Synthesis and characterization of some new Co(II), Ni(II), Cu(II) and Zn(II) with bis (N-methyl benzimidazoliumdithio) alkane iodide

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Abstract: A new type of organic salts and their ionic salts have been recently the subject of intensive research or the extractive desulfurization of model oil (DibenzothiopheneDBT), due to the limitation of hydrodesulfurization process for removing thiophenic sulfur compounds catalytically. This study is to investigate the possible application of the above compounds as extractant for desulfurization of liquid fuel oil. Two novel organic salts are bis (N-methylbenzimidazolium) 1,3-dithiopropane diiodide (L^1) and bis (N-methyl benzimidazolium) 1,4-dithiobutane diiodide(L^2), have been prepared by improved method. Their ionic salts of the type [L][MCl_2I_2] (where L = cations of L^1, L^2, M = Co(II), Ni(II), Cu(II) and Zn(II)) were obtained using (1:1) molar ratio. The prepared organic salts and their ionic salts were characterized by elemental analysis, IR, conductivity measurement, electronic spectra, metal content analysis and magnetic measurements. The conductance data indicate that the organic salts are (1:2) electrolyte where as the complex salt s are (1:1) electrolyte. The electronic spectra and magnetic measurements indicate that the anion of the type $[MCl_2I_2]^{-2}$ have a tetrahedral environment around the metal ions. The result reveals that the ionic salt of the formula $[C_{19}H_{22}N_4S_2][CuCl_2I_2]$ can be used as extractant for desulfurization of model oil. The sulfur removal of DBT- containing model oil can reach to (46.8%) with single extraction under mild condition.

Keywords: ionic liquids, extractive desulfurization, benzimidazolium.

Introduction

Sulfur in the fuels is always organic source of SO_x that contributes to acid rain and air pollution. Therefore, the threshold limit for sulfur in gasoline and diesel oil in expected to be regulated, and this limits becomes increasingly stringent. Therefore, lower sulfur content even free-sulfur will be a trend for the development of quality in fuels[1-3]. Until now, desulfurization can only be obtained via the heterogeneous catalytic hydrodesulfurization (HDS) process in petroleum plants. The main drawbacks of the HDS process include high operating temperature of 300^oC or above, high H_2 pressure of up to MPs, high energy costs and difficulty in removing aromatic heterocyclic sulfur compounds such as benzothiphene (BT) and its derivatives[4]. Therefore, ionic liquids(ILs) may be potential candidates in overcoming HDS, drawbacks in removing aromatic heterocyclic sulfur compounds. Recently, research in ILs is attracting more attention as compared to traditional organic solvents, which could be due to their negligible vapor pressure, non-flammability and thermally stable kind of substance[5-7]. One of the most appealing features of using ILs is their potential to be custom made with preselected characteristics (moisture, stability, density, viscosity and miscibility with other solvents) through careful selection of the cation, anion or both[8].

Ionic liquids (ILs) have recently gained recognition as environmentally being alternative solvents for separations, chemical syntheses, electro chemistry and catalysis. The oxidative desulfurization extraction using ILs, as extractants catalysis to remove sulfur compounds have been reported[9-12]. Lu etal[13] have described oxidative desulfurization of fuel, catalyzed by the acidic IL [Hmim]BF_4 in the presence of H_2O_2. In these desulfurization process, sulfur containing compounds can be oxidative to greater polar sulfoxides and sulfones, which can be extracted easily by IL. The oxidation of sulfur containing compounds in [Bmim] PF_6in the presence of H_2O_2 and UV irradiation has been studied by Zhao etal[11], who found that IL [Bmim] PF_6 was used to be the extractant and photochemical reaction medium to promote the removal of sulfur containing compounds. The results of both experiments showed that the sulfur removal of model oil could reach about (90%), which was superior to the simple extraction with IL[14,15]. In this paper, we have synthesized two new type of organic salts [L1] and [L2] and eight type of their complex salts of Lewis acid ionic liquids [L][MCl_2I_2] and [L][MCl_4], which are utilized as extractants in extractive desulfurization of model.

