



Synthesis and Characterization of the Energetic Compounds Aminoguanidinium-, Triaminoguanidinium- and Azidoformamidinium Perchlorate

Thomas M. KLAPÖTKE* and Jörg STIERSTORFER

Department Chemistry and Biochemistry, Energetic Materials Research, Ludwig-Maximilian University of Munich, Butenandtstr. 5-13, D-81377 Munich, Germany

**E-mail: tmk@cup.uni-muenchen.de*

Abstract: Aminoguanidinium perchlorate (**2**, AGClO₄) was formed by the reaction of aminoguanidinium bicarbonate (**1**) with aqueous perchloric acid solution. Triaminoguanidinium perchlorate (**3**, TAGClO₄) was synthesized by nucleophilic attack of aqueous hydrazine solution on aminoguanidinium perchlorate under release of ammonia. The new and highly explosive azidoformamidinium perchlorate (**4**, AFCIO₄) was formed by the reaction of aminoguanidinium perchlorate with potassium nitrite under acidic conditions. The structures of the perchlorate salts in the crystalline state were determined using low temperature single crystal X-ray diffraction yielding monoclinic as well as orthorhombic structures. The compounds were characterized comprehensively using vibrational spectroscopy (IR and Raman), multinuclear (¹H, ¹³C and ¹⁵N) NMR spectroscopy, elemental analysis and mass spectrometry. The thermal behavior as well as the decompositions were investigated using DSC (differential scanning calorimetry) and the heats of formation were calculated using heats of combustion determined by bomb calorimetric measurements. In addition, the sensitivities were evaluated using BAM methods (drophammer and friction tester), whereby the perchlorate salts are all sensitive towards impact as well as friction.

Keywords: perchlorates, energetic salts, calorimetry, X-ray, DSC

Introduction

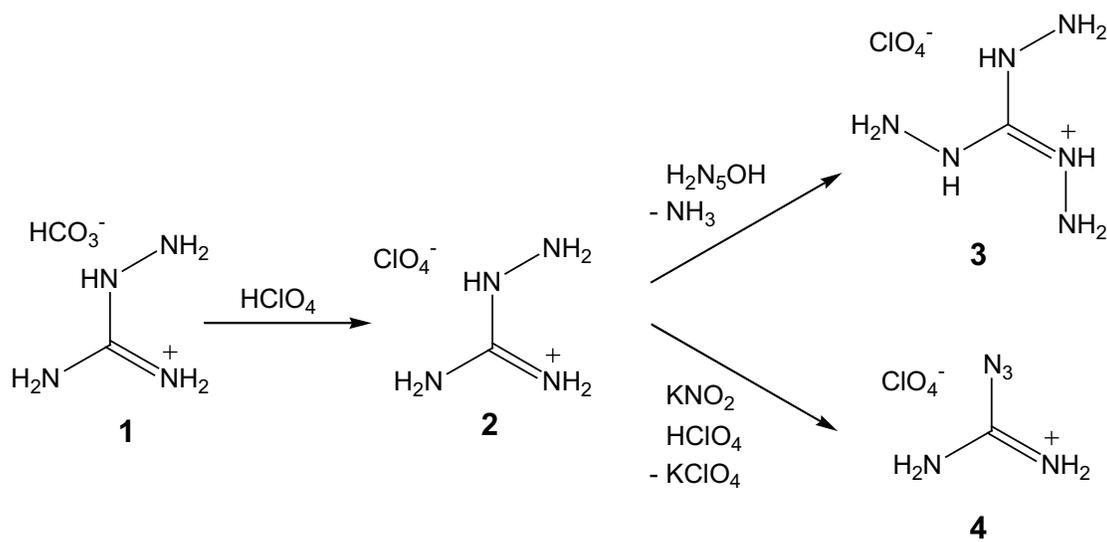
The preparation and characterization of new energetic materials [1] is a constant research topic in our research group [2]. Perchlorate salts are, in spite

of their toxicity [3], still used in many energetic compositions [4] since they are, despite of their high oxygen content, often more stable and less sensitive than the corresponding chlorates due to a steric (kinetic) barrier. [5] Ammonium perchlorate [6] for example is used in combination with aluminium as the solid propellant [7] in boosters of the space shuttle [8]. Potassium perchlorate is still used in pyrotechnic composition for accomplishing a suitable oxygen balance [9]. This and further special energetic properties can be fulfilled by combining nitrogen rich cations with the ClO_4^- anion. Since the pK_s of perchloric acid is very low (-10) [10] salts can be even prepared in combination with different tetrazole derivatives, *e.g.* 1,5-diaminotetrazole or 1-methyl-5-aminotetrazole [11]. Also some guanidinium perchlorate salts are known but rarely described and only a few crystal structures of guanidinium perchlorate [12] as well as 1-carbamoylguanidine [13] and biguanidine [14] have been reported in the literature. In this work we present a full characterization, including the crystal structures and properties, of three cationic derivatives of guanidine as their perchloric salts [15]. These compounds, namely aminoguanidinium perchlorate (**2**, AGClO_4), triaminoguanidinium perchlorate (**3**, TAGClO_4) and azidoformamidinium perchlorate (**4**, AFCIO_4) are not only interesting energetic derivatives but can also be used as synthetic building blocks in the preparation of further nitrogen rich salts by the reaction of potassium salts with the formation of low solubility potassium perchlorate.

