CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201001243

3,4,5-Trinitropyrazole-Based Energetic Salts

Yanqiang Zhang,[a] Yong Guo,[a] Young-Hyuk Joo,[a] Damon A. Parrish,[b] and Jean'ne M. Shreeve*[a]

Abstract: High-density energetic salts that are comprised of nitrogen-rich cations and the 3,4,5-trinitropyrazolate anion were synthesized in high yield by neutralization or metathesis reactions. The resulting salts were fully characterized by ^{1}H, ^{13}C NMR, and IR spectroscopy; differential scanning calorimetry; and elemental analysis. Additionally, the structures of the 3,5-diaminotriazolium and triaminoguanidinium 3,4,5-trinitropyrazolates were confirmed by single-crystal X-ray diffraction. Based on the measured densities and calculated heats of formation, the detonation performances (pressure: 23.74–31.89 GPa; velocity: 7586–8543 ms^{-1}; Cheetah 5.0) of the 3,4,5-trinitropyrazolate salts are comparable with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB; 31.15 GPa and 8114 ms^{-1}). Impact sensitivities were determined to be no less than 35 J by hammer tests, which places these salts in the insensitive class.

Keywords: detonation performance · energetic salts · heterocycles · polynitro compounds · structure–property relationships

Introduction

Energetic nitrogen-rich salts, as families of environmentally benign high energy density materials (HEDM), have attracted considerable interest due to the lower vapor pressures, higher heats of formation, and enhanced thermal stabilities than their atomically similar nonionic analogues.[1–3] They are often prepared by neutralization or metathesis reactions, with N-protonated cations such as ammonium, hydrazinium, guanidium, azolium, azinium, and so forth, and C-, N-, or O-deprotonated anions, for example, nitroformate, azolate, or picrate.[4–5] In pursuit of higher detonation performance and lower sensitivity, many energetic salts with nitrogen-rich cations or nitrogen-containing heterocyclic anions, have been obtained through combination of carefully selected ions.[6–7] Their full characterization provides knowledge of the structure–property relationships in energetic salts.

Both the oxygen balance and density of energetic compounds are enhanced by the presence of the nitro group, which improves the detonation performances (pressure and velocity) that are related to the square of and proportional to the density.[8] Azoles, the five-membered nitrogen-containing heterocycles, can be N-deprotonated, and nitroazolates are excellent anions for energetic salts. A large number of nitroazolate salts have been reported, including fully C-nitrated azolates, for example, 2,4,5-trinitroimidazolate (TNI), 3,5-dinitrotriazolate (DNT), and 5-nitrotetrazolate (NT) salts.[9] Based on calculations, the 3,4,5-trinitropyrazolate (TNP, −63.1 kJ mol^{-1}) has a less negative heat of formation than its isomer, 2,4,5-trinitroimidazolate (−148.5 kJ mol^{-1}), NO_3^- (−307.9 kJmol^{-1}), and ClO_4^- (−277.8 kJ mol^{-1}). 3,4,5-Trinitropyrazole with a calculated density of 1.867 g cm^{-3} is stable up to 200 °C, making its salts potential energetic materials.[10,11] However, 3,4,5-trinitropyrazolate salts were only mentioned in patents without characterization and properties.[10] In our work, a series of high-nitrogen 3,4,5-trinitropyrazolate salts have now been prepared and characterized. Their thermal stabilities, detonation performances, and impact sensitivities were also investigated.

Results and Discussion

3,4,5-Trinitropyrazole (HTNP) was prepared from the nitration of pyrazole with fuming nitric acid, followed by thermal

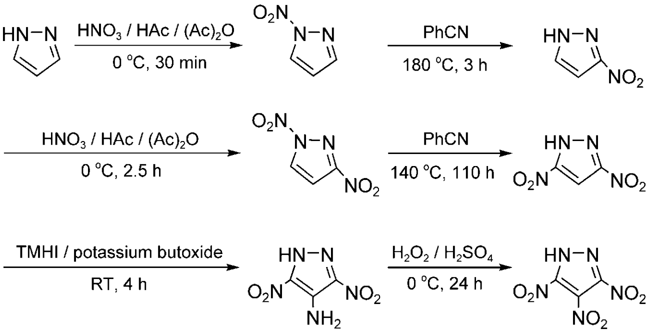
---

[a] Dr. Y. Zhang, Dr. Y. Guo, Dr. 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. D. A. Parrish
Naval Research Laboratory, Code 6030
Washington, D.C. 20375-5001 (USA)

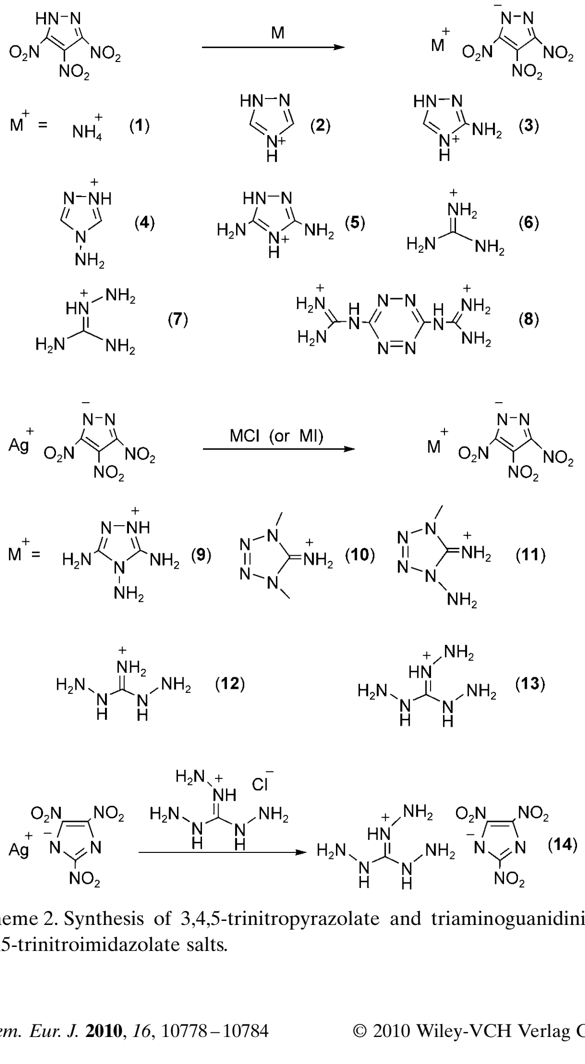
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001243.

rearrangement of N-nitropyrazole in benzonitrile, amination with 1,1,1-trimethylhydrazinium iodide, and finally oxidation with 30 % hydrogen peroxide (Scheme 1).[11,12]



Scheme 1. Synthesis of 3,4,5-trinitropyrazole.

