

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 $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$, where Cat^+ is guanidinium, 4-aminotriazolium, 4-amino-1-methyltriazolium, 4-amino-1-ethyltriazolium, 4-amino-1-butyltriazolium, 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

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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.

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-tetraazocane (HMX), and 1,3,5-trinitroperhydro-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 NO_3^- , ClO_4^- , and $\text{N}(\text{NO}_2)_2^-$ 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

tetranitratoaluminate, was reported.^[3] It shows a glass transition temperature (T_g) 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 NO_2 and oxygen, accompanied by the formation of Al-O-Al bridges, was observed. Its initial preparation involved the highly toxic and corrosive chemicals N_2O_4 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 $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$. 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 polyoxometalate salts $\text{Na}_{13}[\text{Ln}(\text{TiW}_{11}\text{O}_{39})_2] \cdot x\text{H}_2\text{O}$ ($x=27-44$)^[5a] and lanthanide complexes of the pseudohalide SCN^- in the hydrolytically unstable $[\text{bmim}]_4\text{Ln}(\text{SCN})_7 \cdot \text{H}_2\text{O}$ ($\text{bmim} = 1\text{-butyl-3-methylimidazolium}$).^[5b] However, the former exist as hydrates, are not stable in the absence of water of hydration, and are not typi-

[a] Dr. G.-H. Tao, Dr. Y. Huang, Prof. Dr. J. M. Shreeve
Department of Chemistry
University of Idaho
Moscow, Idaho, 83844-2343 (USA)
Fax: (+1) 208-885-9146
E-mail: jshreeve@uidaho.edu

[b] Dr. J. A. Boatz
AFRL/PRSP Space and Missile Propulsion Directorate
10 East Saturn Boulevard, Edwards Air Force Base, CA 93524-7680
(USA)

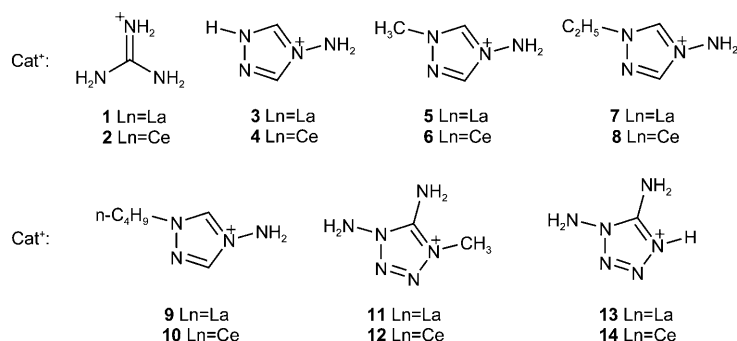
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cal ionic liquids. The instability of $[\text{bmim}]_4\text{Ln}(\text{SCN})_7 \cdot \text{H}_2\text{O}$ to moisture and air also limits their applications. Since our new lanthanide ionic liquids do not present these difficulties, their potential for applications related to electrodeposition, catalysis, energetics or photophysics may be realized.

Results and Discussion

Nitrate is a familiar stable ligand for lanthanides.^[6] It is also an energetic oxidizing anion and can be the oxidizer component in energetic ionic liquids.^[7] Lanthanides coordinate with O-donor ligands more strongly than with N-donor ligands;^[8] for example, ambient moisture irreversibly decomposes $[\text{bmim}]_4\text{Ln}(\text{SCN})_7 \cdot \text{H}_2\text{O}$ ionic liquids by displacing the isothiocyanate ligand.^[5b] 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 $(\text{CH}_6\text{N}_3)_2[\text{La}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ (**1**) and $(\text{CH}_6\text{N}_3)_2[\text{Ce}(\text{NO}_3)_5(\text{H}_2\text{O})_2]$ (**2**). The crystal structure of **1** was reported earlier.^[9]

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 to obtain salts **5–10** by using a minor modification of the literature method (Scheme 1).^[10] Stoichiometric amounts of



Scheme 1. Ionic liquids based on lanthanide nitrate complex anions

triazolium iodide, AgNO_3 , and lanthanum nitrate hexahydrate were heated to reflux in acetonitrile in the absence of light. After the silver iodide and the solvent were removed, a viscous liquid remained. These salts have the characteristics of room-temperature ionic liquids. It was also our aim to increase the energy of these ionic liquids by using energetic cations such as 1,5-diamino-4*H*-1,2,3,4-tetrazolium and 1,5-diamino-4-methyl-1,2,3,4-tetrazolium. The melting points of salts **11** and **12**, which contain the latter cation, of less than 100 °C place them in the class of ionic liquids. This preparative method for metal nitrate complexes is a rela-

tively green procedure that does not involve highly toxic or corrosive chemicals.