Results and Discussion

Synthesis

The perchlorate salts (**2–4**) were synthesized according to Scheme 1. Aminoguanidinium perchlorate AGClO_4 (**2**), is obtained by neutralization of the cheap starting material aminoguanidinium hydrogencarbonate using 1 equivalent of perchloric acid solution. After completion of the CO_2 release the product was isolated by evaporation and was recrystallized from ethanol.



Scheme 1. Synthesis of the perchlorates **2** – **4**.

TAGClO₄ (3) was formed in excellent yields by the reaction of **AGClO₄ (2)** with an excess of hydrazinium hydrate in dioxane as the solvent. The end of reaction can be easily detected by cessation of NH₃ release while refluxing the mixture at ca. 80 °C.

AFCIO₄ (4) was obtained by the reaction of the hydrazine group of **AGClO₄ (2)** with HNO₂, formed from potassium nitrite in dilute aqueous perchloric acid solution. After filtration of KClO₄ the product was isolated simply by removing the solvent.

Crystal Structures

The single crystal X-ray diffraction data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collections were undertaken using the CRYALIS CCD software [16] and the data reductions were performed with the CRYALIS RED software [17]. The structures were solved with SIR-92 [18], refined with SHELXL-97 [19] and finally checked using PLATON [20]. In all structures the hydrogen atoms were located and refined. The absorptions of the structures were corrected using the SCALE3 ABSPACK multi-scan method [21]. Selected data and parameters from the X-ray data collection and refinements are given in Table 1. Further information regarding the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre [22] as supplementary publication Nos. 664916 (**2**), 664917 (**3**) and 664918 (**4**).

Table 1. Crystallographic data

Formula	CH ₇ N ₄ ClO ₄	CH ₉ N ₆ ClO ₄	CH ₄ N ₅ ClO ₄
Form. weight [g mol ⁻¹]	174.56	204.59	185.54
Crystal system	monoclinic	monoclinic	orthorhombic
Space Group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>Pbca</i> (No. 61)
Color / Habit	colorless needles	colorless rods	colorless rods
Size, mm	0.04 x 0.06 x 0.09	0.02 x 0.07 x 0.09	0.02 x 0.07 x 0.11
<i>a</i> [Å]	7.988(1)	10.2506(3)	8.5992(3)
<i>b</i> [Å]	8.498(1)	15.0671(4)	11.0586(4)
<i>c</i> [Å]	9.958(2)	10.3572(3)	14.1919(4)
α [°]	90.0	90.0	90.0
β [°]	103.50(1)	102.443(3)	90.0
γ [°]	90.0	90.0	90.0
<i>V</i> [Å ³]	657.3(2)	1562.06(8)	1349.58(8)
<i>Z</i>	4	8	8
$\rho_{\text{calc.}}$ [g cm ⁻³]	1.764	1.740	1.826
μ [mm ⁻¹]	0.549	0.483	0.545
<i>F</i> (000)	360	848	752
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	200	100	200
Theta Min-Max [°]	4.4, 26.0	3.7, 26.0	4.0, 26.0
Dataset	-9: 9 ; -10: 10 ; -12: 12	-12: 12 ; -18: 18 ; -12: 12	-9: 10 ; -9: 13 ; -17: 16
Reflections collected	6373	15530	6468
Independent reflections	1291	3068	1325
<i>R</i> _{int}	0.030	0.063	0.034
Observed reflections	1214	1930	974
No. parameters	119	289	116
<i>R</i> ₁ (obs)	0.0343	0.0343	0.0297
<i>wR</i> ₂ (all data)	0.0864	0.0844	0.0802
GooF	1.07	0.94	1.02
Resd. Dens. [e/ Å ³]	-0.35, 0.32	-0.36, 0.29	-0.47, 0.19
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	664916	664917	664918

AGClO₄ (2) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell with a density of 1.764 g cm⁻³. The asymmetric unit is shown in Figure 1. The bond lengths in the aminoguanidinium cation are in the same range as observed for example in aminoguanidinium chloride [23] or nitrate [24] in the literature. The C–N bond distances are between 1.30 and 1.33 Å which is crucially shorter than C–N single bonds (1.47 Å) but significantly longer than C=N double bonds (1.22 Å) [25] and show the delocalization of the positive charge. The hydrazine N1–N2 bond has a length of 1.402(3) Å. The Cl–O bond distances in the ClO₄⁻ anion lie between 1.41 and 1.44 Å, which is quite normal and can be found in other perchlorate structures [13, 14].

