Heteroatom Chemistry
Volume 19, Number 3, 2008

The Preparation and Characterization of Guanylurea Nitrate and Perchlorate Salts

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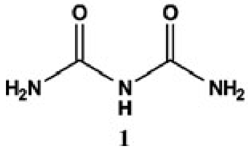
Received 5 November 2007

ABSTRACT: *Guanylurea nitrate (GUN) and guanylurea perchlorate (GUP) were prepared from cyanoguanidine (CG) and concentrated nitric or perchloric acid, respectively. Both compounds were fully characterized by analytical and spectroscopic methods. Crystals of GUP were grown from water, and its crystal structure was determined by single-crystal X-ray diffraction. GUP crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell; different unit cell parameters are $a = 8.0115(2)$ Å, $b = 9.7328(2)$ Å, $c = 9.5770(2)$ Å, and $\beta = 105.89(1)^\circ$. The heats of combustion of both compounds were determined using oxygen bomb calorimetry. Finally, the EXPLO5 computer code was used to determine the detonation velocity ($D = 5734$ m s^{-1}) and pressure ($P = 10.6$ GPa) of GUN as well as those of formulations with ammonium nitrate and dinitramide.* Heteroatom Chem 19:301–306, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20419

INTRODUCTION

The synthesis, characterization, and understanding of the properties of energetic materials are the goal of our research group [1–3]. Recently, we reported on energetic materials based on biuret (**1**) and found them to show interesting explosive properties [4,5]. Many reports have appeared in the literature mentioning about salts of the protonated parent guanylurea (**2**) with chloride [6], nitrate [7], or dinitramide [8] as the counteranion, the last one having shown prospective use as a new insensitive material with a high performance. However, very little is known about the structure and properties of salts of **2** with energetic anions as prospective energetic materials.

In the present work, we would like to report the preparation, characterization, and explosive properties of two salts of **2**, namely with nitrate (GUN) and perchlorate (GUP) anions. In addition, the crystal structure of GUP was determined.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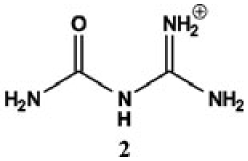
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EXPERIMENTAL SECTION

Materials and Methods

All chemicals and solvents (analytical grade) were used as supplied by Sigma-Aldrich Fine Chemicals Inc. (Taufkirchen, Germany) ^{1}H, ^{13}C, ^{14}N, and ^{35}Cl

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Contract grant sponsor: Ludwig-Maximilian University, Munich, Germany.
Contract grant sponsor: Fonds der Chemischen Industrie.
Contract grant sponsor: European Research Office of the U.S. Army Research Laboratory.
Contract grant numbers: N 62558-05-C-0027 and 9939-AN-01.
Contract grant sponsor: Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants.
Contract grant numbers: E/E210/4D004/X5143 and E/E210/7D002/4F088.

NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-d_6 at or near 25°C. The chemical shifts are given relative to tetramethylsilane (^{1}H and ^{13}C), CH_3NO_2 (^{14}N), and NaCl (^{35}Cl) as external standards. Infrared (IR) spectra were recorded on a Perkin-Elmer spectrum one FT-IR instrument [9] as KBr pellets at 20°C. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), and "weak" (w). Raman spectra were recorded on a Perkin-Elmer spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch simultaneous thermal analyzer STA 429. Melting points were determined by differential scanning calorimetry (Linseis DSC PT-10 instrument [10], calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5°C min^{-1} in closed aluminum sample pans with a 1-μm hole in the top for gas release under a nitrogen flow of 20 mL min^{-1} with an empty identical aluminum sample pan as a reference. For the calorimetric measurements, a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 207A oxygen bomb for the combustion of highly energetic materials was used [11].

Preparation of GUN

Sixty-five percent concentrated nitric acid (11.351 g, 119.02 mmol) was added dropwise to a solution of cyanoguanidine (5.001 g, 59.47 mmol) in 40 mL water by means of a dropping funnel. The solution was stirred for 15 min at room temperature and shortly boiled. Slow cooling to room temperature resulted first in cloudiness and finally in the formation of an insoluble powder that was filtered, washed with acetone, and dried under high vacuum (9.113 g, 93%). No further purification was required.