Reactions of HTNP with ammonia, triazole, 3-aminotriazole, 4-aminotrizole, 3,5-diaminotriazole, guanidine carbonate, aminoguanidine bicarbonate, and 3,6-diguanidinotetrazine, resulted in the formation of salts **1**–**8** (Scheme 2). Other salts **9**–**14** were readily synthesized by metathesis reactions of 3,4,5-triaminotriazolium chloride, 1,4-dimethyl-5-aminotetrazolium, and 1,5-diamino-4-methyltetrazolium iodides, and diaminoguanidium and triaminoguanidinium chlorides with Ag(TNP) (or Ag(TNI), silver trinitroimidazolate), which was obtained from treatment of KTNP (or KTNI) with an equivalent amount of aqueous silver nitrate. All of the salts, which were isolated as crystalline materials in good yields, are nonhygroscopic and stable in air. Unfortunately attempts to isolate the corresponding trinitropyrazolate salt of 1,5-diaminotetrazole (DAT) were unsuccessful due to the extreme hygroscopicity of the product which became a highly sticky material when exposed to air for several seconds. The structures of the salts **1**–**14** were determined by ^{1}H and ^{13}C NMR spectroscopy (some with ^{15}N NMR spectroscopy), IR spectroscopy, and elemental analysis. In the ^{1}H NMR spectra, the hydrogen signals of the cations were observed and easily assigned, since there is no proton associated with the TNP anion. In the ^{13}C NMR spectra, except for two very weak signals ($\delta = \approx 122$ and 147 ppm) assigned to the TNP anion, the other signals are associated with the cations.



Scheme 2. Synthesis of 3,4,5-trinitropyrazolate and triaminoguanidinium 2,4,5-trinitroimidazolate salts.

In the IR spectra, several main absorption bands at around 1520, 1360, 1320, and 850 cm^{-1} are attributed to the TNP anion. The intense absorption bands in the range of 3100–3500 cm^{-1} can be assigned to the N–H bonds of the nitrogen-rich cations. The structures of salts **5** and **13** were confirmed with single-crystal X-ray diffraction.

In the ^{15}N NMR spectra of salts, three signals ($\delta = \approx -9.0$, -9.5, and -44.0 ppm) are assigned to the TNP anion, the other signals are associated with the cations. HTNP, **9**, **13**, and **14** taken as examples were measured in CD_3CN or [D$_6$]DMSO with respect to CH_3NO_2 as external standard (Figure 1). Comparing the TNP anion with HTNP, the signals of pyrazole ring and nitro groups shift downfield with a difference of about 74 and 8 ppm. In comparison with the TNP anion, the TNI anion has a similar chemical shift of the nitro groups, and much lower chemical shift ($\delta = \approx 69$ ppm) of the ring nitrogen atoms. Interestingly, at 30 °C in ([D$_6$]DMSO), there are only five signals ($\delta = -8.9$, -9.5, -43.0, -225.8, and -310.1 ppm) for **9**, but all signals (seven) are resolved at 80 °C.

Properties of TNP salts: The thermal stabilities of the TNP salts were determined by differential scanning calorimetric (DSC) measurements (Table 1). When the decomposition peak in the DSC scan was not sharp, the salts were examined by using thermogravimetric analysis (TGA). While salts **1** and **8** decomposed without melting at 224 and 243 °C, respectively, the other salts have melting and decomposition temperatures ranging from 120 (**11**) to 206 °C (**9**) and 167 (**2** and **11**) to 243 °C (**8**). Densities for the TNP salts were measured with a gas pycnometer, and found in the range between 1.61 (**10**) and 1.77 g cm^{-3} (**4**). The triazolium salts exhibit a higher density than their guanidinium analogues, and 4-aminotriazolium TNP (**4**) has the highest density of 1.77 g cm^{-3}. Among the four guanidinium salts (**6**, **7**, **12**, and **13**), diaminoguanidinium TNP (**12**) has the lowest density at 1.62 g cm^{-3}. The two tetrazolium salts (**10** and **11**) have low

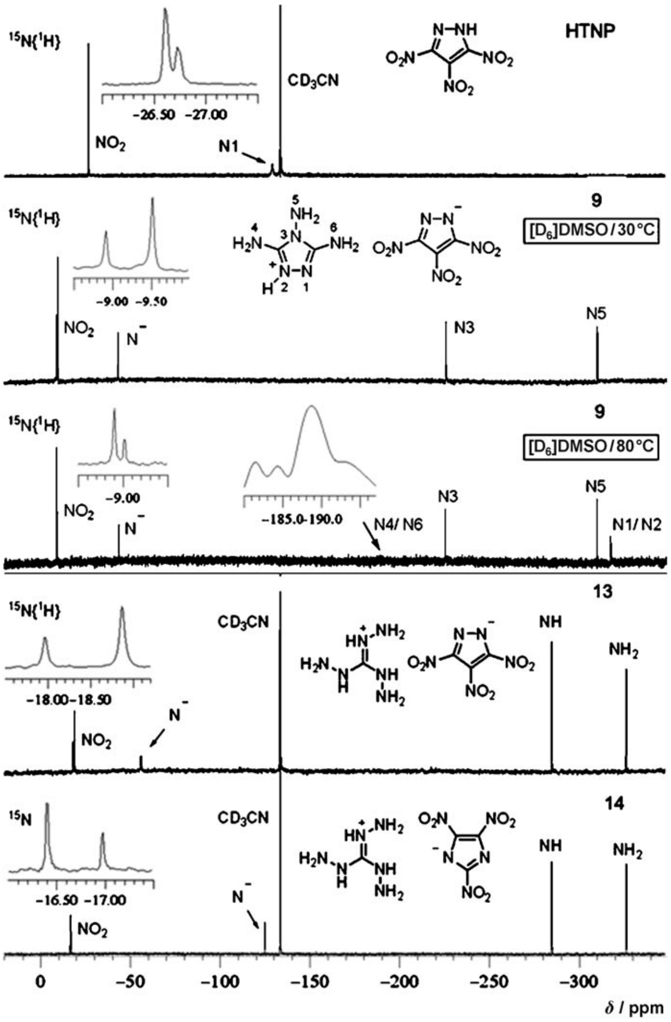


Figure 1. ^{15}N NMR spectra of compounds HTNP, **9**, **13**, and **14**.

densities of 1.61 and 1.64 g cm^{-3}, respectively. These relatively high densities are presumably caused by the high symmetry of the anion and the extensive intra- and intermolecular hydrogen bonds found in these salts. The oxygen balances (OB) of the TNP salts were calculated to fall between −50.6 (**10**) and −14.5 % (**1**).

