Propellants

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Oxygen-Balanced Energetic Ionic Liquid**

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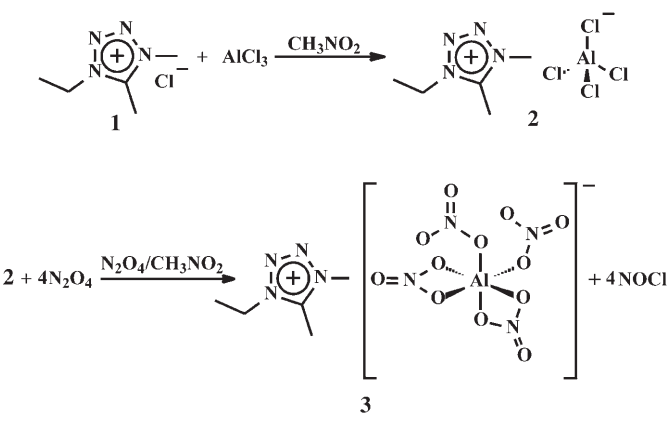
Energetic ionic liquids (EILs) are of great interest.[1–3] They offer enhanced stability, higher densities, no vapor pressure, and, hence, no vapor toxicity. As a general principle, the stability of energetic ionic compounds can be greatly enhanced by making the cation the fuel and the anion the oxidizer. The formal positive charge increases the ionization potential of the fuel cation, and the formal negative charge decreases the electron affinity of the anion. In this manner, the fuel cation becomes more oxidizer-resistant, and the oxidizer anion is protected against premature reduction by the cation. For environmental reasons, it is also desirable to avoid halogen-containing ingredients, such as perchlorates.

The previously known EILs consist of small oxidizing anions, such as ClO_4^-, NO_3^-, or $N(NO_2)_2^-$, and large fuel cations containing quaternary nitrogen heterocycles with long, asymmetric, poorly packing side chains. The most serious drawback of these EILs is that they are underoxidized. The small anions do not carry sufficient oxygen for complete oxidation of the large fuel cations to carbon monoxide, resulting in poor performance. In rocket propulsion, a low molecular weight of the exhaust products is very important.[4,5] Furthermore, at high flame temperatures CO_2 is dissociated almost completely to CO and O_2 (Boudouard equilibrium).[6] Therefore, it is often sufficient to oxidize the carbon content only to CO and not to CO_2 to achieve near-maximum performance.[5] The aim of this study was the preparation of halogen-free, CO-balanced, EILs.

In 1998, the concept of oxidizer-balanced EILs was proposed, and in 2002, its practicability was shown by the preparation of 1-ethyl-3-methylimidazolium tetranitratoborate,[7] a compound that turned out to be indeed an ionic liquid with a freezing point of −25 °C. However, its energy content and thermal stability were marginal. Herein, we report on a significantly improved compound using the tetranitratoaluminate anion as a thermally more stable high-oxygen carrier and the 1-ethyl-4,5-dimethyltetrazolium cation as a more energetic counterion (imidazole, $\Delta H_f^\circ = +49.8\ kJ\,mol^{-1}$;[8] tetrazole, $\Delta H_f^\circ = +237.1\ kJ\,mol^{-1}$ [9]). These are the first CO-balanced EILs. Although an oxygen-balanced tetrazolium salt, 5-aminotetrazolium nitrate, was recently reported,[10] its melting point of 173 °C does not classify it as an ionic liquid.

Polynitratoaluminates were first studied in the 1960s in the USA[11] and, subsequently, during the 1970s in the USSR.[12–23] Several examples of alkali metal,[12–21] NO_2^+,[22,23] and ethylammonium salts[24] of tetra-, penta-, and hexanitratoaluminate anions are known. The tetranitratoaluminate anion contains 12 oxygen atoms; of these, 10.5 are available to oxidize a fuel cation.

