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Energetic Salts Based on Monoanions of *N*,*N*-Bis(1*H*-tetrazol-5-yl)amine and 5,5′-Bis(tetrazole)

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Abstract: High-density energetic salts that contain nitrogen-rich cations and the 5-(tetrazol-5-ylamino)tetrazolate ($HBTA^-$) or the 5-(tetrazol-5-yl)tetrazolate (HBT^-) anion were readily synthesized by the metathesis reactions of sulfate salts with barium compounds, such as bis[5-(tetrazol-5-ylamino)tetrazolate] ($Ba(HBTA)_2$), barium iminobis(5-tetrazolate) (BaBTA), or barium 5,5′-bis(tetrazolate) (BaBT) in aqueous solution. All salts were fully characterized by IR spectroscopy, multinuclear (^1H, ^{13}C, ^{15}N) NMR spectroscopy, elemental analyses, density, differential scanning calorimetry (DSC), and impact sensitivity. $Ba(HBTA)_2{\cdot}4H_2O$ crystallizes in the triclinic space group $P\bar{1}$, as determined by single-crystal X-ray diffraction, with a density of 2.177 g cm^{-3}. The densities of the other organic energetic salts range between 1.55 and 1.75 g cm^{-3} as measured by a gas pycnometer. The detonation pressure (P) values calculated for these salts range from 19.4 to 33.6 GPa, and the detonation velocities (v_D) range from 7677 to 9487 m s^{-1}, which make them competitive energetic materials. Solid-state ^{13}C NMR spectroscopy was used as an effective technique to determine the structure of the products that were obtained from the metathesis reactions of biguanidinium sulfate with barium iminobis(5-tetrazolate) (BaBTA). Thus, the structure was determined as an HBTA salt by the comparison of its solid-state ^{13}C NMR spectroscopy with those of ammonium 5-(tetrazol-5-ylamino)tetrazolate (AHBTA) and diammonium iminobis(5-tetrazolate) (A_2BTA).

Keywords: density functional calculations · energetic materials · nitrogen-rich salts · NMR spectroscopy · tetrazoles

Introduction

Modern high-energy density materials (HEDM), in which energetic nitrogen-rich salts are among the most recent and exciting developments, continue to attract considerable interest (Scheme 1).[1–15] The attractive syntheses of novel energetic products include a wide range of neutral molecules and salts, such as nitrogen-rich salts,[4] 5-azidotetrazoles[5] and their salts,[6] derivatives of 1,5-diaminotetrazole,[7] 1,5-diamino-4-methyltetrazolium dinitramide,[8] mono-, di-, and trisubstituted nitroiminotetrazoles,[9] hypergolic ionic liquids,[10] energetic nitrate ester,[11] polyazido heteroaromatic compounds,[12] salts of pentanitrogen cation,[13] octanitrocubane (ONC),[14] 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20),[15] and salts of *N*,*N*′-dinitrourea (DNU).[16] Novel properties, such as high density, high positive heat of formation, and high thermal stability, suggest energetic organic compounds with high nitrogen content for a variety of unique applications including gas generators,[17] smoke-free pyrotechnic fuels,[18,19] fire extinguishers onboard military aircraft,[20,21] solid fuels in micropropulsion systems,[22,23] effective precursors for carbon nanospheres[24,25] and carbon nitride nanomaterials.[26–29]

5-N-Substituted tetrazoles,[30] for example, 5-aminotetrazoles,[31] 5,5′-azotetrazolates,[32] bis(1*H*-tetrazol-5-yl)amine (H_2BTA),[4,33] 5,5′-bis(1*H*-tetrazolyl)hydrazine (BTH),[34] and 5-azido-1*H*-tetrazole[6] have nitrogen contents greater than 82%, and many of their derivatives that bear tetrazole group(s) are weakly acidic and thus have constituted anionic moieties in energetic salts.[4,31,35,36] Our recent communications[4,37] about dianionic salts of *N*,*N*-bis(1*H*-tetrazol-5-yl)-amine (Scheme 1) have aroused wide interest in many applications, such as high-energetic materials,[31,33,35,36,38–61] metal-

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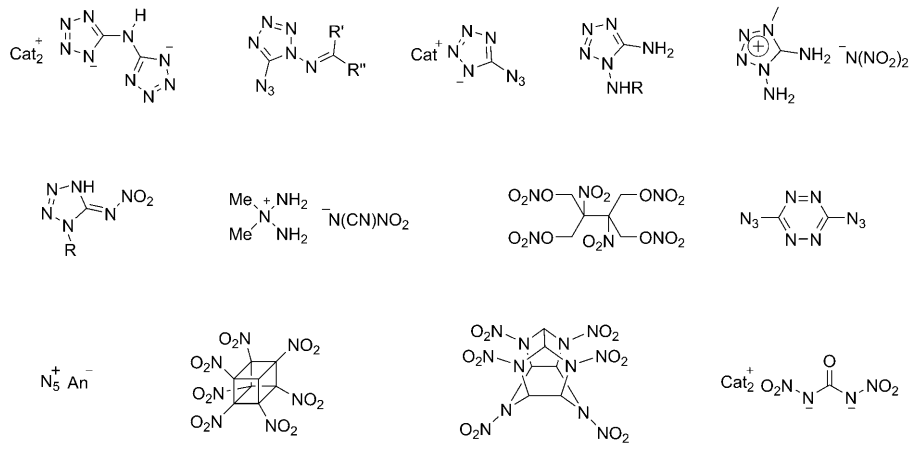
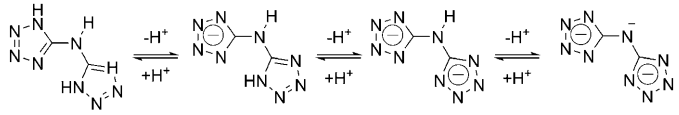


Scheme 1. Recent advances in HEDM (Cat = cation; An = anion).

lic coordination compounds[62–65] and polymers,[66,67] theoretical calculations and physical predictions,[68–72] functional ionic liquids,[73–77] and so on.[78,79]

Recently, the single-crystal X-ray structure of H_2BTA was reported.[33] H_2BTA is an amine substituted with two tetrazole groups, theoretically possessing three reversible types of deprotonated, di-deprotonated, tri-deprotonated modes (Scheme 2).[80] Some metal-containing H_2BTA derivatives



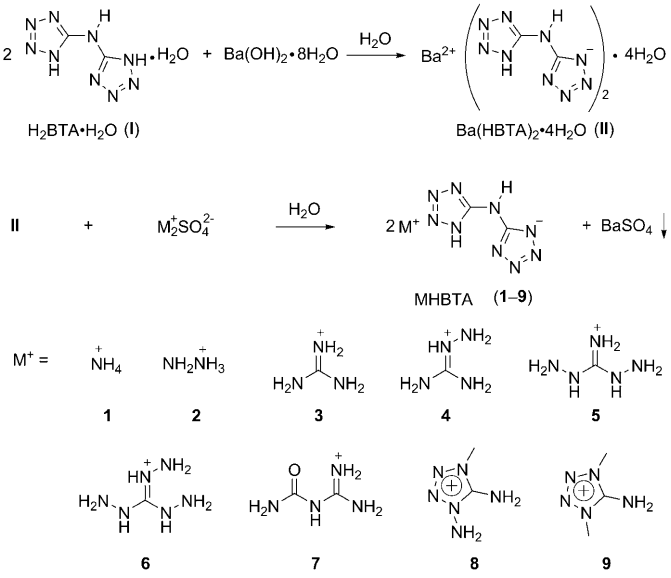
Scheme 2. Three reversible types of deprotonated, di-deprotonated, and tri-deprotonated modes for H_2BTA.

have been readily obtained because a planar H_2BTA functional heterocycle contains nine nitrogen electron-donating atoms.[62–67,80–84] On the other hand, the acidic protons of H_2BTA enable the formation of the corresponding salts by reactions with nitrogen-rich bases. Although there are several reports of salts of H_2BTA, most of them appear in patents or unpublished documents.[85] Previously, we reported bis(4-amino-1,2,4-triazolium) (BTA), which, when subjected to microwave heating, gave rise to a nanopowder.[37] After that, based on the dianion of H_2BTA, we prepared several salts ($M_2^+BTA^{2-}$) with relatively high detonation pressures (17.5–34.9 GPa) and detonation velocities (7636–9926 m s^{-1}).[4] We believe that salts of the monoanion ($HBTA^-$) have not yet been paired with nitrogen-rich cations. The promising detonation properties and interesting applications of $M_2^+BTA^{2-}$ encouraged us to do further research on the monoanionic salts of H_2BTA. In this paper, we describe the syntheses and theoretical calculations of monoanionic salts of H_2BTA (M^+ $HBTA^-$), which were paired with nitrogen-rich energetic cations. Also reported in this work is the formation of M^+ $HBTA^-$ rather than $M^{2+}BTA^{2-}$ when, for example, biguanidinium sulfate was reacted with barium iminobis(5-tetrazolate) (BaBTA). This was confirmed by solid-state ^{13}C NMR spectroscopy.