The heats of formation (ΔH_f) of the cations and anions were calculated by using the Gaussian 03 (Revision D. 01) suite of programs. The calculated ΔH_f of nitrogen-rich cations varies between 575.9 (guanidinium, **6**) and 1903.6 kJ mol^{-1} (diguanidinotetrazinium, **8**). Compared with 2,4,5-trinitroimidazolate anion (−148.5 kJ mol^{-1}),[9a] the calculated ΔH_f of the TNP anion is less negative (−63.1 kJ mol^{-1}). The heats of formation (ΔH_f) of the TNP salts are calculated by using Born–Haber energy cycles (see the Experimental Section). They are positive, and fall in the range 0.11 (**6**) to 1.45 kJ g^{-1} (**11**).

With the data of density, heat of formation, and oxygen balance in hand, the detonation pressure (P) and velocity (νD), and specific impulse (I_{sp}) values of the TNP salts were calculated with Cheetah 5.0. Just as for **13** and **14**, the TNP salts have weaker detonation properties than the corresponding TNI salts arising mainly from lower densities.[9a] Based on the data in Table 1, the calculated detonation pressures and velocities lie in the range of 23.74–31.89 GPa and 7586–8543 m s^{-1}, which are superior to that of trinitrobenzene (TNT, 19.5 GPa and 6881 m s^{-1}). Salt **4**, with a detonation pressure and velocity of 31.89 GPa and 8543 m s^{-1}, is comparable with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 31.15 GPa and 8114 m s^{-1}). The specific impulse values of the TNP salts ranging between 228.9 and 269.6 s suggest application of these energetic materials as propellants. Impact sensitivities of the TNP salts were measured by using a BAM Fallhammer apparatus with a 10 kg drop weight and found to be no less than 35 J, which places them in the insensitive class.

Table 1. Properties of trinitropyrazolate salts compared with triaminoguanidium TNI (**14**), TNT, and TATB.

Salt	T_m[a] [°C]	T_d[b] [°C]	ρ[c] [g cm^{-3}]	ΔH_L[d] [kJ mol^{-1}]	ΔH_f[d] (cation) [kJmol^{-1}]	ΔH_f[d] (salt) [kJ mol^{-1}]/[kJ g^{-1}]	OB[e] [%]	P[f] [Gpa]	νD[g] [ms^{-1}]	I_{sp}[h] [s]	IS[i] [J]
1	–	224	1.73	502.7	626.4	60.5/0.28	−14.5	29.92	8461	263.0	40
2	158	167	1.69	473.1	835.0	299.0/1.10	−35.3	25.64	7871	245.0	>40
3	171	171	1.71	468.0	804.5	273.5/0.95	−36.2	26.00	7972	237.9	>40
4	168	168	1.77	471.9	936.3	401.2/1.40	−36.2	31.89	8543	269.6	>40
5	188	196	1.76	465.2	764.0	235.6/0.78	−37.1	27.67	8216	230.2	>40
6	163	235	1.66	476.5	575.9	28.3/0.11	−30.5	24.74	7865	235.6	>40
7	136	222	1.69	470.9	667.4	133.6/0.48	−31.8	26.85	8134	240.9	>40
8	–	243	1.68	1324.6	1903.6	452.3/0.75	−34.5	24.30	7817	228.9	>40
9	206	206	1.76	459.5	877.6	355.0/1.12	−37.8	28.83	8359	236.5	>40
10	166	219	1.61	449.6	887.7	375.0/1.19	−50.6	23.74	7586	230.5	>40
11	120	167	1.64	451.3	974.3	459.8/1.45	−37.8	25.20	7922	245.2	35
12	122	197	1.62	459.4	769.0	246.5/0.84	−32.9	25.34	7983	246.3	>40
13	125	184	1.65	455.9	871.5	352.7/1.15	−33.9	27.20	8236	250.5	>40
14	125	214	1.71	459.9	871.5	263.1/0.86	−33.9	28.89	8441	243.2	>40
TNT	80.4	295	1.65	–	–	–	−74.0	19.5	6881	–	15
TATB	–	318	1.94	–	–	–	−55.8	31.15	8114	–	50

[a] Melting temperature (nitrogen gas: DSC, 10 °C min^{-1}). [b] Decomposition temperature (nitrogen gas: DSC or TGA, 10 °C min^{-1}). [c] Density (25 °C). [d] Heat of formation. [e] Oxygen balance for $C_aH_bO_cN_d$, 1600-($c-2a-b/2$)/MW, MW = molecular weight of salt. [f] Detonation pressure. [g] Detonation velocity. [h] Specific impulse calculated isobarically at 68 atm. [i] Impact sensitivity.

It is interesting to compare the impact of salt formation on the properties, such as density and heat of formation (and thus detonation properties), of two insensitive explosives (HTNP (1.86 g cm^{-3}) and 3-nitro-1,2,4-triazolate-5-one (NTO, 1.93 g cm^{-3})). Salts **2**, **3**, and **4** have lower densities than the parent at 1.69. 1.71, and 1.77 g cm^{-3}, while the densities of the analogous NTO salts are also markedly reduced to 1.67, 1.71 and 1.68 g cm^{-3}, although it would appear that strong hydrogen bonding should contribute to enhancing the densities.[13] While both parent explosives have slightly negative heats of formation (−0.07 kJ g^{-1}

and $-0.78\,\mathrm{kJ\,g^{-1}}$, respectively), the salts have increased positive values in the 0.95 to $1.40\,\mathrm{kJ\,g^{-1}}$ and 1.70 to $2.33\,\mathrm{kJ\,g^{-1}}$ ranges, respectively. However, while the salts have good thermal stabilities, none have detonation properties equivalent to the parent.