Experimental

General

All reagents used were either analytical grade or chemically pure. Infrared spectra were recorded on a Brucker Tensor 27 CO FTIR spectrophotometer in the 200-4000 cm^{-1}range using CsI, KBr discs. Elemental analysis (CHNS) were carried out using micro analytical techniques on Perkin Elmer 2400 at Al-Al-Bait University (Jorden). Metal contents were determined spectrophotometrically using AA 670 atomic absorption. The chloride content was determined using the method in reference[16] .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 Shimadzu UV- Visible spectrophotometer UV 160 for 10^{-3}M solution of the complexes in DMF at 25°C using (1cm) quartz cell. Magnetic measurements were carried out at 25°C on the solids by Faradays method using Brucker BM6 instrument. The concentration of the sulfur contain before and after extraction was analyzed by Shimadzu UV- Visible spectrophotometer UV 1800 at the corresponding wave length (235 nm).

1.The preparation of organic salts:

The preparation of bis(N-Methyl benzimidazole-2-yl)1,3-dithiopropane and bis(N-Methyl benzimidazole-2-yl)1,4-dithiobutane were prepared in our laboratory [17].

1.1-preparation of organic salts

a-bis(N-methylbenzimidazolium)1,3-dithiopropanediiodide [{($C_7H_5(CH_3)N_2S)_2(CH_2)_3$}].2I(**L^1**)
A solution of bis(N-Methyl benzimidazole-2-yl)1,3-dithiopropane (3026g, 0.01mol) in tetrahydrofuran (10 cm^3) was added dropwise to a solution of (1.2cm^3, 0.02mol) of methyl iodide in ethanol (10 cm^3). The reaction mixture was refluxed for (2h), then left stand at room temperature for (24h)., the solid thus formed was filtered off, washed twice with ethanol then dried under room for several hours.
b- bis(N-methylbenzimidazolium)1,4-dithiobutanediiodide
[{($C_7H_5(CH_3)N_2S)_2(CH_2)_4$}].2I (L^2)
This organic saltwas prepared by the same procedure above but, bis(N-Methyl benzimidazole-2-yl)1,4-dithiobutane was used instead of bis(N-Methyl benzimidazole-2-yl)1,3-dithiopropane.

1.2- preparation of ionic salts [L][MCl$_2$I$_2$]

A solution of CoCl$_2$.6H$_2$O (0.24g, 0.001mol) in ethanol (10 cm^3) was added dropwise to a solution of bis(N-methylbenzimidazolium) 1,3-dithiopropane diiodide (L^1) (0.61g, 0.001mol) in tetrahydrofuran (15 cm^3) or bis(N-methylbenzimidazolium) 1,4-dithiobutane diiodide (L^2) (0.61g, 0.001mol) in tetrahydrofuran (15 cm^3). The mixture was refluxed for (2h)., then the solution was allowed to cool to room temperature. The solid thus firmed 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.

### 2. Extractive desulfurization of the model Diesel Oil

The contained and it Model diesel oil was prepared by dissolving dibenzothiophene (DBT) in n-hexane by weights to give solution with (2000 ppm) of (DBT). Extractive experiment was performed by mixing 10 cm^3 of model fuel and 0.2g of ionic liquids or their ionic salts dissolved in 5 cm^3 of dimethylsulfoxide (DMSO). The mixture was shaked vigorously by using an orbital incubator shaker (DRAGON-LAB-sk-180-Pro) , which operated at 300 rpm and 30°C ($\pm$2°C) for 30 min of extraction. When the reaction finished the upper phase (model oil) was withdrawn and analyzed to determine the concentration of sulfur in model oil liquid fuel. The percentage of removal sulfur can be calculated by the following equation :

$$\% \text{ S removal} = \frac{[DBT]_{initial} - [DBT]_{final}}{[DBT]_{initial}} \times 100$$

Results and discussion

The synthetic rout of the bis (N-methylbenzimidazolium) 1,3-dithiopropane diiodide(L^1) or bis(N-methylbenzimidazolium) 1,4-dithio butane diiodide(L^2) are described in scheme (1). The above organic salts were prepared by the reaction of 2-mercapto benzimidazole and 1,3-dibromopropane or 1,4-dibromobutane 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).

