Energetic Ionic Liquids Based on Lanthanide Nitrate Complex Anions (Postprint)

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Energetic ionic liquids based on anionic rare earth nitrate complexes, Cat+3[Ln(NO3)6]3-, where Cat+ is guanidinium, 4-amino-triazolium, 1-methyl-4-amino-triazolium, 1-ethyl-4-amino-triazolium, 1-butyl-4-amino-triazolium, 1,5-diamino-tetrazolium, and 1,5-diamino-4-methyltetrazolium, were prepared. The hexanitratolanthanum (cerium) salts with the latter two cations are the first CO-balanced energetic ionic liquids that are hydrolytically and air stable with impact sensitivities of ~27 J. For environmental considerations, these ionic liquids were obtained by a simple method using nitrate-containing precursors. All salts are fully characterized by IR, NMR, elemental analysis, thermal stability, phase behavior, density, and water content determinations. Based on theoretical calculations, these new compounds have potential as propellants.
Energetic Ionic Liquids based on Lanthanide Nitrate Complex Anions

Guo-Hong Tao,[a] Yangen Huang,[a] Jerry A. Boatz,[b] and Jean’ne M. Shreeve*[a]

Abstract: Energetic ionic liquids based on anionic lanthanide nitrate complexes Cat3[N(NO3)6]3−, where Cat is guanidinium, 4-aminotriazolium, 4-amino-1-methyltriiazolium, 4-amino-1-ethyltriiazolium, 1,5-diaminotetrazolium, and 1,5-diamino-4-methyltetrazolium, were prepared. The hexanitratolanthanate (-cerate) salts with the last two cations, which are the first CO-balanced energetic ionic liquids that are stable to hydrolysis and air, have impact sensitivities of about 27 J. These ionic liquids were obtained by an environmentally friendly, simple method using nitrate-containing precursors. All salts were fully characterized by IR and NMR spectroscopy, elemental analysis, and determination of thermal stability, phase behavior, density, and water content. According to theoretical calculations, these new compounds have potential as propellants.

Keywords: ab initio calculations · energetic materials · ionic liquids · lanthanides · nitrate complexes

Introduction

Ionic liquids are often considered as greener solvents, electrolytes, and advanced materials.[1] Compared with traditional energetic compounds such as 2,4,6-trinitrotoluene (TNT), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (RDX), and 1,3,5-trinitrohydroperhydro-1,3,5-triazine (RDX), many energetic ionic liquids were reported with several advantages, including enhanced thermal stability, higher density, negligible vapor pressure, and little or no vapor toxicity.[2] The relatively low oxygen content of most known energetic ionic liquids contributes to their poor performance.[3] This arises from the fact that small anions such as NO3−, ClO4−, and N(NO2)2− have insufficient oxygen to completely oxidize the large fuel cations to carbon monoxide. Thus, the preparation of CO-balanced ionic liquids is important for improving their performance as energetic materials. In 2006, the first CO-balanced energetic ionic liquid, 1-ethyl-4,5-dimethyltetrazolium tetranitroaluminate, was reported.[4] It shows a glass transition temperature (Tg) at ~46 °C. However, it is only stable in dry air and thus must be protected from water. At 75 °C, clear weight loss attributed to the loss of NO3 and oxygen, accompanied by the formation of Al-O-Al bridges, was observed. Its initial preparation involved the highly toxic and corrosive chemicals N2O4 and NOCl.

Ligands which coordinate through oxygen atoms to a lanthanide ion give rise to stable complexes. Thus, higher air and thermal stabilities may be obtained by introducing lanthanide nitrates as main components of ionic liquids. We now report new energetic ionic liquids based on anionic lanthanide nitrate complexes Cat+3[N(NO3)6]3−. Based on CO formation, some of these salts have a neutral or positive oxygen balance. Compounds 11 and 12 (see Scheme 1) are the first CO-balanced energetic ionic liquids which are stable to moisture and air. Furthermore, important for ease of synthesis and for environmental reasons, these liquids are prepared by using readily available nitrate salts as precursors.

