

Hypergolic *N,N*-Dimethylhydrazinium Ionic Liquids

Yanqiang Zhang,^[a] Haixiang Gao,^[b] Yong Guo,^[a] Young-Hyuk Joo,^[a] and Jean'ne M. Shreeve^{*[a]}

Abstract: *N,N*-Dimethylhydrazinium dicyanamide and nitrocyanamide ionic liquids (ILs) were prepared by quaternization of *N,N*-dimethylhydrazine with alkyl halides followed by metathesis reactions with silver dicyanamide or silver nitrocyanamide. The key physicochemical properties, such as melting point and decomposition temperatures,

density, viscosity, heat of formation, detonation pressure and velocity, and specific impulse were measured/calculated. The impact of anions and alkyl-

Keywords: bipropellants • density functional calculations • energetic salts • hypergolicity • ionic liquids

substituted cations on these properties is demonstrated. Droplet tests with white-fuming nitric acid (WFNA) as an oxidizer were utilized to show that the 14 new *N,N*-dimethylhydrazinium salts are hypergolic with ignition delay (ID) times ranging from 22 to 1642 ms, thereby suggesting that some may have potential as bipropellants.

Introduction

Combustion of a fuel–oxidizer combination is usually initiated by an igniter such as an electric spark, a hot wire, or a hot surface. There are, however, certain chemicals (fuels) that can ignite spontaneously upon coming into contact with oxidizing substances.^[1–4] These self-ignition systems, also known as ‘hypergolic’ systems, are of special importance in rocket propellants, since such fuel–oxidizer combinations simplify engine design and provide a convenient way of achieving repeated on-and-off capability at no extra cost. The fuel and oxidizer are stored separately, to be brought together subsequently when firing is desired, thus enabling less hazardous systems.

The fuel–oxidizer hypergolic systems have been widely used in biliquid propellants, in which the fuels of choice are hydrazine, monomethylhydrazine (MMH), and *N,N*-dimethylhydrazine (UDMH) with oxidizing agents such as white-fuming nitric acid (WFNA), red-fuming nitric acid (RFNA), or nitrogen tetroxide (N₂O₄).^[5–11] These hypergolic combina-

tions require that a successful fuel have a high energy density per unit mass and a high specific impulse, and that there is a short ignition delay time. Unfortunately, hydrazine and its derivatives, as a class of acutely toxic and carcinogenic substances, have high vapor pressures so that costly safety precautions and handling procedures are required. Therefore, there is an urgent need for alternative nontoxic liquid hypergolic fuels that have low vapor pressures, and high energy densities by which the reaction exhibits concomitant short ignition delays. Considering that energetic ionic liquids have many unique properties, for example, extremely low vapor pressure, high thermal and chemical stability, and tunable physicochemical characteristics, it is likely that they could have potential as liquid hypergolic fuels.^[12–23]

The first ionic liquids reported to be hypergolic were dicyanamide salts with substituted imidazolium, methylpyridinium, and methylpyridinium cations.^[24] It was suggested that the key to the hypergolicity of these ionic liquids was the dicyanamide anion. Through Fourier transform infrared (FTIR) observations, biuret reaction tests, and initial ab initio calculations, a mechanism was proposed for the formation of N₂O, CO₂, and HNCO from the dicyanamide reaction during preignition.^[25] Based on the calculated heats of formation and experiments, the Idaho group prepared a series of 2,2-dimethyltriazanium salts with a variety of anions (including chloride, nitrocyanamide, dicyanamide, dinitrocyanmethanide, nitrodicyanmethanide, tricyanmethanide, and nitrate) and found that with a common cation in addition to the dicyanamide ionic liquid, the nitrocyanamide, nitrate, and chloride salts were also hypergolic.^[26] Ap-

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

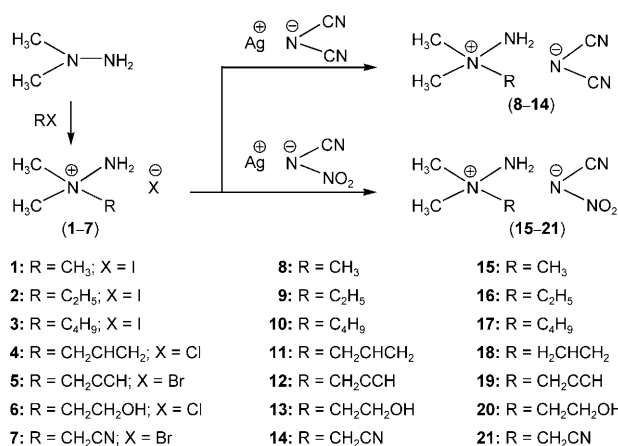
[b] Dr. H. Gao
Department of Applied Chemistry, China Agricultural University
Beijing 100193 (China)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200902725>.

parently not only anions but cations also play an important role in modifying the hypergolic properties of ionic liquids. To examine the phenomenon of hypergolicity, a series of *N,N*-dimethylhydrazinium dicyanamide and nitrocyanamide ionic liquids were prepared and their physicochemical and hypergolic properties determined and compared.

Results and Discussion

The *N,N*-dimethylhydrazinium salts were obtained by quaternizing *N,N*-dimethylhydrazine with alkyl halides followed by metathesis reactions with silver dicyanamide or silver nitrocyanamide (Scheme 1). These salts are hydrophilic and



Scheme 1. Synthesis of *N,N*-dimethylhydrazinium ionic liquids.

soluble in water, methanol, ethanol, acetone, and acetonitrile, yet insoluble in less polar solvents, such as hexane, diethyl ether, and ethyl acetate. The resulting *N,N*-dimethylhydrazinium salts were characterized by ¹H and ¹³C NMR spectroscopy, IR spectroscopy, and elemental analysis. The

characterization data support the expected structures and compositions. The physicochemical properties of the *N,N*-dimethylhydrazinium salts such as phase-transition temperature (*T_m* or *T_g*), thermal decomposition temperature (*T_d*), density (ρ), viscosity (η), ignition delay (ID) time, heat of formation (ΔH_f), detonation pressure (*P*), detonation velocity (v_D), and specific impulse (*I_{sp}*) were measured or calculated (Table 1).