Analytical Data of GUN

IR $\tilde{\nu}$ (cm^{-1}; KBr, rel. int.): 3456(s), 3384(s), 3295(s), 3208(s), 3032(m), 2427(w), 2199(w), 2034(w), 1733(s), 1688(s), 1635(s), 1590(s), 1533(m), 1456(s), 1385(s), 1347(s), 1148(m), 1053(s), 929(m), 817(m), 753(m), 705(m), 624(s), 559(m), 501(m); Raman $\tilde{\nu}$ (cm^{-1}) (rel. int.): 3236(2), 2986(43), 1744(4), 1693(3), 1635(3), 1583(6), 1451(5), 1388(4), 1142(7), 1054(100), 930(8), 718(8), 560(3), 448(20), 287(5), 139(6); ^{1}H NMR (DMSO-d_6, 400.18 MHz, 25°C, TMS) δ (ppm): 9.47 (1H, s, −NH), 8.08 (4H, s, $H_2N{-}C{=}NH_2^+$), 7.10 (2H, s, $-NH_2$); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100.63 MHz, 25°C, TMS) δ (ppm): 155.56 (1C, C1/C2), 154.49 (1C, C2/C1); ^{14}N NMR (DMSO-d_6, 28.92 MHz, 25°C, CH_3NO_2) δ (ppm): −4.95 (1N, NO_3^-); $C_2H_7N_5O_4$ (165.05 g mol^{-1}, calcd/found): C 14.54/14.54, H 4.27/4.05, N 42.42/42.33; *m/z* (FAB$^+$, xenon, 6 keV, m-NBA matrix): 103.2 [GU]$^+$; DSC (5°C min^{-1}): 203°C (mp + dec); Sensitivity data: friction >360 N; shock >30 J; electrostatic discharge insensitive.

Preparation of GUP

Cyanoguanidine (5.001 g, 59.47 mmol) was dissolved in 20 mL water, and 70% concentrated perchloric acid (17.001 g, 119.02 mmol) was added slowly. The reaction mixture was brought to reflux and stirred for 15 min. Crystals (suitable for X-ray diffraction) of the title compound formed upon slow cooling overnight and were washed with ethanol and ether (9.919 g, 82%). No further purification was required.

Analytical Data of GUP

IR $\tilde{\nu}$ (cm^{-1}; KBr, rel. int.): 3459(s), 3378(s), 3256(s), 3187(s), 1736(s), 1679(s), 1654(m), 1583(s), 1527(m), 1465(m), 1345(m), 1108(s), 1089(s), 931(w), 764(w), 713(w), 680(w), 625(m), 559(m), 463(w); Raman $\tilde{\nu}$ (cm^{-1}) (rel. int.): 3277(3), 3072(4), 2986(100), 2187(3), 1725(15), 1618(12), 1576(9), 1532(9), 1466(16), 1335(4), 1124(18), 1081(17), 932(99), 817(4), 782(5), 707(14), 631(21), 551(7), 461(38), 436(33), 338(6), 273(139); ^{1}H NMR (DMSO-d_6, 400.18 MHz, 25°C, TMS) δ (ppm): 9.57 (1H, s, −NH), 8.00 (4H, s, $H_2N{-}C{=}NH_2^+$), 7.08 (2H, s, $-NH_2$); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100.63 MHz, 25°C, TMS) δ (ppm): 155.5 (1C, C1/C2), 154.4 (1C, C2/C1); ^{35}Cl NMR (DMSO-d_6, 400.18 MHz, 25°C, NaCl) δ (ppm): +1000 (ClO_4^-); $C_2H_7N_4O_5Cl$ (202.01 g mol^{-1}, calcd/found): C 11.88/11.79, H 3.49/3.35, N 27.73/27.45; *m/z* (FAB$^+$, xenon, 6 keV, m-NBA matrix): 103.2 [GU]$^+$; DSC (5°C min^{-1}): 204°C (dec), 241°C (mp), 313°C (bp); Sensitivity data: friction >360 N; shock >30 J; electrostatic discharge insensitive.