Lanthanide-doped ionic liquids exhibit interesting luminescence properties and good photochemical stability.[4] In addition to our present work, only one or two families of lanthanide ionic liquids have been prepared,[5] for example, the inorganic polyanowometalate salts Na2[Ln-(TiW11O42)]·xH2O (x = 27–44)[5b] and lanthanide complexes of the pseudohalide SCN− in the hydrolytically unstable [bmim]3[Ln(SCN)4]-H2O (bmim = 1-butyl-3-methylimidazolium).[5c] However, the former exist as hydrates, are not stable in the absence of water of hydration, and are not typi-
cal ionic liquids. The instability of [bmim]_3Ln(SCN)_2-H_2O to moisture and air also limits their applications. Since our new lanthanide ionic liquids do not present these difficulties, their potential for applications related to electrodeposition, catalysis, energetics or photophysics may be realized.

Results and Discussion

Nitrate is a familiar stable ligand for lanthanides. It is also an energetic oxidizing anion and can be the oxidizer component in energetic ionic liquids. Lanthanides coordinate with O-donor ligands more strongly than with N-donor ligands, for example, ambient moisture irreversibly decomposes [bmim]_3Ln(SCN)_2-H_2O ionic liquids by displacing the thiocyanate ligand. In our syntheses, guanidinium nitrate and lanthanum or cerium nitrate are dissolved in acetonitrile and heated to reflux with triethyl orthoformate to give 1 or 2. They are unchanged after being dissolved in water and dried in vacuum. Compounds 1 and 2 can be crystallized from water at room temperature to form colorless blocklike crystals of (CH_3CN)_3[La(NO_3)_3(H_2O)] (1) and (CH_3CN)_3[Ce(NO_3)_3(H_2O)] (2). The crystal structure of 1 was reported earlier.

Because of strong hydrogen-bonding interactions, the melting points of 1 and 2 exceed 100°C. To lower the melting points, 4-amino-1,2,4-triazolium cations were introduced into energetic ionic liquids. Generally, the E mode of the D_{2h} point group in symmetric NO_3^- gives an IR absorbance band around 1385 cm^{-1}. When the oxygen atoms of NO_3^- are coordinated to a lanthanide, the N-O asymmetrical stretching vibration is perturbed and has two different stretching modes. Therefore, in the system with bidentate nitrate ligands, ν_3 is split into two peaks, ν_3 and ν_3^{1470}. In the Cat^+3[Ln(NO_3)_3]^3+ ionic liquids, the band separation ν_3-ν_2 approaches about 130 cm^{-1}. For example, the ν_3 and ν_3 absorbance peaks of NO_3^- in ionic liquids 5 and 8 are at 1454, 1325 cm^{-1} and 1470, 1313 cm^{-1} respectively (Figure 1). No obvious absorbance peak near 1385 cm^{-1} was observed, in support of the fact that no uncoordinated nitrate ions are present in these ionic liquids, which distinguishes them from conventional nitrate ionic liquids without coordination structure.

In the crystal of known tris(tributylammonium) hexanitrolanthanate ([((C_6H_5)NH)_3][Ln(NO_3)_6]), the main nitrate vibrational frequencies are ν_1=1469, ν_1=1305, ν_3=1036, and ν_3=819 cm^{-1}. These are consistent with the IR data of Cat^+3[Ln(NO_3)_3]^3+. Thus, Cat^+3[Ln(NO_3)_3]^3+ has a structure analogous to [((C_6H_5)NH)_3][Ln(NO_3)_6] in which all six of the nitrate ligands are coordinated to the lanthanide ion in a chelating bidentate mode.

Salts Cat^+3[Ln(NO_3)_3]^3+ are thermally stable over the range of 185 to 235°C in a nitrogen atmosphere. The cations
play a more important role than the anions in determining the decomposition temperature because they are less stable than the anions. Their thermal stabilities generally meet the criterion for energetic compounds. Salts 3–12 are all ionic liquids (Table 1). The melting points/glass transition temperatures \( T_m/T_g \) were determined by differential scanning calorimetry (DSC) from the first heating cycle. As the temperature is increased, the solid samples exhibit distinct melting points. The DSC curves of solid samples of 1 \( (T_m = 137^\circ C) \), 4 \( (T_m = 76^\circ C) \), and 12 \( (T_m = 90^\circ C) \) are given in Figure 2. However, on warming from \(-70^\circ C\), liquid samples of 5–10 behave differently. Each displays a gradual step associated with a phase transition temperature \( T_g \) between \(-20 \) and \(-40^\circ C\). Since there is no sharp endothermic peak that can be associated with melting, as was observed in the solid samples, 5 was taken as representative and examined further.