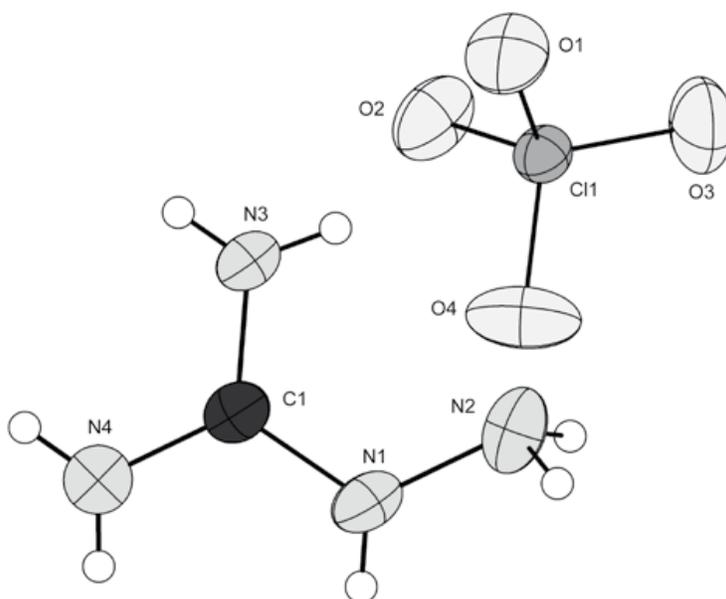


Figure 1. Molecular structure of **2**. Displaced ellipsoids are drawn at the 50% probability level.

The packing of the structure is influenced by several moderate N–H \cdots O hydrogen bonds, in which all oxygen atoms of the perchlorate anions as well as all hydrogen atoms of the cations participate. The coordination of one aminoguanidinium cation is illustrated in Figure 2.

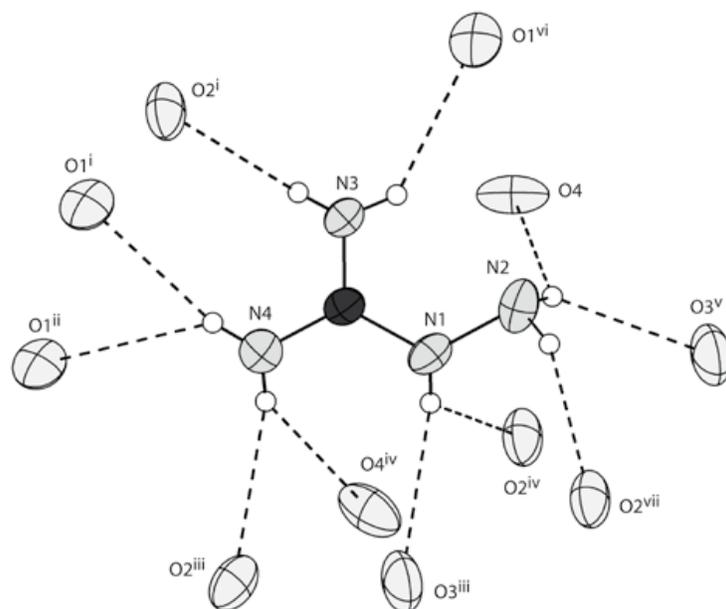


Figure 2. Hydrogen bonding of the aminoguanidinium cation. Symmetry codes: (i) $2-x, 0.5+y, 1.5-z$; (ii) $x, -0.5-y, -0.5+z$; (iii) $x, 1+y, z$; (iv) $1-x, 0.5+y, 1.5-z$; (v) $1-x, -1-y, 2-z$; (vi) $2-x, -1-y, 2-z$; (vii) $x, -0.5-y, 0.5+z$.

TAGClO₄ (3) crystallizes in the monoclinic space group $P2_1/c$, whereby eight molecules can be found in the unit cell. One molecule of the asymmetric unit containing two independent molecular moieties is shown in Figure 3. The Cl–O distances in the perchlorate anions lie again between 1.42 and 1.44 Å.

The geometry of the cation is comparable to those observed for triaminoguanidinium chloride [26] and nitrate [27] in the literature. Again the positive charge is delocalized, which can be seen by the similar C–N bond lengths ($d(\text{C1–N1}) = 1.327(3)$ Å, $d(\text{C1–N3}) = 1.317(3)$ Å, $d(\text{C1–N5}) = 1.332(3)$ Å) building a planar fragment. The hydrazine bonds have similar lengths between 1.40 and 1.42 Å. Again the packing is influenced by several N–H \cdots O and N–H \cdots N hydrogen bonds resulting in a high density of 1.740 g cm⁻³.

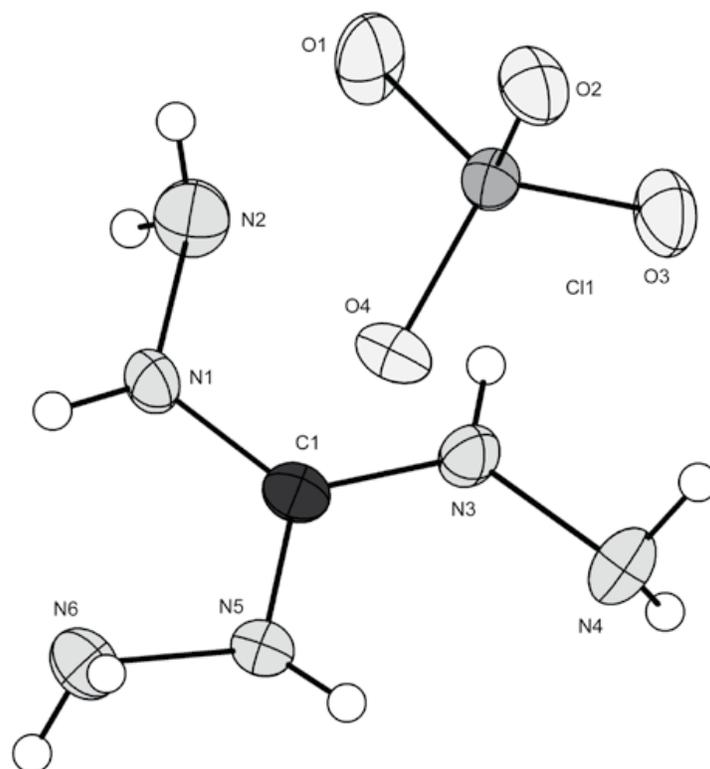


Figure 3. Molecular structure of **3**. Displaced ellipsoids are drawn at the 50% probability level.