In the IR spectra of these energetic ionic liquids, the main N–O stretching modes of the lanthanide complex anions $[\text{Ln}(\text{NO}_3)_6]^{3-}$ are observed at about 1450–1470, 1320–1350, 1034–1040, and 815–820 cm^{-1} . No other N–O stretching mode was found. These observed bands are assigned to the N–O stretching modes ν_4 , ν_1 , ν_2 , and the bending mode ν_6 .^[11] Bands ν_4 and ν_1 are assigned to the N–O asymmetrical stretching vibration. Band ν_2 is due to N–O symmetrical stretching vibration, and ν_6 is the out-of-plane bending vibration.^[11c] Generally, the $\nu_3(E')$ mode of the D_{3h} 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_4 and ν_1 .^[11b] In the $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ ionic liquids, the band separation $\nu_4-\nu_1$ approaches about 130 cm^{-1} . For example, the ν_4 and ν_1 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

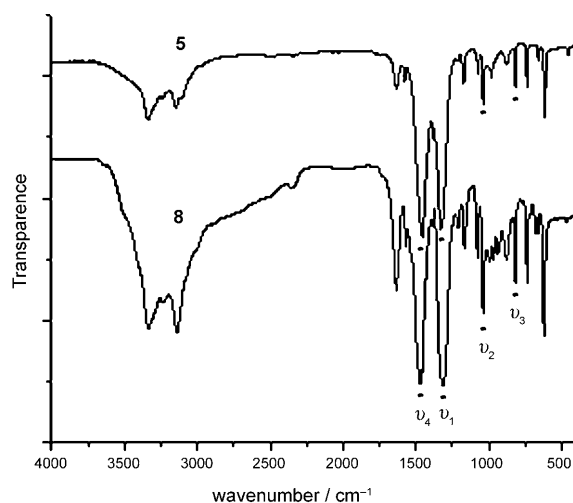


Figure 1. IR spectra of **5** and **8**. The asterisks mark the typical N–O vibration bands of the $[\text{Ln}(\text{NO}_3)_6]^{3-}$ ions.

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.^[13] In the crystal of known tris(tributylammonium) Hexanitratolanthanate $([(\text{C}_4\text{H}_9)_3\text{NH}]_3[\text{Ln}(\text{NO}_3)_6])$, the main nitrate vibrational frequencies are $\nu_4=1469$, $\nu_1=1305$, $\nu_2=1036$, and $\nu_6=819 \text{ cm}^{-1}$.^[12] These are consistent with the IR data of $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$. Thus, $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ has a structure analogous to $[(\text{C}_4\text{H}_9)_3\text{NH}]_3[\text{Ln}(\text{NO}_3)_6]$ in which all six of the nitrate ligands are coordinated to the lanthanide ion in a chelating bidentate mode.

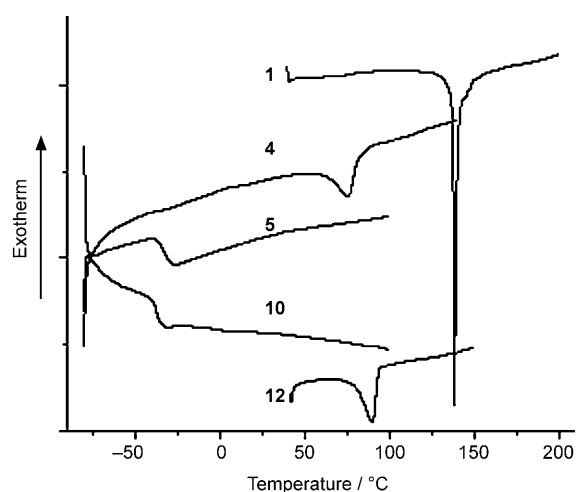
Salts $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ are thermally stable over the range of 185 to 235 °C in a nitrogen atmosphere. The cations

Table 1. Properties of $\text{Cat}^+{}_3[\text{Ln}(\text{NO}_3)_6]^{3-}$.

	T_m (T_g) ^[a] [°C]	T_d ^[b] [°C]	ρ ^[c] [g cm ⁻³]	OB _{CO} ^[d] [%]	$\Delta H_f^{\text{[e]}}$ (cation) [kJ mol ⁻¹]	$\Delta H_f^{\text{[f]}}$ (anion) [kJ mol ⁻¹]	$\Delta H_L^{\text{[g]}}$ [kJ mol ⁻¹]	$\Delta H_f^{\text{[h]}}$ [kJ mol ⁻¹]	$\Delta H_f^{\text{[i]}}$ [kJ g ⁻¹]
1	137	225	1.95	10.4	575.9	-1924.5	2327.2	-2524.0	-3.65
2	138	220	1.96	10.4	575.9	-1911.6	2329.4	-2513.3	-3.63
3	81	211	1.87	6.3	910.7	-1924.5	2233.5	-1425.9	-1.86
4	76	212	1.88	6.3	910.7	-1911.6	2235.9	-1415.4	-1.84
5	(-24)	231	1.76	-5.9	866.6	-1924.5	2162.9	-1487.6	-1.84
6	(-28)	227	1.77	-5.9	866.6	-1911.6	2165.4	-1477.2	-1.82
7	(-32)	232	1.67	-16.9	828.2	-1924.5	2101.3	-1541.2	-1.81
8	(-33)	228	1.67	-16.9	828.2	-1911.6	2100.4	-1527.4	-1.79
9	(-33)	229	1.59	-36.0	782.6	-1924.5	2019.1	-1595.8	-1.71
10	(-37)	230	1.60	-35.9	782.6	-1911.6	2021.9	-1585.7	-1.69
11	88	185	2.06	0	974.3	-1924.5	2224.4	-1226.0	-1.43
12	90	187	2.08	0	974.3	-1911.6	2229.6	-1218.3	-1.42
13	-	187	2.00	11.8	1018.0	-1924.5	2237.6	-1108.1	-1.36
14	-	188	2.02	11.8	1018.0	-1911.6	2242.9	-1100.5	-1.35
OB-EIL3 ^[j]	-	-	-	0	836	-1486	419 ^[j]	-1069	-2.66

