

Preparation and characterization of ionic complex salts based on benzotriazolium cations

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Received
15 / 05 / 2011

Accepted
15 / 09 / 2011

الخلاصة

تم تحضير السوائل الايونية والتي أساسها ايونات البنزوتريازوليم، وتم تشخيصها بواسطة طيف الأشعة تحت الحمراء وفوق البنفسجية والقياسات التوصيلية والتحليل العنصري الدقيق . كذلك الاملاح الايونية ذوات الصيغة العامة $[A]^+_2[MCl_2I_2]$ و $[A]^+$ عندما $A =$ benzotriazolium cation⁺¹ ، $A =$ benzotriazolium cation⁺²، $M = Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}$ وتم تشخيصها بواسطة التحليل العنصري الدقيق، التوصيلية الكهربائية، طيف الأشعة تحت الحمراء وفوق البنفسجية والمحتوى الفلزي والقياسات المغناطيسية. بينت نتائج الطيف الالكتروني و القياسات المغناطيسية بان الايونات ذوات الصيغة $[MCl_2I_2]$ تمتلك بنية رباعية السطوح والمربع المستوي حول الايون الفلزي.

Abstract

Ionic liquid based on benzotriazolium ions were synthesized. these ionic liquids were characterized by IR, UV, Conductivity measurements and elemental analysis. There ionic salts with Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} of

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the types $[A]^+_2[MCl_2I_2]$ and $[A']^+ [MCl_2I_2]$, where $A =$ benzotriazolium cation⁺¹, $A' =$ benzotriazolium cation⁺², $M = Co^{+2}, Ni^{+2}, Cu^{+2}$ and Zn^{+2} were prepared and characterized by elemental analysis, molar conductance, IR, UV/V is, metal content and magnetic measurements. The results of electronic spectra and magnetic measurements showed that the anions of the type $[MCl_2I_2]$ have tetrahedral and square planer geometry around the metal ions.

Introduction

Ionic liquid have been exploited in different research area due to their unique physiochemical properties, such as negligible vapor pressure, thermal and chemical stability, which make them vary promising materials to replace volatile organic solvents in several application such as synthesis and purification[1-4].

Metal containing ionic liquids and ionic liquid crystals based on imidazolium moiety that is metal complexes of imidazolium salts. They have realized as versatile reaction media, catalyst, catalyst precursors and reagents for various chemical processes include nonmaterial[5-6].

The two isomorphism imidazolium salts $[EMIM]_2 [MCl_4]$ ($M = Co$ or Ni) were prepared directly by mixing the corresponding metal chloride with $[EMIM]Cl$ ($EMIM =$ 1-ethyl-3-methyl-imidazolium) [7]. Crystal structure studies showed extended hydrogen bonding net-works were observed between $[MCl_4]^{-2}$ chlorides and hydrogen of the hetero atom ring

Palgunadi et.al.[8] prepared and used the $[RMIM][ZnX_2Y_2]$ ionic liquid system ($R = Me, Et, n.Bu, benzyl, X = Y = Cl$ or $Br, X = Cl, Y = Br$) for the coupling reaction of CO_2 and ethylene to produce cyclic carbonates. Crystal structure of $[Me_2IM][ZnBr_2Cl_2]$ showed that two imidazolium cations paired with $[ZnBr_2Cl_2]$.

Deetleft. et. al. [9] prepared the thiozolium based gold (III) compound $[BMT_2][AuBrCl_3]$ from the reaction of 3-butyl-4-methylthiazolium bromide $[BMT_2]Br$ with $HAuCl_4$ or $NaAuCl_4$.

Formation of mixed ion could be due the substitution of chloride by softer bromide.