AFCIO₄ (**4**) crystallizes in the orthorhombic space group *Pbca* with eight formula moieties in the unit cell and the highest density of 1.826 g cm⁻³ observed in this work. The azidoformamidinium moiety is not planar (torsion angle (N2–N1–C1–N4) = 19.5(3) °) and the azide has a N1–N2–N3 angle of 170.1(2), which is quite common for covalent azide groups and can be explained by hyperconjugation effects [28]. The NH₂ groups are in plane with the carbon atom, displaying a N4–C1–N5 angle of 123.3(2) °. The C–N distances and intratomic angles are similar to those found in 1972 by Bärnighausen who investigated azidoformamidinium chloride [29].

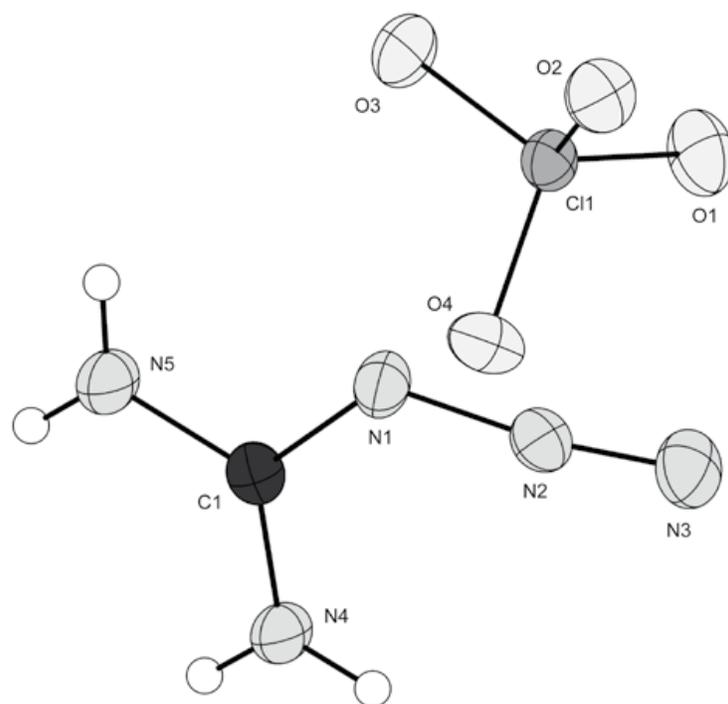


Figure 4. Molecular structure of **4**. Displaced ellipsoids are drawn at the 50% probability level. Selected distances: $d(\text{C1-N1}) = 1.390(3)$, $d(\text{C1-N4}) = 1.306(3)$, $d(\text{C1-N5}) = 1.302$, $d(\text{N1-N2}) = 1.256(2)$, $d(\text{N2-N3}) = 1.116(2)$ Å.