Result and Discussion

Sodium dicyanamide was reacted with sodium azide under Brønsted acidic conditions to yield the corresponding *N,N*-bis(1*H*-tetrazol-5-yl) amine as a monohydrate ($H_2BTA{\cdot}H_2O$, **I**) in 77% yield (Scheme 3).[81,86] The reaction of barium hydroxide with **I** (1:2 molar ratio) in water gave the white salt $Ba(HBTA)_2{\cdot}4H_2O$ (**II**), which was slightly soluble in water at 25 °C and dissolved in hot water. It was purified by recrystallization in water and was characterized by IR spectroscopy, multinuclear NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray diffraction. The NMR spectroscopic data of **II** were collected in [D$_6$]DMSO. ^1H NMR spectroscopy of **II** showed a large, broad peak at $\delta =$ 4.75 ppm and a small peak at $\delta = 10.4$ ppm. A signal at $\delta =$ 156.3 ppm in the ^{13}C NMR spectrum was downfield from **I** ($\delta = 154.7$ ppm),[33,81] which suggests anionic properties of the tetrazole ring of **II**. The ^{15}N NMR spectrum of **II** is given in Figure 1 and discussed below.

The thermal behavior of **II** was investigated by DSC and TGA. The thermal degradation temperature was 312 °C as determined by TGA, which is consistent with the exotherm



Scheme 3. Syntheses of HBTA salts from the metathesis reactions of **II** with sulfates with singly charged cations.

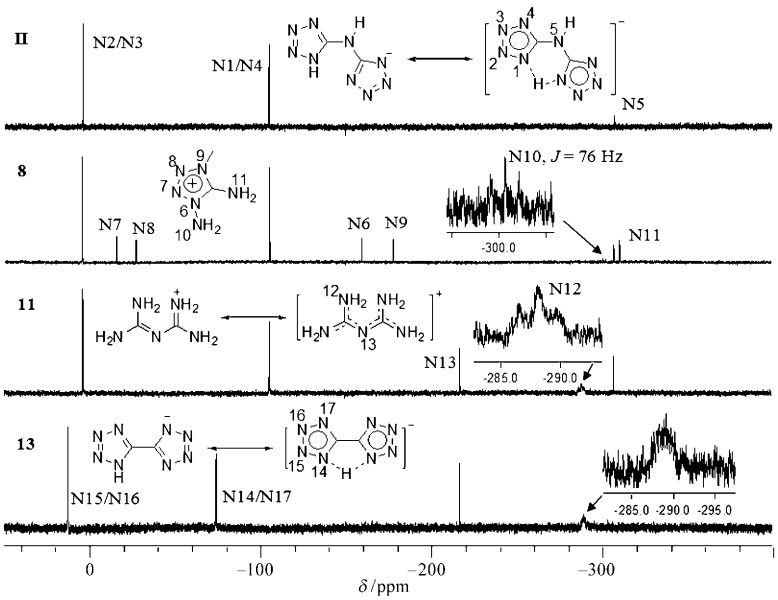


Figure 1. ^{15}N NMR spectra of **II**, **8**, **11**, and **13** measured in [D_6]DMSO. Chemical shifts are given in ppm with respect to $MeNO_2$ as external standard.

found by DSC beginning at around 314 °C. The DSC curve shows an endotherm at 141 °C, which corresponds to the loss of water. This was supported by 11.3 % weight loss from 128 to 175 °C (calcd 14.0 % for four water molecules of crystallization) in its TGA curve. No melting point was observed. The structure was further confirmed by single-crystal X-ray structuring.

A crystal of **II** suitable for X-ray diffraction was obtained by slow recrystallization from water at room temperature. The structure is shown in Figure 2. Crystallographic and structural refinement data for compound **II** are listed in Table 1, and selected bond lengths and angles are included in Table 2. Tables of atomic coordinates and thermal displacement parameters and a complete list of bond angles and distances for **II** can be found in the Supporting Information. Single-crystal X-ray diffraction revealed that compound **II** crystallizes in the triclinic space group $P\bar{1}$. As shown in Figure 2a, the unit cell consists of two barium cations, four HBTA anions, and eight crystal water molecules. In the molecules of **II**, each Ba^{II} ion is nine-coordinated with two oxygen atoms of water as bridges between two barium cations. The Ba–N distance is between 2.8663(15) and 2.9664(16) Å. The bond lengths of the HBTA anion are similar to values in the literature.[83b] The experimental density of **II** is 2.17 g cm^{-3} (calcd 2.177 g cm^{-3}, X-ray).

Several compounds (**1**–**9**) were prepared by the metathesis of sulfate salts with **II** in aqueous solution (Scheme 3). They were characterized by elemental and NMR spectral analysis, DSC, and TGA. ^{13}C NMR spectra occur in a small range from $\delta = 156.1$ to 156.3 ppm, which is very close to that of **II** ($\delta = 156.3$ ppm). Interestingly, the metathesis reactions of barium aminobis(tetrazolate) (**III**) and sulfates with doubly charged cations (**IV** and **V**) gave salts of HBTA anion (**10** and **11**) instead of the expected BTA salts (Scheme 4). Salts **10** and **11** were characterized by elemental and NMR spectral analysis, DSC, and TGA. ^{13}C NMR spectroscopic signals in [D_6]DMSO assigned to **11** occur at $\delta = 156.3$ and 159.7 ppm. The peak at $\delta =$ 159.7 ppm is assigned to the guanylguanidinium cation and is at the same position in guanylguanidinium dinitrourea dianionic salts[16] and guanylguanidinium 5-aminotetrazolate.[31] The other signal at $\delta =$ 156.3 ppm apparently shows that the anionic species is an HBTA anion ($\delta = 156.1$–156.3 ppm) rather than a BTA dianion. To be sure of the structure of **11**, solid-state ^{13}C NMR spectra of salts **1**, **11**, and **14**, were determined (Figure 3). The chemical shift of the BTA dianion in **14** is very different from the HBTA anion in **1**. For **14**, a single peak at $\delta =$ 159.4 ppm was found in solid-state ^{13}C NMR spectroscopy, thereby suggesting the symmetry of the BTA dianion. For **1**, two peaks at $\delta = 157.1$ and 151.2 ppm were found, thereby suggesting the asymmetry of the HBTA anion in the solid state, although there was only one peak at $\delta = 156.1$ ppm because of the free movement of the proton when the ^{13}C NMR spectrum was recorded in [D_6]DMSO. For **11**, there were three peaks at $\delta = 160.2$, 156.2, and 151.7 ppm. The signal at $\delta = 160.2$ ppm, close to that of the guanylguanidinium cation in [D_6]DMSO, was assigned to the guanylguanidinium cation in the solid state. The remainder of the signals at $\delta = 156.2$ and 151.7 ppm, therefore, were assigned to the HBTA anion in the solid state. By using solid-state ^{13}C NMR spectroscopy, we determined the structure of **11** to be the form MHBTA rather than MBTA. This technique is useful in determining the structural information of salts, which may be hard to recystallize.

Salts **1**, **3**, and **4** can also be synthesized by the reaction of **II** with corresponding carbonates. Salt **10** can be obtained by the reaction of **I** and carbohydrazide (Scheme 5). Salts **12** and **13** were synthesized based on 5-(tetrazole-5-yl)tetrazolate (HBT) by the metathesis of barium 5,5′-bis(tetrazolate) (**VI**) with the corresponding sulfates **IV** and **V**. The signals in the ^{13}C NMR spectra in [D_6]DMSO are at $\delta = 149.2$ ppm for **12** and $\delta = 149.3$ ppm for **13** (Scheme 6).