In view of these interesting results and as continuation of our studies on transition metal ionic salts [10-12], we have prepared new ionic salts of $Co^{+2}, Ni^{+2}, Cu^{+2}$ and Zn^{+2} based benzotriazolium cation Fig 1

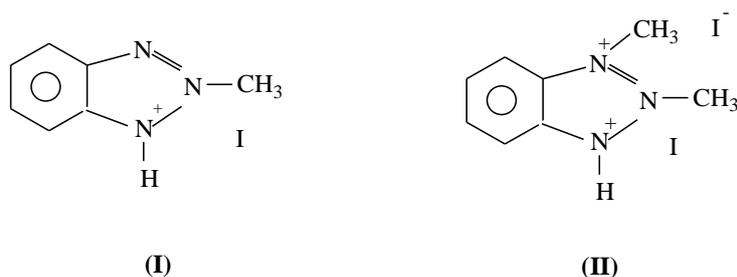


Fig 1. Benzotriazolium iodide (I) and benzotriazolium diiodide (II)

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. Solvents were distilled from appropriate drying agents under nitrogen at Liverpool University (2011).

IR spectra were recorded on Bruker Tensor 27co (FTIR) spectrophotometer in the $250\text{-}4000\text{ cm}^{-1}$ range using CsI discs. Elemental analyses were carried out on CHN Perkin Elmar 2400, AL-Baint University Jordan. Melting points were measured on electrothermal 9300 melting point apparatus. Metal content were determined spectrophotometrically using AA670 atomic absorption, conductivity measurements were made on 10^{-3} M solution of the ionic salts in dimethyl formamide (DMF) using a conductivity meter type PCM3-Jenway. Electronic spectra were recorded on Shimadza UV/Vis. Spectrophotometer UV-160 for 10^{-3} M solutions of the ionic salts in DMSO using 1 cm quartz cell. The magnetic measurements were carried out at 25°C on the solid by Faradays method using Bruker BM6 instrument.

Preparation of organic salts

1- Benzotriazolium iodide [Bzt]I.

a solution of benzotriazole (1.20 g, 0.01 mol) in ethanol (10 cm^3) was added dropwise to a solution of methyl iodide (1.42 g, 0.01 mol) in ethanol (10 cm^3). Addition was continued for 30 min. The reaction mixture was refluxed for 2 h, then left to stand at room temperature. The black solid thus formed was filtered off, washed twice with ethanol then dried under vacuum for several hours.

The analogous salts Benzotriazolium iodide [Bztd].2I was prepared similarly expect by using (2.84g, 0.02 mol) of methyl iodide.

2- Preparation of ionic salts [bzt]₂[CoCl₂I₂].

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24g, 0.001 mol) in ethanol (10 cm^3) was added dropwise to a solution of benzotriazolium iodide (0.26 g, 0.001 mol) in tetrahydrofuran (15 cm^3). The mixture was refluxed for 2h, then the solution was allowed to cool to room temperature. The solid thus formed was filtered off, washed with ethanol (10 cm^3) followed by diethyl ether (10 ml) and dried under vacuum for several hours.

The rest of the ionic salts were prepared in similar manner.

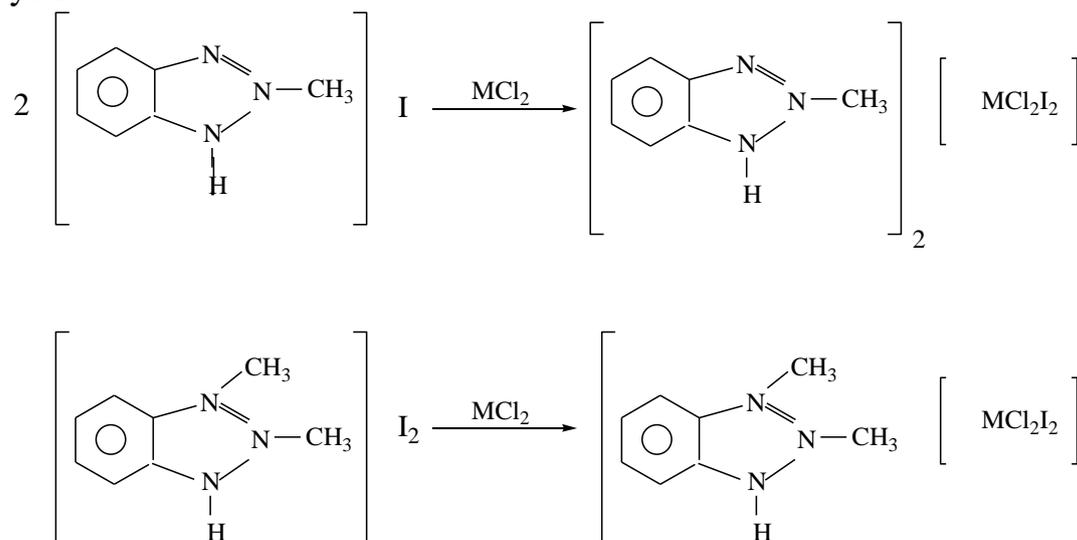
3- Preparation of ionic salts [bztd][CoCl₂I₂]