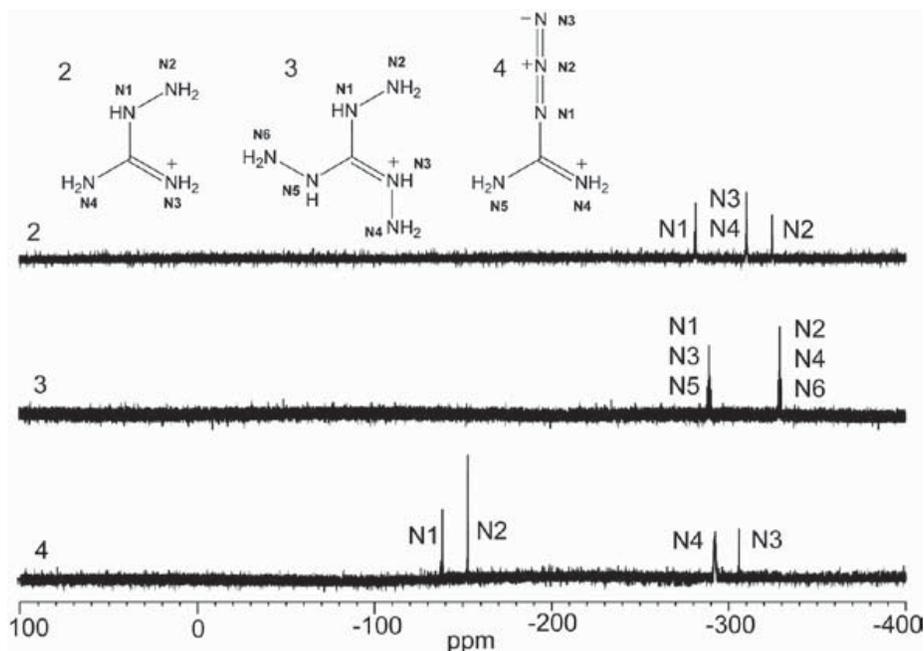
NMR spectroscopy

The ^{13}C and ^{15}N NMR chemical shifts are presented in Table 2. For compounds **2** - **4** the proton coupled as well as the proton decoupled ^{15}N NMR spectra (Figure 5) with full NOE (nuclear overhauser effect) were recorded. The assignments are given based on the values of the ^{15}N - ^1H coupling constants. The chemical shifts are given with respect to CH_3NO_2 (^{15}N) and TMS (^1H , ^{13}C) as external standards. In the case of ^{15}N NMR, negative shifts are upfield from CH_3NO_2 . In all cases D_2O was used as the solvent.

In the ^{15}N NMR spectra of **AGClO₄** three signals are observed which can be assigned to the nitrogen N1 (-285.6 ppm), N2 (-327.6 ppm) as well as N3/N4 (-312.4 ppm). **TAGClO₄** shows only two signals at -289.1 ppm (N1, N3, N5) and -329.4 ppm (N2, N4, N6), while in **AFCIO₄** four different nitrogen shifts are observed. The azide group is shifted in contrast to carbon bonded covalent azides [30] in a different order, which can be explained by the presence of the positive charge building a formal carbenium ion. The azide nitrogen atoms can be found at -138.2 ppm (N3), -152.7 (N2) and -305.9 (N1) ppm. The NH_2 nitrogen shift is found at -292.2 ppm.

Table 2. ^{15}N NMR and ^{13}C NMR chemical shifts

Compound	$\delta(\text{N1})/\text{ppm}$	$\delta(\text{N2})$	$\delta(\text{N3})$	$\delta(\text{N4})$	$\delta(\text{N5})$	$\delta(\text{N6})$	$\delta(\text{C1})/\text{ppm}$
2	-285.6	-327.6	-312.4	-312.4	---	---	159.3
3	-289.1	-329.4	-289.1	-329.4	-289.1	-329.4	159.5
4	-305.9	-152.7	-138.2	-292.2	-292.2	---	159.2

**Figure 5.** ^{15}N NMR spectra of **2** - **4**.

Vibrational spectroscopy

The investigated compounds **2-4** can be easily identified using vibrational spectroscopy such as IR and Raman spectroscopy. In the Raman spectra (Figure 6) the most intense band at about 930 cm^{-1} is caused by the $\nu_s(\text{ClO}_4^-)$ vibration, which is not active in the IR spectra. The perchlorate anion shows further characteristic vibrations at about 459 cm^{-1} (δ_s), 625 cm^{-1} (δ_{as}) and 1119 cm^{-1} (ν_{as}). The N–H stretch vibrations can only be obtained as weak peaks in the Raman spectra in the range of $3200\text{-}3400\text{ cm}^{-1}$. The azidoformamidinium cation in **4** causes the characteristic vibrations at 2189 and 2128 cm^{-1} in the Raman spectra, which can be assigned to the ν_{sym} and ν_{asym} of the covalent azide. The very weak vibrations in the range of $1400\text{-}1700\text{ cm}^{-1}$ can be assigned to C–N and N–N stretching vibrations of the cations.

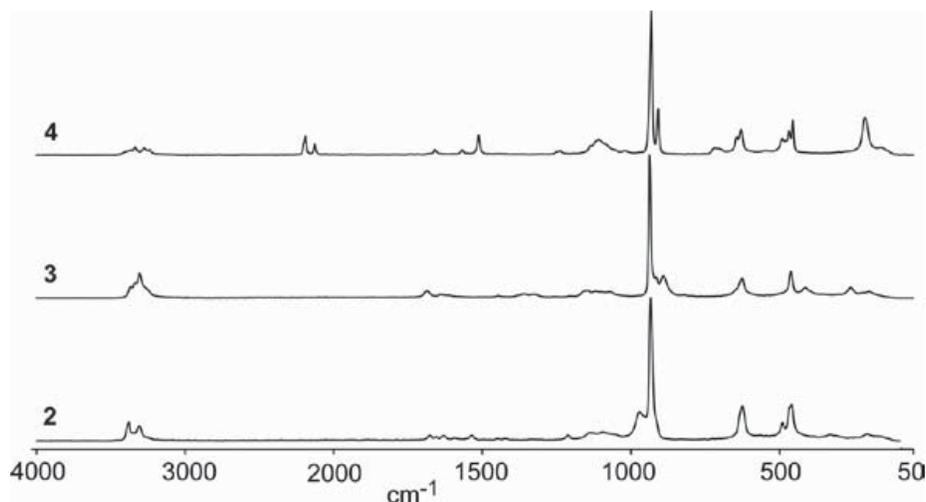


Figure 6. Raman spectra of **2** - **4**.