The ^{15}N NMR spectra of barium salt **II**, HBTA salts **8** and **11**, and HBT salt **13** were obtained in [D_6]DMSO (Figure 1). The chemical shifts are given with respect to CH_3NO_2 as external standard. The ^{15}N NMR spectrum of **II** shows three signals at $\delta = -307.0$ (N5), −104.7 (N1/N4), and 4.3 ppm (N2/N3). The signals are farther downfield than

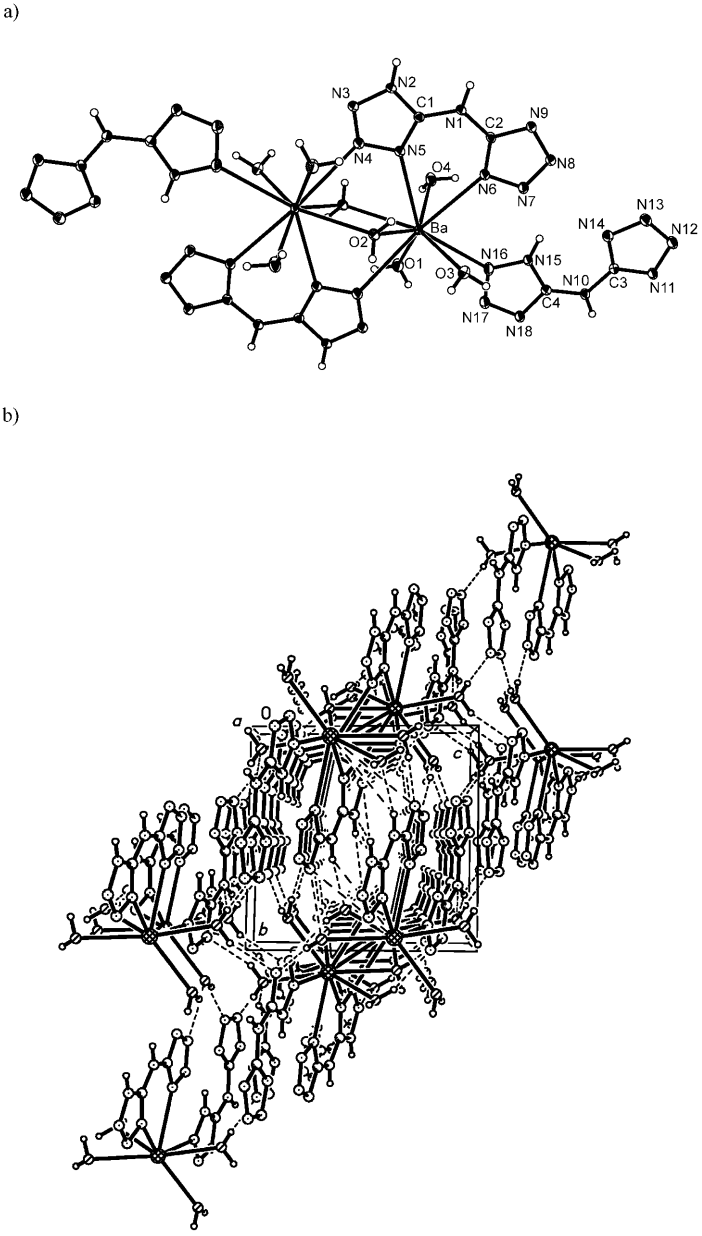


Figure 2. a) Molecular structure of **II** (thermal displacement at 30% probability). Hydrogen atoms are shown. b) Ball-and-stick packing diagram of **II** viewed down the *a* axis. Dashed lines indicate hydrogen bonding.

Table 1. Crystal data and structure refinement for **II**.

empirical formula	$C_4H_{12}BaN_{18}O_4$
M_r	513.66
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	8.9204(8)
b [Å]	9.5202(9)
c [Å]	9.5760(9)
α [°]	89.0880(10)
β [°]	81.5120(10)
γ [°]	76.9750(10)
V [Å^3]	783.50(13)
Z	2
ρ_{calcd} (20 °C) [Mg m^{-3}]	2.177
μ [mm^{-1}]	2.600
θ range [°]	3.80 to 67.92°
independent reflns	3874 (R_{int} = 0.0147)
data/restraints/parameters	3874/9/268
GOF	1.094
R_1 ($I > 2\sigma(I)$)[a]	0.0171
wR_2 ($I > 2\sigma(I)$)	0.0431
R_1 (all data)	0.0176
wR_2 (all data)	0.0435
largest differential peak and hole [e Å^{-3}]	0.683 and −0.607

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

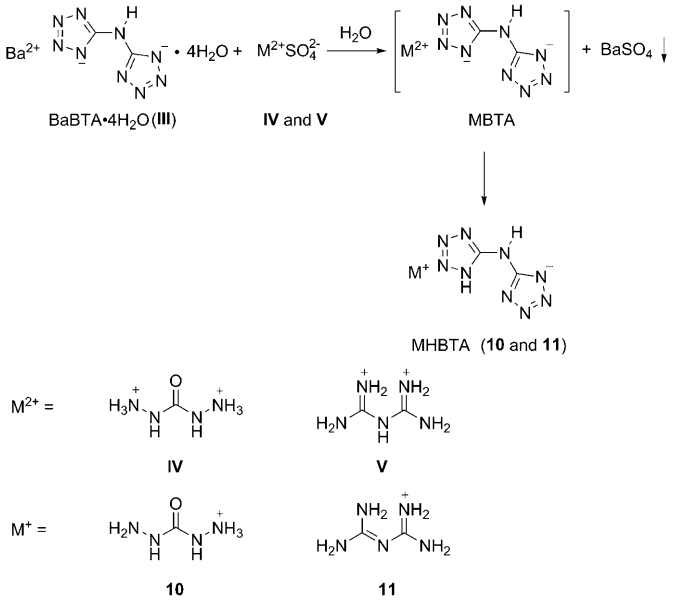
Table 2. Selected bond lengths [Å] and angles [°] for **II**.[a]

Ba–N5	2.8663(15)	N4–N5	1.365(2)
Ba–N6	2.8792(16)	C1–N1	1.364(2)
Ba–N16	2.9509(16)	C2–N1	1.384(2)
Ba–N4#1	2.9664(16)	C2–N6	1.332(2)
C1–N5	1.334(2)	C2–N9	1.340(2)
C1–N2	1.343(2)	N6–N7	1.370(2)
N2–N3	1.344(2)	N7–N8	1.304(2)
N3–N4	1.296(2)	N8–N9	1.352(2)
N5-Ba-N6	61.26(4)	N4-N3-N2	108.78(15)
N5-Ba-N4#1	115.17(4)	N3-N4-N5	110.19(15)
N6-Ba-N16	76.05(4)	C1-N5-N4	104.47(14)
N16-Ba-N4#1	106.82(4)	N6-C2-N9	112.61(16)
O2#1-Ba-O2	78.30(4)	N6-C2-N1	127.54(16)
Ba#1-O2-Ba	101.70(4)	N9-C2-N1	119.86(16)
N5-C1-N2	110.50(16)	C2-N6-N7	103.56(15)
N5-C1-N1	126.85(16)	N8-N7-N6	109.84(14)
N2-C1-N1	122.65(16)	N7-N8-N9	109.64(14)
C1-N2-N3	106.05(14)	C2-N9-N8	104.35(14)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+1$

that of **I** ($\delta = -315.7$, -123.8, -17.9 ppm).[33] The ^{15}N NMR signal of **8** can be divided into two sets of data: one set for the 1,5-diamino-4-methyltetrazolium cation is six signals at $\delta = -310.5$(N11), -300.7(N10), -177.8(N9), -159.2(N6), -27.1(N8), and -15.7(N7), and the other set for the HBTA anion close to that of **II** is three signals at $\delta = -307.1$, -105.4, and 4.5 ppm. In the ^{15}N NMR spectrum of **11**, the HBTA signals are also found at $\delta = -307.0$, -105.4, and 3.9 ppm, and the remaining signals at $\delta = -288.1$(N12) and -217.1 ppm (N13) belong to the highly symmetric guanylguanidinium cation. For salt **13**, in addition to the similar signals of cation as **11** at $\delta = -288.1$ and -216.7 ppm, the HBT signals are at $\delta = -74.2$ (N14/N17) and 12.6 ppm (N15/N16).

Physical properties of the energetic salts: The phase-transition temperatures (midpoint of melting point) and thermal stabilities of salts **1**–**13** were determined by using DSC and TGA, respectively. As shown in Table 3, ammonium salt **1** is the most thermally stable (T_d = 269 °C). For guanidinium-derivatized salts **1**–**13**, thermal degradation temperatures are in the range of 189–269 °C. Except for salts **8** and **13**, for which no melting points were detected, the melting points of other salts fall in the range 187–263 °C. For the guanidini-



Scheme 4. HBTA-salt synthesis from the metathesis of **III** and sulfates with doubly charged cations.

