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SYNTHESIS AND CHARACTERIZATION OF SOME CUPRIC CHLORIDE PIPERIDINIUM COMPLEX SALTS, APPLICATION ON EXTRACTIVE DESULFURIZATION

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ABSTRACT. In this study, organic salts [*m*amPipe]Br (**1**) and [*p*amPipe]Br (**2**) are reacted with cupric chloride to create inorganic salts, which are compounds derived from piperidinium's nitrogenous base. Spectroscopic and physical methods were used to characterize the produced compounds, including mass spectrometry, infrared FT-IR, magnetic measurements, micro-elemental analysis, and nuclear magnetic resonance spectroscopy. The extractive desulfurization method was applied, and the generated compounds were analyzed using model oil containing 1000 ppm of the sulfur compound. After dissolving dibenzothiophene (DBT) in n-hexane as a solvent, the percentages of sulfur removal were determined using ultraviolet (UV) quantitative analysis. These studies might improve the sulfur removal rate and yield a satisfactory outcome.

KEY WORDS: Ionic liquids, Organic salts, Cupric chloride, Lewis's acid, Desulfurisation

INTRODUCTION

As environmental awareness has grown globally, stringent laws and guidelines have been implemented to lessen the harmful effects of vehicle exhaust on the environment and public health [1]. Around the world, restrictions on fuel sulfur content have been imposed due to growing environmental awareness. The treatments must proceed to meet the strict regulations regarding the sulfur content of liquid fuels. To address the shortcomings above of monolayer ILS, SiO_2-immobilized bilayer ILS (SiO_2-Bill) was developed [2]. The state of the world's atmosphere steadily declined as industry expanded. Fuel oil's sulfur content produces sulfur oxides, which gravely contaminate the atmosphere.

Hydrodesulfurization (HDS) is the primary desulfurization technique [3]. Fossil fuels are used extensively in industries and other domains, such as transportation, power plants, engines, aircraft, agriculture, etc., to support social development. It is proven that sulfur compounds in fossil fuels release gaseous SO_x into the atmosphere when burned. This gaseous SO_x causes acid rain, air pollution, and other hazardous products that harm human health [4-6].

The global consumption of fossil fuels has significantly increased due to modern industrial development and urbanization. Numerous techniques, such as hydro, bio-absorptive, extractive, and oxidative desulfurization (ODS), have been tried for desulfurization. Hydro-desulfurization (HDS), the most widely used removal technique for OSCs, is commonly used in fossil fuel refining facilities across the globe. For almost a century, the HDS technology has been regarded as an effective way to remove sulfurous compounds from various fuel sources. This process removes sulfur as H_2S gas, so facilities for capturing and eliminating H_2S are part of hydro-desulfurization [7, 8].

Because of their unique qualities, ionic liquids have been found to have extensive application

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in extraction procedures. The mercury removal process, for instance, used the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [9], and the composition of lipophilic wood extractives used the ionic liquids 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium chloride [10]. These highlights show the importance of ionic liquids in studies on extractive desulfurization and environmental treatments.

Because of their high sensitivity to organic sulfur compounds and selectivity, ionic liquids have been used extensively in the desulfurization of fuels. Pyridinium compounds such as [MEPy]I and [MEPy]I/Cu_2Cl_2 have tested on extractive desulfurization with efficiency 22% and 54% of sulfur removal, respectively [11], benzotriazole compounds [diMBt]I, [AMBt]I and [AMBt]I_3 gave efficiency of sulfur removal 22%, 13% and 26%, respectively [12]. The piperidinium compounds are examples of these ionic liquids [MMPip]I/3$FeCl_3$ gave up to 45% of sulfur removal [13]. These compounds have demonstrated different levels of extractive desulfurization efficiency. Lewis acid-containing compounds have been proven more effective in the extractive desulfurization process. The strong attraction between the π electron on the sulfur compound and the metal orbitals is considered to be responsible for this.

