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Identification of radical structures on 1pentamethylbenzyl-3-ethylimidazoliumsilver(I) bromide and 1,3-bis(pentamethylbenzyl)-4,5dimethylbenzimidazoliumsilver(I)bromide exposed to gamma rays: an EPR study

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1-Pentamethylbenzyl-3-ethylimidazoliumsilver(I)bromide and 1,3-bis(pentamethylbenzyl)-4,5dimethylbenzimidazoliumsilver(I) bromide and their Ag⁺ complexes were synthesized and their polycrystal forms were produced by recrystallization in dichloromethane/Et₂O solvent system. Structural determinations were carried out by ¹H NMR and ¹³C NMR with a Varian 400 NMR system using tetramethylsilane as internal standard and CDCl₃ as solvent. The disappearance of acidic N-heterocyclic carbene proton showed the formation of Ag(I) complexes. Also, elemental analyses were carried out. Electron paramagnetic resonance (EPR) measurements were performed to determine the formed radical structure on the samples irradiated at the room temperature for 72 h by using ⁶⁰Co-source with dose rate of 0.680 kGy. The EPR measurements were carried out in the temperature range of 200 K-450 K. Identical radicals were determined on the irradiated compounds. It was observed that the shapes of the spectra of the samples were independent of the temperature but, the resonance line intensities changed linearly with the temperature. Also, it was detected that the free radical on the 1-pentamethylbenzyl-3-ethylimidazoliumsilver(I)bromide is not stable compared to that on the 1,3-bis(pentamethylbenzyl)-4,5dimethylbenzimidazoliumsilver(I)bromide. Copyright © 2016 John Wiley & Sons, Ltd.

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Introduction

N-heterocyclic carbene (NHC) salts (mainly imidazolium and benzimidazolium salts) have given a new route to chemists since 1968. These versatile compounds both as metal free compounds and as their transition metal complexes have got many properties, making them attractive for researchers.^[11] Their antimicrobial, antihelmintic, antifungal and anticancer activities and potentials in catalytic applications made them noteworthy compounds. NHC salts have three main parts and can be changed for gaining different properties. So NHC salts and their metal complexes can be fine-tuned for the most suitable properties (Scheme 1).

It has been known for a long time that silver(I)NHC complexes have antimicrobial activity.^[2] In recent studies, these complexes have been examined for their catalytic activity. And during these studies, some research groups have achieved promising results.^[3] These versatile compounds have exhibited very good results in anti-tumor (anticancer) activities in the last decade.^[4,5]

In recent years, electron paramagnetic resonance (EPR) technique has been widely used for characterization of various materials.^[6–11] Researchers have investigated compounds containing Ag and Br by using EPR method. For instance, Samokhvalov *et al.*^[12] have studied surface characterization of Ag and have found

that the majority of Ag was presented in diamagnetic Ag⁺¹ form. In the study of Arcon *et al.*,^[13] the sample containing Br was investigated and observed that EPR signals were temperature dependent and the signals exhibited a dramatic narrowing.

It is known that irradiation changes a number of physical and chemical properties of the irradiated materials such as electrical resistivity, magnetic susceptibility, etc..^[14,15] The purpose of this

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Scheme 1. The 'property forming' sites of a NHC salt and NHC-M complex (CA⁻ = Counter Anion).

study is to give information about the radical structures of 1-pentamethylbenzyl-3-ethylimidazoliumsilver(I)bromide (Complex.1) and 1,3-bis(pentamethylbenzyl)-4,5 dimethylbenzimidazoliumsilver(I)bromide (Complex 2) by means of EPR.

Experimental

All solvents and reagents were commercially obtained from the suppliers and were used without further purification. Melting points were measured using an Electrothermal 9100 melting point detection apparatus. ¹H NMR and ¹³C NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as internal standard solution and recorded at room temperature using a Varian 400 MHz spectrometer.