Alkylated tetrazolium cations were used in this work because of their large positive heats of formation and their potential to form ionic liquids. Ionic salts of the tetranitratoaluminate anion can be prepared in essentially quantitative yields in one-pot reactions in nitromethane solution. The starting materials are the chloride salt of the cation, aluminum trichloride, and dinitrogen tetroxide. The synthesis of 1-ethyl-4,5-dimethyltetrazolium tetranitratoaluminate (**3**) is shown in Scheme 1. The starting material 1-ethyl-4,5-dimethyltetrazolium chloride (**1**) was prepared by alkylation of 1,5-dimethyltetrazole with ethyl iodide, followed by anion exchange of iodide for chloride using an anion-exchange resin. The alkylation places the ethyl group primarily into the 1 position, but 16% is also found at the 2 position of the tetrazolium cation. The percentage of the minor isomer was reduced to 6% by recrystallization from ethanol and might be reduced further by additional recrystallizations. This relatively small isomeric impurity was not removed from the product. It offers the benefit of lowering the melting point of the salt without drastically altering its energetic or chemical properties.



Scheme 1. Synthesis of 1-ethyl-4,5-dimethyltetrazolium tetranitratoaluminate (**3**).

The reaction of the tetrazolium chloride in nitromethane with one equivalent of anhydrous aluminum trichloride gives the tetrachloroaluminate salt **2**, which is a viscous ionic liquid. This intermediate can then be reacted directly with an excess of N_2O_4 in nitromethane. Compound **3** is obtained as a clear, nearly colorless, viscous liquid by pumping off the volatile

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compounds, NOCl, CH_3NO_2, and excess N_2O_4, at ambient temperature. It is stable in dry air, hydrolyzes in water, and is soluble in CH_3NO_2 and moderately soluble in CH_2Cl_2. The identity and purity of the product were established by Raman, infrared, ^1H, ^{14}N, ^{15}N, and ^{13}C NMR spectroscopy, and the observed material balance.

The ^{14}N NMR spectrum of **3** shows a strong signal at $\delta = -25$ ppm, which is attributed to the four nitrogen atoms of the tetranitratoaluminate anion. The signals at $\delta = -134$ and -144 ppm, assigned to N1 and N4, respectively, of the tetrazolium cation, are much broader. Additional signals from N2 and N3 of the tetrazolium cation are obscured by the strong broad signal at $\delta = -25$ ppm.

The ^{15}N NMR spectrum of the neat liquid shows the expected five signals, at $\delta = -15.6$ (N2), -18.2 (N3), -25.3 ($Al(NO_3)_4^-$), -134.2 (N1), and -145.8 (N4) ppm. The tetranitratoaluminate anion contains two monodentate and two bidentate nitrato ligands, as shown by us by a crystal structure analysis of $[N(CH_3)_4][Al(NO_3)_4]$.[25] In this pseudo-octahedral structure, the two monodentate ligands are *cis* to each other. The observation of a single nitrogen resonance for the monodentate and bidentate nitrato groups is attributed to fast intramolecular exchange. Even at $-30\,^\circ C$ in CH_3NO_2, this exchange could not be slowed sufficiently to observe line broadening or separate signals for the nitrato groups. The assignments for the ^1H and ^{13}C NMR signals are given in the Experimental Section.

The presence of the tetranitratoaluminate anion was also confirmed by vibrational spectroscopy. The observed infrared and Raman spectra are shown in Figure 1, and the frequencies are listed in the Experimental Section. The anion part of the infrared spectrum is in good agreement with those previously reported for $Rb[Al(NO_3)_4]$[15] and $Cs[Al(NO_3)_4]$.[12] Additional support came from calculations at the MP2/6-311+G(d) level of theory. Two minimum-energy structures were obtained with C_2 and C_1 symmetry, respectively. Contrary to the tetranitratoborate anion, which possesses four monodentate nitrato ligands,[26] both tetranitratoaluminate isomers are hexacoordinated with two monodentate and two bidentate ligands in *cis* configuration. These isomers differ only in the orientation of the NO_2 groups of the monodentate ligands with respect to each other and, at the MP2 level, differ only by 2.5 kJ mol^{-1}. The energetically favored C_2 structure agrees with the crystal structure of $[N(CH_3)_4][Al(NO_3)_4]$,[25] and its calculated spectra are in better agreement with the observed ones.