EXPERIMENTAL

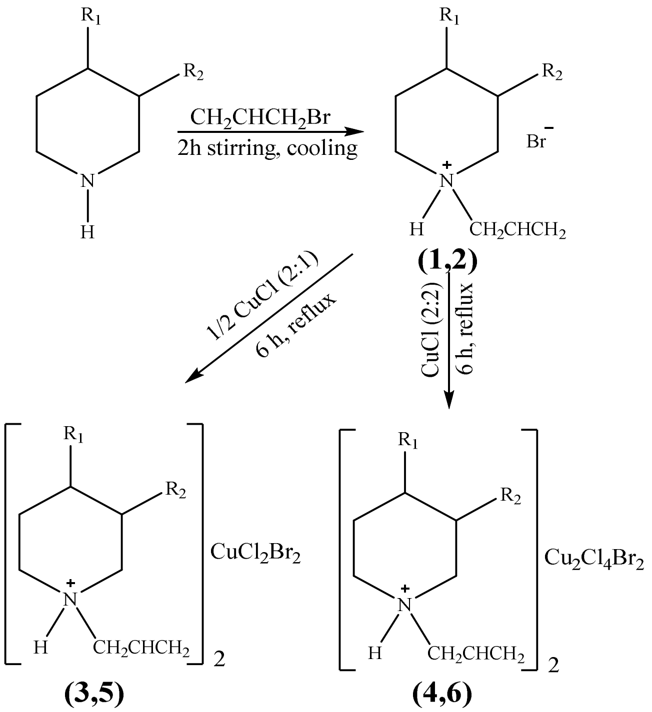
Each chemical that is used comes from an authentic, ultra-pure source. The JASCO Canvas FT/IR 4200 infrared spectrophotometer obtained the FT-IR spectra. ^{1}H-NMR spectra were recorded on a Bruker 400MHz spectrometer with tetramethylsilane (TMS) as an internal reference and DMSO-d_6 as a solvent. The microanalysis was performed at Thermo Electron Corporation's Flash EA 1112 Series using a Trio-1000 mass spectrometer. SensAA was used for atomic absorption analysis, and MSB MK1 Sherwood was used for effective magnetic moments.

Establishing complexes and organic salts of copper(II)

1-Allyl-3-methylpiperidinium bromide [*m*amPipe]Br (**1**) and 1-Allyl-4-methylpiperidinium bromide **[***p*amPipe]Br (**2**) ionic liquids, or organic salts, have been made following the literature [13-17], considering that the reaction is exothermic and its yield rises with cooling. Allylmethylpiperidinium bromide [amPip]Br, was prepared by dissolving 3-methyl or 4-methyl piperidine in absolute ethanol, then gradually adding allyl bromide while stirring constantly for two hours and cooling the mixture. This reaction is exothermal. Evaporation and a rotary evaporator set at 80 °C concentrated the solution and eliminated any leftover solvent after the reaction. Subsequently, ionic salts of copper were produced by reacting various ratios of organic salt [amPip]Br with cupric chloride in ratios of (2:1) and (2:2), respectively, compounds (**3-6**). The following table shows the prepared compounds' physical properties and the results of their elemental microanalysis. Scheme 1 displays the equation for the reaction.

Extractive desulfurization

Dibenzothiophene (DBT), a sulfur compound, must first be dissolved in a hexane solvent to reach the initial concentration of 1000 ppm and to prepare the model oil sample. The next step is determining the circumstances of the ideal sulfur removal procedure.



Compound 1: $R_1 = H, R_2 = CH_3$, **[*m*amPi]Br**
Compound 2: $R_1 = CH_3$, $R_2 = H$, **[*p*amPi]Br**
Compound 3: $R_1 = H, R_2 = CH_3$, **[*m*amPipe]$_2$CuCl$_2$Br$_2$**
Compound 4: $R_1 = CH_3$, $R_2 = H$, **[*m*amPipe]$_2$Cu$_2$Cl$_4$Br$_2$**
Compound 5: $R_1 = H, R_2 = CH_3$, **[*p*amPipe]$_2$CuCl$_2$Br$_2$**
Compound 6: $R_1 = CH_3$, $R_2 = H$, **[*p*amPipe]$_2$Cu$_2$Cl$_4$Br$_2$**

Scheme 1. The route of prepared salts (**1-6**).