Physicochemical properties of *N,N*-dimethylhydrazinium ionic liquids

Phase-transition temperatures (*T_m* or *T_g*) and thermal stabilities of the *N,N*-dimethylhydrazinium salts were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). As shown in Table 1, the *N,N*-dimethylhydrazinium salts are liquids at room temperature except for **8**, **9**, **15**, and **16**, which exhibit *T_m* at lower than 100 °C. These salts may therefore be classified as room-temperature ionic liquids. Although **9** is a solid at 25 °C, it does form a long-lived supercooled phase and solidifies only after standing at room temperature for many days. Surprisingly, there are no detectable *T_m* or *T_g* transitions for compounds **11–14** and **18–21** over a temperature range between –60 and 25 °C. With the increasing length of the alkyl side chain of the cation from methyl (**8**) to butyl (**10**), the *T_m* decreases from 60.5 to 20.4 °C, and for (**15**) to (**17**) from 35.2 to 9.0 °C, respectively. The decomposition temperatures of the *N,N*-dimethylhydrazinium salts vary from 296.9 (**16**) to 144.8 °C (**14**), with the nitrocyanamide salts exhibiting greater thermal stability than their dicyanamide analogues.

Density and viscosity of the *N,N*-dimethylhydrazinium ionic liquids vary from 1.01 to 1.28 g cm^{–3} and 67.5 to 1310 mPa, respectively. The nitrocyanamide salts have a higher density and viscosity than the corresponding dicyanamides due to the presence of the nitro group with its greater proclivity to form hydrogen bonds. As a function of the alkyl substituent, density of the *N,N*-dimethylhydrazinium salts increases according to CH₂CN > CH₂CH₂OH >

Table 1. Properties of *N,N*-dimethylhydrazinium ILs.

Salts	<i>T_m</i> (<i>T_g</i>) ^[a] [°C]	<i>T_d</i> ^[b] [°C]	ρ ^[c] [g cm ^{–3}]	η ^[d] [mPas]	ID ^[e] [ms]	ΔH_f ^[f] [kJ mol ^{–1}]	ΔH_f ^[f] (cation) [kJ mol ^{–1}]	ΔH_f ^[f] (anion) [kJ mol ^{–1}]	ΔH_f ^[g] (salt) [kJ g ^{–1}]	<i>P</i> ^[h] [GPa]	v_D ^[i] [ms ^{–1}]	<i>I_{sp}</i> ^[j] [s]
8	60.5	253.5	1.10	–	58	501.6	646.5	113.4	1.83	10.82	6317	189.4
9	30.9	267.1	1.06	67.5	22	484.2	613.9	113.4	1.57	9.79	6131	184.6
10	20.4	263.3	1.01	113.9	46	458.8	578.3	113.4	1.27	8.58	5932	180.0
11	–	199.2	1.05	78.6	24	474.4	814.6	113.4	2.71	9.09	6057	204.0
12	–	174.3	1.13	228.6	30	484.6	909.4	113.4	3.26	10.08	6191	210.0
13	–	236.0	1.15	161.8	40	482.9	478.3	113.4	0.64	10.88	6281	185.8
14	–	144.8	1.17	1057.0	1286	488.7	844.9	113.4	2.83	11.03	6318	202.1
15	35.2	292.4	1.24	–	126	499.6	646.5	–27.1	0.74	14.71	7029	213.4
16	25.4	296.9	1.17	–	198	481.3	613.9	–27.1	0.60	12.56	6681	208.0
17	9.0	285.5	1.11	119.5	228	457.2	578.3	–27.1	0.46	10.89	6408	201.2
18	–	208.2	1.16	84.9	130	472.9	814.6	–27.1	1.68	12.19	6596	221.5
19	–	189.3	1.21	269.8	134	479.5	909.4	–27.1	2.18	12.78	6611	227.2
20	–	269.1	1.26	185.9	247	480.3	478.3	–27.1	–0.15	14.09	6880	206.2
21	–	193.5	1.28	1310.0	1642	485.4	844.9	–27.1	1.79	14.52	6899	220.4

[a] Phase-transition temperature. [b] Decomposition temperature. [c] Density (25 °C). [d] Viscosity (25 °C). [e] Ignition delay time (WFNA). [f] Heat of formation (cation or anion). [g] Heat of formation (salt). [h] Detonation pressure (CHEETAH 5.0). [i] Detonation velocity (CHEETAH 5.0). [j] Specific impulse (CHEETAH 5.0, for monopropellants).

$\text{CH}_3\text{CCH} > \text{CH}_3 > \text{CH}_2\text{CHCH}_2 > \text{C}_2\text{H}_5 > \text{C}_4\text{H}_9$; viscosity:
 $\text{CH}_2\text{CN} > \text{CH}_3\text{CCH} > \text{CH}_2\text{CH}_2\text{OH} > \text{C}_4\text{H}_9 > \text{CH}_2\text{CHCH}_2$.

Hypergolic test: Because it is flexible, accurate, simply constructed, and very useful for screening materials, the droplet test was selected to assess the potential hypergolic characteristics of the *N,N*-dimethylhydrazinium salts and to measure their actual ignition delay (ID) times.^[2,27] Using a pipette, the ionic liquid sample (10–50 μL) was dropped into a 25 mL beaker containing an excess amount (1.5 mL) of WFNA. The ignition process was recorded at 500 frames per second with a high-speed camera. Then the ignition delay time, the time from fuel contact with the liquid surface of the oxidizer until a visible flame is recorded, could be measured. Figure 1 depicts a sequence of pictures that show a falling droplet of compound **10** into a pool of liquid WFNA, thereby demonstrating that the hypergolic compounds can undergo self-sustained combustion after ignition.

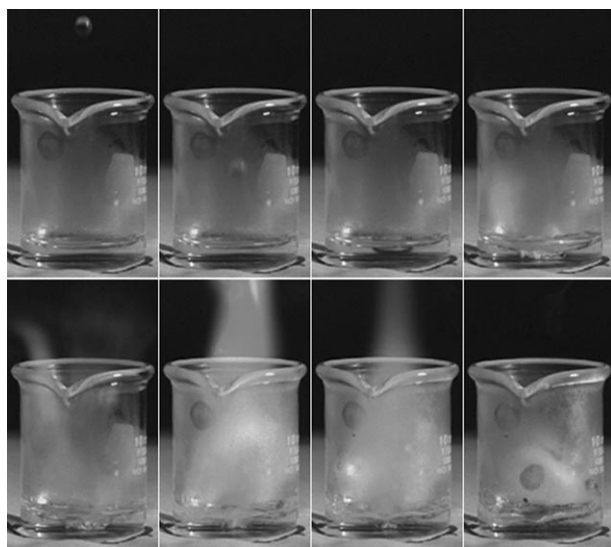


Figure 1. The ID test process shown with a series of high-speed camera photos (a droplet of **10** falling into liquid WFNA).