The synthesis of 1-pentamethylbenzyl-3ethylimidazoliumbromide (Salt 1)

Pentamethylbenzylbromide and 1-ethylimidazole were synthesized according to conventional methods in literature^[16] (Scheme 2). Salt 1-pentamethylbenzyl-3-ethylimidazoliumbromide was



Scheme 2. Synhesis routes for Salt 1, Complex 1 (a); Salt 2, Complex 2 (b) i = KOH, Acetone, 1 eq. EtBr, 24 h. reflux ii = Toluene, pentamethyl benzylbromide 45–50 °C, 3–4 h. iii = 0.5 eq. Ag₂CO₃, DCM, 24 h. iv = DMF, pentamethyl benzylbromide 10–12 h. 50–60 °C.

synthesized according to the route in Scheme 2.^[16] In a 50 ml Schlenk tube, 2.41 g (0.01 mole) of penta methyl benzylbromide was dissolved in 20 ml of toluene. Stirring and heating at 50 °C 0.96 g (0.01 mole) of 1-ethylimidazole was added. The reaction mixture was stirred in constant temperature for 2 h. A white dense milkiness was observed. Toluene was distilled off under vacuum and a dirty-white solid was obtained. This solid was washed and redissolved in 1 ml of dichloromethane (DCM) and hexane was added to the solution until it became cloudy. The white substance achieved after 24 h of crystallization was dried under vacuum. Yield = 2.8 g (83%), mp = $135-137 \degree C^{-1}H$ NMR (400 MHz, CDCl₃, 25 °C) δ = 10.35 (s, 1H, CcarbeneH), 7.26–6.85 (s, 2H, backbones), 2.24-2.19 (s, 15H, Me₅Ph Hs), 1.61 (t, 3H, N-CH₂-CH₃), 4.50 (q, 2H, NCH₂—CH₃), 5.65 (s, 2H, N—CH₂—Bzyl), ¹³C NMR δ = 137.32 (Ccarbene), 125.2 and 120.81 (backbones) 77.38-76.75(CDCl₃-solvent) 49.10-45.47 (N-C*H2-CH3) 17.24-15.62 (Bzl-(CH3) and (N-CH₂-C*H₃), 133.78-133.56 (Bzl-Arom).

The synthesis of 1,3-bis(pentamethylbenzy)-4,5dimethylbenzimidazoliumbromide (Salt 2)

Instead of the conventional method with strong base, a more practical way can be used. To perform this, DMF (N-N'-dimethyl formamide) was used as both a solvent and basic reagent (Scheme 2); 1.46 g (0.01 mole) of 4,5-dimethylbenzimidazole was dissolved in 10 ml of DMF in a 50 ml Schlenk type tube stirring at 70 °C. After stirring for 30 min, two eq. of pentamethyl benzylbromide (4.82 g or 0.02 mole) was added and the reaction mixture was stirred at constant temperature for 10 h. Solvent was distilled off under vacuum and then a dirty-white yellowish solid was obtained. This solid was washed with hexane (5 ml ×3 times) and dried under vacuum. No further recrystallization was needed. Yield 4.5 g (86%). mp = 208–210 °C, ¹H NMR δ = 9.56 (s, 1 H, C carbene), 8.07 (s, 2 H, aromatic part of benzimidazol), 5.7 (s, 4 H, N-CH₂-), 2.15 (s, 30 H, Me₅), 2,61 (s, 6H, back methyls), ¹³C NMR δ = 137.70(Ccarbene), 77.34-76.70(CDCl₃-solvent) 125.06 (backbones) 47.74 (N—C*H₂—Bzl) 20.81–16.94 (Bzl—(CH₃), 133.32–130.54 (Bzl-Arom)

The synthesis of silver(I)NHC complexes

Both complexes have been synthesized by reaction between 1 mmol of the corresponding NHC salt and 0.5 mmol (138 mg) of Ag₂CO₃ (Scheme 2). Ag₂CO₃ was used in such reactions as both a Ag⁺ ion supplier and basic salt for stripping the acidic proton of the carbene. Both of the complexes have been recrystallized in DCM/Et₂O in 24 h. For both complexes, the formation of complexes was monitored by ¹H NMR spectra, ¹³C NMR spectra and elemental analysis methods.