[a] Melting point (phase-transition temperature). [b] Thermal degradation. [c] Density, gas pycnometer, 25°C. [d] CO oxygen balance: index of the deficiency or excess of oxygen in a compound relative to the amount required to convert all C to CO, all H to H₂O, and all Ln to Ln₂O₃. For a compound with molecular formula C_aH_bN_cO_dLn_e, OB_{CO} [%] = 1600[(d - a - b/2 - 3e/2)/M] (M = formula weight of salt). [e] Molar enthalpy of formation of cation. [f] Molar enthalpy of formation of anion. [g] Lattice energy. [h] Molar enthalpy of formation of salt. [i] Ref. [3] (**OB-EIL**: oxygen-balanced energetic ionic liquid). [j] Not considering the enthalpy of vaporization.

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** ($T_m = 137^\circ\text{C}$), **4** ($T_m = 76^\circ\text{C}$), and **12** ($T_m = 90^\circ\text{C}$) are given in Figure 2. However, on warming from -70°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°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.

Figure 2. DSC curves of some typical $\text{Cat}^+{}_3[\text{Ln}(\text{NO}_3)_6]^{3-}$ ionic liquids.

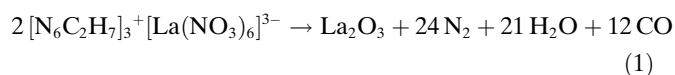
When **5** was cooled to -70°C , it became a glassy, transparent solid. After being warmed to above -25°C , it gradually became a very viscous transparent liquid. This indicates a glasslike character similar to that of conventional ionic liquids below the glass transition temperature.^[14] Furthermore, different cations clearly affect T_m and T_g . When the substituent on the 1-amino-1,2,4-triazolium cation is H (**3**) or CH₃ (**5**), the product has a very different phase-transition point; however, as expected, the difference in this property due to different alkyl substituents (CH₃, C₂H₅, and C₄H₉) is negligible. This phenomenon arises from the greater opportunity for hydrogen bonding in **3**. Although **3**, **4**, **11**, and **12** are solids, they readily form long-lived supercooled phases and solidify only after standing at room temperature for several days. The DSC and TGA spectra show no peaks or steps for water of crystallization. This also confirms that the water from the starting materials was removed under reflux with triethyl orthoformate. In addition, there are no peaks which can be assigned to the melting points of the corresponding $\text{Cat}^+\text{NO}_3^-$, that is, these ionic liquids are single-component systems.

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-diamino-4-methyl-1,2,3,4-tetrazolium cation strongly enhances the density. The cation:anion ratio of 3:1 in the $\text{Cat}^+{}_3[\text{Ln}(\text{NO}_3)_6]^{3-}$ 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%,^[3] 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

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 nitrate 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 H₂O, and all Ln to Ln₂O₃. The OB_{CO} data of these ionic liquids are shown in Table 1. The OB_{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)].



The theoretical performance of Cat⁺₃[Ln(NO₃)₆]³⁻ as propellants can be estimated from data calculated by the GAMESS^[16] and Gaussian 03 suites of programs. The heat of formation of the anions ΔH_f^o (anion) were estimated on the basis of the gas-phase experimental heats of formation of NO₃⁻, F⁻, Cl⁻, LaF₄⁻, and LaCl₄⁻. 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–Jaisén–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 shell^[19] and a d-type polarization function.^[20] The heats of formation of the cations ΔH_f^o(cation) were determined by using the method of isodesmic reactions (Scheme 2).^[21] Geometric opti-

mization 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 ΔH_L could be predicted by the formula suggested by Jenkins et al. [Eqs. (3) and (4)].^[23]