The results show that all the *N,N*-dimethylhydrazinium salts are hypergolic with WFNA. Among these, **9**, **11**, and **12** are good hypergolic materials with relatively short ignition delay times at 22, 24, and 30 ms, respectively (Table 1). These results appear to support use of salts with lower carbon content and that, not surprisingly, the liquid samples ignite more readily than the solid ones. The nitrocyanamide salts have a longer ID than the corresponding dicyanamide salts; for example, the shortest ID of a nitrocyanamide salt (**15**) is 126 ms.

Theoretical study: Calculations were performed with the Gaussian 03 (Revision D.01) suite of programs.^[28] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were car-

ried out using the B3LYP functional with 6-31+G** basis set,^[29] and single energy points were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Based on a Born–Haber energy cycle (Scheme 2), the heat of formation of a salt can be simplified by the formula given in Equation (1):

$$\Delta H_f^\circ(\text{salt}, 298\text{K}) = \Delta H_f^\circ(\text{cation}, 298\text{K}) + \Delta H_f^\circ(\text{anion}, 298\text{K}) - \Delta H_L \quad (1)$$

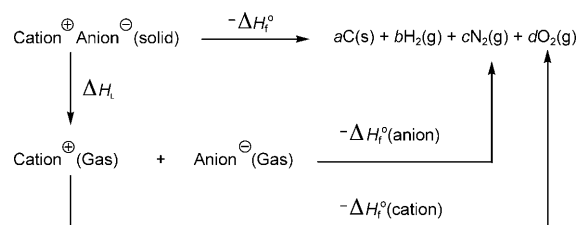
in which ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]:^[30]

$$\Delta H_L = U_{\text{pot}} + \{p[(n_M/2) - 2] + q[(n_X/2) - 2]\}RT \quad (2)$$

in which n_M and n_X depend on the nature of the ions M_p^+ and X_q^- , respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy (U_{pot}) has the form [Eq. (3)]:

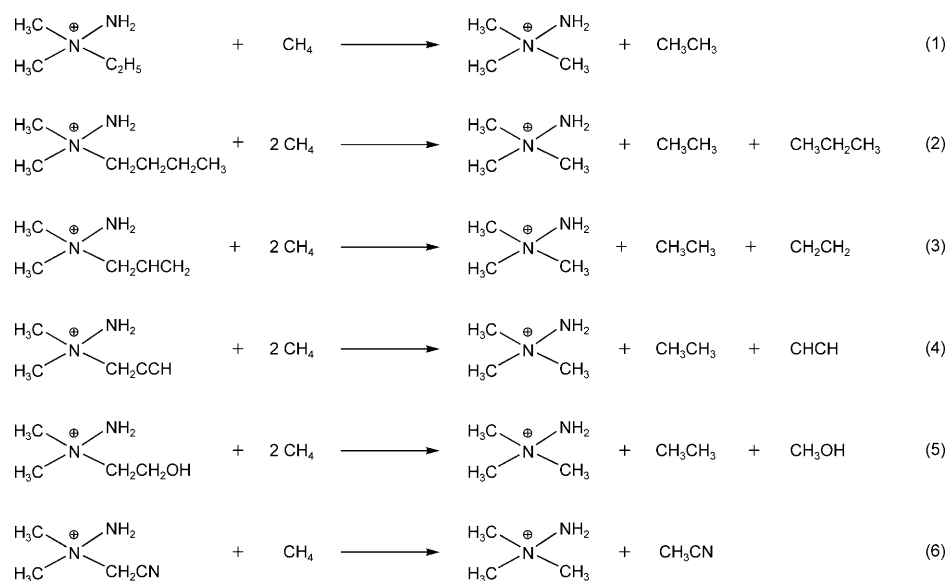
$$U_{\text{pot}}[\text{kJmol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

in which ρ_m [g cm^{-3}] is the density, M_m is the chemical formula mass of the ionic material, and values for γ and the coefficients γ [$\text{kJmol}^{-1} \text{cm}$] and δ [kJ mol^{-1}] are taken from the literature.



Scheme 2. Born–Haber cycle for the formation of energetic salts.

The heats of formation of the cations were computed by using the method of isodesmic reactions. The isodesmic reactions for *N,N*-dimethylhydrazinium cations are shown in Scheme 3. The heats of formation of the anions are literature values.^[26] The enthalpy of reaction ($\Delta_r H_{298}^\circ$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors. Thus, the heats of formation of the species being investigated can be readily extracted. With values of the heats of formation and densities, the detonation pressure (P) and velocity (ν_D), and specific impulse (I_{sp}) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory using CHEETAH 5.0.^[31] The values of the heats of formation and detonation pressures

Scheme 3. Isodesmic reactions for calculating the heat of formation of *N,N*-dimethylhydrazinium cations.

and velocities and specific impulses, which are summarized in Table 1, show that with the exception of heats of formation, the nitrocyanoamide salts have higher values for these properties than the corresponding dicyanamide salts. For the dicyanamide salts, the highest heat of formation, detonation pressure, detonation velocity, and specific impulse are 3.26 kJ g^{-1} (**12**), 11.03 GPa (**14**), 6318 ms^{-1} (**14**), and 210.0 s (**12**), respectively. The analogous values for the nitrocyanoamide salts are 2.18 kJ g^{-1} (**19**), 14.71 GPa (**15**), 7029 ms^{-1} (**15**), and 227.2 s (**19**).

Conclusion

A series of *N,N*-dimethylhydrazinium dicyanamide and nitrocyanoamide ionic liquids were synthesized in good yields. The resulting salts were fully characterized by spectroscopic and analytical methods, thereby showing that the anions and the different alkyl substitutions of cations have a major impact on their physicochemical properties. The droplet tests demonstrated that all the *N,N*-dimethylhydrazinium salts are hypergolic with WFNA as the oxidizer and some may have potential as bipropellants, especially the dicyanamide compound **11**, with properties such as T_g lower than -60°C , viscosity 78.6 mPa, and ID 24 ms.