X-Ray Structure Determination of GUP

Crystal Data. Guanylurea perchlorate, $C_2H_7N_4O_5Cl$, $M = 202.01$ g mol^{-1}, $a = 8.0115(2)$, $b = 9.7328(2)$, $c = 9.5770(2)$ Å, and $\beta = 105.895(2)°$; $U = 718.21(3)$ Å^{-3}, space group $P2_1/c$, $Z = 4$, $D_c = 1.873$ g cm^{-3}. Crystal dimensions 0.20 × 0.10 × 0.10 mm. $\mu(\mathrm{Mo} - K_\alpha) = 0.21$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 416$.

Single crystals of GUP were grown as described in the preparation section. The X-ray crystallographic data for GUP was collected on an Oxford diffraction Xcalibur 3 diffractometer equipped with a CCD detector at –173°C. All data were collected using graphite-monochromated Mo Kα radiation, 5373 independent measured reflections, 1397 unique reflections, 1229 reflections with [$I_{\text{net}} > 2\sigma\ I_{\text{net}}$], θ range: 4.19°–26.00°, index range: $-9 \le h \le 9$, $-12 \le k \le 11$, and $-11 \le l \le 11$. No absorption correction was applied to the data sets collected.

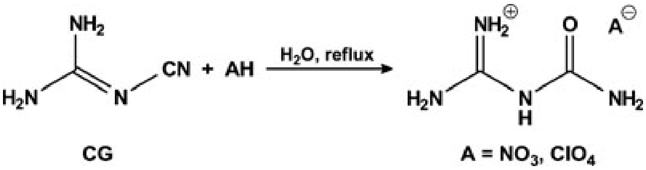
Structure Solution and Refinement. The crystal structure of GUP was solved by direct methods (SHELXS-97 and SIR97) [12] and refined by means of full-matrix least-squares procedures using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Refinement converged to $R_F = 0.0257$ ($R_F = \sum[F_0 - F_c]/\sum[F_0]$), $R_w = 0.0286$, ($R_w = \text{Sqrt}.[\sum\{w[F_0 - F_c]^2\}/\sum\{wF_0^2\}]$; for all reflections: $R_F = 0.0706$, $R_w = 0.0718$, and goodness of fit = 1.098.

Further information on the crystal structure determination (excluding structure factors) has been deposited at the Cambridge Crystallographic Data Centre (CCDC 665842) and is available free of charge by request from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (+44) 1223–336-033, e-mail deposit@ccdc.cam.ac.uk]. Crystallographic data in CIF format are also available as supporting information.

RESULTS AND DISCUSSION

Guanylurea nitrate (GUN) and perchlorate (GUP) were prepared in high purity by hydrolysis of cyanoguanidine (CG) with the corresponding concentrated acid in aqueous solution (Scheme 1). Both compounds precipitated out of the reaction mixture in high-isolated yields (>80%).

The nitrate anion in GUN shows a strong, broad, and a sharp IR absorptions centered at 1345 and 817 cm^{-1}, respectively, and a sharp band at 1055 cm^{-1} in the Raman spectrum [13–15]. The perchlorate anion in GUP shows a strong broad stretch with its maximum at 1108 cm^{-1} in the infrared spectrum and strong, sharp bands at 932 and 461 cm^{-1} in the Raman spectrum [15–16]. Both compounds show complex NH vibration bands in the range from about 3180–3460 cm^{-1} indicative of complex hydrogen bonding in the crystal structures of both compounds (see X-ray discussion below). In the double bond absorption region, several bands of different intensities are found due to C=O (GUN: 1733, GUP: 1736 cm^{-1}) and C=N (GUN: 1635, GUP: 1651 cm^{-1}) stretching modes. This region appears to be rather complicated due to the many resonating structures of the cation.



SCHEME 1 Synthesis of GUN and GUP from cyanoguanidine (CG).

The ^{1}H NMR spectra of GUN and GUP in DMSO-d_6 show three well-resolved resonances at around 9.5, 8.1, and 7.1 ppm corresponding to NH and the protons in the guanidine and urea moieties. In the ^{13}C NMR spectra, signals of the guanidine and urea carbon atoms occur at around 155.5 and 154.4 ppm and cannot be differentiated. The resonances for the anions can be found at −4.9 (^{14}N NMR, GUN) and +1000 (^{35}Cl NMR, GUP) [17], ClO_4^- (aq) +946, +1000, +1003) ppm.