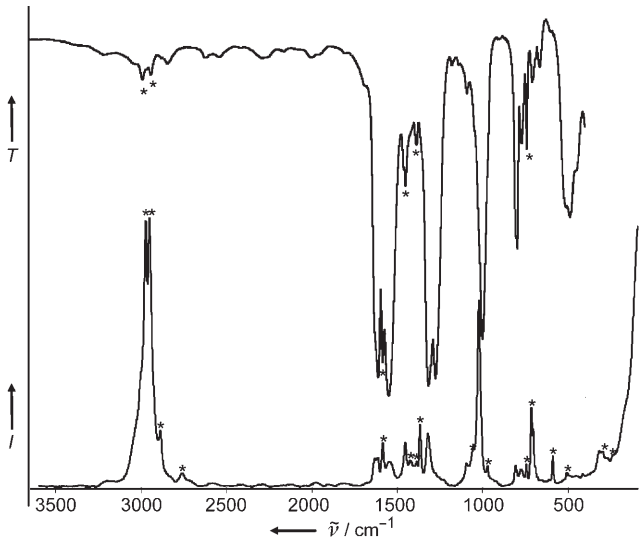

Figure 1. IR (upper trace) and Raman (lower trace) spectra of liquid **3**. The stars indicate bands assigned to the cation.

Individual modes are difficult to assign because of the size of the anion and strong vibrational coupling. In the region of the N–O stretching modes, three clusters are observed at about 1650–1500, 1350–1290, and 1030–990 cm^{-1}, with each cluster containing four fundamental vibrations. These clusters are characteristic for covalently bound mono- and bidentate nitrato ligands and distinguish them from ionic nitrates.[27] The highest-frequency cluster contains the N=O stretching vibration of the bidentate ligands and the antisymmetric stretching vibration of the terminal NO_2 part of the monodentate ligands. The medium-frequency cluster contains the O–N–O antisymmetric stretching vibration of the bidentate ligands and the symmetric stretching vibration of the terminal NO_2 part of the monodentate ligands, while the lowest-frequency cluster is composed of the O–N–O symmetric stretching vibration of the bidentate ligands and the stretching vibration of the coordinating N–O part of the monodentate ligands. Although the spectra of the mono- and bidentate ligands exhibit different intensity patterns and the frequency separation between the first and the second cluster is somewhat larger for the bidentate nitrates, distinction between monodentate and bidentate nitrato ligands becomes difficult when dealing with molecules that contain both types of ligands at the same time.

For energetic materials, stability and physical properties are very important. The thermal stability of **3** was investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The DSC trace showed a glass transition temperature (T_g) at $-46\,^\circ C$ and a strongly exothermic decomposition with a maximum at 217 °C and an onset at 183 °C. In accord with the DSC data, the TGA showed catastrophic weight loss to start at 183 °C; however, very slow weight loss also occurred at much lower temperatures, but the exact onset was difficult to ascertain. When a sample of **3** was held isothermally in the TGA apparatus at 75 °C for 4 h, a 10.4 % weight loss was observed. This slow weight loss is attributed to the loss of NO_2 and oxygen, accompanied by the formation of Al–O–Al bridges. Similar observations were previously reported by Shirokova and Rosolovskii for the cesium polynitratoaluminates.[13]

Ignition of EILs often presents major problems. The ignition of compound **3** and self-sustained burning were readily achieved by either thermal heating of **3** to about 200 °C or by the use of a hot 40-gauge Ni/Cr wire wrapped around the sample container, a glass melting-point capillary. The capillary was filled to the top with the sample, and a direct current passed through the wire. After a few seconds, compound **3** ignited quite spectacularly, giving off flames and light, fluffy alumina, in accord with the predicted idealized combustion process [Eq. (1)]. Obviously, the composition of

the combustion products at a given flame temperature would significantly deviate from those given in Equation (1).

$$2\,[N_4C_5H_{11}]^+[Al(NO_3)_4]^- \rightarrow Al_2O_3 + 8\,N_2 + 11\,H_2O + 10\,CO \qquad (1)$$

When samples were heated in the TGA apparatus to their decomposition temperature, a false small mass increase was observed right before the catastrophic mass loss, due to the thrust of the burning liquid pushing down the TGA pan.

The theoretical performance of **3** as a propellant can be estimated from the calculated heats of formation of the free gaseous cation (836 kJ mol^{-1}) and anion (−1486 kJ mol^{-1}), calculated at the MP2/6-311 + G(d) level of theory, an estimate[28] of the Coulomb energy of the ions in the liquid of about 419 kJ mol^{-1}, using publicly available performance calculation codes.[29] Based on these estimates, the performance of this system significantly exceeds those of state-of-the-art materials, such as hydrazine.[30]

Experimental Section

Caution! *Although no difficulties were encountered when handling these materials, they are highly energetic and potentially explosive! They should be handled on a small scale while using appropriate safety precautions (safety shields, face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs).*

Materials and apparatus: All reactions were carried out in Pyrex glass ampoules that were closed by Teflon/glass high-vacuum valves. Volatile materials were handled in a Pyrex glass vacuum line. Nonvolatile materials were handled in the dry argon atmosphere of a glove box.