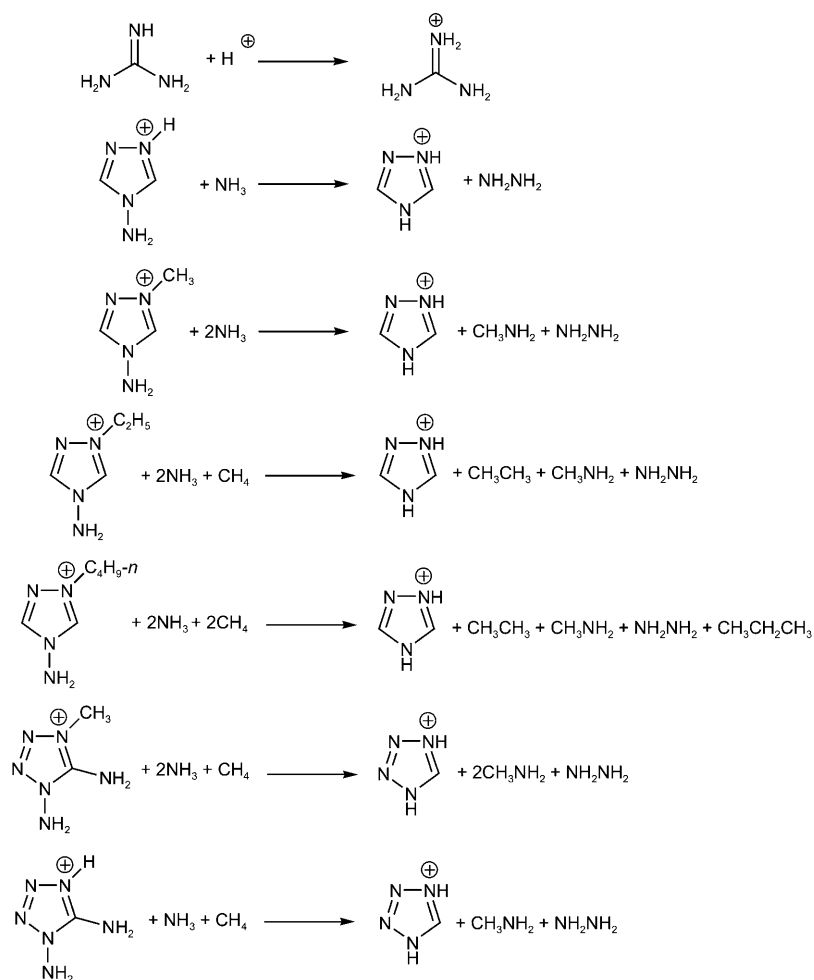
$$\Delta H_f^o(\text{ionic salts, 298 K}) = \sum \Delta H_f^o(\text{cation, 298 K}) + \sum \Delta H_f^o(\text{anion, 298 K}) - \Delta H_L \quad (2)$$

$$\Delta H_L = U_{\text{POT}} + [p(nM/2-2) + q(n_x/2-2)]RT \quad (3)$$

$$U_{\text{POT}} [\text{kJ mol}^{-1}] = 2342.6I(\rho_m/M_m)^{1/3} + 55.2I \quad (4)$$

The calculated heats of formation for Cat⁺₃[Ln(NO₃)₆]³⁻ are summarized in Table 1. Compound **14** has the highest value, and the data show that the performance of Cat⁺₃[Ln(NO₃)₆]³⁻ may be better than some important energetic materials, for example, hydrazine.^[3]

The impact sensitivities of **11** and **12** were measured by the BAM method.^[24] The impact sensitivities of **11** and **12** of



Scheme 2. Isodesmic reactions and protonation reactions for calculating heats of formation of cations.

27 J (3/6 and 2/6 explosions) show that they are impact-sensitive energetic materials.^[25]

Conclusion

Lanthanide nitrate complex anions are suitable for preparation of energetic ionic liquids. Ionic liquids $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ 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 $\text{Cat}^+[\text{Ln}(\text{NO}_3)_6]^{3-}$ 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 Biorad model 3000 FTS spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 and 75 MHz, respectively, by using CD_3CN , D_2O , or $[\text{D}_6]\text{DMSO}$ as locking solvent. Chemical shifts are reported in parts per million relative to TMS. The densities of the solid salts were measured at 25 °C on a Micromeritics Accucyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed on a calorimeter equipped with an auto-cool accessory and calibrated against indium. The following procedure was used in experiments for each sample: cooling from 40 °C to -80 °C and heating to 400 °C at 10 °C min⁻¹. Thermogravimetric analysis (TGA) was carried out by heating samples at 10 °C min⁻¹ from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate 70 mL min⁻¹). Elemental analyses (H, C, N) were performed on a CE-440 Elemental Analyzer. The metal content was determined by titration with ethylenediaminetetraacetic acid. The water content was determined by coulometric Karl-Fischer titration on a Mettler Toledo DL39 Coulometer with a Hydranal Coulomat reagent. Computations were performed by using the GAMESS^[16] and Gaussian 03^[26] suites of programs.