Experimental Section

Caution: Although none of the compounds described herein has demonstrated unstable characteristics, these materials should be handled with care using the appropriate safety practices.

Reactants: *N,N*-Dimethylhydrazine 98% (Aldrich), iodomethane 99% (Alfa Aesar), iodoethane 98% (Acros), 1-iodobutane 99%, (Aldrich), allyl chloride 99% (Acros), propargyl bromide 80 wt % solution in toluene (Acros), 2-chloroethanol 99% (Acros), bromoacetonitrile 97%

(Acros), silver nitrate 99.95% (Salt Lake Metals), and sodium dicyanamide 97% (Acros), were used as received.

General methods: ^1H and ^{13}C NMR spectra were recorded using a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, with $[\text{D}_6]\text{DMSO}$ as a locking solvent unless otherwise stated. Chemical shifts were reported relative to Me_4Si . The melting and decomposition points were recorded using a differential scanning calorimeter (DSC) at a scan rate of $10^\circ\text{C min}^{-1}$ in closed aluminum containers. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at $10^\circ\text{C min}^{-1}$ from 25 to 600°C . IR spectra were recorded by using KBr pellets. Densities were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical).

X-ray analyses: A clear colorless prism of dimensions $0.43 \times 0.42 \times 0.23 \text{ mm}^3$ was obtained by cooling a saturated solution of **8** in acetone, and was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected using a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). An Oxford Cobra low-temperature device was used to keep the crystals at a constant -100°C during data collection. Data collection was performed and the unit cell was initially refined using APEX2 (v2009.3-0).^[32] Data reduction was carried out using SAINT (v7.60A)^[33] and XPREP (v2008/2).^[34] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS (v2008/1).^[35] The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) software suite.^[36] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The H atoms were included using a riding model.

Compound **8** is in the orthorhombic *Pbca* space group with one trimethylhydrazinium cation per dicyanamide anion. The structure is shown in Figure 2a. The N–N bond length in the cation is $1.4592(15) \text{ \AA}$ (similar to literature value: $1.453(3) \text{ \AA}$).^[37] There is only hydrogen bonding between the ion pair (N3...N10: $3.1316(18) \text{ \AA}$) (Figure 2b). Details of the data collection and refinement are given in Table 2. Further crystallographic data are provided in the Supporting Information. CCDC-749800 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N,N,N*-Trimethylhydrazinium iodide (1):** A solution of *N,N*-dimethylhydrazine (1.26 g, 20.1 mmol) in THF (15 mL) was cooled in an ice–water bath, and a solution of iodomethane (2.98 g, 20.1 mmol) in THF (15 mL) was added dropwise with stirring. After the mixture was left at reflux at 25°C for 8 h, the precipitate was filtered, washed with THF (20 mL), and dried under vacuum to give a white solid (4.04 g, 95%). ^1H NMR: $\delta = 3.29$ (s, 9H; CH_3), 6.10 ppm (s, 2H; NH_2); ^{13}C NMR: $\delta = 57.3$ ppm; IR (KBr): $\tilde{\nu} = 3434, 3290, 3146, 3014, 1609, 1473, 1055, 942, 897, 671 \text{ cm}^{-1}$; elemental analysis calcd (%) for $\text{C}_3\text{H}_{11}\text{N}_2\text{I}$ (202.04): C 17.83, H 5.49, N 13.87; found: C 18.00, H 5.63, N 13.87.

***N*-Ethyl-*N,N*-dimethylhydrazinium iodide (2):** The same procedure was used as for **1**. *N,N*-Dimethylhydrazine (1.19 g, 19.8 mmol) and iodoethane (3.09 g, 19.8 mmol) were reacted to give a white solid (3.88 g, 91%). ^1H NMR: $\delta = 1.27$ (t, $J = 14.5 \text{ Hz}$, 3H; CH_3), 3.21 (s, 6H; CH_3), 3.50 (m,

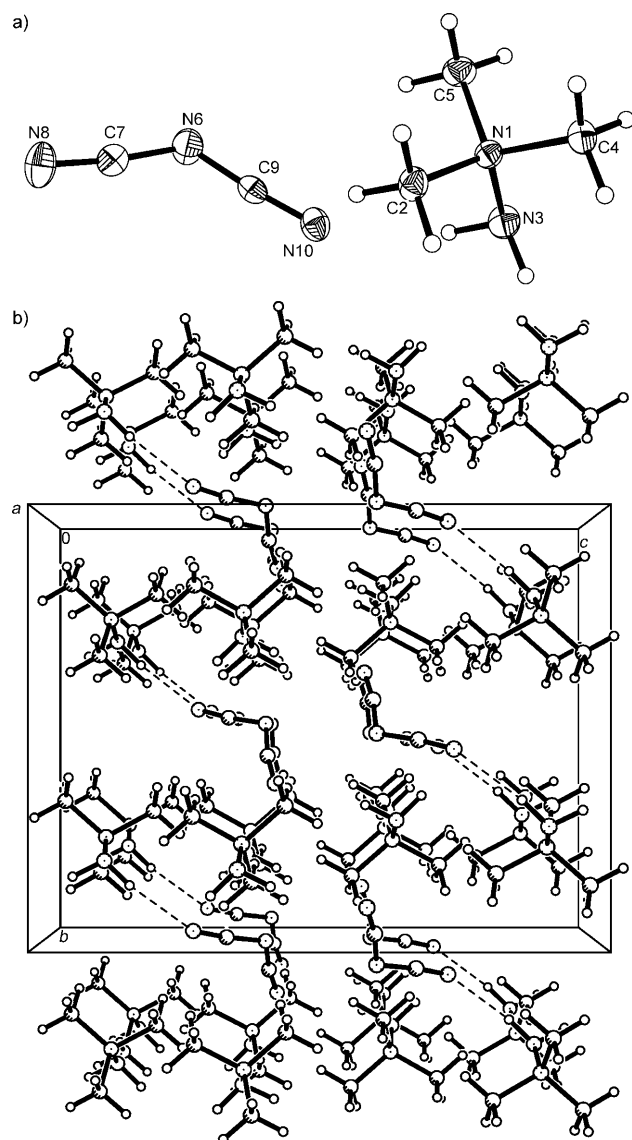


Figure 2. a) Thermal ellipsoid plot (30%) of **8**. The hydrogen atoms are included but unlabeled for clarity. b) Ball-and-stick packing diagram of **8** viewed down the *a* axis. The dashed lines indicate hydrogen bonding.