When 5 was cooled to \(-70^\circ C\), it became a glassy, transparent solid. After being warmed to above \(-25^\circ C\), it gradually became a very viscous transparent liquid. This indicates a glasslike character similar to that of conventional ionic liquids below the glass transition temperature.\(^{[10]}\) Furthermore, different cations clearly affect the decomposition temperature (Figure 2). The densities of these lanthanide ionic liquids vary from about 1.6 \( (9, 10) \) to about 2.1 g cm\(^{-3}\) \( (11 \) and 12\). The 1,5-di- amino-4-methyl-1,2,3,4-tetrazolium cation strongly enhances the density. The cation/anion ratio of 3:1 in the Cat\(^+\)[Ln(NO\(_3\)\(_3\)]\(^-\) ionic liquids increases the nitrogen content, since most of the nitrogen atoms are present in the cation. The calculated nitrogen content for CO-balanced aluminum-containing ionic liquids is 28 \%,\(^{[11]}\) while the nitrogen content of CO-balanced salts 11 and 12 is around 40 \%. This will improve their energetic performance.

These ionic liquids are hydrophilic and are soluble in water and lower alcohols. Their water content was determined by using a Karl–Fischer coulometer. The water content, determined after the ionic liquid was dried under

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**Table 1. Properties of Cat\(^+\)[Ln(NO\(_3\)\(_3\)]\(^-\) ionic liquids.**

<table>
<thead>
<tr>
<th>Cat(^+)[Ln(NO(_3)(_3)](^-)</th>
<th>(T_m(T_g))</th>
<th>(T_g)</th>
<th>(\rho)</th>
<th>OB(_{\text{cat}})</th>
<th>(\Delta H_m) (cation)</th>
<th>(\Delta H_m) (anion)</th>
<th>(\Delta H_l)</th>
<th>(\Delta H_h)</th>
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<tr>
<td></td>
<td>[(^\circ C)]</td>
<td>[(^\circ C)]</td>
<td>[g cm(^{-3})]</td>
<td>[%]</td>
<td>[kJ mol(^{-1})]</td>
<td>[kJ mol(^{-1})]</td>
<td>[kJ mol(^{-1})]</td>
<td>[kJ mol(^{-1})]</td>
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<tr>
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<td>225</td>
<td>1.95</td>
<td>10.4</td>
<td>575.9</td>
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<td>1.96</td>
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<td>2329.4</td>
<td>-2513.3</td>
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<td>76</td>
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<td>1.88</td>
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<td>-</td>
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<td>-1486</td>
<td>419(^h)</td>
<td>-1069</td>
<td>-2.66</td>
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</tbody>
</table>


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**Figure 2. DSC curves of some typical Cat\(^+\)[Ln(NO\(_3\)\(_3\)]\(^-\) ionic liquids.**

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vacuum, ranges between 1900 and 4500 ppm. This is slightly higher than is found in conventional ionic liquids.[13,15] In aqueous solution, the IR spectra show an absorbance peak at 1385 cm\(^{-1}\) assignable to the nitrate anion. After the liquids were dried, the IR absorbance peaks of the bidentate nitrato ligands near 1450 cm\(^{-1}\) and 1325 cm\(^{-1}\) reappeared concomitantly. At the same time, the peak at 1385 cm\(^{-1}\) disappeared. This is a reversible process and indicates that these ionic liquids are moisture-stable.

Oxygen balance (OB) reveals the deficiency or excess of oxygen in an energetic compound. In a CO-balanced ionic liquid, the oxygen present must convert all of C to CO, all H to H\(_2\)O, and all Ln to Ln\(_2\)O\(_3\). The OB\(_{\text{CO}}\) data of these ionic liquids are shown in Table 1. The OB\(_{\text{CO}}\) values of 11 and 12 are zero, which indicates they are CO-balanced ionic liquids.

When 1 mg of 11 was heated to 200°C in a micro melting point apparatus, gases rapidly evolved to leave white lanthanum oxide powder. The decomposition process is in accord with the predicted idealized combustion process [Eq. (1)].

\[
2\left[\text{N}_2\text{C}_2\text{H}_3\right]_3^+\text{[La(NO}_3)_6\text{]}^3^+ \rightarrow \text{La}_2\text{O}_3 + 24\text{N}_2 + 21\text{H}_2\text{O} + 12\text{CO}
\]  