Triguanidinium hexanitratolanthanate (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 remove coordinated water. After being concentrated in vacuo, the resulting crude solid was washed with acetonitrile/diethyl ether. A quantitative yield of **1** as a white solid was obtained after drying under vacuum (692 mg). IR (KBr): $\tilde{\nu}$ = 3493, 3417, 3383, 3214, 1695, 1660, 1581, 1472, 1420, 1355, 1323, 1294, 1034, 816, 743, 525 cm⁻¹; ^{13}C NMR (D_2O): δ = 167.1 ppm; elemental analysis (%) calcd for $\text{C}_3\text{H}_{18}\text{LaN}_{15}\text{O}_{18}$ (691.17): C 5.21, H 2.62, N 30.40, La 20.10; found: C 5.80, H 2.86, N 30.01, La 20.11.

Triguanidinium hexanitratocerate (2): The same procedure was used as for **1**. Guanidinium nitrate (3 mmol, 366 mg) and cerium nitrate hexahydrate (1 mmol, 434 mg) were used to obtain a quantitative yield of **2** as a white solid (692 mg). IR (KBr): $\tilde{\nu}$ = 3493, 3416, 3380, 3214, 1693, 1660, 1580, 1472, 1418, 1358, 1325, 1296, 1035, 815, 743, 522 cm⁻¹; ^{13}C NMR (D_2O): δ = 166.9 ppm; elemental analysis (%) calcd for $\text{C}_3\text{H}_{18}\text{CeN}_{15}\text{O}_{18}$

(692.38): C 5.20, H 2.62, N 30.34, Ce 20.24; found: C 5.39, H 3.01, N 30.24, Ce, 20.13.

Tris(4-amino-1H-1,2,4-triazolium) hexanitratolanthanate (3): The same procedure was used as for **1**. 4-Amino-1H-1,2,4-triazolium nitrate (3 mmol, 441 mg) and lanthanum nitrate hexahydrate (1 mmol, 433 mg) were used to obtain a quantitative yield of **3** as a colorless, viscous, transparent liquid (760 mg) which became a light yellow solid after standing at 25 °C for one week. IR (KBr): $\tilde{\nu}$ = 3397, 3144, 1635, 1458, 1341, 1075, 1038, 939, 879, 825, 738, 617 cm⁻¹; ^1H NMR (CD_3CN): δ = 8.97 (s, 2H), 3.84 ppm (br, 2H); ^{13}C NMR (CD_3CN): δ = 145.1 ppm; elemental analysis (%) calcd for $\text{C}_6\text{H}_{15}\text{LaN}_{18}\text{O}_{18}$ (766.20): C 9.41, H 1.97, N 32.91, La 18.13; found: C 9.53, H 2.06, N 33.66, La 17.91.

Tris(4-amino-1H-1,2,4-triazolium) hexanitratocerate (4): The same procedure was used as for **1**. 4-Amino-1H-1,2,4-triazolium nitrate (3 mmol, 441 mg) and cerium nitrate hexahydrate (1 mmol, 434 mg) were used to obtain a quantitative yield of **4** as a colorless, viscous, transparent liquid (764 mg) which became a light yellow solid after standing at 25 °C for one week. IR (KBr): $\tilde{\nu}$ = 3200, 3136, 1636, 1456, 1323, 1075, 1039, 934, 878, 816, 738, 621 cm⁻¹; ^1H NMR (CD_3CN): δ = 8.98 (s, 2H), 3.20 ppm (br, 2H); ^{13}C NMR (CD_3CN): δ = 145.2 ppm; elemental analysis (%) calcd for $\text{C}_6\text{H}_{15}\text{CeN}_{18}\text{O}_{18}$ (767.41): C 9.39, H 1.97, N 32.85, Ce 18.26; found: C 9.57, H 1.96, N 32.67; Ce 18.13.

Tris(4-amino-1-methyl-1,2,4-triazolium) hexanitratolanthanate (5): The basic technique used follows closely that employed in preparing tetra-butylammonium hexanitratolanthanide complexes.^[10] 4-Amino-1-methyl-1,2,4-triazolium iodide was obtained by using a slightly modified literature procedure.^[27] A mixture of 4-amino-1,2,4-triazole (2 mmol, 168 mg) and iodomethane (2 mmol, 284 mg) in acetonitrile (20 mL) was stirred at room temperature for 5 days. 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 solvent was removed from the lower layer in vacuo to obtain a white solid (442 mg, 98%). IR (KBr): $\tilde{\nu}$ = 3484, 3223, 3119, 1609, 1567, 1443, 1405, 1170, 1067, 973, 867, 730, 610 cm⁻¹; ^1H NMR (CD_3CN): δ = 9.54 (s, 1H), 8.66 (s, 1H), 6.15 (s, 2H), 4.06 ppm (s, 3H); ^{13}C NMR (CD_3CN): δ = 145.9, 143.9, 40.1 ppm. 4-Amino-1-methyl-1,2,4-triazolium iodide (0.3 mmol, 68 mg), AgNO_3 (0.3 mmol, 51 mg), and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were held at reflux in acetonitrile for 12 h with complete exclusion of light. An excess of triethyl orthoformate was added during reflux to remove coordinated water. After the silver iodide was filtered off, the filtrate was concentrated. The resulting crude liquid was purified by dissolving in methanol (ca. 10 mL), filtering, and adding the filtrate to diethyl ether (3–5 times the volume of filtrate). The mixture was shaken, allowed to separate, and the top layer was decanted off. This process was repeated as often necessary to ensure removal of traces of silver iodide. Light yellow, viscous liquid **5** was obtained after drying under vacuum. Yield: 36 mg (45%). IR (KBr): $\tilde{\nu}$ = 3332, 3241, 3148, 1632, 1574, 1454, 1325, 1172, 1072, 1038, 981, 877, 819, 735, 615 cm⁻¹; ^1H NMR (CD_3CN): δ = 9.43 (s, 1H), 8.58 (s, 1H), 6.13 (br, 2H), 4.07 ppm (s, 3H); ^{13}C NMR (CD_3CN): δ = 145.9, 144.0, 40.0 ppm; elemental analysis (%) calcd for $\text{C}_9\text{H}_{21}\text{LaN}_{18}\text{O}_{18}$ (808.28): C 13.37, H 2.62, N 31.19, La 17.19; found: C 13.42, H 2.63, N 31.27, La 17.19.