X-ray crystallography: Crystals of both **5** and **13**, suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of aqueous solutions at room temperature. Their structures are shown in Figures 2 and 3, and crystallographic data are summarized in Table 2. Both of them crystallize in the triclinic $P\bar{1}$ space group with one cation per TNP anion. The transfer of each proton from the NH group of HTNP to the ring nitrogen of 3,5-diaminotriazole and triaminoguanidine is confirmed in Figures 2a and 3a. For **5**,

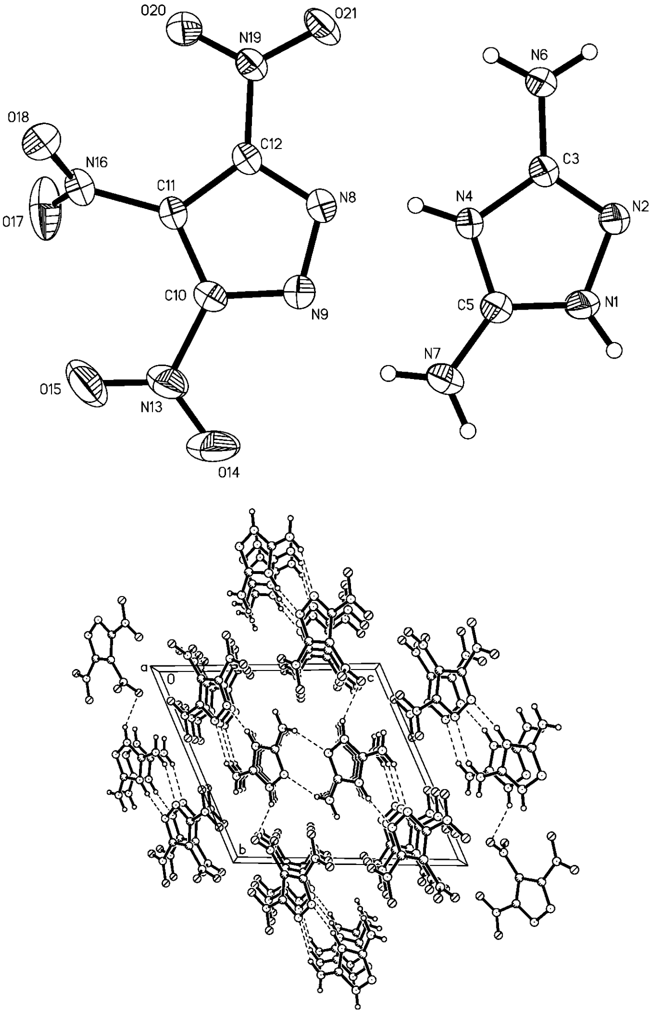


Figure 2. a) Thermal ellipsoid plot (30%) and labeling scheme for 3,5-diaminotriazolium TNP (**5**). Hydrogen atoms included but are unlabelled for clarity. b) Ball and stick packing diagram of **5** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

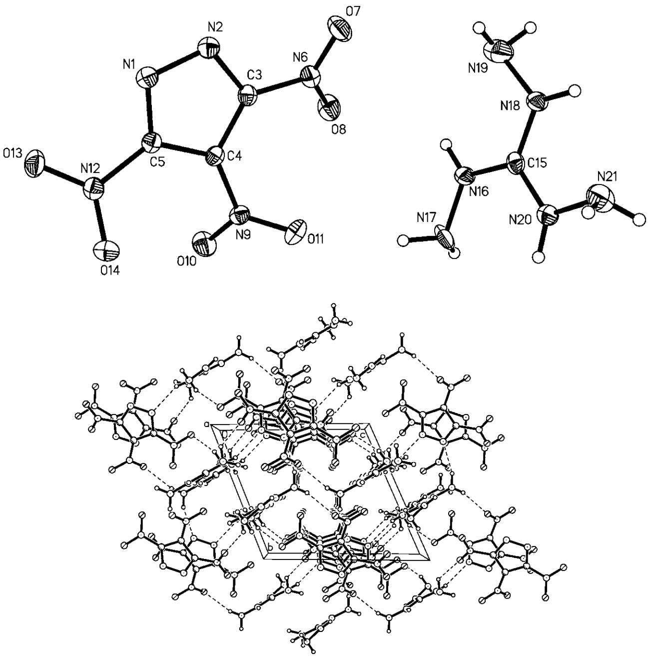


Figure 3. a) Thermal ellipsoid plot (30%) and labeling scheme for triaminoguanidium TNP (**13**). Hydrogen atoms included but are unlabelled for clarity. b) Ball and stick packing diagram of **13** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

Table 2. Crystallographic data for **5** and **13**.

	5	**13**
formula	$C_5H_6N_{10}O_6$	$C_4H_9N_{11}O_6$
CCDC number[a]	768959	768960
M_r	302.20	307.18
crystal size [$\mathrm{mm^{-3}}$]	$0.21\times0.14\times0.03$	$0.50\times0.17\times0.11$
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	5.1125(17)	7.4774(17)
b [Å]	10.676(4)	9.402(2)
c [Å]	11.579(4)	9.848(2)
α [°]	66.294(5)	65.955(3)
β [°]	78.501(5)	81.813(3)
γ [°]	84.852(5)	70.094(3)
V [Å^3]	567.1(3)	594.5(2)
Z	2	2
T [K]	293(2)	100(2)
ρ_{calcd} [$\mathrm{mg\,m^{-3}}$]	1.770 (20°C)	1.660 (20°C)
μ [$\mathrm{mm^{-1}}$]	0.160	0.155
$F(000)$	308	314
θ [°]	1.95 to 26.35	2.26 to 28.42
index ranges	$-6\leq h\leq6$ $-12\leq k\leq13$ $-14\leq l\leq14$	$-9\leq h\leq9$ $-12\leq k\leq12$ $-11\leq l\leq13$
reflections collected	5161	6292
independent reflections (R_{int})	2312 (0.0206)	2911 (0.0123)
data/restraints/parameters	2312/0/190	2911/12/237
GOF on F^2	1.033	1.056
R_1 ($I>2\delta(I)$)[b]	0.0536	0.0313,
wR_2 ($I>2\delta(I)$)[c]	0.1414	0.0838
R_1 (all data)	0.0827	0.0344
wR_2 (all data)	0.1618	0.0862
Largest diff. peak and hole [e Å^{-3}]	0.244 and −0.249	0.349 and 0.331

[a] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [b] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. [c] $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

the pyrazole and the triazole rings are in the same plane. In the TNP anion, 3(5)-nitro groups are in the plane of the pyrazole ring, and the 4-nitro group is twisted out of the plane of the pyrazole ring (116.2°). Each cation in **5** can form a variety of hydrogen bonds (N1···O18, 2.911(3); N4···N8, 2.777(3); N6···N2, 2.995(3); N7···N9, 3.029(3) Å). For **13**, all three nitro groups are tilted to the plane of the pyrazole (19.7, 43.3, and 22.6°). Its packing structure is configured by hydrogen bonds (N17···N1, 2.965(3); N17···O11, 3.172(3); N18···N2, 2.8997(15); N19···O14, 2.960(5); N21···O7, 3.169(4); N21···O10, 3.141(4); N16B···O10, 2.995(6); N18B···N2, 3.121(6); N20B···O11, 3.259(6) Å). The extensive hydrogen-bonding interactions between cations and anions form a complex 3D network. Further details are provided in the Supporting Information.