The theoretical performance of Cat\(^+\)\(_{\text{d}}\)\([\text{Ln(NO}_3)_6\text{]}\)\(^{3^-}\) as propellants can be estimated from data calculated by the GAMESS\(^{[8]}\) and Gaussian 03 suites of programs. The heat of formation of the anions \(\Delta H_f^\circ\) (anion) were estimated on the basis of the gas-phase experimental heats of formation of NO\(_3^-\), F\(_2\), Cl\(_2\), LaF\(_4\), and LaCl\(_4\). Geometry optimizations and single-point calculations on the anions were performed by using second-order many-body perturbation theory (MBPT(2))\(^{[17]}\) also known as MP2 in conjunction with the Stevens–Basch–Krauss–Jaisen–Cundari (SBKJC) effective core potentials and corresponding valence-only basis sets\(^{[18]}\). The SBKJC basis sets for carbon, nitrogen, oxygen, fluorine, and chlorine were augmented with a diffuse s p 4 p shell\(^{[19]}\) and a d-type polarization function\(^{[20]}\).

The heats of formation of the cations \(\Delta H_f^\circ\) (cation) were determined by using the method of isodesmic reactions (Scheme 2).\(^{[21]}\) Geometric optimization and the frequency analyses are carried out at the B3LYP level up to 6-31+G(d,p) basis sets\(^{[22]}\). Single-point energies were calculated at the MP2/6-311+G(d,p) level\(^{[17a,b]}\). Heat of formation can be estimated on the basis of Born–Haber energy cycles [Eq. (2)]\(^{[19]}\). The lattice energy \(\Delta H_L\) could be predicted by the formula suggested by Jenkins et al. [Eqs. (3) and (4)]\(^{[23]}\).

\[
\Delta H_f^\circ\text{(ionic salts, 298 K)} = \sum \Delta H_f^\circ\text{(cation, 298 K)} + \sum \Delta H_f^\circ\text{(anion, 298 K)} - \Delta H_L
\]

\[
\Delta H_L = U_{\text{pot}} + [p(nM/2 - 2) + q(n_N/2 - 2)]RT
\]

\[
U_{\text{pot}} [\text{kJ mol}\text{ }^{-1}] = 2342.6I(\rho_{\text{ion}}/M_{\text{an}})^{1/3} + 55.2I
\]

The calculated heats of formation for Cat\(^+\)\(_{\text{d}}\)\([\text{Ln(NO}_3)_6\text{]}\)\(^{3^-}\) are summarized in Table 1. Compound 14 has the highest value, and the data show that the performance of Cat\(^+\)\(_{\text{d}}\)\([\text{Ln(NO}_3)_6\text{]}\)\(^{3^-}\) may be better than some important energetic materials, for example, hydrazine.\(^{[11]}\)

The impact sensitivities of 11 and 12 were measured by the BAM method\(^{[24]}\). The impact sensitivities of 11 and 12 of

\[
\text{Scheme 2. Isodesmic reactions and protonation reactions for calculating heats of formation of cations.}
\]
Lanthanide nitrate complex anions are suitable for preparation of energetic ionic liquids. Ionic liquids Cat+ [Ln(NO3)6]3− were obtained by an environmentally benign preparative method from nitrate salts. Compounds 11 and 12 are the first CO-balanced metal ionic liquids which are stable to moisture and air. According to theoretical calculations, these liquids are potential propellants. Their thermal stabilities, phase behavior, densities, and water content were investigated. Salts Cat+ [Ln(NO3)6]3− may retain lanthanides in a stable liquid and thus have potential for applications related to electrodeposition, catalysis, and photophysics.

Experimental Section

Caution! Although we have not experienced any problems in handling these compounds, with the exception of 11 and 12 their shock and impact sensitivities have not been determined. Therefore, they should be synthesized in amounts of less than 1 mmol and handled with extreme care.

General methods: All chemicals were obtained commercially as analytical-grade materials and used as received. Solvents were dried by standard procedures. IR spectra were recorded by using KBr plates for neat liquids and KBr pellets for solids on a Bio-Rad model 3000 FTIR spectrometer.

Lanthanide nitrate complex anions are suitable for preparation of energetic ionic liquids. Ionic liquids Cat+ [Ln(NO3)6]3− were obtained by an environmentally benign preparative method from nitrate salts. Compounds 11 and 12 are the first CO-balanced metal ionic liquids which are stable to moisture and air. According to theoretical calculations, these liquids are potential propellants. Their thermal stabilities, phase behavior, densities, and water content were investigated. Salts Cat+ [Ln(NO3)6]3− may retain lanthanides in a stable liquid and thus have potential for applications related to electrodeposition, catalysis, and photophysics.