Tris(4-amino-1-methyl-1,2,4-triazolium) hexanitratocerate (6): The same procedure was used as for **5**. 4-Amino-1-methyl-1,2,4-triazolium iodide (0.3 mmol, 68 mg), AgNO_3 (0.3 mmol, 51 mg), and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain **6** as a light yellow, viscous liquid. Yield: 39 mg (48%). IR (KBr): $\tilde{\nu}$ = 3338, 3238, 3148, 1634, 1574, 1456, 1323, 1172, 1073, 1038, 981, 878, 818, 736, 616 cm⁻¹; ^1H NMR (CD_3CN): δ = 9.62 (s, 1H), 8.71 (s, 1H), 6.30 (br, 2H), 4.20 ppm (s, 3H); ^{13}C NMR (CD_3CN): δ = 146.0, 144.2, 40.2 ppm; elemental analysis (%) calcd for $\text{C}_9\text{H}_{21}\text{CeN}_{18}\text{O}_{18}$ (809.49): C 13.35, H 2.61, N 31.05, Ce 17.31; found: C 13.68, H 2.56, N 30.90, Ce 17.25.

Tris(4-amino-1-ethyl-1,2,4-triazolium) hexanitratolanthanate (7): The same procedure was used as for **5**. 4-Amino-1-ethyl-1,2,4-triazolium iodide was prepared by the method used for 4-amino-1-methyl-1,2,4-triazolium iodide. A mixture of 4-amino-1,2,4-triazole (2 mmol, 168 mg) and iodoethane (2 mmol, 312 mg) in acetonitrile (20 mL) was heated at 50 °C 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, any residual solvent was removed from the lower layer in vacuo to obtain a yellow liquid (462 mg, 96%). IR (KBr): $\tilde{\nu}$ = 3455, 3233, 3121, 3051, 1621, 1560, 1449, 1406, 1165, 1074, 989, 964, 872, 722, 619 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 9.89 (s, 1H), 8.81 (s, 1H), 6.39 (s, 2H), 4.43 (t, 2H, J = 7.2 Hz), 1.53 ppm (t, 3H, J = 7.2 Hz); $^{13}\text{C NMR}$ (CD_3CN): δ = 146.1, 143.3, 49.2, 14.2 ppm. 4-Amino-1-ethyl-1,2,4-triazolium iodide (0.3 mmol, 72 mg), AgNO_3 (0.3 mmol, 51 mg), and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain **7** as colorless, viscous liquid. Yield: 47 mg (55%). IR (KBr): $\tilde{\nu}$ = 3332, 3233, 3135, 1631, 1566, 1459, 1323, 1198, 1167, 1075, 1038, 990, 872, 819, 735, 621 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 9.46 (s, 1H), 8.61 (s, 1H), 4.40 (t, 2H, J = 7.2 Hz), 3.68 (br, 2H), 1.53 ppm (t, 3H, J = 7.2 Hz); $^{13}\text{C NMR}$ (CD_3CN): δ = 145.9, 143.2, 49.1, 13.9 ppm; elemental analysis (%) calcd for $\text{C}_{12}\text{H}_{27}\text{LaN}_8\text{O}_{18}$ (850.36): C 16.95, H 3.20, N 29.65, La 16.33; found: C 17.01, H 3.50, N 29.68, La 16.29.