$R= -CH_2CH_2CH_2-$ (L^1)
$-CH_2CH_2CH_2CH_2-$ (L^2)
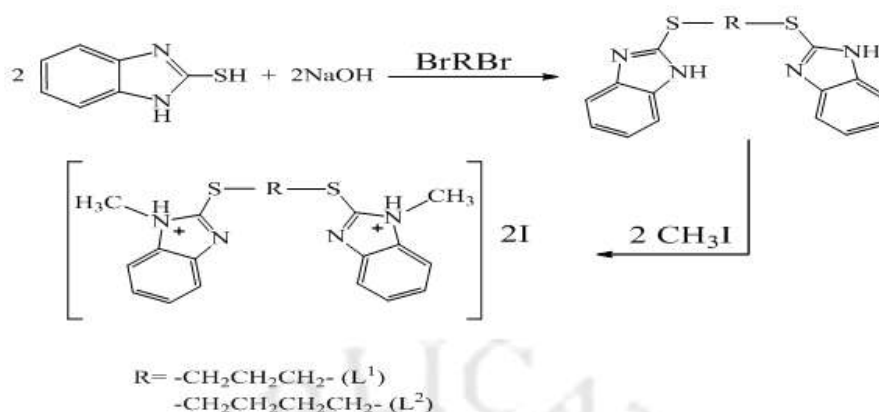
Scheme (1) : Synthesis of the organic salts

The ionic salts of the general formula [L][MCl_2I_2] (where L = cations of L^1, L^2, M = Co(II), Ni(II), Cu(II) and Zn(II)) were prepared by reaction of metal chloride with above organic salts (L). The physical properties of these ionic salts are listed in Table (1).

Table (1) : Analytical data and physical propertiesof the prepared compounds

No.	Chemical formula	M. P. °C	Color	Yield	Elemental analysis (found) / calculated						Λ (10^{-3}M) $Ohm^{-1}.mol^{-1}.cm^2$
					C%	H%	N%	S%	Cl%	M%	
L^1	$[C_{19}H_{22}N_4S_2].2I$	145-146	Brown	76	36.52 (36.12)	3.52 (3.81)	9.96 (9.36)	10.27 (10.85)	---	---	135
L^2	$[C_{20}H_{24}N_4S_2].2I$	186-187	Dark yellow	63	37.59 (37.88)	3.75 (3.98)	8.77 (8.90)	10.04 (9.51)	---	---	142
1	$[C_{19}H_{22}N_4S_2][CoCl_2I_2]$	112-113	Dark green	57	30.32 (30.20)	2.92 (2.87)	7.44 (7.41)	8.52 (8.37)	9.42 (9.33)	7.83 (7.75)	83
2	$[C_{19}H_{22}N_4S_2][NiCl_2I_2]$	108-110	Dark brown	56	30.33 (30.30)	2.92 (2.89)	7.44 (7.16)	8.52 (8.21)	9.43 (9.32)	7.80 (7.71)	87
3	$[C_{19}H_{22}N_4S_2][CuCl_2I_2]$	138-139	Dark brown	56	30.13 (30.20)	2.90 (2.84)	7.40 (7.33)	8.47 (8.32)	9.37 (9.11)	8.39 (8.22)	81
4	$[C_{19}H_{22}N_4S_2][ZnCl_2I_2]$	107-109	Light yellow	76	30.06 (29.97)	2.90 (2.87)	7.38 (7.22)	8.45 (8.32)	9.34 (9.29)	8.62 (8.54)	70
5	$[C_{20}H_{24}N_4S_2][CoCl_2I_2]$	165^d	Dark green	86	31.33 (31.23)	3.13 (3.09)	7.31 (7.26)	8.37 (8.29)	9.25 (9.17)	7.69 (7.65)	85
6	$[C_{20}H_{24}N_4S_2][NiCl_2I_2]$	211^d	Dark brown	63	31.34 (31.29)	3.13 (3.04)	7.31 (7.22)	8.37 (8.28)	9.25 (9.19)	7.66 (7.54)	76
7	$[C_{20}H_{24}N_4S_2][CuCl_2I_2]$	180^d	Dark brown	89	31.14 (31.07)	3.11 (3.09)	7.26 (7.21)	8.32 (8.27)	9.20 (9.17)	8.24 (8.18)	89
8	$[C_{20}H_{24}N_4S_2][ZnCl_2I_2]$	275^d	Light yellow	85	31.07 (29.88)	3.10 (3.07)	7.25 (7.19)	8.30 (8.25)	9.17 (9.06)	8.46 (8.33)	71

d= decomposition temperature

The conductance data showed that the organic salts are (1:2) and the ionic salts are (1:1) electrolytic nature [18]. The formation of organic salts was investigated by FTIR spectra. Table (2) shows the more characteristic infrared spectral bands. The assignment of the IR of the organic salts show band at 2540-2650 cm^{-1} and 1618-1637 cm^{-1}, assigned to $\upsilon(NH^+CH_3)$ and $\upsilon(C=N)$ respectively [19] that means the quarternide salts with methyl group was at the NH groups. The spectra of the ionic salts also reveal the presence of the above bands at similar position, as well as the presence of new bands at 290-330cm^{-1} and 210-230cm^{-1} which was assigned to υ(M-Cl) and υ(M-I) respectively [20].