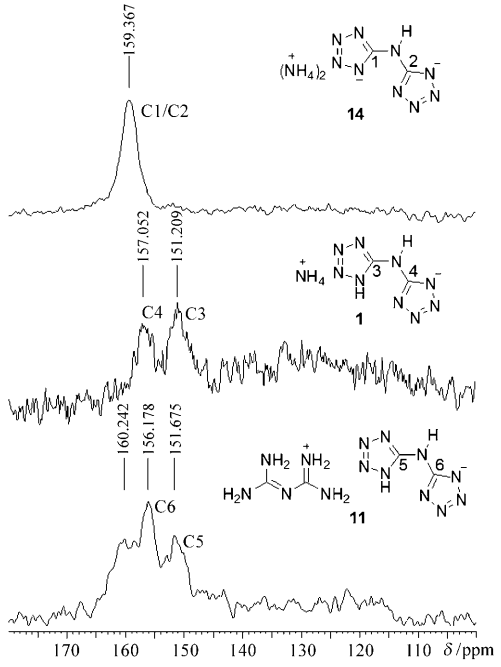
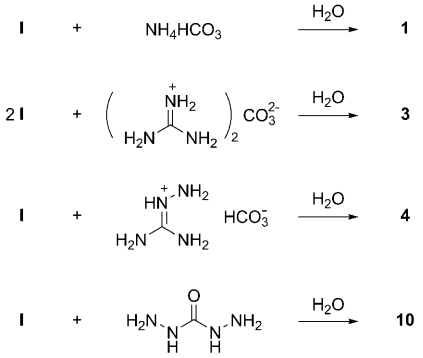
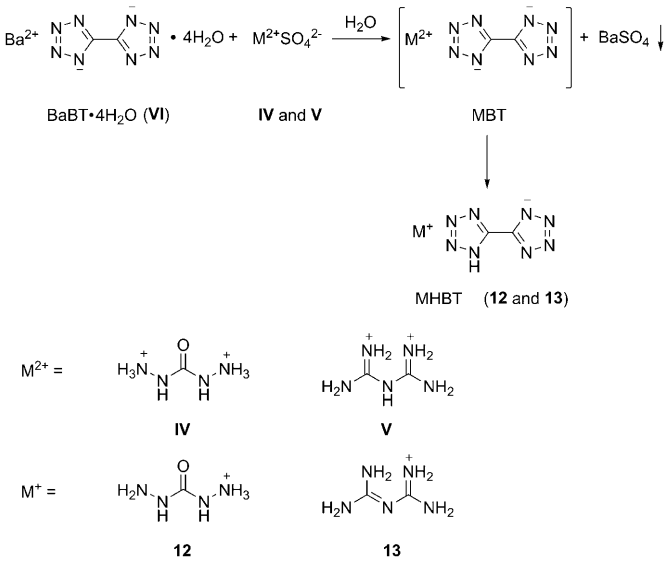


Figure 3. Solid-state ^{13}C NMR spectra of salts **1**, **11**, and **14**.



Scheme 5. Alternative routes to MHBTA salts.



Scheme 6. Syntheses of HBTA salts from the metathesis of **VI** and sulfates with doubly charged cations.

um salt **3**, in addition to an endotherm at 263 °C, the DSC trace shows a second endotherm at 139 °C that corresponds to the loss of water. This was further shown by a 6.4% weight loss over the temperature range 82 to 108 °C (calcd 7.1%). This was duplicated in the TGA curve. Similarly, DSC and TGA curves showed loss of water of salts **3**–**5**, **7**, and **9**.

Density is one of the most important factors that determines the performance of energetic compounds. The densities of salts **1**–**13** are in the range of 1.55–1.75 g cm^{-3}. The densities were also estimated by employing our tabulated volume parameters,[71] which agree reasonably well with the experimental values. Oxygen balance (OB) is used to indicate the degree to which a compound can be oxidized. Owing to the presence of only two nitro groups in the salts. All compounds possess negative OB_{co}, and are in the range from −42.1 to −60.1%, which are more negative than TNT (−24.7%).

Impact sensitivities of the salts were determined using a BAM Fallhammer with approximately 20 mg samples. When a 10 kg mass was dropped from 40 cm, no explosion occurred, thereby indicating that salts **10**–**13** are insensitive to impact.[87]

Heat of formation is another important parameter in evaluating the performance of energetic salts. This property of the salts can be calculated with good accuracy (including the heat of formation of the cation and anion, and the lattice energy of salts).[69,70,88,89] The heats of formation of the HBTA and HBT anions were calculated. Calculations were

Table 3. Physical properties and thermochemical values of energetic salts based on the HBTA and BT anion.

Salt	Cation	T_m[a]	T_d[b]	d_{meas}[c]	OB[d]	$\Delta_f H_{cation}$[e]	$\Delta_f H_L$[f]	$\Delta_f H_{sal}$[g]	P[h]	v_D[i]
	HBTA salts 550.1 ($\Delta_f H$ of HBTA anion, kJ mol^{-1})									
1	ammonium	decomp	269	1.66	−52.8	626.4	532.1	594.4, 3.5	28.1	8936
2	hydrazinium	248	249	1.66	−52.8	770.0	520.3	749.8, 4.0	30.7	9257
3	guanidinium	263	268	1.62	−52.8	563.7	498.9	565.0, 2.7	23.2	8343
4	aminoguanidinium	210	234	1.64	−52.9	660.3	491.6	668.8, 2.9	25.7	8696
5	diaminoguanidinium	205	213	1.55	−47.0	769.0	476.6	792.5, 3.3	24.0	8413
6	triaminoguanidinium	211	213	1.58	−50.9	871.5	471.6	900.0, 3.5	26.3	8748
7	*N*-carbamoylguanidinium	227	231	1.63	−60.1	350.6	476.3	374.4, 1.5	19.4	7677
8	1,5-diamino-4-methyltetrazolium	decomp	201	1.64	−42.8	974.3	471.5	1002.9, 3.8	24.7	8401
9	5-amino-1,4-dimethyltetrazolium	257	258	1.58	−56.6	887.7	467.4	920.3, 3.5	21.3	7860
10	carbonic hydrazylhydrazidinium	187	189	1.75	−42.8	663.4	491.2	672.3, 2.8	33.6	9487
11	guanylguanidinium	257	258	1.69	−56.6	620.9	486.2	634.8, 2.5	25.1	8645
	HBT salts 424.9 ($\Delta_f H$ of HBT anion, kJ mol^{-1})									
12	carbonic hydrazylhydrazidinium	200	224	1.68	−42.1	663.4	499.1	589.2, 2.6	27.2	8749
13	guanylguanidinium	decomp	251	1.60	−56.9	620.9	487.0	558.8, 2.3	20.4	7906
	BTA salts 630.0 ($\Delta_f H$ of BTA dianion, kJ mol^{-1})									
14	ammonium	142	230	1.56	−55.6	626.4	1526.8	356.0, 1.9	22.0	8341
15	hydrazinium	216	235	1.72	−55.2	770.0	1498.1	671.9, 3.1	35.2	9952
16	guanidinium	259	260	1.52	−61.9	563.7	1316.3	465.4, 1.7	18.4	7717
17	aminoguanidinium	192	218	1.59	−61.1	660.3	1286.9	678.0, 2.3	23.4	8525
18	diaminoguanidinium	159	196	1.55	−60.4	769.0	1229.4	938.6, 2.8	24.5	8623
19	triaminoguanidinium	170	180	1.51	−59.8	871.5	1177.7	1195.2, 3.3	25.1	8658

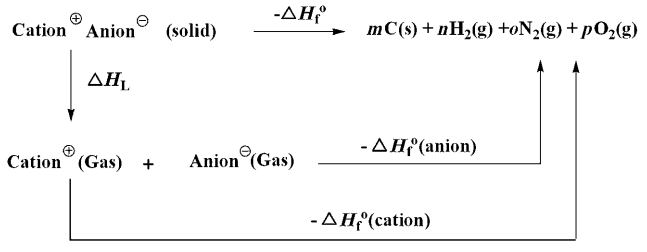
[a] Melting point [°C]. [b] Thermal degradation [°C]. [c] Measured density or density corrected from hydrate [g cm^{-3}]. [d] CO oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$ (without crystal water), OB [%] = $1600[\{(d-a-b)/2\}/M_r]$. [e] Calculated molar enthalpy of formation of cation [kJ mol^{-1}]. [f] Calculated molar lattice energy [kJ mol^{-1}]. [g] Calculated molar enthalpy of formation of salts [kJ mol^{-1}]; specific enthalpy of formation of salts [kJ g^{-1}]. [h] Detonation pressure [GPa]. [i] Detonation velocity [m s^{-1}].

carried out using the Gaussian 03 (Revision D.01) suite of programs.[90] The geometric optimization of the structures and frequency analyses were carried out using B3-LYP functional with the 6-31+G** basis set,[91] and single-point energies 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 7), the heat of formation of a salt can be simplified by the formula given in Equation (1):

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

in which ΔH_L is the lattice energy of the salt, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]:[92]



Scheme 7. Born–Haber cycle for the formation of energetic salts.