Tris(4-amino-1-ethyl-1,2,4-triazolium) hexanitratocerate (8): The same procedure was used as for **7**. 4-Amino-1-ethyl-1,2,4-triazolium iodide (0.3 mmol, 72 mg), AgNO_3 (0.3 mmol, 51 mg), and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were reacted to obtain **8** as a colorless, viscous liquid. Yield: 45 mg (53%). IR (KBr): $\tilde{\nu}$ = 3335, 3239, 3139, 1634, 1567, 1470, 1313, 1209, 1165, 1076, 1038, 992, 878, 819, 737, 621 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 9.72 (s, 1H), 8.75 (s, 1H), 4.52 (t, 2H, J = 7.2 Hz), 2.73 (br, 2H), 1.61 ppm (t, 3H, J = 7.2 Hz); $^{13}\text{C NMR}$ (CD_3CN): δ = 145.3, 143.5, 49.3, 14.0 ppm; elemental analysis (%) calcd for $\text{C}_{12}\text{H}_{27}\text{CeN}_8\text{O}_{18}$ (851.57): C 16.93, H 3.20, N 29.61, Ce 16.45; found: C 16.94, H 3.32, N 29.62, Ce 16.32.

Tris(4-amino-1-butyl-1,2,4-triazolium) hexanitratolanthanate (9): The same procedure was used as for **5**. 4-Amino-1-butyl-1,2,4-triazolium iodide was prepared according to a similar method as for 4-amino-1-methyl-1,2,4-triazolium iodide. A mixture of 4-amino-1,2,4-triazole (2 mmol, 168 mg) and iodobutane (2 mmol, 368 mg) in acetonitrile (20 mL) was stirred at 70°C for 12 h. The solution was concentrated and added to excess ethyl acetate (3–5 times the volume of solution). After decanting the solvent, any residual solvent was removed from the lower layer in vacuo to obtain a yellow liquid (516 mg, 96%). IR (KBr): $\tilde{\nu}$ = 3460, 3246, 3120, 2961, 2874, 1622, 1561, 1524, 1462, 1407, 1381, 1163, 1073, 988, 864, 755, 617 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 9.87 (s, 1H), 8.77 (s, 1H), 6.40 (s, 2H), 4.39 (t, 2H, J = 7.2 Hz), 1.86–1.97 (m, 2H), 1.34–1.42 (m, 2H), 0.95 ppm (t, 3H, J = 7.2 Hz); $^{13}\text{C NMR}$ (CD_3CN): δ = 146.1, 143.6, 53.4, 31.1, 19.8, 13.6 ppm. 4-Amino-1-butyl-1,2,4-triazolium iodide (0.3 mmol, 80 mg), AgNO_3 (0.3 mmol, 51 mg), and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain **9** as colorless viscous liquid. Yield: 49 mg (52%). IR (KBr): $\tilde{\nu}$ = 3333, 3220, 3131, 2965, 2877, 1643, 1562, 1450, 1322, 1142, 1073, 1034, 993, 871, 820, 734, 631 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 9.46 (s, 1H), 8.60 (s, 1H), 6.11 (br, 2H), 4.37 (t, 2H, J = 7.2 Hz), 1.86–1.92 (m, 2H), 1.35–1.42 (m, 2H), 0.97 ppm (t, 3H, J = 7.2 Hz); $^{13}\text{C NMR}$ (CD_3CN): δ = 146.0, 143.5, 53.4, 31.1, 19.8, 13.5 ppm; elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{39}\text{LaN}_8\text{O}_{18}$ (934.52): C 23.13, H 4.21, N 26.98, La 14.86; found: C 23.04, H 3.97, N 27.13, La 14.71.

Tris(4-amino-1-butyl-1,2,4-triazolium) hexanitratocerate (10): The same procedure was used as for **9**. 4-Amino-1-butyl-1,2,4-triazolium iodide (0.3 mmol, 80 mg), AgNO_3 (0.3 mmol, 51 mg) and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain **10** as a colorless, viscous liquid. Yield: 52 mg (56%). IR (KBr): $\tilde{\nu}$ = 3332, 3231, 3137, 2964, 2876, 1635, 1565, 1450, 1321, 1165, 1076, 1037, 990, 877, 819, 735, 618 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 9.73 (s, 1H), 8.73 (s, 1H), 6.30 (br, 2H), 4.50 (t, 2H, J = 7.2 Hz), 1.96–2.05 (m, 2H), 1.38–1.50 (m, 2H), 1.00 ppm (t, 3H, J = 7.2 Hz); $^{13}\text{C NMR}$ (CD_3CN): δ = 146.1, 143.7, 53.5, 31.2, 19.8, 13.5 ppm; elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{39}\text{CeN}_8\text{O}_{18}$ (935.73): C 23.10, H 4.20, N 26.94, Ce 14.97; found: C 23.08, H 4.34, N 27.23, Ce 14.59.