Raman spectra were recorded directly in the glass reactors in the range 3600–80 cm^{-1} on a Bruker Equinox 55 FRA 106/S FT-RA spectrometer, using a Nd-YAG laser at 1064 nm with power levels of 400 mW. Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Midac, M Series, FT-IR spectrometer. For liquid samples, a Wilks minicell with AgCl windows was used. Solids were recorded as AgCl or KBr pellets. The cells were filled inside the glove box using an Econo minipress (Barnes Engineering Co.) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample. ^{14}N and ^{15}N NMR spectra were recorded at 36.13 and 50.68 MHz, respectively, on a Bruker AMX 500 spectrometer. Samples were either externally referenced to CH_3NO_2 or dissolved in CH_3NO_2. TGA thermograms were measured on a Shimadzu TGA-50 instrument using a flow rate of 20 mL min^{-1} of nitrogen. DSC measurements were recorded on a Shimadzu DSC-50(SH); the temperature was ramped at a rate of 10 K min^{-1}. Densities were measured with a pycnometer.

The starting materials, N_2O_4 (Matheson), ethyl iodide, $AlCl_3$, and 5-methyltetrazole (Aldrich), were used without further purification. Deuterated solvents (Cambridge Isotopes) were dried using standard methods. Nitromethane (Fisher) was dried over $CaCl_2$, vacuum-distilled and stored over 4-Å molecular sieves before use. All volatile materials were handled using standard high-vacuum techniques. 1,5-dimethyltetrazole was prepared by a literature method;[31] its identity and purity were confirmed by IR, Raman, and ^{1}H NMR spectroscopy.

1-Ethyl-4,5-dimethyltetrazolium chloride (**1**): 1,5-dimethyltetrazole (28 mmol) and ethyl iodide (15 mL) were placed into a 250-mL glass ampoule equipped with a high-vacuum valve and degassed by three freeze-pump-thaw cycles. The ampoule was immersed into a hot water bath at 100 °C for 10 h. The volatile material was removed under vacuum at room temperature, to give a yellow solid (5.466 g). The solid was dissolved in a minimum amount of methanol, and passed through a column containing 15 g (55.5 meq) AMBERJET 4200 (Cl) ion-exchange resin, using methanol as eluent. The bulk of the methanol was removed under vacuum, and the anion exchange was repeated until the effluent was free of iodide, as shown by the absence of an NH_3-insoluble precipitate with $AgNO_3$. All volatile material was pumped off, and the residue was recrystallized from ethanol. Yield: 1.412 g (31 %); ^{1}H NMR (CD_3CN): $\delta = 1.56$ (t, $^3J = 7.4$ Hz, 3H, CH_3), 2.95 (s, 3H, CH_3), 4.23 (s, 3H, CH_3), 4.61 ppm (q, $^3J = 7.4$ Hz, 2H, CH_2); minor isomer, 2-ethyl-4,5-dimethyltetrazolium chloride: ^{1}H NMR (CD_3CN): $\delta = 1.60$ (t, $^3J = 7.4$ Hz, 3H, CH_3), 3.00 (s, 3H, CH_3), 4.27 (s, 3H, CH_3), 4.86 ppm (q, $^3J = 7.4$ Hz, 2H, CH_2). Raman (400 mW): $\tilde{\nu} = 2986$ (7.4), 2953 (10.0), 2887 (2.5), 2814 (1.0), 2763 (0.4), 1589 (1.8), 1530 (1.0), 1474 (sh), 1456 (1.8), 1416 (1.0), 1396 (0.8), 1363 (2.9), 1324 (0.5), 1307 (0.5), 1287 (0.7), 1229 (0.2), 1116 (0.3), 1088 (0.3), 1065 (0.8), 1041 (0.5), 980 (0.8), 808 (0.3), 788 (0.2), 747 (1.0), 724 (3.9), 699 (0.6), 655 (0.6), 594 (1.1), 503 (0.7), 388 (0.6), 296 (1.5), 246 (0.8), 229 (0.8), 153 (sh) cm^{-1}. IR (KBr): $\tilde{\nu} =$ 2997 (m), 2946 (w), 2888 (w), 1629 (br), 1587 (s), 1526 (m), 1467 (sh), 1453 (m), 1409 (w), 1388 (w), 1360 (m), 1323 (w), 1287 (w), 1229 (w), 1181 (w), 1151 (w), 1113 (w), 1084 (vw), 1058 (sh), 1034 (s), 975 (m), 805 (w), 745 (s), 720 (w), 696 (vw), 648 (w) cm^{-1}.