Thermodynamic and energetic properties

Differential Scanning Calorimetry (DSC)

DSC measurements to determine the decomposition temperatures of **2**, **3** and **4** were performed in pressed Al-containers, containing a hole (0.1 mm) for the gas release, with a nitrogen flow of 20 mL/min on a Linseis PT-10 DSC [31] calibrated by standard pure indium and zinc at heating rates of 5 °K/min. The DSC plots in Figure 7 show the thermal behavior of ca. 2.0 mg of **2**, **3** and **4** in the 50-400 °C temperature range. The temperature of decomposition can be related to the sensitivity of the compounds. **AFCIO₄** has the lowest decomposition point (125 °C), **TAGCIO₄** is the second (180 °C) and **AGCIO₄** is the most stable compound and decomposes at 250 °C. The investigated salts have discrete melting points, whereby melting temperatures do not follow the same trend of the decomposition temperatures. **TAGCIO₄** has the highest melting point within this row (**2**: 72 °C, **3**: 125 °C, **4**: 75 °C), which can be explained by the many hydrogen bonds observed in this structure.

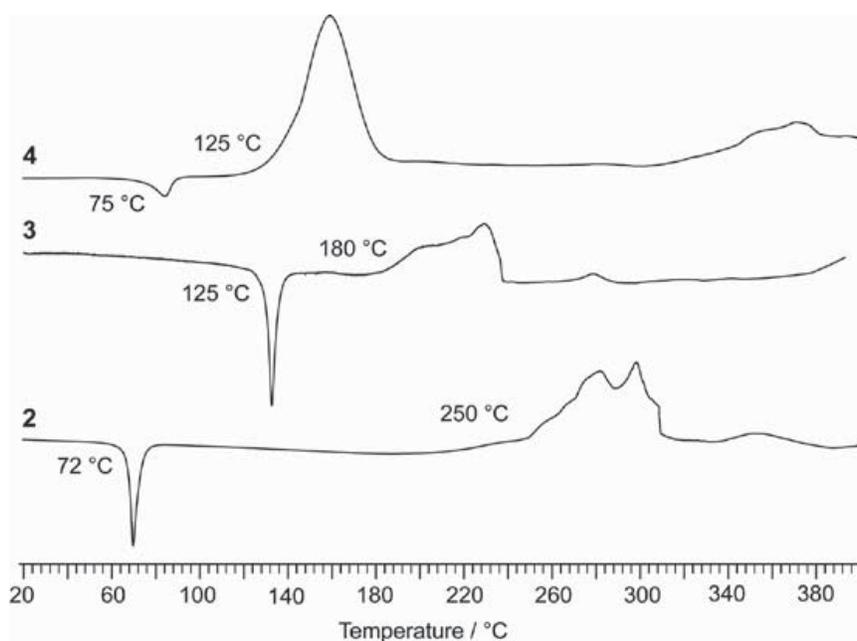
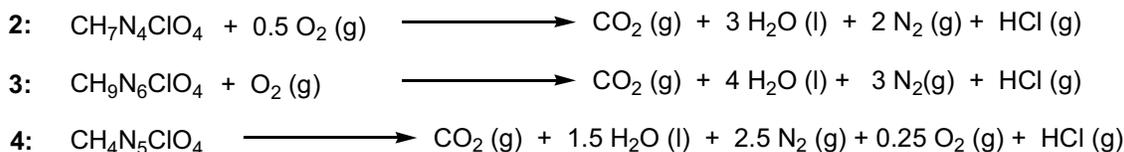


Figure 7. DSC plots of **2** - **4** ($\beta = 5 \text{ K min}^{-1}$).

Bomb Calorimetry

The heats of combustion for compounds **2**, **3** and **4** were determined experimentally, using a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb [32]. To ensure better combustion the samples (ca. 200 mg) were pressed with a defined amount of benzoic acid (ca. 800 mg) forming a tablet and a Parr 45C10 alloy fuse wire was used for ignition. In all measurements, a correction of 2.3 cal cm^{-1} wire burned has been applied, and the bomb was examined for evidence of noncombusted carbon after each run. A Parr 1755 printer was furnished with the Parr 1356 calorimeter to produce a permanent record of all activities within the calorimeter. The reported values are the average of three separate measurements. The calorimeter was calibrated by combustion of certified benzoic acid (SRM, 39i, NIST) in an oxygen atmosphere at a pressure of 3.05 MPa. The experimental results of the constant volume combustion energy ($\Delta_c U$) of the salts are summarized in Table 3. The standard molar enthalpy of combustion ($\Delta_c H^\circ$) was derived from $\Delta_c H^\circ = \Delta_c U + \Delta nRT$ ($\Delta n = \Delta n_i$ (products, g) - Δn_i (reactants, g); Δn_i is the total molar amount of gases in the products or reactants). The enthalpy of formation, $\Delta_f H^\circ$, for each of the salts was calculated at 298.15 K using Hess' law whereby the following combustion reactions (Scheme 2) were used. The enthalpies of formations show that **2** is formed exothermically, whereby **3** and **4** are endothermic compounds ($\Delta_f H^\circ$ **2**: -161 ± 7 , **3**: 121 ± 17 , **4**: $71 \pm 27 \text{ kJ/mol}$).



Scheme 2. Combustion equations.