2H; CH₂), 5.91 ppm (s, 2H; NH₂); ¹³C NMR: δ = 8.1, 54.6, 63.4 ppm; IR (KBr): $\tilde{\nu}$ = 3459, 3238, 3132, 3019, 1624, 1466, 1079, 1015, 871, 814 cm⁻¹; elemental analysis calcd (%) for C₄H₁₃N₂I (216.06): C 22.24, H 6.06, N 12.97; found: C 22.23, H 6.26, N 13.11.

N-Butyl-N,N-dimethylhydrazinium iodide (3): The same procedure was used as for **1**. *N,N*-Dimethylhydrazine (1.67 g, 27.7 mmol) and iodobutane (5.10 g, 27.7 mmol) were reacted to give a white solid (4.11 g, 61%). ¹H NMR: δ = 0.91 (t, *J* = 14.7 Hz, 3H; CH₃), 1.30 (m, 2H; CH₂), 1.71 (m, 2H; CH₂), 3.23 (s, 6H; CH₃), 3.45 (m, 2H; CH₂), 5.94 ppm (s, 2H; NH₂); ¹³C NMR: δ = 13.4, 18.8, 23.9, 55.2, 67.5 ppm; IR (KBr): $\tilde{\nu}$ = 3435, 3253, 3128, 3012, 2959, 2872, 1618, 1469, 1384, 1091, 983, 910, 734, 543, 414 cm⁻¹; elemental analysis calcd (%) for C₆H₁₇N₂I (244.12): C 29.52, H 7.02, N 11.48; found: C 29.49, H 7.10, N 11.20.

N-Allyl-N,N-dimethylhydrazinium chloride (4): Allyl chloride (1.75 g, 22.9 mmol) was added to a stirring solution of *N,N*-dimethylhydrazine (1.38 g, 23.0 mmol) in THF (50 mL). The mixture was heated at reflux at 70 °C for 8 h. After decanting the solvent, the residue was washed twice with THF (20 mL) and dried under vacuum to afford a yellow liquid (2.73 g, 87%). ¹H NMR: δ = 3.28 (s, 6H; CH₃), 4.28 (d, *J* = 7.1 Hz, 2H;

Table 2. Crystallographic data and structure-refinement parameters of **8**.

empirical formula	C ₅ H ₁₁ N ₅
<i>M_r</i>	141.19
crystal size [mm]	0.43 × 0.42 × 0.23
crystal system	orthorhombic
space group	<i>Pbca</i>
<i>a</i> [Å]	8.4205(19)
<i>b</i> [Å]	12.085(3)
<i>c</i> [Å]	15.666(4)
α [°]	90
β [°]	90
γ [°]	90
<i>V</i> [Å ³]	1594.1(6)
<i>Z</i>	8
<i>T</i> [K]	173 (2)
ρ_{calcd} [Mg m ⁻³]	1.177
μ [mm ⁻¹]	0.081
<i>F</i> (000)	608
θ range [°]	2.60 to 26.48
index ranges	−10 ≤ <i>h</i> ≤ 10 −15 ≤ <i>k</i> ≤ 15 −19 ≤ <i>l</i> ≤ 19
reflns collected	13246
independent reflns	1645 (<i>R</i> _{int} = 0.0270)
GOF	1.072
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0394
<i>wR</i> ₂ (all data) ^[b]	0.1045
largest differential peak and hole [e Å ⁻³]	0.292 and −0.184

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

CH₂), 5.57 (m, 2H; CH₂), 6.07 (m, 1H; CH), 6.52 ppm (s, 2H; NH₂); ¹³C NMR: δ = 54.3, 69.2, 126.5, 126.6 ppm; IR (KBr): $\tilde{\nu}$ = 3438, 3252, 3140, 3039, 1629, 1473, 1092, 958, 888, 770, 634 cm⁻¹; elemental analysis calcd (%) for C₅H₁₃N₂Cl (136.62): C 43.96, H 9.59, N 20.50; found: C 43.70, H 9.87, N 19.39.

N-Propargyl-N,N-dimethylhydrazinium bromide (5): The same procedure was used as for compound **1**. *N,N*-Dimethylhydrazine (1.41 g, 23.5 mmol) and propargyl bromide (2.77 g, 23.3 mmol) were reacted to give a brown solid (3.64 g, 87%). ¹H NMR: δ = 3.37 (s, 6H; CH₃), 4.00 (s, 1H; CH), 4.67 (s, 2H; CH₂), 6.30 ppm (s, 2H; NH₂); ¹³C NMR: δ = 54.7, 57.9, 72.3, 82.5 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3209, 3100, 3032, 2958, 2127, 1629, 1468, 1236, 1089, 972, 892, 698 cm⁻¹; elemental analysis calcd (%) for C₅H₁₁N₂Br (179.06): C 33.54, H 6.19, N 15.64; found: C 33.54, H 6.17, N 15.84.

N-(2-Hydroxyethyl)-N,N-dimethylhydrazinium chloride (6): The same procedure was used as for **4**. *N,N*-Dimethylhydrazine (1.28 g, 21.3 mmol) and 2-chloroethanol (1.71 g, 21.2 mmol) were reacted to give a white solid (2.55 g, 86%). ¹H NMR: δ = 3.33 (s, 6H; CH₃), 3.61 (t, *J* = 9.9 Hz, 2H; CH₂), 3.83 (t, *J* = 9.5 Hz, 2H; CH₂), 5.53 (s, 1H; OH), 6.42 ppm (s, 2H; NH₂); ¹³C NMR: δ = 56.1, 57.1, 70.8 ppm; IR (KBr): $\tilde{\nu}$ = 3402, 3303, 3126, 3027, 1626, 1473, 1085, 1007, 956, 863 cm⁻¹; elemental analysis calcd (%) for C₄H₁₃N₂OCl (140.61): C 34.17, H 9.32, N 19.92; found: C 34.23, H 9.76, N 19.46.