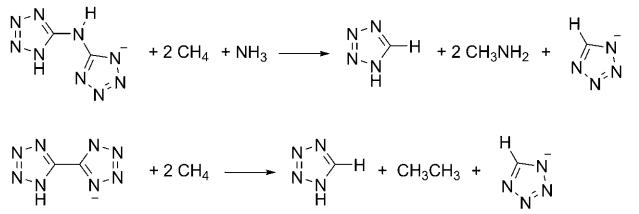
$$\Delta H_L = U_{pot} + \{p[(n_M/2) - 2] + q[(n_X/2) - 2]\}RT \quad (2)$$

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)]:

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

in which density, ρ_m [g cm^{-3}], M_m is the chemical formula mass of the ionic material [g], and the coefficients γ [kJ mol^{-1} cm] and δ [kJ mol^{-1}] are assigned literature values.[92]

All the heats of formation of cations are taken from literature data.[16,35] The task that remains is to determine the heats of formation of anions, which are computed by using the method of isodesmic reactions. The enthalpy of isodesmic reactions ($\Delta_r H_{298}^o$) (Scheme 8) are obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**; see the Supporting Information). The calculated heat of formation of the HBTA anion is 500.1 kJ mol^{-1} and that of the HBT anion is 424.9 kJ mol^{-1}, both of which are lower than the iminobis(5-tetrazolate) (BTA dianion, 630 kJ mol^{-1}).[79] All of the HBTA and HBT salts exhibit positive heats of formation, with **2** having the highest at 4.0 kJ g^{-1} (1,3,5-trinitro-1,3,5-triazine (RDX): 0.42 kJ g^{-1}; 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX): 0.35 kJ g^{-1}).



Scheme 8. Isodesmic reactions of HBTA and HBT anions.

The energetic properties of the new salts are characterized by their detonation velocities and pressures. These parameters are directly related to density, heat of formation, and oxygen balance of salts. The detonation pressure and velocity values (based on the traditional Chapman–Jouget thermodynamic detonation theory) were obtained by using CHEETAH 5.0.[93] As shown in Table 3, for salts **1–13**, the calculated detonation pressures (P) fall in the range of 19.4–33.6 GPa, which is comparable to that of TNT (19.9 GPa) and RDX (33.3 GPa). Detonation velocities (ν_D) are found in the range from 7677 $m\,s^{-1}$ (comparable to TNT, 6881 $m\,s^{-1}$) to 9487 $m\,s^{-1}$ (comparable to HMX, 9486 $m\,s^{-1}$). Comparison of HBTA salts **1–6** with BTA salts **14–19**,[4] when paired with the same cations, is interesting. HBTA salts **1–6** are more thermally stable with 20 °C higher decomposition temperatures on average than that of the BTA salts **14–19** (240 > 220 °C). The mean measured density of HBTA salts **1–6** is higher than that of BTA salts **14–19** (1.62 > 1.58 $g\,cm^{-3}$). The computed specific heats of formation of salts **1–6** are larger on average than those of BTA salts **14–19** (3.3 > 2.5 $kJ\,g^{-1}$). The average predicted detonation pressure and velocity of salts **1–6** are comparable to that of salt **14–19** (26.3 vs. 26.7 GPa and 8732 vs. 8636 $m\,s^{-1}$). Therefore, salts of HBTA are comparable to those of BTA with respect to detonation properties.

The detonation properties of HBTA salts are superior to those of HBT salts (**10** vs. **12** and **11** vs. **13**) because of higher physical densities and energy densities. These HBTA and HBT compounds have rather high nitrogen content that exceeds 71 % and can be as high as 83 %. Polynitrogen compounds are of significant interest as high-energy materials for propulsion or explosive applications.[6,13,94–98] In the past several years, the single most important breakthrough has been the synthesis and study of the N_5^+ cation. A large number of salts with polyazide anions compete very well as materials with highest nitrogen content.[1,6,13,94–98] However, compared to such compounds, the HBTA and HBT salts have superior thermal and hydrolytic stabilities, which suggests promise for practical applications. Contributing to these properties is the anionic nature of the HBTA (HBT) anion, which requires the presence of a stabilizing cation.

Conclusion

Salts of HBTA and HBT **1–13** were successfully synthesized and fully characterized. All the new salts exhibit reasonable physical properties, such as high densities (1.55 to 1.75 $g\,cm^{-3}$) and good thermal stabilities (T_d = 189 to 269 °C). Their detonation properties were evaluated by a combination of theoretical and empirical calculations. These materials exhibit a wide range of heats of formation (374.4 to 1002.9 $kJ\,mol^{-1}$) and energy densities (1.5 to 4.0 $kJ\,g^{-1}$). Their calculated detonation velocities (7677 to 9487 $m\,s^{-1}$) and detonation pressures (19.4 to 33.6 $kJ\,mol^{-1}$) are comparable to those of energetics such as TNT, RDX, and HMX.

Experimental Section

Caution: Although we experienced no difficulties in handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged!

General methods: IR spectra were recorded with KBr plates using a BIORAD model 3000 FTS spectrometer. ^1H and ^{13}C NMR spectra were recorded using spectrometers at 300 and 75.5 MHz, respectively, by using [D_6]DMSO as the locking solvent except as noted. Chemical shifts were reported in ppm relative to TMS. Densities were measured at 25 °C using a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an auto-cool accessory and calibrated using indium. The samples were heated from 40 to 400 °C at 10 °C min^{-1}. The transition temperature, T_m, was taken as peak maximum. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C min^{-1} from 25 to 600 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL min^{-1}). Elemental analyses were performed using a CE-440 Elemental Analyzer.

X-ray crystallography: An irregular colorless crystal of dimensions 0.35 × 0.21 × 0.14 mm^2 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 $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). An MSC X-Stream low-temperature device was used to keep the crystals at a constant 173(2) K during data collection.

Data collection was performed and the unit cell was initially refined using APEX2 [v2.1-0].[99] Data reduction was performed using SAINT (v7.34A)[100] and XPREP (v6.12).[101] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS (v2.10).[102] The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v6.12) system of programs.[103] 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 using a riding model.

CCDC-749624 (**II**) 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.

$Ba(HBTA)_2{\cdot}4H_2O$ (II): A mixture of **I** (6.84 g, 40 mmol) and $Ba(OH)_2{\cdot}8H_2O$ (6.31 g, 20 mmol) in H_2O (40 mL) was stirred at room temperature overnight. After filtration, a solid product was obtained. The crude product was added to water (150 mL) and heated at reflux to dissolve. After a second filtration, the filtrate was collected and concentrated to approximately 60 mL. The condensed solution was cooled to give white crystals (8.60 g, 16.7 mmol, 84 %). ^1H NMR: δ = 4.75 (br), 10.4 ppm (br); ^1H NMR (concd): δ = 5.07 ppm (br); ^{13}C NMR δ = 156.3 ppm; ^{13}C NMR (concd): δ = 156.6 ppm; ^{15}N NMR: δ = −307.0, −104.7, 4.3 ppm; IR (KBr): $\tilde{\nu}$ = 3458, 3309, 1637, 1504, 1034 cm^{-1}.

General procedures for the preparation of energetic compounds 1–9: A mixture of **II** (514 mg, 1 mmol) and the sulfate salt (1 mmol) in water (10 mL) was stirred and heated at reflux for a short time. After cooling,

the $BaSO_4$ was filtered off. The clear filtrate was evaporated slowly in the hood to give a white solid product.

Ammonium HBTA salt (1): White solid, yield: 323 mg (95%). ^{1}H NMR: δ=6.09 (br), 7.90 ppm (br); ^{13}C NMR: δ=156.1 ppm; ^{13}C NMR (solid, internal standard tetrakistrimethylsilylsilane, δ=2.7 ppm): δ=151.2, 157.0 ppm; IR (KBr): $\tilde{\nu}$=3247, 3049, 1655, 1508, 1452, 1043 cm^{-1}; elemental analysis calcd (%) for $C_2H_6N_{10}$ (M_r=170.14): C 14.12, H 3.55, N 82.33; found: C 14.40, H 3.54, N 81.32.