1-Ethyl-4,5-dimethyltetrazolium tetrachloroaluminate (**2**): In the glove box, compound **1** (3.25 mmol) and $AlCl_3$ (3.25 mmol) were placed into a 9-mm (outer diameter) glass ampoule. The ampoule was connected to the vacuum line, and evacuated at −196 °C. Nitromethane (≈1 mL) was added at −196 °C, and the ampoule was allowed to warm slowly to room temperature, which led to an orange solution. The nitromethane was removed under a dynamic vacuum overnight at ambient temperature, giving a quantitative yield of **2** as an amber viscous liquid.

1-Ethyl-4,5-dimethyltetrazolium tetranitratoaluminate (**3**): In the glove box, compound **2** (1.68 mmol) was loaded into a 9-mm glass ampoule. The ampoule was connected to the glass vacuum line and evacuated. After cooling to −196 °C, N_2O_4 (39.92 mmol) was condensed in, followed by CH_3NO_2 (27.06 mmol). The mixture was allowed to slowly warm to room temperature and stirred for 1.5 h. The volatile material was removed under a dynamic vacuum for 24 h, giving an almost colorless clear viscous oil. Expected mass 0.674 g, found mass 0.651 g. ^{1}H NMR (CD_3NO_2): $\delta = 1.62$ (t, $^3J = 7.4$ Hz, 3H, CH_3), 2.95 (s, 3H, CH_3), 4.90 (s, 3H, CH_3), 4.67 ppm (q, $^3J = 7.4$ Hz, 2H, CH_2); minor isomer, 2-ethyl-4,5-dimethyltetrazolium tetranitratoaluminate: ^{1}H NMR (CD_3NO_2): $\delta = 1.70$ (t, $^3J = 7.4$ Hz, 3H, CH_3), 2.82 (s, 3H, CH_3), 4.33 (s, 3H, CH_3), 4.91 ppm (q, $^3J = 7.4$ Hz, 2H, CH_2); ^{13}C NMR: $\delta = 8.77$, 13.95, 37.53, 47.84, 153.87 ppm; ^{14}N NMR (CD_3NO_2): $\delta = -144$, −134, −25 ppm; ^{14}N NMR (CD_2Cl_2): −141, −26 ppm; ^{15}N NMR (neat liquid): $\delta = -145.8$ (s, 1N, N4), −134.2 (s, 1N, N1), −25.3 (s, 4N, $Al(NO_3)_4$), −18.2 (s, 1N, N3), −15.6 ppm (s, 1N, N2). Raman (400 mW): $\tilde{\nu} = 2973$ (9.9), 2951 (10.0), 2887 (1.0), 2761 (0.5), 1630 (1.0), 1611 (1.0), 1585 (1.6), 1547 (0.9), 1453 (1.6), 1422 (1.0), 1387 (1.0), 1367 (2.3), 1321 (2.0), 1092 (0.9), 1057 (sh), 1021 (7.0), 970 (0.8), 808 (0.8), 775 (0.7), 743 (0.9), 715 (3.0), 703 (2.0), 703 (2.0), 589 (1.2), 508 (0.5), 317 (1.3), 300 (1.2), 271 (0.9), 237 (1.1) cm^{-1}. IR (AgCl plates): $\tilde{\nu} = 3032$ (sh), 2995 (w), 2944 (w), 2850 (w,br), 2627 (w,br), 2547 (w,br), 2282 (w,br), 2004 (w,br), 1945 (sh), 1694 (sh), 1630 (sh), 1611 (s), 1583 (s), 1550 (s), 1466 (w), 1451 (m), 1388 (w), 1320 (s), 1275 (s), 1182 (w), 1142 (w), 1093 (w), 1047 (sh), 1021 (sh), 1001 (s), 806 (sh), 796 (m), 773 (w), 739 (m), 711 (w), 664 (w), 516 (sh), 489 (m), 450 (sh) cm^{-1}.

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