Conclusion

A family of energetic salts based on nitrogen-rich cations and the TNP anion was prepared and fully characterized. The structures of **5** and **13** were confirmed by single-crystal X-ray diffraction, which showed that there are extensive hydrogen-bonding interactions between the cation and anion in these salts. Densities for the TNP salts, measured with a gas pycnometer, were found to fall in the range between 1.61 (**10**) and 1.77 $g\,cm^{-3}$ (**4**), which places them in a class of relatively dense compounds. By using Cheetah 5, their detonation pressures and velocities were calculated to fall in the range of 23.74–31.9 GPa and 7586–8543 $m\,s^{-1}$. Salt **4**, with a detonation pressure and velocity of 31.89 GPa and 8543 $m\,s^{-1}$, is comparable with TATB (31.15 GPa and 8114 $m\,s^{-1}$). The specific impulse values of the TNP salts range between 228.9 and 269.6 s. Except for **1** (40 J) and **11** (35 J), the impact sensitivities of the TNP salts are more than 40 J. Based on rather high detonation properties, low impact sensitivities, and high stabilities, the TNP salts have potential as energetic materials.

Experimental Section

Caution! Although none of the compounds described herein have exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices.

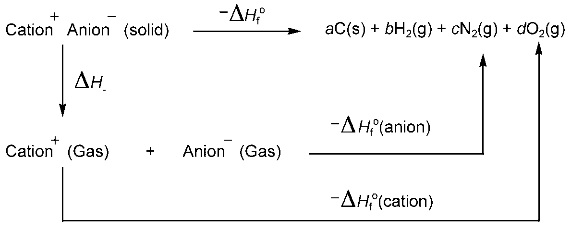
Reactants: Pyrazole (98 %, Alfa Aesar), aqueous ammonia (28–30 %, EMD), 1,2,4-1*H*-triazole (99.5 %), 3-amino-1,2,4-1*H*-triazole (95 %), 4-amino-1,2,4-4*H*-triazole (99 %), 3,5-diamino-1,2,4-1*H*-triazole (98 %), guanidinium carbonate (99 %), aminoguanidinium bicarbonate (98.5 %), (all from Acros), and silver nitrate (99.95 %, Salt Lake Metals) were used as received.

General methods: ^1H, ^{13}C, and ^{15}N NMR spectra were recorded on a 300 (Brucker AVANCE 300) and 500 MHz (Brucker AVANCE 500) NMR spectrometer operating at 300.13, 75.48, and 50.69 MHz, respectively, using [D$_6$]DMSO as a locking solvent unless otherwise stated. Chemical shifts were reported relative to Me_4Si. The melting and decomposition points were recorded on a differential scanning calorimeter at a scan rate of 10 °C min^{-1} in closed aluminum containers. TGA measurements were carried out by heating samples at 10 °C min^{-1} from 25 to 600 °C. IR spectra were recorded by using KBr pellets on a Bio-Rad model 3000 FTS spectrometer. Densities were measured at room temperature with a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical).

X-ray crystallography: An orange plate of dimensions $0.21\times0.14\times0.03\ mm^3$ (**5**) and a yellow prism of dimensions $0.50\times0.17\times0.11\ mm^3$ (**13**) were mounted on a MiteGen MicroMesh by using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated by using graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$). An Oxford Cobra low-temperature device was used to keep the crystals at a constant 293(2) and 100(2) K during data collection. Data collection was performed and the unit cell was initially refined by using APEX2 [v2009.3-0].[14] Data reduction was performed by using SAINT [v7.60 A][15] and XPREP [v2008/2].[16] Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS [v2008/1].[17] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v2008/4] system of programs.[18] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included by using a riding model.

Theoretical study: Calculations were performed with the Gaussian 03 (Revision D.01) suite of programs.[19] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out by using the B3LYP functional with 6-31+G** basis set,[20] 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 3), the heat of formation of a salt can be simplified by the formula given in Equation (1):

$$\Delta H_f^0(\text{salt},298\text{K}) = \Delta H_f^0(\text{cation},298\text{K}) + \Delta H_f^0(\text{anion},298\text{K}) - \Delta H_L \tag{1}$$



Scheme 3. Born–Haber cycle for the formation of energetic salts.

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)]:[21]

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

in which n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

$$U_{POT}\ [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \tag{3}$$

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

The heats of formation of the cations were computed by using the method of isodesmic reactions. The enthalpy of reaction (ΔH_{r298°) 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 (vD), and specific impulse (I_{sp}) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory by using Cheetah 5.0.[22]

3,4,5-Trinitropyrazole: 4-Amino-3,5-dinitropyrazole[12c] (0.50 g, 2.6 mmol, H_2O monosolvate) was added to a mixture of 30% H_2O_2 (3.5 mL) and concentrated H_2SO_4 (6.8 mL), with stirring and cooling in an ice bath. After 24 h, the reaction mixture was poured into cold water (35 mL) and extracted with diethyl ether (3 x15 mL). The organic solution was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the product was isolated as a light yellow solid (0.49 g, 2.4 mmol, 93%), which can be recrystallized from diethyl ether and benzene. ^{1}H NMR: $\delta = 9.42$ ppm (s, 1H); ^{13}C NMR: $\delta = 147.2$, 122.5 ppm; ^{15}N NMR (CD_3CN): $\delta = -26.6$, -26.7, -129.6 ppm; IR (KBr pellet): 3147, 1595, 1554, 1494, 1455, 1359, 1334, 1202, 1128, 1024, 843, 790, 763, 558, 505 cm^{-1}.