Table 3. Physicochemical properties of **2**, **3** and **4**

Formula	CH ₇ N ₄ ClO ₄	CH ₉ N ₆ ClO ₄	CH ₄ N ₅ ClO ₄
Molecular Mass	174.56	204.59	185.54
Impact sensitivity (J) ^a	4	3	2
Friction sensitivity (N) ^b	110	45	5
N (%) ^c	32.10	41.08	37.75
Ω (%) ^d	-9.17	-15.64	4.31
Combustion	yes	yes	yes
T _{dec.} (°C) ^e	250	180	125
Density (g cm ⁻³) ^f	1.764	1.740	1.826
-ΔU _{comb.} (cal g ⁻¹) ^g	1632 ± 8	2058 ± 19	1285 ± 27
-ΔH _{comb.} ^o (kJ mol ⁻¹) ^h	1184 ± 8	1752 ± 16	987 ± 20
ΔH _f ^o (kJ mol ⁻¹) ⁱ	-161 ± 7	121 ± 17	71 ± 27

^{a,b} BAM methods, see ref. [33,34]; ^c Nitrogen content; ^d Oxygen balance; ^e Decomposition temperature from DSC (β = 5 K min⁻¹); ^f estimated from X-ray diffraction; ^g Experimental (constant volume) combustion energy; ^h Experimental molar enthalpy of combustion; ⁱ Molar enthalpy of formation.

Sensitivities

For initial safety testing, the impact and friction sensitivities were tested according to BAM methods [33, 34] using the “BAM Fallhammer” and “BAM friction tester”. Compound **2**, as well as compound **3** are sensitive towards impact (**2**: > 4 J, **3**: > 3 J) and therefore are classified as “sensitive”. Since the impact sensitivity (> 2 J) of **4** is lower than that of lead azide [35], it is classified as “extremely sensitive” and should be considered to be a primary explosive. Therefore, **4** should only be handled with appropriate precautions! Also the extreme friction sensitivity determined to be 5 N is the highest observed in this work. Compounds **2** and **3** are significantly less sensitive towards friction (**2**: > 110 N, **3**: > 45 N).

Experimental

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting points were measured with a Linseis PT-10 DSC, using heating rates of 5 deg min⁻¹ and are checked with a Büchi Melting Point B-450 apparatus. ¹H, ¹³C and ¹⁵N NMR spectra were recorded in D₂O with a Jeol Eclipse 270, Jeol EX 400 or Jeol Eclipse 400 instrument. All chemical shifts are quoted in ppm relative to TMS (¹H, ¹³C) or nitromethane (¹⁵N). Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum One FT-IR instrument. Raman spectra were measured using a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental Analyses were performed with a Netsch STA 429 Simultaneous Thermal Analyzer and mass spectrometry was done at a JEOL MStation MS-700. Bomb Calorimetry measurements were performed using a Parr 1356 Bomb calorimeter with a Parr 1108CL oxygen bomb. The sensitivity data were investigated using the BAM drophammer and friction tester.

CAUTION !

The prepared perchlorates are energetic materials which show increased sensitivities towards various stimuli. Proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar[®] gloves and ear plugs) should be used when handling compound 2, 3 and 4. Extra safety precautions should be taken, especially when compound 4 is prepared on a larger scale.

2: To aminoguanidinium bicarbonate (13.61 g, 0.10 mol) 1 M perchloric acid solution (100 mL) was added under continuous stirring. After the release of CO₂ stopped, the solvent was evaporated and the crude product was recrystallized from ethanol yielding colorless **2** (16.80 g, 96 % yield).

M.p.: 72 °C, 250 °C (dec.); **IR** (ATR, cm⁻¹): $\tilde{\nu}$ = 3459 (s), 3371 (vs), 1652 (s), 1599 (m), 1537 (w), 1420 (w), 1204 (w), 1039 (s), 930 (m), 622 (m); **Raman** (1064 nm, cm⁻¹): $\tilde{\nu}$ = 3377 (13), 3307 (10), 1676 (4), 1533 (4), 1213 (4), 1137 (5), 1096 (6), 970 (20), 933 (100), 625 (24), 490 (12), 459 (25); **¹H NMR** (D₂O, 25°C): δ = 8.49 (s, 1H, NH-NH₂), 7.15 (s, 2H, NH₂), 6.65 (s, 2H, NH₂), 4.60 (s, 2H, NH-NH₂); **¹³C NMR** (D₂O, 25°C): δ = 159.3 (C1); **¹⁵N NMR** (D₂O, 25°C): δ = -285.6 (N1), -312.4 (N3, N4), -327.6 (N2); ***m/z*** (FAB⁺): 75 (cation); ***m/z*** (FAB⁻): 99 (ClO₄⁻); **EA** (CH₇N₄ClO₄, M = 174.56) calc.: C 6.88, H 4.04, N 32.10 %; found: C 6.71, H 4.34, N 31.57 %; **BAM-Drophammer**: > 4 J; **BAM-Friction Test**: > 110 N, $\Delta U_{\text{comb.}}$: 1632 cal g⁻¹.

3: Aminoguanidinium perchlorate (8.73 g, 0.05 mol) was suspended in 40 mL of dioxane and 3 eq. of hydrazine hydrate (7.50 g, 0.15 mole, 7.3 mL) were added. The mixture was refluxed for 4 h at 90 °C until the release of NH₃ stopped. Afterwards the solvent was evaporated and the crude product was recrystallized from hot ethanol yielding **3** (9.72 g, 95 % yield).