Table 1. The prepared compounds' physical characteristics and elemental microanalysis outcomes.

Compounds	Formula	m.p. (°C)	CHN (theoretical)/calculated			
			C%	H%	N%	Cu%
(**1**) [*m*amPipe]Br	$C_9H_{18}BrN$	157-159	(49.10) 48.24	(8.24) 8.23	(6.63) 6.33	---
(**2**) [*p*amPipe]Br	$C_9H_{18}BrN$	144-146	(49.10) 46.39	(8.24) 7.86	(6.63) 7.76	---
(**3**) [*m*amPipe]CuCl$_2$Br$_2$	$C_{18}H_{36}Br_2Cl_2CuN_2$	160-162	(37.62) 37.32	(6.31) 6.75	(4.87) 4.95	(11.06) 10.86
(**4**) [*m*amPipe]Cu$_2$Cl$_4$Br$_2$	$C_{18}H_{36}Br_2Cl_4Cu_2N_2$	145-148	(30.48) 31.50	(5.12) 4.88	(3.95) 3.75	(17.92) 18.50
(**5**) [*p*amPipe]CuCl$_2$Br$_2$	$C_{18}H_{36}Br_2Cl_2CuN_2$	165-167	(37.62) 37.60	(6.31) 6.80	(4.87) 5.20	(11.06) 10.60
(**6**) [*p*amPipe]Cu$_2$Cl$_4$Br$_2$	$C_{18}H_{36}Br_2Cl_4Cu_2N_2$	149-153	(37.62) 36.75	(6.31) 6.70	(4.87) 5.15	(11.06) 10.85

RESULTS AND DISCUSSION

One of the primary features of piperidinium ionic liquids is their capacity to remove sulfur from petroleum derivatives. Lewis's acids, specifically iron, are present in these liquids. Every prepared compound was thoroughly characterized and found to be consistent with the data presented in the references [11, 18-20]. (DMSO-d_6, 400 MHz), δ 0.88 (3H, C-CH_3, s), δ 1.066 (1H, CH-C, bs), δ 1.06, δ 1.73, δ 3.29, δ 3.70 (cyclic, 2H, CH_2, bs), δ 3.70 (2H, CH_2 for terminal group, bs), δ 4.010 (2H, CH_2, d, for allylic group), δ 5.74 (1H, = CH, bs), δ 9.59 (1H, NH, s) are the ^{1}H-NMR characterization data for organic salts (**1**, **2**). The following GC-mass data (*m/z*, intensity%) can be retrieved for organic salt (**1**), [*m*amPipe]Br, $C_9H_{18}BrN$: (140, 100%), (138.2, 1.04%), (126.1, 0.11%), (124.1, 0.39%), (112, 1.08%), (98.1, 0.5%), (84, 0.32%), (82, 0.19%), (70, 0.06%), (68, 0.05%). (DMSO-d_6, 400 MHz), δ 0.90 (3H, C-CH_3, s), δ 1.066 (1H, CH-C, bs), δ 1.06, δ 1.73, δ 3.29, δ 3.70 (cyclic, 2H, CH_2, bs), δ3.21 (2H, CH_2, d, for allylic group), δ 5.38 (1H, =CH, bs), δ 5.18 (2H, for terminal CH_2 group, bs) δ 8.53 (1H, NH, s). The organic salt (**2**) GC-mass data, [*p*amPipe]Br, $C_9H_{18}BrN$, the intensity percentages are (*m/z*, 140.2, 4.41%), (138.2, 0.15%), (100.1, 100%), (98.1, 2.26%), (96.1, 0.01%), (94.1, 0.03%), (82, 0.04%), (82, 0.02%), (70, 0.06%), and (58, 0.04%). Figure (1) shows the NMR of organic salts **1**, **2**. All these results match the literature well [13].