Ammonium 3,4,5-trinitropyrazolate (1): 3,4,5-Trinitropyrazole (203 mg, 1 mmol) and aqueous ammonia (61 mg, 1 mmol) were placed in water (5 mL). The mixture was stirred at room temperature for 0.5 h; water was removed under reduced pressure. The residual solid was crystallized with ethyl acetate (white plates, 187 mg, 85%). ^{1}H NMR: $\delta = 7.09$ ppm (t, $J = 98.76$ Hz, 4H); ^{13}C NMR: $\delta = 122.1$, 147.0 ppm; IR (KBr pellet): 765, 806, 849, 1026, 1128, 1165, 1318, 1355, 1421, 1456, 1512, 1527, 2812, 3262, 3318 cm^{-1}; elemental analysis calcd (%) for $C_3H_4N_6O_6$ (220.10): C 16.37, H 1.83, N 38.18; found: C 16.39, H 1.67, N 37.90.

General procedure for synthesis of the salts 2–8: Triazole (1 mmol), 3-aminotriazole (1 mmol), 4-aminotriazole (1 mmol), 3,5-diaminotriazole (1 mmol), or aminoguanidinium bicarbonate (1 mmol), or guanidinudium carbonate (0.5 mmol) or 3,6-diguanidino-1,2,4,5-tetrazine (0.5 mmol) was added to a solution of 3,4,5-trinitropyrazole (1 mmol) in water (10 mL). The mixtures were stirred at room temperature until transparent solutions were formed. If not, more water was added to the mixtures. Then, water was slowly evaporated to leave the solid product in good yield.

1,2,4–1*H*-Triazolium 3,4,5-trinitropyrazolate (2): Light yellow plates (253 mg, 93%); ^{1}H NMR: $\delta = 9.39$ (s, 2H), 14.75 ppm (s, 2H); ^{13}C NMR: $\delta = 122.1$, 142.9, 147.0 ppm; ^{15}N NMR: $\delta = -9.0$, -9.6, -43.8, -113.3, -181.5 ppm; IR (KBr pellet): 628, 846, 941, 1126, 1323, 1353, 1462, 1525, 1555, 2638, 2904, 3154 cm^{-1}; elemental analysis calcd (%) for $C_5H_4N_8O_6$ (272.14): C 22.07, H 1.48, N 41.18; found: C 22.10, H 1.35, N 40.69.

3-Amino-1,2,4–1*H*-Triazolium 3,4,5-trinitropyrazolate (3): Yellow plates (261 mg, 91%); ^{1}H NMR: $\delta = 8.27$ ppm (s, 1H; CH); ^{13}C NMR: $\delta =$ 122.1, 139.1, 147.0, 150.7 ppm; ^{15}N NMR: $\delta = -9.2$, -9.8, -45.1, -97.4, -192.5, -221.7, -310.2 ppm; IR (KBr pellet): 470, 615, 678, 847, 947, 1132, 1323, 1349, 1456, 1520, 1672, 3120, 3365, 3429 cm^{-1}; elemental analysis calcd (%) for $C_5H_5N_9O_6$ (287.15): C 20.91, H 1.76, N 43.90; found: C 20.90, H 1.62, N 43.66.

4-Amino-1,2,4–4*H*-triazolium 3,4,5-trinitropyrazolate (4): Light yellow needles (273 mg, 95%); ^{1}H NMR: $\delta = 6.71$ (br s, 3H), 9.50 ppm (s, 2H; CH); ^{13}C: $\delta = 122.0$, 143.9, 146.9 ppm; ^{15}N NMR: $\delta = -9.1$, -9.8, -44.9, -113.6, -175.3, -295.0 ppm; IR (KBr pellet): 615, 762, 845, 927, 1020, 1203, 1327, 1365, 1454, 1523, 3170, 3297, 3426 cm^{-1}; elemental analysis calcd (%) for $C_5H_5N_9O_6$ (287.15): C 20.91, H 1.76, N 43.90; found: C 20.92, H 1.59, N 43.60.

3,5-Diamino-1,2,4–1*H*- triazolium 3,4,5-trinitropyrazolate (5): Orange plates (278 mg, 92%); ^{1}H NMR: $\delta = 6.58$ ppm (br s, 4H; NH_2); ^{13}C: $\delta =$ 122.1, 147.1, 151.4 ppm; ^{15}N NMR: $\delta = -9.1$, -9.8, -44.7, -187.2, -231.6, -314.9 ppm; IR (KBr pellet): 765, 800, 846, 1128, 1322, 1361, 1451, 1510, 1668, 1691, 3261, 3440 cm^{-1}; elemental analysis calcd (%) for $C_5H_6N_{10}O_6$ (302.16): C 19.87, H 2.00, N 46.35; found: C 19.85, H 1.87, N 46.02.

Guanidinium 3,4,5-trinitropyrazolate (6): Light yellow plates (246 mg, 94%); ^{1}H NMR: $\delta = 6.89$ ppm (s); ^{13}C NMR: $\delta = 122.1$, 147.0, 158.0 ppm; IR (KBr pellet): 579, 677, 761, 849, 1024, 1128, 1315, 1353, 1452, 1514, 1546, 1655, 3177, 3427, 3477 cm^{-1}; elemental analysis calcd (%) for $C_4H_6N_8O_6$ (262.14): C 18.33, H 2.31, N 42.75; found: C 18.39, H 2.17, N 42.48.

Aminoguanidinium 3,4,5-trinitropyrazolate (7): Light yellow plates (258 mg, 93%); ^{1}H NMR: $\delta = 8.53$ (s, 1H; NH), 7.12 (s, 2H; NH_2), 6.75 (s, 2H; NH_2), 4.67 ppm (s, 2H; NH_2); ^{13}C NMR: $\delta = 158.7$, 147.0, 122.1 ppm; IR (KBr pellet): 3500, 3468, 3372, 1663, 1513, 1455, 1361, 1313, 1128, 959, 844, 646 cm^{-1}; elemental analysis calcd (%) for $C_4H_7N_9O_6$ (277.16): C 17.33, H 2.55, N 45.48; found: C 17.26; H 2.47; N 45.24.

3,6-Diguanidino-1,2,4,5-tetrazine di-3,4,5-trinitropyrazolate (8): Red plates (306 mg, 96%); ^{1}H NMR: $\delta = 8.17$ ppm (s); ^{13}C NMR: $\delta = 122.1$, 147.0, 154.3, 158.5 ppm; IR (KBr pellet): 601, 846, 1035, 1075, 1320, 1358, 1518, 1541, 1616, 1698, 3431 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{10}N_{20}O_{12}{\cdot}2H_2O$ (638.34): C 18.82, H 2.21, N 43.88; found: C 18.81, H 2.03, N 43.73.