N-Cyanomethyl-N,N-dimethylhydrazinium bromide (7): The same procedure was used as for **1**. *N,N*-Dimethylhydrazine (1.33 g, 22.1 mmol) and bromoacetonitrile (2.65 g, 22.1 mmol) were reacted to give a white solid (3.59 g, 90%). ¹H NMR: δ = 3.48 (s, 6H; CH₃), 5.14 (s, 2H; CH₂), 6.59 ppm (s, 2H; NH₂); ¹³C NMR: δ = 55.4, 56.2, 112.0 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3227, 3111, 3026, 2960, 1624, 1471, 1091, 977, 898, 760 cm⁻¹; elemental analysis calcd (%) for C₄H₁₀N₃Br (180.05): C 26.68, H 5.60, N 23.34; found: C 26.59, H 5.61, N 22.45.

General procedure for preparation of ILs (8–21): Silver dicyanamide (1.04 g, 6 mmol) or silver nitrocyanamide (1.16 g, 6 mmol) was suspended in methanol (15 mL) and a solution of **1–7** (6 mmol) in methanol (15 mL) was added dropwise. After stirring at room temperature for 6 h, the insoluble silver halide was removed by filtration. The solvent was removed

under reduced pressure to yield the crude product, which was dissolved in acetone (5 mL), and diethyl ether (1–3 mL) was added to the solution until permanent cloudiness was obtained. The solution was stored at room temperature for 3 h and filtered. Additional diethyl ether (5 mL) was added to the filtrate to form two phases. The upper phase was decanted, and the residue was dried under vacuum at 70 °C to give the final product.

***N,N,N*-Trimethylhydrazinium dicyanamide (8):** White solid (0.799 g, 94 %). ¹H NMR: δ = 3.25 (s, 9H; CH₃), 6.06 ppm (s, 2H; NH₂); ¹³C NMR: δ = 57.3, 119.0 ppm; IR (KBr): $\tilde{\nu}$ = 3212, 3111, 3020, 2260, 2213, 2140, 1631, 1478, 1324, 1092, 943, 915, 522 cm⁻¹; elemental analysis calcd (%) for C₅H₁₁N₅ (141.17): C 42.54, H 7.85, N 49.61; found: C 42.15, H 7.85, N 49.19.

***N*-Ethyl-*N,N*-dimethylhydrazinium dicyanamide (9):** Yellow supercooled liquid (0.859 g, 92 %). ¹H NMR: δ = 1.28 (t, J = 14.5 Hz, 3H; CH₃), 3.16 (s, 6H; CH₂), 3.44 (m, 2H; CH₂), 5.88 ppm (s, 2H; NH₂); ¹³C NMR: δ = 8.0, 54.6, 63.6, 119.0 ppm; IR (KBr): $\tilde{\nu}$ = 3441, 3276, 3160, 3035, 2247, 2203, 2142, 1633, 1471, 1323, 1087, 1015, 915, 525 cm⁻¹; elemental analysis calcd (%) for C₆H₁₃N₅ (155.20): C 46.43; H 8.44; N 45.12; found: C 45.51, H 8.61, N 44.36.

***N*-Butyl-*N,N*-dimethylhydrazinium dicyanamide (10):** Colorless liquid (0.995 g, 90 %). ¹H NMR: δ = 0.91 (t, J = 14.7 Hz, 3H; CH₃), 1.31 (m, 2H; CH₂), 1.70 (m, 2H; CH₂), 3.17 (s, 6H; CH₃), 3.37 (m, 2H; CH₂), 5.90 ppm (s, 2H; NH₂); ¹³C NMR: δ = 13.4, 19.0, 24.1, 55.2, 67.8, 119.0 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3264, 3156, 2966, 2877, 2248, 2201, 2141, 1633, 1475, 1325, 1092, 910, 522 cm⁻¹; elemental analysis calcd (%) for C₈H₁₇N₅ (183.25): C 52.43, H 9.35, N 38.22; found: C 51.85, H 9.52, N 38.35.

***N*-Allyl-*N,N*-dimethylhydrazinium dicyanamide (11):** Amber liquid (0.896 g, 89 %). ¹H NMR: δ = 3.16 (s, 6H; CH₃), 4.04 (d, J = 7.2 Hz, 2H; CH₂), 5.62 (m, 2H; CH₂), 5.95 (s, 2H; NH₂), 6.03 ppm (m, 1H; CH); ¹³C NMR: δ = 54.8, 70.0, 119.1, 126.0, 127.5 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3263, 3151, 3032, 2243, 2198, 2139, 1631, 1473, 1318, 1090, 958, 905, 772, 520 cm⁻¹; elemental analysis calcd (%) for C₇H₁₃N₅ (167.21): C 50.28, H 7.84, N 41.88; found: C 49.31, H 7.97, N 41.83.

***N*-Propargyl-*N,N*-dimethylhydrazinium dicyanamide (12):** Amber liquid (0.878 g, 89 %). ¹H NMR: δ = 3.25 (s, 6H; CH₃), 3.65 (s, 1H; CH), 4.37 (s, 2H; CH₂), 5.98 ppm (s, 2H; NH₂); ¹³C NMR: δ = 55.2, 58.9, 72.3, 82.7, 119.3 ppm; IR (KBr): $\tilde{\nu}$ = 3433, 3268, 3159, 3035, 2978, 2247, 2202, 2142, 1624, 1472, 1321, 1092, 995, 896, 665, 524 cm⁻¹; elemental analysis calcd (%) for C₇H₁₁N₅ (165.20): C 50.89, H 6.71, N 42.39; found: C 50.04, H 6.79, N 41.76.

***N*-(2-Hydroxyethyl)-*N,N*-dimethylhydrazinium dicyanamide (13):** Amber liquid (0.922 g, 90 %). ¹H NMR: δ = 3.24 (s, 6H; CH₃), 3.50 (t, J = 10.1 Hz, 2H; CH₂), 3.86 (m, 2H; CH₂), 5.24 (t, J = 9.2 Hz, 1H; OH), 5.99 ppm (s, 2H; NH₂); ¹³C NMR: δ = 55.0, 56.1, 69.7, 119.0 ppm; IR (KBr): $\tilde{\nu}$ = 3286, 3161, 3034, 2964, 2247, 2202, 2140, 1628, 1471, 1325, 1084, 957, 913, 662, 522 cm⁻¹; elemental analysis calcd (%) for C₆H₁₃N₅O (171.20): C 42.09, H 7.65, N 40.91; found: C 41.56, H 7.76, N 40.73.

