temperature suggest the electrolytic nature (1:1) for complexes (1-12). The conductance data showed that the organic salts are (1:2) and for the ionic salts are 1:1 electrolytic nature(31).The conductivities of the ionic liquids salts are significantly higher than those observed for 1-n-butyl-3-methylimidazolium- tetrachloroaluminate(32). This indicated that the interactions between the cation and anion essentially electrostatic with small contribution of hydrogen bond.

The formation of organic di-iodide salts was investigated by FTIR spectra. (Table 2) shows the more characteristic infrared spectral bands of the organic salts and there ionic salts. The assignment of the infrared spectra of the organic salts show a band at 2423-2560 and 1597-1618cm^{-1}, assigned to υ(N^+CH_3) and υ(C=N)(33),that means that the quantized salts with methyl iodide was at the nitrogen atom . The spectra of the ionic salts also reveal the presence of the above bands at similar position , as well as the presence of new band at 278-318 and 210-230 cm^{-1} which was assigned to υ(M-Cl) and υ(M-I) respectively(34,35).

The magnetic properties of the complexes provide valuable information for distinguishing their stereochemistry. The magnetic moment (μ_{eff}) of the Co(II) complex salts (1,5 & 9) $3d^7$ system showed an effective magnetic moments of (4.32-4.64)B.M, confirming a tetrahedral geometries which is related to three unpaired electrons. The magnetic moments of the Ni(II) ionic salts were found to be (2.94-3.54) B.M suggest tetrahedral geometry(36). The magnetic moment values of the Cu(II) ionic salts (2.07-2.18) B.M , these values reveals the presence of one unpaired electron, suggest a tetrahedral structure for the ionic salts(37). The Zn(II) ionic salts were diamagnetic.

The electronic spectral bands of the organic salts and their ionic salts are listed in (Table 2). The Uv-visible spectra of the organic salts showed a bands at (31055-33783) cm^{-1} assigned to π-π^*, n-π^* and charge transfer transition within the molecules, respectively(37). The band of the organic salts were slightly blue shifted in all complexes, while new bands were observed in the visible region for Co(II),Ni(II) and Cu(II) complexes salts due to d-d transition.

For Co(II) ionic salts (1,5 and9), few d-d transition were observed around 400-700nm.Bands at 16447-16455cm^{-1} assigned to $^4A_2(F) \longrightarrow {}^4T_1(P)$ transition , in addition a charge transfer bands at (31250-33557) Cm^{-1} suggest tetrahedral geometry for Co(II) ionic salts. The Ni(II) ionic salts (2,6,10) shows bands in the visible region at 14409-14450 cm^{-1} correspond to $^3T_1(F) \longrightarrow {}^3T_1(p)$ transition and charge transfer bands was observed at 30303-33333 cm^{-1}. The electronic spectra and the magnetic moment support the tetrahedral structure for Ni(II) ionic salts.

In case of Cu(II) complexes (3,7 and 11), only one band of lower energy observed at 10683-11820 cm^{-1} was assigned to d-d transition, correspond to the $^2T_2g \longrightarrow {}^2Eg$ transition and a charge transfer band at 31446-32935 cm^{-1} .The magnetic moment and electronic spectra of Cu(II) complexes support a tetrahedral geometry around Cu(II).The spectra of diamagnetic Zn(II) complex salts are dominated by the ligands bands indicating a tetrahedral geometry(38).

The prepared organic salts and their ionic salts will be used as effective extractants for desulfurization of real diesel oil from Iraqi refinery.

The results of this study clearly indicated that the M^{2+} ion is surrounded tetrahedraly by two Cl^- and two I^- ions and there is electrostatic interaction between the cation and the anion. There may a hydrogen bonding between the complex anion and the Bis-(N-methylbenzothiazolium -2-thio) cations or Bis-(N-methylbenzoxazolium-2-thio) cation.

(Table 1): Physical properties of organic salts and their ionic salts

Comp. no.	**Chemical formula**	**Color**	**m.p°C**	**Molar conductivity $\Omega^{-1}.cm^2.mol^{-1}$**	**μ_{eff}**
L_1I	$[C_{18}H_{18}N_2S_4]$ $2I^-$	White	140-142	148	---
L_2I	$[C_{18}H_{18}N_2S_2O_2]$ $2I^-$	Pale brown	128-130	155	---
L_3I	$[C_{21}H_{17}N_3S_4]$ $2I^-$	White	200^d	162	---
1	$[C_{18}H_{18}N_2S_4]^{+2}[CoCl_2I_2]^{-2}$	Purple	148-150	85	4.64
2	$[C_{18}H_{18}N_2S_4]^{+2}[NiCl_2I_2]$-2	Green	146-149	80	2.94
3	$[C_{18}H_{18}N_2S_4]^{+2}[CuCl_2I_2]^{-2}$	Olive green	155-157	75	2.07
4	$[C^{18}H_{18}N_2S_4]^{+2}[ZnCl_2I_2]^{-2}$	Pale white	122-124	79	Dia
5	$[C_{18}H_{18}N_2S_2O_2]^{+2}[CoCl_2I_2]^{-2}$	Dark green	238-241	77	4.32
6	$[C_{18}H_{18}N_2S_2O_2]^{+2}[NiCl_2I_2]^{-2}$	Green	1154-156	89	3.44
7	$[C_{18}H_{18}N_2S_2O_2]^{+2}[CuCl_2I_2]^{-2}$	Yellowish green	125-127	71	2.18
8	$[C_{18}H_{18}N_2S_2O_2]^{+2}[ZnCl_2I_2]^{-2}$	Pale white	228-230	76	Dia
9	$[C_{21}H_{17}N_3S_4]^{+2}[CoCl_2I_2]^{-2}$	Olive green	130-131	70	4.48
10	$[C_{21}H_{17}N_3S_4]^{+2}[NiCl_2I_2]^{-2}$	Brown	230^d	83	3.54
11	$[C_{21}H_{17}N_3S_4]^{+2}[CuCl_2I_2]^{-2}$	Dark brown	110-112	73	2.09
12	$[C_{21}H_{17}N_3S_4]^{+2}[ZnCl_2I_2]^{-2}$	Pale white	170-173	78	Dia

d= decomposition temperature

(Table 2): Electronic and infrared spectral data organic salts and their ionic salts

Compound no.	Band maxima (λ_{max}) Cm^{-1}	IR spectra Cm^{-1}			
		$\upsilon(CH_3N^+)$	$\upsilon(C{=}N)$	$\upsilon(M\text{-}Cl)$	$\upsilon(M\text{-}I)$
L_1I	32051	2533_S	1618_S	---	---
L_2I	33783	2560_m	1599_S	---	---
L_3I	31055	2423_S	1597_m	---	---
1	16447,32585	2550_m	1620_m	315_w	228_m
2	14409,30303	2493_S	1618_m	295_m	218_S
3	10683,32041	2446_S	1615_S	290_m	225_m
4	30674	2548_w	1612_S	278_S	230_m
5	16451,33557	2487_m	1630_S	305_m	220_m
6	14450,33333	2435_m	1635_S	311_m	216_m
7	10752,31446	2350_S	1601_m	318_m	229_m
8	34246	2439_m	1626_m	279_m	228_m
9	16455,32674	2554_w	1603_m	308_w	214_m
10	14450,31847	2425_w	1600_m	314_m	230_w
11	11820,32935	2348_m	1594_m	300_m	225_m
12	30674	2524_m	1597	285_w	210_m

S= strong, m=medium, w= weak

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