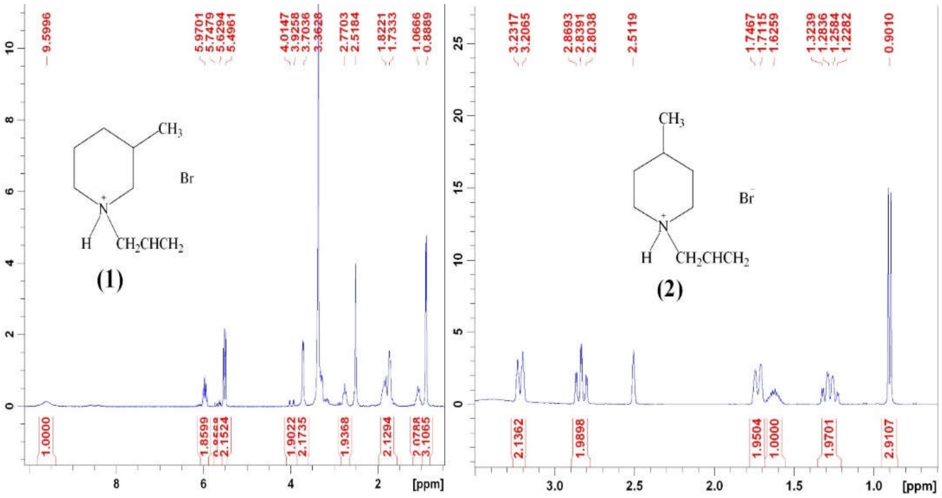


Figure 1. The ^{1}H-NMR of compounds **1** and **2**.

Consequently, the compounds mentioned in Table 1 were prepared and well characterized in addition to the properties listed in Tables 1 and 2 [14, 21-24]. Physical and spectroscopic methods are applied, as indicated in Table 2.

Table 2. Various details related to the prepared compounds' characteristics.

Comp. No.	IR data (cm^{-1})				μ$_{eff}$ (BM)	Conductivity** ohm^{-1}.cm^{2}.mol^{-1}
	C-N	N^{+}-R*	N-H	M-X		
1	1600	2553	3436	---	---	67
2	1600	2510	3436	---	---	72
3	1643	2854	3320	273, 300	1.92	82
4	1646	2368	3336	262, 289	1.88	84
5	1600	2356	3444	254, 293	2.20	84
6	1596	2372	3374	258, 293	2.15	87

* R = CH_2CHCH_2. ** (DMF) as solvent at 25°C, (10^{-3} M).

The prepared compounds have been characterized using the results attached to the supporting files. In addition to determining the percentage of copper through atomic absorption measurements, these magnetic susceptibility results demonstrated that the complex salts of copper adopt a tetrahedral structure around the copper's central ion, which matches the results described in the literature [15, 25, 26].

Desulfurization with extraction

By determining the concentration of the prepared and used salt, the extraction time, and the temperature, the ideal conditions for the extractive desulfurization process were established beforehand. The findings indicated the ideal parameters, which were 30 degrees Celsius, 60 minutes of extraction time, and grams of concentration. Dibenzothiophene (DBT) dissolved in hexane solvent at a concentration of 1000 ppm was used as the starting concentration for the petroleum model of sulfur when creating a standard curve plot, as illustrated in the following figures, using ultraviolet technology with a Shimadzu UV 1800 device. The UV spectra of several dibenzothiophene standerd solutions (250, 500, 750, 1000 ppm) at varying concentrations are displayed in Figure 2. The standard calibration curve for these standard solutions can be seen in Figure 3.