Hydrazinium HBTA salt (2): White solid, yield: 351 mg (95%). ^{1}H NMR: δ=7.48 ppm (brs); ^{13}C NMR: δ=156.2 ppm; IR (KBr): $\tilde{\nu}$=3305, 3037, 1655 cm^{-1}; elemental analysis calcd (%) for $C_2H_7N_{11}$ (M_r=185.15): C 12.97, H 3.81, N 83.22; found: C 13.06, H 3.76, N 81.47.

Guanidinium HBTA salt·H_2O (3): White solid, yield: 412 mg (97%). ^{1}H NMR: δ=5.7–7.0 (br), 7.09 ppm (s); ^{13}C NMR: δ=156.2, 157.9 ppm; IR (KBr): $\tilde{\nu}$=3413, 3169, 1658, 1591, 1509 cm^{-1}; elemental analysis calcd (%) for $C_3H_{10}N_{12}O$ (M_r=230.19): C 15.65, H 4.38, N 73.02; found: C 15.85, H 4.38, N 72.79.

Aminoguanidinium HBTA salt·H_2O (4): White solid, yield: 412 mg (97%). ^{1}H NMR: δ=4.4–6.6 (br), 6.95 (br), 7.27 (br), 8.7 ppm (br); ^{13}C NMR: δ=156.2, 158.8 ppm; IR (KBr): $\tilde{\nu}$=3348, 3201, 3151, 1662, 1624, 1502 cm^{-1}; elemental analysis calcd (%) for $C_3H_{11}N_{13}O$ (M_r=245.21): C 14.69, H 4.52, N 74.26; found: C 14.86, H 4.52, N 73.28.

Diaminoguanidinium HBTA salt·H_2O (5): White solid, yield: 500 mg (96%). ^{1}H NMR: δ=4.9 (br), 7.18 (s), 8.62 ppm (br); ^{13}C NMR: δ=156.3, 159.8 ppm; IR (KBr): $\tilde{\nu}$=3308, 3147, 2995, 1645, 1498, 1041 cm^{-1}; elemental analysis calcd (%) for $C_3H_{12}N_{14}O$ (M_r=260.22): C 13.85, H 4.65, N 74.86; found: C 14.05, H 4.66, N 74.86.

Triaminoguanidinium HBTA salt·H_2O (6): White solid, yield: 370 mg (72%). ^{1}H NMR: δ=4.47 (br), 5.44 (br), 8.57 (br), 10.4 ppm (br); ^{13}C NMR: δ=156.3, 159.0 ppm; IR (KBr): $\tilde{\nu}$=3320, 3212, 1683, 1638, 1494, 1330, 1126, 1036, 951 cm^{-1}; elemental analysis calcd (%) for $C_3H_{11}N_{15}$ (M_r=257.22): C 14.01, H 4.31, N 81.68; found: C 14.01, H 4.23, N 79.08.

***N*-Carbamoylguanidinium HBTA salt·H_2O (7)**: White solid, yield: 514 mg (94%). ^{1}H NMR: δ=3.60 (br), 7.15 (br), 8.03 ppm (br); ^{13}C NMR: δ=154.5, 155.5, 156.1 ppm; IR (KBr): $\tilde{\nu}$=3375, 3331, 3109, 1707, 1648, 1608 cm^{-1}; elemental analysis calcd (%) for $C_4H_{11}N_{13}O_2$ (M_r=273.22): C 17.58, H 4.06, N 66.65; found: C 17.89, H 4.01, N 65.98.

1,5-Diamino-4-methyltetrazolium HBTA salt (8): White solid, yield: 454 mg (85%). ^{1}H NMR: δ=3.84 (s, 3H), 7.00 (s, 2H), 8.78 ppm (br, 2H); ^{1}H NMR (concd): δ=3.85 (s), 7.05 (s), 8.28 ppm (brs); ^{13}C NMR: δ=34.4, 147.5, 156.2 ppm; ^{15}N NMR: δ=−310.5, −307.1, −300.7, −177.8, −159.2, −105.4, −27.1, −15.7, 4.5 ppm; IR (KBr): $\tilde{\nu}$=3358, 3307, 3191, 3032, 2932, 1717, 1647, 1491, 1032 cm^{-1}; elemental analysis calcd (%) for $C_4H_9N_{15}$ (M_r=267.21): C 17.98, H 3.39, N 78.63; found: C 17.93, H 3.31, N 77.92.

5-Amino-1,4-dimethyltetrazolium HBTA salt·H_2O (9): White solid, yield: 540 mg (95%). ^{1}H NMR: δ=3.85 (s, 6H), 6.95 ppm (br); ^{13}C NMR: δ=33.9, 148.5, 156.2 ppm; IR (KBr): $\tilde{\nu}$=3420, 3211, 3147, 3030, 2828, 2865, 1707, 1638, 1493, 1026, 785 cm^{-1}; elemental analysis calcd (%) for $C_5H_{12}N_{14}O$ (M_r=284.24): C 21.13, H 4.26, N 68.99; found: C 20.86, H 4.25, N 67.90.

General procedures for the preparation of energetic compounds 10–13: A mixture of **III/IV** (2 mmol) and the sulfate salt (2 mmol) in water (10 mL) was stirred and heated at reflux for a short time. After cooling, the $BaSO_4$ was filtered off. The clear colorless filtrate was evaporated slowly in the hood to give white solid product.

Carbonic hydrazylhydrazidinium HBTA salt (10): White solid, yield: 292 mg (60%). ^{1}H NMR: δ=5.73 (br), 7.86 ppm (br); ^{13}C NMR: δ=154.9, 159.9 ppm; IR (KBr): $\tilde{\nu}$=3329, 1666, 1507, 1168, 1026 cm^{-1}; elemental analysis calcd (%) for $C_3H_9N_{13}O$ (M_r=243.19): C 14.82, H 3.73, N 74.87; found: C 14.72, H 3.63, N 73.86.

Guanylguanidinium HBTA salt (11): White solid, yield: 503 mg (99%). ^{1}H NMR: δ=5.93 (br), 6.80 (s), 10.5 ppm (br); ^{1}H NMR (concd): δ=7.03 (brs), 11.7 ppm (br); ^{13}C NMR: δ=156.3, 159.7 ppm; ^{13}C NMR (concd): δ=156.4, 160.1 ppm; ^{15}N NMR: δ=−307.0, −288.1, −217.1, −105.4, 3.9 ppm; IR (KBr): $\tilde{\nu}$=3406, 3346, 3175, 1638, 1561, 1030 cm^{-1}; elemental analysis calcd (%) for $C_4H_{10}N_{14}$ (M_r=254.22): C 18.90, H 3.96, N 77.14; found: C 19.04, H 3.88, N 77.05.

Carbonic hydrazylhydrazidinium HBT salt (12): White solid, yield: 429 mg (94%). ^{1}H NMR: δ=4.3 (br), 8.4 ppm (br); ^{13}C NMR: δ=149.2, 159.1 ppm; IR (KBr): $\tilde{\nu}$=3263, 1672, 1563, 1509, 1438, 1350, 1152, 1117, 1064, 977 cm^{-1}; elemental analysis calcd (%) for $C_3H_8N_{12}O$ (M_r=228.18): C 15.79, H 3.53, N 73.66; found: C 15.54, H 3.41, N 71.53.

Guanylguanidinium HBT salt (13): White solid, yield: 469 mg (98%). ^{1}H NMR: δ=5.7 (br), 6.8 ppm (s); ^{1}H NMR (concd): δ=6.94 (brs), 12.2 ppm (br); ^{13}C NMR: δ=149.3, 159.7 ppm; ^{15}N NMR: δ=−288.1, −216.7, −74.2, 12.6 ppm; IR (KBr): $\tilde{\nu}$=3434, 3349, 1707, 1334 cm^{-1}; elemental analysis calcd (%) for $C_4H_{10}N_{14}$ (M_r=254.22): C 18.90, H 3.96, N 77.14; found: C 19.04, H 3.88, N 77.05.