General procedure for synthesis of the salts 9–13: A solution of 3,4,5-triaminotriazolium chloride, 1,4-dimethyl-5-aminotetrazolium iodide, 1,5-diamino-4-methyltetrazolium iodide, diaminoguanidinium chloride, or triaminoguanidinium chloride in water (15 mL) was added dropwise to a silver 3,4,5-trinitropyrazolate (1 mmol) suspension in water (25 mL). After the mixture was stirred at room temperature for 6 h, silver chloride was removed by filtration, and washed with water. The filtrate was slowly evaporated to leave the solid product in a good yield.

3,4,5-Triaminotriazolium 3,4,5-trinitropyrazolate (9): Light yellow needles (304 mg, 96%); ^{1}H NMR: $\delta = 5.57$ (s, 2H, NH_2), 7.06 ppm (br s, 4H, NH_2); ^{13}C NMR: $\delta = 122.1$, 147.0, 150.0 ppm; ^{15}N NMR (30 °C): $\delta = -8.9$, -9.5, -43.0, -225.7, -310.0 ppm; ^{15}N NMR (80 °C): $\delta = -8.9$, -9.0, -43.3, -188.5, -225.2, -310.0, -317.5 ppm; IR (KBr pellet): 3458, 3418, 3365, 3328, 1677, 1631, 1554, 1519, 1455, 1354, 1319, 1172, 962, 848 cm^{-1}; elemental analysis calcd (%) for $C_5H_7N_{11}O_6$ (317.18): C 18.93, H 2.22, N 48.58; found: C 18.94, H 2.07, N 48.49.

1,4-Dimethyl-5-aminotetrazolium 3,4,5-trinitropyrazolate (10): Light yellow needles (297 mg, 94%); ^{1}H NMR: $\delta = 3.86$ (s, 6H, CH_3), 9.09 ppm (br s, 2H, NH_2); ^{13}C NMR: $\delta = 33.9$, 122.1, 146.8, 148.4 ppm; IR (KBr pellet): 504, 847, 1309, 1350, 1452, 1510, 1545, 1699, 3017, 3376, 3392 cm^{-1}; elemental analysis calcd (%) for $C_6H_8N_{10}O_6$ (316.19): C 22.79, H 2.55, N 44.30; found: C 22.95, H 2.55, N 43.96.

1,5-Diamino-4-methyltetrazolium 3,4,5-trinitropyrazolate (11): Light yellow plates (292 mg, 92%); ^{1}H NMR: $\delta = 3.86$ (s, 3H, CH_3), 7.01 (s, 2H, NH_2), 8.99 ppm (s, 2H, NH_2); ^{13}C NMR: $\delta = 34.5$, 122.0, 146.9, 147.5 ppm; IR (KBr pellet): 507, 767, 846, 1301, 1327, 1365, 1455, 1515, 1709, 2957, 3184, 3336, 3435 cm^{-1}; elemental analysis calcd (%) for $C_5H_7N_{11}O_6$ (317.18): C 18.93, H 2.22, N 48.58; found: C 19.24, H 2.26, N 48.48.

Diaminoguanidinium 3,4,5-trinitropyrazolate (12): Light yellow plates (277 mg, 95%); ^{1}H NMR: $\delta = 4.54$ (s, 4H; NH_2), 7.13 (s, 2H; NH_2), 8.54 ppm (s, 2H, NH); ^{13}C NMR: $\delta = 122.1$, 147.1, 159.9 ppm; IR (KBr pellet): 677, 846, 924, 1201, 1320, 1357, 1451, 1516, 1678, 3212, 3385, 3503 cm^{-1}; elemental analysis calcd (%) for $C_4H_8N_{10}O_6$ (292.17): C 16.44, H 2.76, N 47.94; found: C 16.48, H 2.63, N 47.83.

Triaminoguanidinium 3,4,5-trinitropyrazolate (13): Light yellow plates (261 mg, 85%); ^{1}H NMR: $\delta = 4.47$ (s, 6H, NH_2), 8.58 ppm (s, 3H, NH); ^{13}C NMR: $\delta = 122.1$, 147.0, 159.0 ppm; ^{15}N NMR (CD_3CN): $\delta = -17.9$, -18.8, -286.2, -327.9 ppm; IR (KBr pellet): 545, 636, 798, 844, 951, 1129, 1296, 1324, 1364, 1452, 1509, 1684, 3211, 3362 cm^{-1}; elemental analysis calcd (%) for $C_4H_9N_{11}O_6$ (307.18): C 15.64, H 2.95, N 50.16; found: C 15.70, H 2.82, N 49.85.

Triaminoguanidinium 2,4,5-trinitroimidazolate (14): A solution of triaminoguanidinium chloride (1 mmol) was added dropwise to a silver 2,4,5-trinitroimidazolate (1 mmol) suspension in water (25 mL). After the mixture was stirred at room temperature for 6 h, silver chloride was filtered off and washed with water. The filtrate was slowly evaporated to leave light yellow plates (267 mg, 87%). ^{1}H NMR: $\delta = 4.48$ (s, 6H, NH_2), 8.58 ppm (s, 3H, NH); ^{13}C NMR: $\delta = 137.8$, 146.4, 159.0 ppm; ^{15}N NMR (CD_3CN): $\delta = -16.3$, 16.9, -125.4, -286.3, -328.0 ppm; IR (KBr pellet): 648, 806, 864, 943, 1014, 1139, 1290, 1325, 1462, 1536, 1686, 3334, 3379 cm^{-1}; elemental analysis calcd (%) for $C_4H_9N_{11}O_6$ (307.18): C 15.64, H 2.95, N 50.16; found: C 15.73, H 2.87, N 49.83.

Acknowledgements

The authors gratefully acknowledge the support of DTRA (HDTRA1-07-1-0024), and ONR (N00014-10-1-0097).

---

[1] a) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112–2118; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004–2009; b) D. E. Chavez, M. A. Hiskey, R. D. Gilardi, *Angew. Chem.* **2000**, *112*, 1861–1863; *Angew. Chem. Int. Ed.* **2000**, *39*, 1791–1793; c) J. Giles, *Nature* **2004**, *427*, 580–581; d) M. H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.* **2004**, *116*, 5032–5036; *Angew. Chem. Int. Ed.* **2004**, *43*, 4924–4928.