The structure of GUP was determined experimentally by X-ray diffraction analysis. Repeated attempts to grow crystals of GUN were unsuccessful. Figure 1 shows a formula unit, and Figs. 2 and 3 represent the packing in the unit cell and the hydrogen bonding around the guanylurea cation, respectively, for GUP. The perchlorate salt crystallizes in a monoclinic cell in the space group $P2_1/c$ with $Z = 4$. The

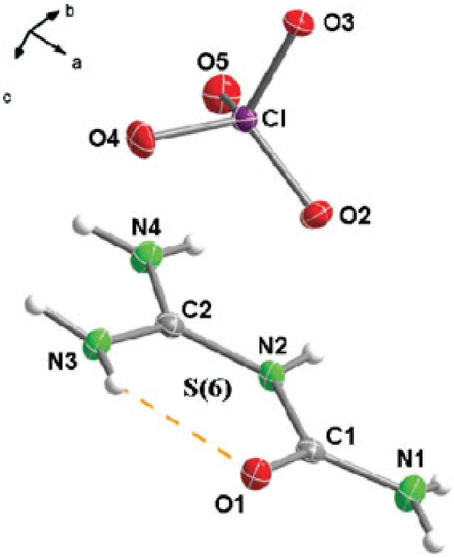


FIGURE 1 Asymmetric unit of GUP with the labeling scheme showing an intramolecular S(6) graph-set (ellipsoids represent 50% probability).

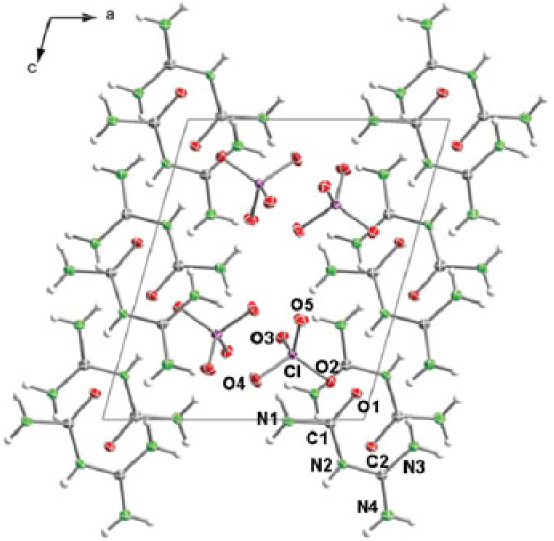


FIGURE 2 View of the unit cell of GUP along the *b* axis.

distances and angles in the cation (Tables 1 and 2) are in agreement with the previously reported chloride salt [6].

Figure 2 shows a view of the packing in the unit cell of GUP along the *b* axis. The planar cations form layers in two different directions, but the nonplanar structure of the anions does not allow an efficient packing forming layers as found in the structure of the chloride salt [6] and as it would be expected from a salt with a planar anion such as nitrate.

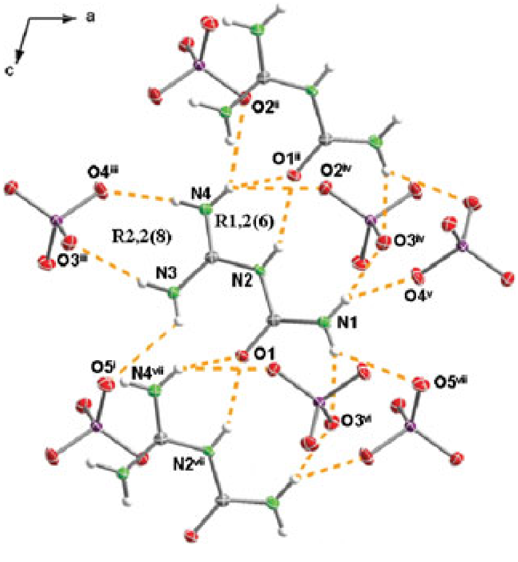


FIGURE 3 View along the *b* axis of the hydrogen bonding around the guanylurea cation in GUP (symmetry codes: (i) x, $-y + 1/2$, $z + 1/2$; (ii) x, $-y + 1/2$, $z - 1/2$; (iii) $-x - 1$, $y - 1/2$, $-z + 1/2$; (iv) $-x$, $y - 1/2$, $-z + 1/2$; (v) $+1$, y, z, (vi) $-x$, $-y + 1$, $-z + 1$; (vii) $x + 1$, $-y + 1/2$, $z + 1/2$).