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[1] 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.
[2] M. A. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout, C. A. Bolme, *Proc. Int. Pyrotech. Semin.* **2000**, *27*, 3–14.
[3] P. F. Pagoria, G. S. Lee, A. R. Mitchell, R. D. Schmidt, *Thermochim. Acta* **2002**, *384*, 187–204.
[4] Y. Guo, H. Gao, B. Twamley, J. M. Shreeve, *Adv. Mater.* **2007**, *19*, 2884–2888.
[5] T. Abe, G.-H. Tao, Y.-H. Joo, Y. Huang, B. Twamley, J. M. Shreeve, *Angew. Chem.* **2008**, *120*, 7195–7198; *Angew. Chem. Int. Ed.* **2008**, *47*, 7087–7090.
[6] T. M. Klapötke, J. Stierstorfer, *J. Am. Chem. Soc.* **2009**, *131*, 1122–1134.
[7] Y.-H. Joo, B. Twamley, S. Garg, J. M. Shreeve, *Angew. Chem.* **2008**, *120*, 6332–6335; *Angew. Chem. Int. Ed.* **2008**, *47*, 6236–6239.
[8] T. M. Klapötke, P. Mayer, A. Schulz, J. J. Weigand, *J. Am. Chem. Soc.* **2005**, *127*, 2032–2033.
[9] Y.-H. Joo, J. M. Shreeve, *Angew. Chem.* **2009**, *121*, 572–575; *Angew. Chem. Int. Ed.* **2009**, *48*, 564–567.
[10] 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.
[11] D. E. Chavez, M. A. Hiskey, D. L. Naud, D. Parrish, *Angew. Chem.* **2008**, *120*, 8431–8433; *Angew. Chem. Int. Ed.* **2008**, *47*, 8307–8309.
[12] M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, *J. Am. Chem. Soc.* **2005**, *127*, 12537–12543.
[13] R. Haiges, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2004**, *116*, 5027–5032; *Angew. Chem. Int. Ed.* **2004**, *43*, 4919–4924.
[14] a) M. X. Zhang, P. E. Eaton, R. Gilardi, *Angew. Chem.* **2000**, *112*, 422–426; *Angew. Chem. Int. Ed.* **2000**, *39*, 401–404; b) P. E. Eaton, R. Gilardi, M. X. Zhang, *Adv. Mater.* **2000**, *12*, 1143–1148.
[15] A. K. Mandal, C. S. Pant, S. M. Kasar, T. Soman, *J. Energ. Mater.* **2009**, *27*, 231–246.
[16] Y. Guo, G.-H. Tao, Y.-H. Joo, R. Wang, B. Twamley, D. A. Parrish, J. M. Shreeve, *Energy Fuels* **2009**, *23*, 4567–4574, and reference therein.
[17] K. Iwakuma, Y. Miyata, S. Date, M. Kohga, K. Hasue, *Sci. Technol. Energ. Mater.* **2007**, *68*, 95–101.
[18] D. E. Chavez, M. A. Hiskey, D. L. Naud, *J. Pyrotech.* **1999**, *10*, 17–36.
[19] D. E. Chavez, M. A. Hiskey, *J. Pyrotech.* **1998**, *7*, 11–14.
[20] G. Bennett, M. L. Kolleck, J. M. Bennett, Fire in the Air Military Aerospace Technology, **2003**.
[21] S. Fallis, R. Reed, Y.-C. F. Lu, P. H. Wierenga, G. F. Holland, *Proceedings of Halon Options Technical Working Conference*, National

Institute of Standards and Technology, Albuquerque NM (USA), **2000**, pp. 361–370.
[22] A. N. Ali, S. F. Son, M. A. Hiskey, D. L. Naud, *J. Propul. Power* **2004**, *20*, 120–126.
[23] S. F. Son, H. L. Berghout, C. A. Bolme, D. E. Chavez, D. L. Naud, M. A. Hiskey, *Proc. Combust. Inst.* **2000**, *28*, 919–924.
[24] M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. D. Gilardi, *Angew. Chem.* **2004**, *116*, 5776–5779; *Angew. Chem. Int. Ed.* **2004**, *43*, 5658–5661.
[25] C. Ye, H. Gao, J. A. Boatz, G. W. Drake, B. Twamley and J. M. Shreeve, *Angew. Chem.* **2006**, *118*, 7420–7423; *Angew. Chem. Int. Ed.* **2006**, *45*, 7262–7265;.
[26] M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, *Angew. Chem.* **2005**, *117*, 747–749; *Angew. Chem. Int. Ed.* **2005**, *44*, 737–739.
[27] E. G. Gillan, *Chem. Mater.* **2000**, *12*, 3906–3912.
[28] T. Sato, A. Narazaki, Y. Kawaguchi, H. Niino, *Appl. Phys. A* **2004**, *79*, 1477–1479.
[29] D. R. Miller, D. C. Swenson, E. G. Gillan, *J. Am. Chem. Soc.* **2004**, *126*, 5372–5373.
[30] J. Stierstorfer, K. R. Tarantik, T. M. Klapötke, *Chem. Eur. J.* **2009**, *15*, 5775–5792.
[31] G.-H. Tao, Y. Guo, Y.-H. Joo, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* **2008**, *18*, 5524–5530.
[32] a) A. Hammerl, T. M. Klapötke, H. Nöth, M. Warchhold, G. Holl, M. Kaiser, U. Ticmanis, *Inorg. Chem.* **2001**, *40*, 3570–3575; b) A. Hammerl, M. A. Hiskey, G. Holl, T. M. Klapötke, K. Polborn, J. Stierstorfer, J. J. Weigand, *Chem. Mater.* **2005**, *17*, 3784–3793.
[33] T. M. Klapötke, P. Mayer, J. Stierstorfer, J. J. Weigand, *J. Mater. Chem.* **2008**, *18*, 5248–5258.
[34] T. M. Klapötke, C. M. Sabaté, *Chem. Mater.* **2008**, *20*, 3629–3637.
[35] R. Wang, Y. Guo, Z. Zeng, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 2625–2634.
[36] R. Wang, Y. Guo, Z. Zeng, J. M. Shreeve, *Chem. Commun.* **2009**, 2697–2699.
[37] C. Ye, J.-C. Xiao, B. Twamley, J. M. Shreeve, *Chem. Commun.* **2005**, *2750–2752*.
[38] T. Abe, G.-H. Tao, Y.-H. Joo, R. W. Winter, G. L. Gard, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 9897–9904.
[39] Y.-H. Joo, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 9097–9104.
[40] M. Eberspächer, T. M. Klapötke, C. M. Sabaté, *Helv. Chim. Acta* **2009**, *92*, 977–996.
[41] M.-J. Crawford, K. Karaghiosoff, T. M. Klapötke, F. A. Martin, *Inorg. Chem.* **2009**, *48*, 1731–1743.
[42] T. M. Klapötke, C. M. Sabaté, M. Rasp, *J. Mater. Chem.* **2009**, *19*, 2240–2252.
[43] T. M. Klapötke, C. M. Sabaté, J. Stierstorfer, *New J. Chem.* **2009**, *33*, 136–147.
[44] D. E. Chavez, D. A. Parrish, *J. Heterocycl. Chem.* **2009**, *46*, 88–90.
[45] D. E. Chavez, R. D. Gilardi, *J. Energ. Mater.* **2009**, *27*, 110–117.
[46] T. M. Klapötke, C. M. Sabaté, A. Penger, M. Rusan, J. M. Welch, *Eur. J. Inorg. Chem.* **2009**, *880–896*.
[47] M. Göbel, T. M. Klapötke, *Adv. Funct. Mater.* **2009**, *19*, 347–365.
[48] T. M. Klapötke, C. M. Sabaté, M. Rasp, *Dalton Trans.* **2009**, *1825–1834*.
[49] Y. Huang, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 917–923.
[50] C. Ye, H. Gao, B. Twamley, J. M. Shreeve, *New J. Chem.* **2008**, *32*, 317–322.
[51] Z. Zeng, R. Wang, B. Twamley, D. A. Parrish, J. M. Shreeve, *Chem. Mater.* **2008**, *20*, 6176–6182.
[52] H. Gao, Y. Huang, C. Ye, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2008**, *14*, 5596–5603.
[53] Y. Huang, H. Gao, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2008**, *2560–2568*.
[54] H. Gao, Y. Huang, B. Twamley, C. Ye, J. M. Shreeve, *ChemSusChem* **2008**, *1*, 222–227.
[55] C. Ye, H. Gao, J. M. Shreeve, *J. Fluorine Chem.* **2007**, *128*, 1410–1415.
[56] Y. Huang, H. Gao, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2007**, 2025–2030.
[57] R. Wang, H. Gao, C. Ye, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2007**, *46*, 932–938.
[58] Y. Gao, C. Ye, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2006**, *12*, 9010–9018.
[59] R. Wang, H. Gao, C. Ye, J. M. Shreeve, *Chem. Mater.* **2007**, *19*, 144–152.
[60] H. Gao, R. Wang, B. Twamley, M. A. Hiskey, J. M. Shreeve, *Chem. Commun.* **2006**, 4007–4009.
[61] C.-M. Jin, C. Ye, C. Piekarski, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.* **2005**, 3760–3767.
[62] N. Liu, Q. Yue, Y.-Q. Wang, A.-L. Cheng, E.-Q. Gao, *Dalton Trans.* **2008**, 4621–4629.
[63] Y. Cui, J.-G. Zhang, T.-L. Zhang, L. Yang, Y. Zang, Y.-J. Shu, *Chin. J. Chem.* **2008**, *26*, 2029–2034.
[64] Y. Cui, T.-L. Zhang, J.-G. Zhang, L. Yang, *Chin. J. Chem.* **2008**, *26*, 2021–2028.
[65] Z. Zeng, B. Twamley, J. M. Shreeve, *Organometallics* **2007**, *26*, 1782–1787.
[66] Q.-X. Jia, X.-B. Qian, H.-H. Wu, Q.-L. Wang, E.-Q. Gao, *Inorg. Chim. Acta* **2009**, *362*, 2213–2216.
[67] W. Yang, X. Lin, A. J. Blake, C. Wilson, P. Hubberstey, N. R. Champness, *CrystEngComm* **2009**, *11*, 67–81.
[68] M. Ponikvar, J. F. Liebman, *Struct. Chem.* **2008**, *19*, 849–872.
[69] H. Gao, C. Ye, C. Piekarski, J. M. Shreeve, *J. Phys. Chem. A* **2007**, *111*, 10718–10731.
[70] a) K. E. Gutowski, R. D. Rogers, D. A. Dixon, *J. Phys. Chem. A* **2006**, *110*, 11890–11897; b) K. E. Gutowski, R. D. Rogers, D. A. Dixon, *J. Phys. Chem. B* **2007**, *111*, 4788–4800.
[71] C. Ye, J. M. Shreeve, *J. Phys. Chem. A* **2007**, *111*, 1456–1461.
[72] K. K. Govender, I. Cukrowski, *J. Phys. Chem. A* **2009**, *113*, 3639–3647.
[73] Z.-Q. Zhu, S. Xiang, Q.-Y. Chen, C. Chen, Z. Zeng, Y.-P. Cui, J.-C. Xiao, *Chem. Commun.* **2008**, 5016–5018.
[74] M. Smiglak, J. D. Holbrey, S. T. Griffin, W. M. Reichert, R. P. Swatloski, A. R. Katritzky, H. Yang, D. Zhang, K. Kirichenko, R. D. Rogers, *Green Chem.* **2007**, *9*, 90–98.
[75] A. R. Katritzky, S. Singh, K. Kirichenko, M. Smiglak, J. D. Holbrey, W. M. Reichert, S. K. Spear, R. D. Rogers, *Chem. Eur. J.* **2006**, *12*, 4630–4641.
[76] M. Smiglak, W. M. Reichert, J. D. Holbrey, J. S. Wilkes, L. Sun, J. S. Thrasher, K. Kirichenko, S. Singh, A. R. Katritzky, R. D. Rogers, *Chem. Commun.* **2006**, *2554–2556*.
[77] G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacka, H. Roeder, T. Roeder, H. Sixta, *Lenzinger Ber.* **2005**, *84*, 71–85.
[78] X.-C. Hang, Q.-Y. Chen, J.-C. Xiao, *Eur. J. Org. Chem.* **2008**, 1101–1106.
[79] S. V. Voitekhovich, P. N. Gaponik, A. S. Lyakhov, O. A. Ivashkevich, *Tetrahedron* **2008**, *64*, 8721–8725.
[80] J.-M. Lin, Y.-F. Guan, D.-Y. Wang, W. Dong, X.-T. Wang, S. Gao, *Dalton Trans.* **2008**, 6165–6169.
[81] M. Friedrich, J. C. Gálvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 8044–8052.
[82] Y.-B. Lu, M.-S. Wang, W.-W. Zhou, G. Xu, G.-C. Guo, J.-S. Huang, *Inorg. Chem.* **2008**, *47*, 8935–8942.
[83] a) J.-M. Lin, Y.-F. Guan, W. Dong, *Acta Crystallogr. Sect. E* **2007**, *64*, m238; b) J.-M. Lin, Y.-F. Guan, W. Dong, *Acta Crystallogr. Sect. E* **2007**, *63*, m3017; c) X.-P. Liu, C. Zhang, *Acta Crystallogr. Sect. E* **2007**, *63*, m3063; d) Y.-F. Guan, D.-Y. Wang, W. Dong, *Acta Crystallogr. Sect. E* **2007**, *63*, m3150.
[84] L.-L. Zheng, H.-X. Li, J.-D. Leng, J. Wang, M.-L. Tong, *Eur. J. Inorg. Chem.* **2008**, 213–217.
[85] a) B. C. Tappan, M. H. V. Huynh, M. A. Hiskey, S. F. Son, D. M. Oschwald, D. E. Chavez, US 20060413, **2006**; [*Chem. Abstr.* **2006**, *144*, 395919]; b) M. A. Hiskey, D. E. Chavez, D. L. Naud, US