M.p.: 125 °C, 180 °C (dec.); **IR** (ATR, cm⁻¹): $\tilde{\nu}$ = 3293 (vs), 1680 (s), 1359 (w), 1218 (w), 1056 (s), 955 (m), 936 (m), 707 (w), 618 (m); **Raman** (1064 nm, cm⁻¹): $\tilde{\nu}$ = 3363 (8), 3305 (17), 1686 (4), 1638 (2), 1361 (2), 1146 (4), 937 (100), 890 (15), 626 (13), 461 (18), 414 (7), 260 (7); **¹H NMR** (D₂O, 25°C): δ = 8.55 (NH-NH₂), 4.43 (NH-NH₂); **¹³C NMR** ([D₂O, 25°C): δ = 159.5 (C1); **¹⁵N NMR** (D₂O, 25°C): δ = -291.2 (N1, N3, N5), -333.6 (N2, N4 N6); ***m/z*** (FAB⁺): 105; ***m/z*** (FAB⁻): 99 (ClO₄⁻); **EA** (CH₉N₆ClO₄, M = 204.57) calc.: C 5.87, H 4.43, N 41.08 %; found: C 6.02, H 4.42, N 40.58 %. **BAM-Drophammer:** > 3 J, **BAM-Friction Test:** > 45 N, $\Delta U_{\text{comb.}}$: 2058 cal g⁻¹.

4: Aminoguanidinium perchlorate (6.98 g, 0.04 mol) was dissolved in 40 mL 1 M perchloric acid solution (0.04 mol). To this, a solution of potassium nitrite (3.40 g, 0.04 mol) in 20 mL of water was added dropwise while cooling the solution at 0°C. The ice bath was removed and the mixture was stirred for 30 min at RT. Afterwards urea (150 mg) was added, the precipitated potassium perchlorate was filtered off and the solvent was removed using a rotating evaporator, equipped with a water bath not hotter than 60 °C. The crude product was dissolved in a small amount of ethanol, again filtered and the ethanol was removed using high vacuum yielding colorless **4** (6.53 g, 88 % yield). Single crystals suitable for X-ray diffraction were obtained by recrystallization from 2-propanol.

M.p.: 75 °C, 125 °C (dec.); **IR** (ATR, cm⁻¹): $\tilde{\nu}$ = 3394 (vs), 3336 (s), 3260 (s), 3198 (s), 2474 (w), 2410 (w), 2189 (s), 2128 (m), 1685 (vs), 1651 (m), 1503 (s), 1240 (m), 1048 (s), 928 (w), 904 (w), 714 (w), 629 (m); **Raman** (1064 nm, cm⁻¹): $\tilde{\nu}$ = 3337 (5), 3275 (5), 3237 (3), 2189 (13), 2128 (7), 1659 (3), 1567 (3), 1512 (14), 1238 (3), 1108 (11), 1019 (3), 931 (100), 908 (32), 719 (5), 644 (12), 629 (18), 491 (11), 468 (17), 456 (24), 212 (26); **¹H NMR** ([D₂O, 25°C): δ = 8.99 (s, 2H, NH₂), 8.56 (s, 2H, NH₂); **¹³C NMR** (D₂O, 25°C): δ = 159.2 (C1); **¹⁵N NMR** (D₂O, 25°C): δ = -138.2 (N3), -152.7 (N2), -292.2 (N4, N5), -305.9 (N1); ***m/z*** (FAB⁺): 86; ***m/z*** (FAB⁻): 99 (ClO₄⁻); **EA** (CH₄N₅ClO₄, M = 185.53) calc.: C 6.47, H 2.17, N 37.75 %; found: not determined. **BAM-Drophammer:** > 2 J, **BAM-Friction Test:** > 5 N, $\Delta U_{\text{comb.}}$: 1285 cal g⁻¹.

Conclusions

From this experimental study the following conclusions can be drawn:

- Aminoguanidinium perchlorate (**2**), triaminoguanidinium perchlorate (**3**) and azidoformamidinium perchlorate (**4**) can be synthesized in high yields and purity by facile and cheap routes starting from aminoguanidinium bicarbonate.
- Compounds **2-4** can be recrystallized from aqueous ethanolic solutions obtaining single crystals suitable for X-ray diffraction. All compounds crystallize without inclusion of crystal water in monoclinic (**2**, **3**) and orthorhombic (**4**) space groups.
- The investigated compounds and especially **AFCIO₄** are very sensitive towards impact and friction and should only be handled with suitable safety precautions.
- **2-4** show melting points between 72 and 125 °C and are stable up to temperatures of 125 °C for **4** and 250 °C for **2**, whereby only moderate explosions could be detected in the DSC instrument.

Supporting Information

Crystallographic data for the structures **2**, **3** and **4** reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of the data can be obtained free of charge by quoting the numbers 664916 for **2**, 664917 for **3** and 664918 for **4** from CCDC(12 Union Road, Cambridge, CB2 1EZ, UK [fax (internat.) +44(0)1223 /336033; e-mail: deposit@ccdc.cam.ac.uk].

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