TABLE 1 Selected Measured (X-ray) Bond Lengths (Å) for GUP[a]

Cl–O5	1.432(1)	N2–C1	1.398(2)
Cl–O2	1.439(1)	N3–C2	1.317(2)
Cl–O4	1.444(1)	N1–C1	1.330(2)
Cl–O3	1.461(1)	N4–C2	1.319(2)
O1–C1	1.233(2)	O1–N3	2.659(2)
N2–C2	1.357(2)	O2–N3	3.518(2)

[a] Atomic labeling in analogy to Fig. 1.

The guanylurea cation in GUP is involved in a total of 12 hydrogen bonds (Table 3) with the perchlorate anion or other cations, one of which is intramolecular (Fig. 1; N3—H3A···O1 = 2.659(2) Å). The two hydrogen bonds formed with the cations are one of very strong (N2—H2···O1^{ii} = 2.824(2) Å; symmetry code: (ii) x, $-y + 1/2$, $z - 1/2$) and the other of weak (N4—H4B···O1^{ii} = 3.204(2) Å) nature. The bonds formed with the anions have distances between donor and acceptor, which vary in the range between 2.9 and 3.2 Å.

Complete description of the reasonably complex hydrogen-bonding network in **1** is facilitated by the use of graph-set analysis as described by Berstein et al. [18]. For **1**, the computer program *RPLUTO* [19] identifies the 12 hydrogen bonds tabulated in Table 3. Most of these hydrogen bonds are simple dimeric interactions of the type D1,1(2). Besides, there are two C1,1(4) and C1,1(6) chain graph-sets and the above-mentioned intramolecular hydrogen bond describes a pattern that takes the label S(6). At the secondary level, there are several characteristic two hydrogen bonds (binary) D3,3 finite patterns, C2,2 chain motifs and, more interesting, ring graph-sets including R1,2(6), R2,2(8), R4,4(12), R4,4(16), and R4,4(20). In Fig. 3, the two smallest ring patterns formed are presented. The R1,2(6) motif is formed between the carbonyl oxygen (O1^{ii}, symmetry code: (ii) x, $-y + 1/2$, $z - 1/2$) of one cation and the nitrogen atoms labeled as N2 and N4 of another cation, whereas the larger R2,2(8) motif is formed by two hydrogen bonds between the cation and the anion (N3—H3B···O3^{iii} = 2.964(2)

TABLE 2 Selected Measured (X-ray) Bond Angles (°) for GUP[a]

O5–Cl–O2	110.3(1)	N3–C2–N4	121.2(2)
O5–Cl–O4	110.2(1)	N3–C2–N2	121.0(1)
O2–Cl–O4	110.2(1)	N4–C2–N2	117.8(1)
O5–Cl–O3	109.4(1)	O1–C1–N1	124.4(1)
O2–Cl–O3	108.9(1)	O1–C1–N2	122.0(1)
O4–Cl–O3	107.9(1)	N1–C1–N2	113.6(1)
C2–N2–C1	126.0(1)		

[a] Atomic labeling in analogy to Fig. 1.

TABLE 3 Hydrogen-Bonding Geometry in GUP

D—H···A[a]	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
N3—H3A···O1	0.81(2)	2.04(2)	2.659(2)	133(2)
N3—H3A···O5^{i}	0.81(2)	2.46(2)	2.947(2)	120(2)
N2—H2···O1^{ii}	0.78(3)	2.14(3)	2.824(2)	147(2)
N4—H4B···O2^{ii}	0.83(3)	2.33(2)	3.013(2)	140(2)
N4—H4B···O1^{ii}	0.83(3)	2.64(2)	3.204(2)	127(2)
N3—H3B···O3^{iii}	0.87(2)	2.13(3)	2.964(2)	160(2)
N4—H4A···O4^{iii}	0.85(2)	2.31(2)	3.141(2)	166(2)
N4—H4B···O2^{iv}	0.83(3)	2.65(2)	3.247(2)	130(2)
N1—H1B···O3^{iv}	0.84(2)	2.26(2)	3.029(2)	152(2)
N1—H1B···O4^{v}	0.84(2)	2.52(2)	3.028(2)	120(2)
N1—H1A···O3^{vi}	0.82(2)	2.31(2)	3.060(2)	152(2)
N1—H1A···O5^{vii}	0.82(2)	2.65(2)	3.084(2)	115(2)