Triguanidinium hexanitratocerate (1): Guanidinium nitrate (3 mmol, 366 mg) and lanthanum nitrate hexahydrate (1 mmol, 433 mg) were heated to reflux in acetonitrile for 12 h. An excess of triethyl orthoformate was added during reflux to a mixture with the formula for 1 d. The solution was concentrated and added to an excess of ethyl acetate (3–5 times the volume of solution). After decanting the solvent, the residual solid was removed from the lower layer in vacuo to obtain a white solid (442 mg, 98%). IR (KBr): v = 3484, 3223, 3119, 1609, 1574, 1454, 1325, 1172, 1038, 877, 819, 736, 616 cm−1; 1H NMR (CD3CN): δ = 9.54 (s, 1H), 8.66 (s, 1H), 6.15 (s, 2H), 4.06 ppm (s, 3H); 13C NMR (CD3CN): δ = 145.9, 143.9, 40.1 ppm; IR (KBr): v = 3493, 3417, 3380, 3214, 1643, 1535, 1420, 1355, 1323, 1294, 1034, 816, 743, 525 cm−1; 13C NMR (D2O): δ = 167.1 ppm; elemental analysis (%) calc. for C9H21CeN18O18: C 13.35, H 2.61, N 31.05, Ce 17.31; found: C 13.68, H 2.56, N 30.93, Ce 17.25.

H-Lanthanide nitrate complex anions are suitable for preparation of energetic ionic liquids. Ionic liquids Cat+ [Ln(NO3)6]3− were obtained by an environmentally benign preparative method from nitrate salts. Compounds 11 and 12 are the first CO-balanced metal ionic liquids which are stable to moisture and air. According to theoretical calculations, these liquids are potential propellants. Their thermal stabilities, phase behavior, densities, and water content were investigated. Salts Cat+ [Ln(NO3)6]3− may retain lanthanides in a stable liquid and thus have potential for applications related to electrodeposition, catalysis, and photophysics.

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ethyl acetate (3–5 times the volume of solution). After decanting the solvent, any residual solid was removed from the lower layer in vacuo to obtain a yellow liquid (462 mg, 96%). IR (KBr): 3355, 3233, 3133, 2965, 2877, 1700, 1617, 1466, 1330, 1110, 1038, 904, 843, 742, 627 cm⁻¹; ¹H NMR (CD₃CN): δ = 9.73 (s, 1H), 8.74 (s, 1H), 3.89 ppm (s, 3H); ¹³C NMR (CD₃CN): δ = 154.3 ppm; elemental analysis (%) calcd for C₆H₂₁LaN₂₄O₁₈ (856.28): C 4.43, H 1.85, N 41.32, La 16.86; found: C 4.38, H 1.82, N 41.29, La 16.78.

Tris(4-amino-1-ethyl-1,2,4-triazolium) hexanitratocerate (8): The same procedure was used for 7. 4-Amino-1-ethyl-1,2,4-triazolium iodide (0.3 mmol, 72 mg), AgNO₃ (0.3 mmol, 51 mg), and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain 9 as a colorless, viscous liquid, which became a white solid after standing at 25°C for 1 day. Yield: 430 mg (89%). IR (KBr): δ = 3343, 3266, 1717, 1629, 1466, 1330, 1110, 1038, 904, 843, 627 cm⁻¹; ¹H NMR (CD₃CN): δ = 9.67 (s, 1H), 6.02 (s, 2H), 3.89 ppm (s, 3H); ¹³C NMR (CD₃CN): δ = 154.4 ppm; elemental analysis (%) calcd for C₆H₂₁LaN₂₄O₁₈ (856.28): C 4.40, H 1.85, N 41.29, La 16.78.

Acknowledgement

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References


Lanthanide-Based Ionic Liquids

G.-H. Tao, Y. Huang, J. A. Boatz, J. M. Shreeve*

Energetic Ionic Liquids based on Lanthanide Nitrate Complex Anions

Well balanced: A series of ionic liquids Cat+\{Ln(NO3)6\}2− (Ln=La, Ce) such as those shown in the picture were synthesized by a simple method using nitrate-containing precursors. According to theoretical calculations, they have potential as propellants, and the salts in which Cat+ is 1,5-diamino-4-methyltetrazolium are the first CO-balanced energetic ionic liquids that are stable to hydrolysis and air.