The NMR data are: For complex 1, ,¹H NMR δ = 7.26–6.91 (s, 2H, backbones), 2.26–2.19 (s, 15H, (benzylic methyl Hs), 1.44 (t, 3H, methyl of ethyl group), 4.15 (q, 2H, methylene of ethyl group), 5.34 (s, 2H, ethylene of benze group). ¹³C NMR δ = 186.08(Ccarbene), 125.24 and 121.68 (backbones) 77.39–76.75(CDCl₃–solvent) 46.78 and 45.37 (N—C*H₂—Bzl/N—C*H₂—CH₃) 17.24–15.46 (Bzl—(CH₃) and —CH₂—CH₃ of ethyl), 137.31–133.54 (Bzl-Arom). Elemental Analysis(Theo/Exp.) = C, 60.47/61,05; H, 6.61/6,84; N, 4.27/4.46).; For complex 2, , ¹H NMR δ = 8.03 (s, 2 H, aromatic part of benzimidazol), 5.59 (s, 4 H, methylenes of benzylic groups), 2.06–2.33 (s, 30 H, methyls of penta methyl benzenes), 2,55 (s, 6 H, methyls of benzimidazol). ¹³C NMR δ = 182.28(Ccarbene), 125.02(backbones) 77.38–76.75(CDCl₃–solvent) 47.69 (N—C*H₂—Bzl)

20.77–16.85 (Bzl—(CH₃)), 137.14–130.45 (Bzl-Arom). Elemental Analysis: (Theo/Exp.) = C, 45.87/46.16; H, 5.66/5.42; N, 6.29/6.74

EPR measurements

The polycrystal forms of complex 1 and complex 2 samples were irradiated for 72 h by using ⁶⁰Co-gamma ray source with dose rate of 0.680 kGy. The measurements were performed by X-band EPR spectrometer in Saraykoy laboratory of TAEK (Turkish Atomic Energy Authority). In the measurements, the spectrometer was set as follows: the microwave power was 5 mW, the modulation frequency was 100 kHz and modulation amplitude was 0.30 G. The high and low temperature measurements were carried out between 200 K and 450 K by using temperature control unit of the spectrometer. For verification of the values obtained from the recorded spectra, WINEPR simulation program was used.

Results and Discussion

Chemical analysis

¹H NMR and ¹³C NMR data for the compounds were recorded in CDCl₃ for all compounds. From the ¹H NMR spectra of salt 1 the singlet peak was observed at 10.35 and it was assigned to acidic proton of the carbene ring. The two peaks observed at 4.50 (m, 2H), 5.65 (s, 2H) ppm were assigned to CH₂ protons bridging the ring to other groups. The singlet at 2.23 ppm was assigned to methyl protons on the benzene ring. The methyl group of the tail gave a triplet at 1.61 ppm. The protons of backbone of the ring were separately observed at 6.85–7.59 ppm. Because of asymmetry of the molecule, a difference was seen (Fig. 1). From the ¹³C NMR spectra of salt 1 the most significant peaks were interpreted as the peak observed at 137.32 ppm shows the carbene carbon which is highly diagnostic for NHCs; also the peaks at 125.20 and 133.60 refer to the



Figure 1. ¹H-NMR of salt 1.



Figure 2. ¹H-NMR of complex 1.



Figure 3. a. ¹H-NMR of salt 2. b ¹H-NMR of complex 2.



Figure 4. Molecular structures of complex 1 and complex 2.

backbone carbon atoms and 49.10 ppm shows the benzylic $-CH_2$ carbon, which is attached to a phenyl.

The most important detail on the ¹H NMR spectra is the disappearance of the peak at 10.35 as the complexation reaction forms the Ag(I)NHC complex. Other peaks have remained in the spectra. The biggest change was observed on the ring protons and bridging protons. The two peaks observed at 4.15 (m, 2H) and 5.34 (s, 2H) ppm were assigned to CH_2 protons bridging the ring to other groups. The singlet at 2.20 ppm was assigned to methyl protons on the benzene ring. The methyl group of the tail was observed as a triplet at 1.44 ppm. The protons of backbone of the ring were observed at 6.57–6.91 ppm separately. It can be noticed from the values that the signals have shifted in different amounts (Fig. 2).



Figure 5. The EPR spectra at 260 K (a), 320 K (b) for complex 2.

MRC



Figure 6. The molecular structures (a) and radical structures (b) for complex 2 (A) and complex 1 (B).



Figure 7. For complex 2, the experimental EPR spectra (a) and its simulations (b).