***N*-Cyanomethyl-*N,N*-dimethylhydrazinium dicyanamide (14):** Dark red liquid (0.904 g, 91 %). ¹H NMR: δ = 3.35 (s, 6H; CH₃), 4.81 (s, 2H; CH₂), 6.29 ppm (s, 2H; NH₂); ¹³C NMR: δ = 56.1, 56.8, 111.9, 119.3 ppm; IR (KBr): $\tilde{\nu}$ = 3269, 3145, 3038, 2983, 2247, 2198, 2140, 1714, 1621, 1464, 1295, 1084, 900, 788, 525 cm⁻¹; elemental analysis calcd (%) for C₆H₁₀N₆ (166.18): C 43.36, H 6.07, N 50.57; found: C 42.65, H 6.17, N 49.72.

***N,N,N*-Trimethylhydrazinium dicyanamide (15):** White solid (0.887 g, 92 %). ¹H NMR: δ = 3.26 (s, 9H; CH₃), 6.03 ppm (s, 2H; NH₂); ¹³C NMR: δ = 57.3, 116.6 ppm; IR (KBr): $\tilde{\nu}$ = 3462, 3301, 3220, 3113, 3021, 2190, 1630, 1446, 1292, 1159, 1089, 945, 771, 547 cm⁻¹; elemental analysis calcd (%) for C₄H₁₁N₅O₂ (161.16): C 29.81, H 6.88, N 43.46; found: C 29.35, H 6.75, N 42.98.

***N*-Ethyl-*N,N*-dimethylhydrazinium nitrocyanamide (16):** Colorless solid, (0.945 g, 90 %). ¹H NMR: δ = 1.28 (t, J = 14.5 Hz, 3H; CH₃), 3.17 (s, 6H; CH₃), 3.45 (m, 2H; CH₂), 5.81 ppm (s, 2H; NH₂); ¹³C NMR: δ = 8.2, 54.8, 64.1, 116.9 ppm; IR (KBr): $\tilde{\nu}$ = 3468, 3300, 3176, 2246, 2181, 2142, 1629, 1434, 1277, 1157, 1082, 1015, 961, 873, 769 cm⁻¹; elemental analysis calcd

(%) for C₅H₁₃N₅O₂ (175.19): C 34.28, H 7.48, N 39.98; found: C 33.53, H 7.67, N 39.04.

***N*-Butyl-*N,N*-dimethylhydrazinium nitrocyanamide (17):** Colorless liquid (1.05 g, 86 %). ¹H NMR: δ = 0.89 (t, J = 14.6 Hz, 3H; CH₃), 1.30 (m, 2H; CH₂), 1.71 (m, 2H; CH₂), 3.20 (s, 6H; CH₃), 3.38 (m, 2H; CH₂), 5.86 ppm (s, 2H; NH₂); ¹³C NMR: δ = 13.4, 19.1, 24.3, 55.3, 68.2, 117.0 ppm; IR (KBr): $\tilde{\nu}$ = 3474, 3295, 3180, 2966, 2178, 2147, 1629, 1431, 1275, 1156, 1086, 955, 911, 796, 544 cm⁻¹; elemental analysis calcd (%) for C₇H₁₇N₅O₂ (203.24): C 41.37, H 8.43, N 34.46; found: C 40.61, H 8.54, N 34.10.

***N*-Allyl-*N,N*-dimethylhydrazinium nitrocyanamide (18):** Amber liquid (0.963 g, 86 %). ¹H NMR: δ = 3.20 (s, 6H; CH₃), 4.05 (d, J = 7.3 Hz, 2H; CH₂), 5.59 (m, 2H; CH₂), 5.77 (s, 2H; NH₂), 5.98 ppm (m, 1H; CH); ¹³C NMR: δ = 55.2, 70.7, 116.9, 125.6, 128.5 ppm; IR (KBr): $\tilde{\nu}$ = 3464, 3297, 3176, 3039, 2180, 2141, 1627, 1436, 1276, 1157, 1088, 957, 887, 769, 544 cm⁻¹; elemental analysis calcd (%) for C₆H₁₃N₅O₂ (187.20): C 38.50, H 7.00, N 37.41; found: C 38.28, H 7.16, N 36.82.

***N*-Propargyl-*N,N*-dimethylhydrazinium nitrocyanamide (19):** Amber liquid (0.948 g, 85 %). ¹H NMR: δ = 3.30 (s, 6H; CH₃), 3.68 (s, 1H; CH), 4.41 (s, 2H; CH₂), 5.98 ppm (s, 2H; NH₂); ¹³C NMR: δ = 55.3, 59.0, 72.4, 82.6, 116.8 ppm; IR (KBr): $\tilde{\nu}$ = 3460, 3270, 3178, 3041, 2980, 2248, 2181, 2142, 1625, 1434, 1277, 1157, 1091, 958, 893, 762, 543 cm⁻¹; elemental analysis calcd (%) for C₆H₁₁N₅O₂ (185.18): C 38.91, H 5.99, N 37.82; found: C 37.95, H 6.02, N 37.47.

***N*-(2-Hydroxyethyl)-*N,N*-dimethylhydrazinium nitrocyanamide (20):** Amber liquid (1.00 g, 87 %). ¹H NMR: δ = 3.25 (s, 6H; CH₃), 3.51 (t, J = 9.7 Hz, 2H; CH₂), 3.89 (t, J = 9.6 Hz, 2H; CH₂), 5.10 (s, 1H; OH), 5.88 ppm (s, 2H; NH₂); ¹³C NMR: δ = 55.6, 56.5, 70.2, 116.9 ppm; IR (KBr): $\tilde{\nu}$ = 3392, 3304, 3185, 3042, 2967, 2181, 2144, 1625, 1436, 1277, 1158, 1083, 957, 769, 543 cm⁻¹; elemental analysis calcd (%) for C₅H₁₃N₅O₃ (191.19): C 31.41, H 6.85, N 36.63; found: C 30.86, H 6.85, N 36.29.