Tris(1,5-diamino-4-methyl-1,2,3,4-tetrazolium) hexanitratolanthanate (11): The same procedure was used as for **5**. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide was obtained by a minor modification of the literature procedure.^[28] A mixture of 1,5-diamino-1,2,3,4-tetrazole (2 mmol, 0.200 mg) and an excess of iodomethane (10 mmol, 1.42 g) in

acetonitrile (60 mL) was heated to reflux for 18 h. The solution was concentrated and added to an excess of diethyl ether (5 times the volume of solution). The crude product was isolated by filtration. After washing with diethyl ether, any residual solvent was removed in vacuo to obtain a white solid (430 mg, 89%). IR (KBr): $\tilde{\nu}$ = 3240, 3090, 1700, 1609, 1571, 1390, 1115, 1025, 785, 605, 522 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 7.65 (s), 6.12 (s, 2H), 4.00 ppm (s, 3H); $^{13}\text{C NMR}$: δ = 152.6, 36.7 ppm. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (0.3 mmol, 73 mg), AgNO_3 (0.3 mmol, 51 mg), and lanthanum nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain **11** as a colorless, viscous liquid, which became a white solid after standing for 3 d. Yield: 41 mg (48%). IR (KBr): $\tilde{\nu}$ = 3335, 3233, 3055, 1700, 1616, 1451, 1352, 1118, 1037, 912, 818, 735, 581 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 7.61 (s), 6.02 (s, 2H), 3.89 ppm (s, 3H); $^{13}\text{C NMR}$ (CD_3CN): δ = 149.0, 35.6 ppm; elemental analysis (%) calcd for $\text{C}_6\text{H}_{21}\text{LaN}_{24}\text{O}_{18}$ (856.28): C 8.42, H 2.47, N 39.26, La 16.22; found: C 8.43, H 2.52, N 38.38, La 16.11.

Tris(1,5-diamino-4-methyl-1,2,3,4-tetrazolium) hexanitratocerate (12): The same procedure was used as for **11**. 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium iodide (0.3 mmol, 73 mg), AgNO_3 (0.3 mmol, 51 mg), and cerium nitrate hexahydrate (0.1 mmol, 43 mg) were used to obtain **12** as a colorless, viscous liquid which became a white solid after standing at 25°C for 1 day. Yield: 43 mg (50%). IR (KBr): $\tilde{\nu}$ = 3339, 3260, 3050, 1700, 1617, 1459, 1350, 1118, 1038, 909, 818, 736, 576 cm^{-1} ; $^1\text{H NMR}$ (CD_3CN): δ = 7.61 (s), 6.12 (s, 2H), 3.96 ppm (s, 3H); $^{13}\text{C NMR}$ (CD_3CN): δ = 149.1, 35.7 ppm; elemental analysis (%) calcd for $\text{C}_6\text{H}_{21}\text{CeN}_{24}\text{O}_{18}$ (857.49): C 8.40, H 2.47, N 39.20, Ce 16.34; found: C 8.36, H 2.49, N 38.72, Ce 16.32.

Tris(1,5-diamino-4H-1,2,3,4-tetrazolium) hexanitratolanthanate (13): The same procedure was used as for **1**. 1,5-Diamino-4H-1,2,3,4-tetrazolium nitrate was obtained on the basis of the literature procedure.^[28] 1,5-Diamino-4H-1,2,3,4-tetrazolium nitrate (0.15 mmol, 27 mg) and lanthanum nitrate hexahydrate (0.05 mmol, 22 mg) were used to obtain **13** as a white solid. Yield: 47 mg (96%). IR (KBr): $\tilde{\nu}$ = 3324, 3273, 3156, 1721, 1658, 1467, 1330, 1110, 1038, 1004, 932, 816, 742, 689, 627 cm^{-1} ; $^1\text{H NMR}$ ($[\text{D}_6]\text{DMSO}$): δ = 4.83 ppm (s); $^{13}\text{C NMR}$ ($[\text{D}_6]\text{DMSO}$): δ = 155.2 ppm; elemental analysis (%) calcd for $\text{C}_6\text{H}_{21}\text{LaN}_{24}\text{O}_{18}$ (856.28): C 4.43, H 1.86, N 41.29, La 17.06; found: C 4.77, H 1.85, N 41.09, La 16.91.

Tris(1,5-diamino-4H-1,2,3,4-tetrazolium) hexanitratocerate (14): The same procedure was used as for **13**. 1,5-Diamino-4H-1,2,3,4-tetrazolium nitrate (0.15 mmol, 27 mg) and lanthanum nitrate hexahydrate (0.05 mmol, 22 mg) were used to obtain **14** as a white solid. Yield: 48 mg (98%). IR (KBr): $\tilde{\nu}$ = 3343, 3266, 1717, 1629, 1466, 1329, 1130, 1037, 998, 925, 817, 740, 690, 623 cm^{-1} ; $^1\text{H NMR}$ ($[\text{D}_6]\text{DMSO}$): δ = 4.95 ppm (s); $^{13}\text{C NMR}$ ($[\text{D}_6]\text{DMSO}$): δ = 155.4 ppm; elemental analysis (%) calcd for $\text{C}_6\text{H}_{21}\text{CeN}_{24}\text{O}_{18}$ (857.49): C 4.42, H 1.85, N 41.23, Ce 17.18; found: C 4.67, H 1.84, N 41.12, Ce 17.12.

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