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24g, 0.001 mol) in ethanol (10 cm^3) was added drop wise to a solution benzotriazolium diiodide (0.40 g, 0.001

mol) in tetrahydrofuran (15 cm³). Then following the procedure for preparation of [bzt]₂[CoCl₂I₂]. The rest of the ionic salts were prepared similarly.

Results and discussion

The reaction of benzotriazolium cation with Co⁺², Ni⁺², Cu⁺² and Zn⁺² metal salts in ethanol afford the ionic salts of the following types [Bzt]₂[MCl₂I₂] and [Bztd][MCl₂I₂], where Bzt= benzotriazolium cation, Bztd = benzotriazolium dication, M= Co⁺², Ni⁺², Cu⁺² and Zn⁺² in high yields.



Scheme 1: Synthesis of the ionic salts
M= Co, Ni, Cu, Zn

The method used in the preparation normally efficient for the preparation of ionic salts. These salts are stable, non hygroscopic, colored solids. The melting points, elemental analysis, conductance and magnetic measurements are listed in Table 1.

The conductance data show that the ionic salts are of 1:2 or 1:1 electrolytes. Conductivity were measured also at various concentration the plot of Λ_c vis $N^{1/2}$ being linear over the concentration rang 10- 0.1 mM, A and A° values (330-345 ohm⁻¹ cm² equiv⁻¹ N^{+1/2} and 102 – 108 ohm⁻¹ cm² equiv⁻¹ N^{-1/2} receptivity) from the Ohsager equation $\Lambda^\circ = \Lambda_e + A N^{-1/2}$ which a gree with those 1:2 or 1:1 electrolytes [13].

The conductivities of the ionic salts are significantly higher than those observed for 1-n-butyl-3-methyl imidazolium tetrachloroaluminate [14]. This indicated that the interactions between the anion and cation is essentially electrostatic with a small contribution of hydrogen bonds.

Infrared 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 2590 and 1625 cm^{-1} , assigned to $\nu(\text{N}^+-\text{CH}_3)$ [15] and $\nu(\text{C}=\text{N})$ [16] respectively. 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 observed at 280-320 and 210-230 cm^{-1} which was assigned to $\nu(\text{M}-\text{Cl})$ and $\nu(\text{M}-\text{I})$ respectively [17].

Magnetic measurements and electronic spectra

The UV/ Vis spectra of the organic salts shows strong absorption bands at 32051 and 31250 cm^{-1} which correspond to $\pi-\pi^*$ transition.

cobalt (II) ionic salts.

The magnetic moment values of the cobalt ionic salts are 2.51 and 2.14 B.M. more than that of low spin octahedral and lower than the values characteristic of square planar cobalt (II) complexes. Furthermore, these values are similar to that reported for the square planar cobalt (II) complexes [18].

The electronic spectrum of the complexes exhibit a bands at 14837 and 11236 cm^{-1} , characteristic of square planar cobalt (II) complexes.

Nickel (II) ionic salts.

The magnetic moments values 3.36 and 3.01 B.M. at room temperature for the ionic salts suggest the presence of two unpaired electrons, which reveals the spin free nature of the ionic salts corresponding a tetrahedral stereochemistry [10].