[2] a) T. M. Klapötke, C. M. Rienacker, *Propellants Explos. Pyrotech.* **2001**, *26*, 43–47; b) A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, P. Mayer, H. Noth, M. Warchhold, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1477–1482; c) A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, H. Piotrowskia, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2117–2121; d) T. M. Klapötke, C. Kuffer, P. Mayer, K. Polborn, A. Schulz, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 5949–5958; e) T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *J. Am. Chem. Soc.* **2005**, *127*, 2032–2033; f) T. M. Klapötke, K. Karaghiosoff, P. Mayer, A. Penger, J. M. Welch, *Propellants Explos. Pyrotech.* **2006**, *31*, 188–195.

[3] a) H. Xue, S. W. Arritt, B. Twalmley, J. M. Shreeve, *Inorg. Chem.* **2004**, *43*, 7972–7977; b) C. M. Jin, C. F. Ye, C. Piekarski, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2005**, 3760–3767; c) H. Xue, J. M. Shreeve, *Adv. Mater.* **2005**, *17*, 2142- 2146; d) H. X. Gao, C. F. Ye, R. W. Winter, G. L. Gard, M. E. Sitzmann, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2006**, 3221–3226; e) Y. Gao, C. F. Ye, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2006**, *12*, 9010–9018; f) 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; g) H. Xue, H. X. Gao, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2006**, 2959–2965.

[4] a) T. M. Klapötke, J. Stierstorfer, *Helv. Chim. Acta* **2007**, *90*, 2132–2150; b) M. Göbel, T. M. Klapötke, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1006–1017; c) G. Steinhauser, T. M. Klapötke, *Angew. Chem.* **2008**, *120*, 3376–3394; *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347; d) C. Darwich, T. M. Klapötke, C. M. Sabate, *Chem. Eur. J.* **2008**, *14*, 5756–5771; e) T. M. Klapötke, C. M. Sabate, *Eur. J. Inorg. Chem.* **2008**, 5350–5366; f) T. M. Klapötke, J. Stierstorfer, A. U. Wallek, *Chem. Mater.* **2008**, *20*, 4519–4530.

[5] a) Z. Zeng, H. X. Gao, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* **2007**, *17*, 3819–3826; b) Y. Guo, H. X. Gao, B. Twamley, J. M. Shreeve, *Adv. Mater.* **2007**, *19*, 2884–2888; c) Y. G. Huang, H. X. Gao, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2007**, 2025–2030; d) H. X. Gao, Y. G. Huang, C. F. Ye, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2008**, *14*, 5596–5603; e) H. X. Gao, Z. Zeng, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2008**, *14*, 1282–1290; f) Y. Huang, H. X. Gao, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2008**, 2560–2568.

[6] a) J. Stierstorfer, K. R. Tarantik, T. M. Klapötke, *Chem. Eur. J.* **2009**, *15*, 5775–5792; b) T. M. Klapötke, C. M. Sabate, *New J. Chem.* **2009**, *33*, 1605–1617; c) T. M. Klapötke, C. M. Sabate, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1812–1822; d) T. M. Klapötke, J. Stierstorfer, *Dalton Trans.* **2009**, 643–653; e) T. M. Klapötke, C. M. Sabate, A. Penger, M. Rusan, J. M. Welch, *Eur. J. Inorg. Chem.* **2009**, 880–896; f) T. M. Klapötke, C. M. Sabate, *Z. Anorg. Allg. Chem.* **2010**, *636*, 163–175.

[7] a) H. X. Gao, Y. H. Joo, B. Twamley, Z. Q. Zhou, J. M. Shreeve, *Angew. Chem.* **2009**, *121*, 2830–2833; *Angew. Chem. Int. Ed.* **2009**, *48*, 2792–2795; b) Y. G. Huang, H. X. Gao, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 917–923; c) Y. H. Joo, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 3198–3203; d) R. H. Wang, Y. Guo, Z. Zeng, J. M. Shreeve, *Chem. Commun.* **2009**, 2697–2699; e) Y. H. Joo, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 9097–9104; f) R. H. Wang, Y. Guo, Z. Zeng, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 2625–2634.

[8] a) M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys.* **1968**, *48*, 23–35; b) M. J. Kamlet, J. E. Ablard, *J. Chem. Phys.* **1968**, *48*, 36–42; c) M. J. Kamlet, Dickinso. C, *J. Chem. Phys.* **1968**, *48*, 43–50.

[9] a) H. X. Gao, C. F. Ye, O. D. Gupta, J. C. Xiao, M. A. Hiskey, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2007**, *13*, 3853–3860; b) H. Xue, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* **2005**, *15*, 3459–3465; c) C. Darwich, T. M. Klapötke, J. M. Welch, M. Suceska, *Propellants Explos. Pyrotech.* **2007**, *32*, 235–243; d) T. M. Klapötke, P. Mayer, C. M. Sabate, J. M. Welch, N. Wiegand, *Inorg. Chem.* **2008**, *47*, 6014–6027.

[10] a) G. Hervé, FR Patent 2917409, **2008**; b) G. Hervé, WO Patent 2008152525, **2008**; c) G. Hervé, US Patent 20090186931, **2009**.

[11] G. Hervé, C. Roussel, H. Graindorge, *Angew. Chem.* **2010**, *122*, 3245–3249; *Angew. Chem. Int. Ed.* **2010**, *49*, 3177–3181.

[12] a) J. W. A. Janssen, C. L. Habraken, *J. Org. Chem.* **1971**, *36*, 3081–3084; b) J. W. A. Janssen, H. J. Koeners, C. G. Kruse, C. L. Habraken, *J. Org. Chem.* **1973**, *38*, 1777–1782; c) R. D. Schmidt, G. S. Lee, P. R. Pagoria, A. R. Mitchell, R. Gilardi, *J. Heterocycl. Chem.* **2001**, *38*, 1227–1230.

[13] H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2007**, *19*, 1731–1739.

[14] Bruker, APEX2 v2009/3-0, Bruker AXS Inc., Madison, **2009**.

[15] Bruker, SAINT v7.60A, Bruker AXS Inc., Madison, **2009**.

[16] Bruker, XPREP v2008/2, Bruker AXS Inc., Madison, **2008**.

[17] Bruker, SADABS v2008/1, Bruker AXS Inc., Madison, **2008**.

[18] Bruker, SHELXTL v2008/4, Bruker AXS Inc., Madison, **2008**.

[19] 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**.

[20] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**.

[21] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367.

[22] 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**.

Received: May 8, 2010