Table (2) : Infrared, electronic spectra of the organic and ionic salts cm^{-1}

No.	ν (C-S)	ν(C=N)	ν (C-H)	ν (CH$_3$NH$^+$)	ν (M-Cl)	ν(M-I)	UV/Vis ν (cm^{-1})
L^1	748(s)	1618(s)	2958(w)	2580(s)	----	----	31056
L^2	748(s)	1623(s)	2968(m)	2532(s)	----	----	32689
1	-----	1626(s)	-----	2641(s)	290(s)	210(s)	16447
2	-----	1622(s)	-----	2632(m)	311(m)	218(s)	14369
3	-----	1637(m)	-----	2648(s)	317(m)	229(s)	10917
4	-----	1630(m)	-----	2590(s)	275(m)	212(w)	37778
5	-----	1635(s)	-----	2632(s)	305(w)	216(w)	16393
6	-----	1624(m)	-----	2643(m)	312(w)	230(m)	14619
7	-----	1628(m)	-----	2603(m)	300(w)	221(m)	10917
8	-----	1637(s)	-----	2639(m)	279(m)	210(m)	32680

w= week , m=medium , s=strong

The magnetic moment of the Co(II) ionic salt (1,5) showed an effective magnetic moment of (4.57,4.56) B.M confirming tetrahedral geometry. The magnetic moment of the Ni(II) ionic salt (2,6) were found to be (3.40,3.60) B.M suggested a tetrahedral geometry, while for Cu(II) ionic salt (3,7) are (2.01,2.16) B.M suggested a tetrahedral geometry for ionic salts [21]. The Zn(II) ionic salts (4,8) are diamagnetic.

The electronic spectra organic and ionic salt are listed in Table (2). The organic salts showed a band at (31056,32689 cm^{-1}) assigned to π-π^* or n-π^*.

For Co(II) ionic salts (1,5) show a bands at (14493-16393cm^{-1}) were assigned to $^4A_2(F) \longrightarrow {}^4T_1(P)$ translation suggest a tetrahedral geometry. The Ni (II) ionic salts (2,6) show a bands at (14493-14612cm^{-1}) corresponding to $^3T_1(F) \longrightarrow {}^3T_1(P)$ translation, the electronic spectra and magnetic moment support the tetrahedral structure for Ni(II) ionic salts.