***N*-Cyanomethyl-*N,N*-dimethylhydrazinium nitrocyanamide (21):** Yellow liquid (0.952 g, 85 %). ¹H NMR: δ = 3.39 (s, 6H; CH₃), 4.89 (s, 2H; CH₂), 6.37 ppm (s, 2H; NH₂); ¹³C NMR: δ = 56.0, 56.7, 112.0, 116.7 ppm; IR (KBr): $\tilde{\nu}$ = 3456, 3281, 3171, 3043, 2990, 2181, 2143, 1625, 1434, 1279, 1159, 1085, 962, 897, 764, 543 cm⁻¹; elemental analysis calcd (%) for C₅H₁₀N₆O₂ (186.17): C 32.26, H 5.41, N 45.14; found: C 31.53, H 5.41, N 44.22.

Acknowledgements

The authors gratefully acknowledge the support of DTRA (HDTRA1-07-1-0024), NSF (CHE-0315275), and ONR (N00014-06-1-1032).

- [1] M. Tanaka, W. Daimon, I. Kimura, *J. Propul. Power* **1985**, *1*, 314–316.
- [2] W. Daimon, Y. Gotoh, I. Kimura, *J. Propul. Power* **1991**, *7*, 946–952.
- [3] O. de Bonn, A. Hammerl, T. M. Klapötke, P. Mayer, H. Piotrowski, H. Zewen, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2011–2015.
- [4] S. Pichon, L. Catoire, N. Chaumeix, C. Paillard, *J. Propul. Power* **2005**, *21*, 1057–1061.
- [5] A. Osmont, L. Catoire, T. M. Klapötke, G. L. Vaghjani, M. T. Swihart, *Propellants Explos. Pyrotech.* **2008**, *33*, 209–212.
- [6] G. P. Sutton, *J. Propul. Power* **2003**, *19*, 978–1007.
- [7] L. Catoire, N. Chaumeix, C. Paillard, *J. Propul. Power* **2004**, *20*, 87–92.
- [8] I. Frank, A. Hammerl, T. M. Klapötke, C. Nonnenberg, H. Zewen, *Propellants Explos. Pyrotech.* **2005**, *30*, 44–52.
- [9] C. Nonnenberg, I. Frank, T. M. Klapötke, *Angew. Chem.* **2004**, *116*, 4686–4689; *Angew. Chem. Int. Ed.* **2004**, *43*, 4586–4589.
- [10] Y. Ishikawa, M. J. McQuaid, *J. Mol. Struct.* **2007**, *825–846*, 119–124.
- [11] L. Catoire, N. Chaumeix, S. Pichon, C. Paillard, *J. Propul. Power* **2006**, *22*, 120–126.

- [12] M. Freemantle, *Chem. Eng. News* **2007**, 85, 23–26.
- [13] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem.* **2006**, 118, 3664–3682; *Angew. Chem. Int. Ed.* **2006**, 45, 3584–3601.
- [14] C. B. Jones, R. Haiges, T. Schroer, K. O. Christe, *Angew. Chem.* **2006**, 118, 5103–5106; *Angew. Chem. Int. Ed.* **2006**, 45, 4981–4984.
- [15] T. Hawkins, L. Hall, K. Tollison, A. Brand, M. McKay, G. W. Drakes, *Propellants Explos. Pyrotech.* **2006**, 31, 196–204.
- [16] G. Steinhauser, T. M. Klapötke, *Angew. Chem.* **2008**, 120, 3376–3394; *Angew. Chem. Int. Ed.* **2008**, 47, 3330–3347.
- [17] G. Tao, Y. Guo, Y.-H. Joo, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* **2008**, 18, 5524–5530.
- [18] G. Tao, Y. Huang, J. A. Boatz, J. M. Shreeve, *Chem. Eur. J.* **2008**, 14, 11167–11173.
- [19] S. Schneider, T. Hawkins, M. Rosander, J. Mills, G. Vaghjiani, S. Chambreau, *Inorg. Chem.* **2008**, 47, 6082–6089.
- [20] R. Wang, H. Gao, C. Ye, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2007**, 46, 932–938.
- [21] H. Xue, J. M. Shreeve, *Adv. Mater.* **2005**, 17, 2142–2146.
- [22] Y. Gao, S. W. Arritt, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2005**, 44, 1704–1712.
- [23] P. F. Pagoria, G. S. Lee, A. R. Mitchell, R. D. Schmidt, *Thermochim. Acta* **2002**, 384, 187–204.
- [24] S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. Drake, *Energy Fuels* **2008**, 22, 2871–2872.
- [25] S. D. Chambreau, S. Schneider, M. Rosander, T. Hawkins, C. J. Gallegos, M. F. Pastewait, G. L. Vaghjiani, *J. Phys. Chem. A* **2008**, 112, 7816–7824.
- [26] H. Gao, Y.-H. Joo, B. Twamley, Z. Zhou, J. M. Shreeve, *Angew. Chem.* **2009**, 121, 2830–2833; *Angew. Chem. Int. Ed.* **2009**, 48, 2792–2795.
- [27] A. J. Alfano, J. D. Mills, G. L. Vaghjiani, *Rev. Sci. Instrum.* **2006**, 77, 045109/1–5.
- [28] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. L. G. Liu, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [29] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.
- [30] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, 41, 2364–2367.
- [31] CHEETAH 5.0 User's Manual, S. Bastea, L. E. Fried, K. R. Glaesemann, W. M. Howard, P. C. Souers, P. A. Vitello, Lawrence Livermore National Laboratory, **2007**.
- [32] APEX2 v2009/3-0, Bruker AXS Inc., Madison, **2009**.
- [33] SAINT v7.60A, Bruker AXS Inc., Madison, **2009**.
- [34] XPREP v2008/2, Bruker AXS Inc., Madison, **2008**.
- [35] SADABS v2008/1, Bruker AXS Inc., Madison, **2008**.
- [36] SHELXTL v2008/4, Bruker AXS Inc., Madison, **2008**.
- [37] A. Hammerl, T. M. Klapötke, H. Noth, M. Warchhold, G. Holl, M. Kaiser, U. Ticmanis, *Inorg. Chem.* **2001**, 40, 3570–3575.

Received: October 4, 2009

Published online: February 4, 2010