6214139, **2001**; [*Chem. Abstr.* **2001**, *134*, 282929]; c) S. Oga, S. Nakagawa, O. Mitsui, Jpn. Kokai Tokkyo Kobo, JP 2004323392, **2004**; [*Chem. Abstr.* **2004**, *141*, 424196]; d) S. Hyoda, M. Kita, A. Sugino, S. Nemugaki, T. Ueta, K. Sato, EP 1162198, **2001**; [*Chem. Abstr.* **2001**, *136*, 20077]; e) S. Torii, M. Tsuyama, Y. Miyawaki, Y. Kubo, T. Ogawa, Jpn. Kokai Tokkyo Kobo, JP 2000281662, **2000**; [*Chem. Abstr.* **2000**, *133*, 252440]; f) S. Hyoda, M. Kita, H. Sawada, S. Nemugaki, T. Ueta, K. Satoh, S. Otsuka, Y. Miyawaki, H. Taniguchi, Eur. Pat. Appl., EP 1016662, **2000**; [*Chem. Abstr.* **2000**, *133*, 74021]; g) S. Hyoda, M. Kita, H. Sawada, S. Nemugaki, S. Otsuka, Y. Miyawaki, T. Ogawa, Y. Kubo, US Patent 6040453, **2000**; [*Chem. Abstr.* **2000**, *132*, 207845].

[86] W. P. Norris, R. A. Henry, *J. Am. Chem. Soc.* **1963**, *85*, 650.

[87] J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Löhnwitz, P. Mayer, H. Nöth, K. Polborn, C. J. Rohbogner, M. Suter and J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 4237–4253.

[88] M. W. Schmidt, M. S. Gordon, J. A. Boatz, *J. Phys. Chem. A* **2005**, *109*, 7285–7295.

[89] K. E. Gutowski, J. D. Holbrey, R. D. Rogers, D. A. Dixon, *J. Phys. Chem. B* **2005**, *109*, 23196–23208.

[90] 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., T. Vreven, 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, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

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

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

[93] a) CHEETAH 5.0 User's Manual, L. E. Fried, K. R. Glaesemann, W. M. Howard, P. C. Souers, Lawrence Livermore National Laboratory, **2007**; b) J. P. Lu, *Evaluation of the Thermochemical Code -CHEETAH 2.0 for Modelling Explosives Performance*, Fishermans Bend, Victoria, **2001**.

[94] T. M. Klapötke, *Angew. Chem.* **1999**, *111*, 2694–2696; *Angew. Chem. Int. Ed.* **1999**, *38*, 2536–2538.

[95] W. Fraenk, T. Habereder, A. Hammerl, T. M. Klapötke, B. Krumm, P. Mayer, H. Nöth, M. Warchold, *Inorg. Chem.* **2001**, *40*, 1334.

[96] 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.

[97] A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, *J. Am. Chem. Soc.* **2001**, *123*, 6308–6313.

[98] R. Haiges, R. Bau, S. Schneider, T. Schroer, M. Yousufuddin, K. O. Christe, *Angew. Chem.* **2005**, *117*, 1894–1899; *Angew. Chem. Int. Ed.* **2005**, *44*, 1860–1865.

[99] APEX2 v2.1-0, Bruker, Bruker AXS Inc., Madison, **2006**.

[100] SAINT v7.34A, Bruker, Bruker AXS Inc., Madison, **2005**.

[101] SADABS v2.10, Bruker, Bruker AXS Inc., Madison, **2000**.

[102] XPREP v6.12, Bruker, Bruker AXS Inc., Madison, **2001**.

[103] SHELXTL v6.12, Bruker, Bruker AXS Inc., Madison, **2000**.

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