In case of Cu(II) ionic salts (3,7) show a bands at (10438-11990 cm^{-1}) corresponding to $^2T_2 \longrightarrow {}^2E$ translation, the electronic spectra and magnetic moment support the tetrahedral structure for Cu(II) ionic salts [22].
Determination of optimum condition for (λmax 235 nm).
The maximum wave length (λmax 235 nm) was determined as shown in (Fig 1) and the calibration curve diagram was made from the relation between the ratio of absorption of dibenzothiphene (DBT) and the concentration of the stander solution as shown as in diagram (1).
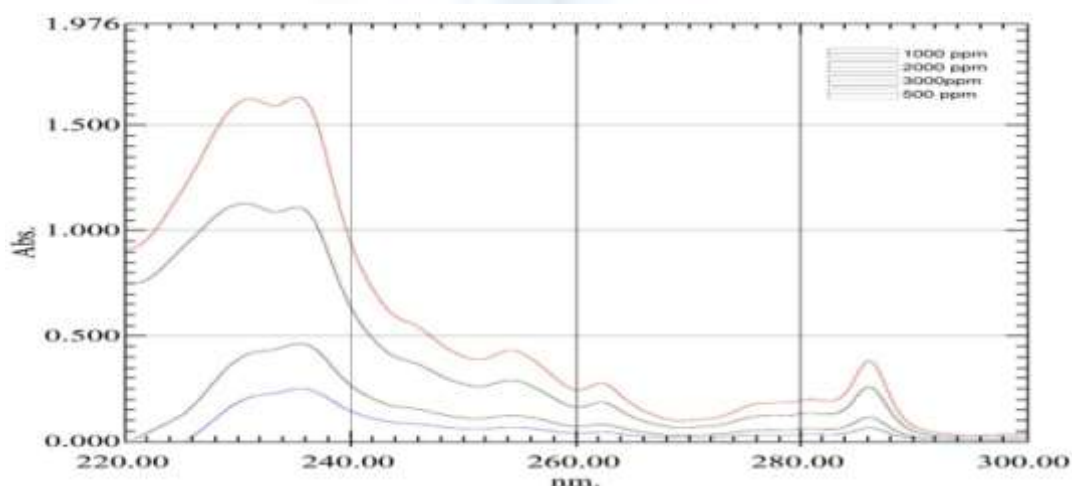
Fig (1): Absorption and wave length for different Concentration of (DBT)
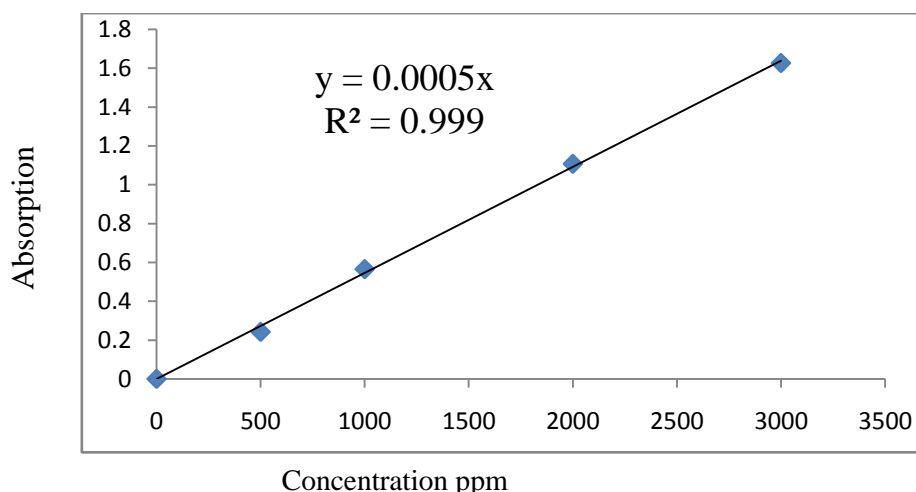
Diagram (1): Calibration curve of stander solution

In this work, two organic salts and eight ionic salts were synthesized with the object of evaluation of the effect of different structural aspects of these compounds in their efficiency for removing sulfur from fuels. In Table (3) the content of the total sulfur after the liquid-liquid extraction experiments are described.

Table (3): The removal sulfur % for model and real oil

No.	Absorption	DBT conc.	S removal % for model oil	S removal % for real oil
L^1	0.715	1430	28.5	36
L^2	0.717	1434	28.3	34
1	0.682	1364	31.8	40
2	0.723	1446	27.7	36
3	0.532	1064	46.8	36
4	0.648	1296	35.2	32
5	0.634	1268	36.6	35
6	0.612	1224	38.8	34
7	0.625	1250	37.5	36
8	0.692	1384	30.8	30

It is obvious from Table (3), that the cupperate **(3)** and nickelate **(6)** anions showed an excellent performance for desulfurization of model oil, as was observed for other research group using model diesel and naphtha from catalytic cracking process [23], however, presumably the same mechanism of extraction for sulfur compounds take place.

Considering that the reactivity between the sulfur organic molecules, mercaptanes ,thiophene and a halogen metalate based ionic liquid, is through the direct interaction of the sulfur atom with the metallic center, it is possible that a donation – retrodonation Dewar-Chatt-Duncanson like [24] mechanism occurs.

Another interesting observation is the performance of the ionic salts for desulfurization is highly depended on the ratio of organic salts to halogen as anion$[MCl_2I_2]^{-2}$ on the metathesis reaction and the acidity of above anion [25]. The enhance ability of acidity of ionic liquid could be treated with the capacity of the cations to be coordinated with sulfur atoms in this case.

From Table (3) we conclude the following observations :

1- Ionic salts containing $[CuCl_2I_2]^{-2}$ and $[NiCl_2I_2]^{-2}$ as anion are good extracting phase for desulfurization of model oil.
2- The extracting phase efficiency decrease when anion containing other metals like (Co , Zn).
3- The cations with the methyl substituent is best with copper(II) ion.

Conclusion

Ionic liquids contains benzimidazoliumcation and halogen cupprate and nickelate anions showed remarkable efficiencies to remove sulfur compound from model oil, however these compounds are air and moisture sensitive ionic liquids. The prepared organic and ionic salts can be easily regenerated and recycled.

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