The most important difference between two spectra was disappearance of the peak in 10.35 ppm of acidic proton in the salt. This shows the formation of NHC—Ag (I) complex from the NHC salt. Other peaks in the spectra have shifted to different values. The

most considerable differences were in the protons, neighboring the main ring of the NHC. The differences reach 0.37 ppm. The hydrogen protons on the main body and the benzene ring showed minor differences (0.04 ppm or less). Also similar observations were seen in the ¹³C NMR spectra. For example, the peak observed at 177.90 ppm shows that the carbene carbon atom has bonded to the Ag(I) ion to form a complex. In ¹³C NMR, the other peaks changed slightly.

For salt 2 and complex 2, the same analysis was carried out using ¹H and ¹³C NMR and elemental analysis as well. For salt 2 the most significant peak in the ¹H NMR spectrum is at 9.26 ppm, which shows acidic proton of the carbene. The other important peaks are 7.26 for backbones, 5.68 for the protons neighboring to N¹ and Ph in benzylic groups. A major number of peaks were massed between 2.61 and 2.15 ppm which refers to the methyl groups on benzene rings. After complex formation the most remarkable change was the disappearance of the peak at 9.26 ppm. Other peaks changed slightly (about 0.05 ppm) (Fig. 3a,b).

In ¹³C NMR spectra, the most remarkable peaks are examined in a similar way to salt 1 and complex 1. The most striking peaks are the ones at 137.70 ppm and 125.06 ppm, those show carbene carbon and backbone carbons respectively. After complex formation a peak at 182.28 ppm appeared. The other peaks changed their value up to 0.20 ppm as well.

EPR analysis

Complex 1 and complex 2 (Fig. 4) were irradiated for 72 h. EPR experiments were performed to determine change in the structures. It was observed that the EPR spectra of the complex 2 are generally similar to those of complex 1. The measurements were performed in the temperature range of 200 K - 450 K. A temperature dependence of the number of EPR lines was not observed for both compounds, but the line intensities changed with temperature (Fig. 5).

From analysis of the spectra and the molecular structures, it was determined that chemical reaction of both samples with gamma rays gave rise to one radical type; these radicals were similar for both compounds and also the produced unpaired electrons were mainly localized on the Ag atom. Considering the spectra, the EPR line splits into a doublet of 1:1 intensity ratios because of Ag nucleus, then each line splits twice into 1:1:1 intensity ratios because of the magnetic unequivalence of the nitrogen atoms. Then each line splits into 1:1 intensity ratios because of the magnetically inequivalent hydrogen protons. But, because of the overlapping, these splittings were not observed clearly in the spectra.



to analysis based on the results obtained from the spectra and the molecular structures of the samples, the effect of the gamma irradiation on the molecular structure was attributed as shown in Fig. 6.

In addition, these obtained results were verified by a computer simulation using the code WINEPR (Fig. 7). The hyperfine parameters and g-factor values were found for both samples as follows: g = 2.0134, $A_{Ag} = 15.30$ Gauss (G), $A_{N1} = 9.05$ G, $A_{N2} = 11.62$ G, $A_{H1} = 6.37$ G, $A_{H2} = 8.04$ G. Some of our obtained data is in good agreement with the literature.^[12,13,17] Also, we have calculated the change of unpaired electron concentration over the samples with temperature (Fig. 8). It was shown in Fig. 8 that complex 1 has more unpaired electron concentration than complex 2. Moreover, it was observed that the color of the irradiated complex 2 changed from white to yellow at the room temperature, but the color of irradiated complex 1 did not change.

Conclusions

The radical structures produced by irradiation were investigated by using the EPR method. The obtained EPR spectra supported the presence of one type of radical structure on both 1-pentamethylbenzyl-3-ethylimidazoliumsilver(I)bromide (complex.1) and 1,3-bis(pentamethylbenzyl)-4,5 dimethylbenzimidazo-liumsilver(I)bromide (complex 2). It was understood from change of color that the irradiation produced color centers on complex 2. According to the obtained results, it can be said that Complex2 was less resistant to irradiation than complex 1. We hope that the results reported, (i.e. characterization of the material irradiated by using the EPR technique) will contribute to the understanding of the such materials in chemistry, physics, etc.

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