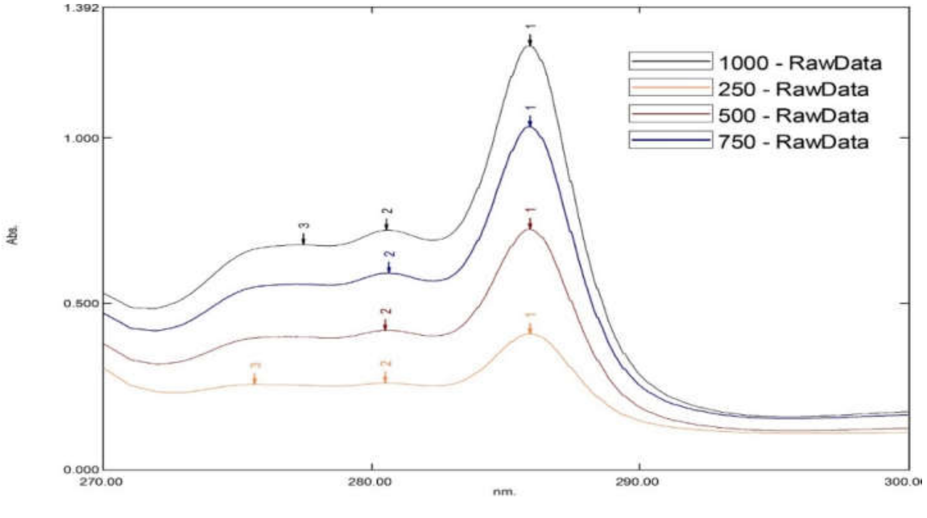


Figure 2. The DBT calibration curve using varying concentrations (standard solutions).

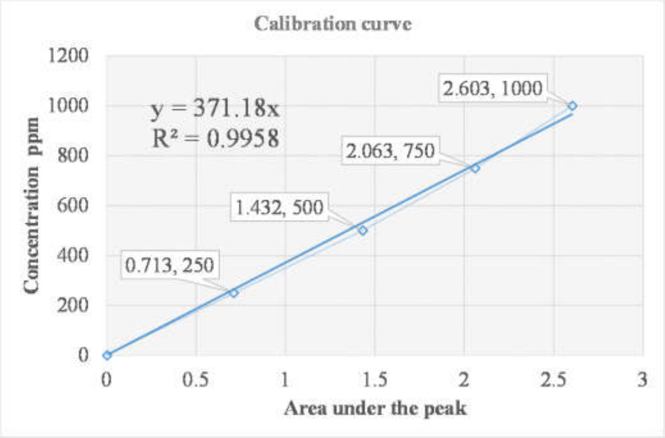


Figure 3. The extraction desulfurization process's calibration curve.

The efficiency of the extraction process was assessed by comparing the prepared compounds' test results with those of previously published literature, as shown in the following table [11, 27-29].

Table 3. The results of the salt extraction tests conducted under ideal circumstances (285 nm, 60 min, 0.1 g of extractant at 30 °C).

Comp. No.	The area under the peak	$S_{content}$ ppm	$S_{removal}$ %
1	2.310	857.4258	14.25
2	2.164	803.2335	19.67
3	2.464	914.5875	08.54
4	2.246	833.6703	16.63
5	2.063	765.7443	23.42
6	1.997	741.2465	25.87

The results of the sulfur extraction process show that complex salts with copper ions are more effective than organic salts without them and that the efficiency of sulfur removal rises as the complex salts' percentage of Lewis acids increases. The results agree with previous field study research [25, 30, 31]. In the optimal situation, the removal rate is not more than 26%, but this is still regarded as a good result,

It could be improved by adjusting the extraction factors, experimenting with different compounds, or loading them onto a carrier like charcoal from activated carbon or clay to increase productivity and lower the sulfur removal process's monetary expense [25, 32, 33].

CONCLUSION

Contrasting the prepared salts with previous research [16, 20, 27-29], the previous results clearly show that they have a respectable level of efficiency in the sulfur removal process. It is also clear that there is no difference in the extraction efficiency when comparing organic salts to one another. It is found that there are no differences in efficiency because of a change in the methyl group's replacement location on the ring. Furthermore, it has been noted that the extraction efficiency increases as iron salt is added and the amount of iron salt increases [16, 17, 34]. This is exactly precisely the same as what was found in the literature.

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