The nickel ionic salts show a bands at 11236 and 12236 cm^{-1} due to ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{p}) \nu_3$ transition indicated for tetrahedral geometry of nickel (II) ionic salts.

Copper (II) ionic salts.

The magnetic moments for the copper (II) ionic salts have been found to be 1.67 and 2.01 B.M. These values corresponding to presence of unpaired electron in the ionic salts which is in a agreement with distorted tetrahedral geometry [19]. The ionic salts show the presence of two bands at 11547 and 19987 cm^{-1} which correspond to the transition of the ${}^2\text{T}_2\text{g} \longrightarrow {}^2\text{E}_2\text{g}$, consistent with distorted tetrahedral geometry [20].

Zinc (II) complex

The ionic salts of Zn(II) are diamagnetic do not show d-d transition indicating a tetrahedral geometry.

Table 1: Analytical, magnetic moments and conductance data for the organic salts and ionic salts

No.	Compound	Melting point (°C)	Color	Analysis found (calc.) %				Λ Ohm ⁻¹ . cm ² .mol ⁻¹	yield	μ_{eff} (B.M)
				C	H	N	M			
1	[Bzt]I	91	Black	32.00 (32.06)	3.40 (3.44)	17.00 (16.03)	---	68.5	85	---
2	[Bzt] ₂ [CoCl ₂ I ₂]	280	Black	25.59 (25.69)	2.70 (2.75)	12.79 (12.84)	8.92 (9.00)	140	86	2.51
3	[Bzt] ₂ [NiCl ₂ I ₂]	236	Yellowish black	25.63 (25.69)	2.71 (2.76)	12.79 (12.84)	8.92 (8.98)	152	75	3.36
4	[Bzt] ₂ [CuCl ₂ I ₂]	170	Dark green	25.50 (25.54)	2.70 (2.73)	12.72 (12.77)	9.43 (9.51)	160	80	1.67
5	[Bzt] ₂ [ZnCl ₂ I ₂]	30	Light brown	25.39 (25.44)	2.71 (2.75)	12.78 (12.72)	9.82 (9.89)	143	82	---
6	[Bztd].2I	87-89	Black	23.73 (23.76)	2.92 (2.97)	10.35 (10.39)	---	145	82	---
7	[Bztd] ₂ [CoCl ₂ I ₂]	153 ^d	Dark green	18.55 (19.10)	1.28 (2.18)	7.52 (8.35)	10.85 (11.72)	78	79	2.14
8	[Bztd] ₂ [NiCl ₂ I ₂]	150	Light brown	18.35 (19.11)	1.84 (2.19)	7.41 (8.36)	10.31 (11.68)	70	70	3.01
9	[Bztd] ₂ [CuCl ₂ I ₂]	264 ^d	Light brown	17.37 (18.93)	1.95 (2.16)	7.65 (8.28)	11.42 (12.52)	68.5	80	2.01
10	[Bztd] ₂ [ZnCl ₂ I ₂]	35	Light brown	17.59 (18.86)	1.87 (2.17)	7.85 (8.25)	11.64 (12.83)	98	72	---

d=decomposition temperature.

Table 2: IR absorption (cm⁻¹) and electronic data for the organic salts and their ionic salt

Compound	IR				UV/Visible bands Maxima in (cm ⁻¹)
	$\nu(\text{N-CH}_3)$	$\nu(\text{C=N})$	$\nu(\text{M-Cl})$	$\nu(\text{M-I})$	
1	2590	1625	---	---	32051
2	2585	160	280	216	14837,30675,34965
3	2589	1622	300	210	11236,36232
4	2580	1625	290	212	11547,30675
5	2585	1620	300	220	33333
6	2590	1625	295	210	31250
7	2588	1620	285	222	11236,36496
8	2582	1625	280	230	11236,27473
9	2588	1627	300	228	19987
10	2590	1629	320	225	34014

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