[a] Symmetry codes: (i) $x, -y + 1/2, z + 1/2$; (ii) $x, -y + 1/2, z - 1/2$; (iii) $-x - 1, y - 1/2, -z + 1/2$; (iv) $-x, y - 1/2, -z + 1/2$; (v) $+1, y, z$; (vi) $-x, -y + 1, -z + 1$; (vii) $x + 1, -y + 1/2, z + 1/2$.

TABLE 4 Thermodynamic and Explosive Properties of Pure GUN and Formulations with Ammonium Nitrate (AN) and Dinitramide (ADN), Calculated with EXPLO5

	GUN	GUN + AN[a]	GUN + ADN[b]
ρ (g cm^{-3})[c]	1.567	1.665	1.704
M(g mol^{-1})	165.11	111.50	141.70
Ω(%)[d]	−33.9	0.0	+0.1
$\Delta U^{\circ}{}_{f}$ (kJ kg^{-1})[e]	−4242	−4356	−2444
$\Delta H^{\circ}{}_{f}$ (kJ mol^{-1})[f]	−721	−500	−364
T_{ex} (K)[g]	1577	2533	3169
V_0 (L kg^{-1})[h]	849	931	880
D (m s^{-1})[i]	5734	7424	8027
P (GPa)[j]	10.6	20.2	24.8

[a] 63% AN + 37% GUN.
[b] 57% ADN + 43% GUN.
[c] The density of pure GUN was measured experimentally using a picnometer.
[d] Oxygen balance according to [21].
[e] Calculated energy of formation.
[f] Calculated enthalpy of formation.
[g] Temperature of the explosion gases.
[h] Volume of the explosion gases.
[i] Detonation velocity.
[j] Detonation pressure.

Å and N4–H4A··· O4^{iii} = 3.141(2) Å; symmetry code: (iii) $-x - 1, y - 1/2, -z + 1/2$).

To assess the energetic properties of GUN and GUP, its thermal stabilities, sensitivity to friction, impact, electrostatic discharge (BAM tests) [14–16], and thermal shock were experimentally determined. Figure 4 shows the DSC thermographs for both salts. At a heating rate of 5°C min^{-1}, GUN melts at 203°C with concomitant decomposition, whereas the DSC graph for GUP shows decomposition at around 201°C and two endotherms at around 241°C and 313°C corresponding to the melting and boiling of the decomposition product, respectively.

No detonation was observed neither in the drop-hammer (~30 J) nor in the friction test (~360 N). No explosion occurred either when grounding the compound in a mortar or when applying an electrostatic discharge by spraying sparks across a small sample of the material using a tesla coil (~20 kV). Thermal shock in a Bunser burner flame results in rapid burning with no explosion in both cases.

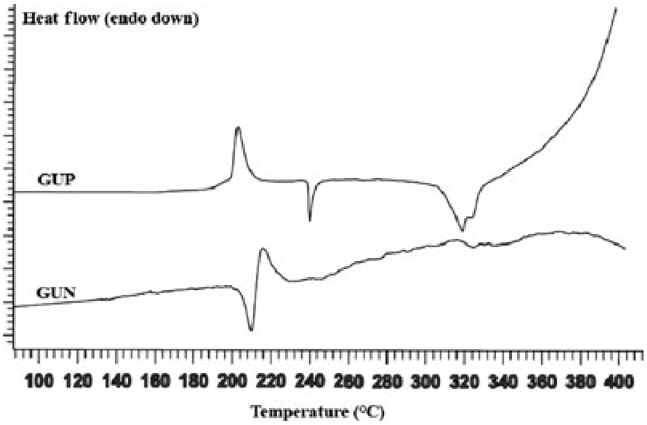


FIGURE 4 DSC thermographs of guanylurea nitrate and perchlorate at a heating rate of 5°C min^{-1}.

The heats of combustion (ΔH_{comb}) of GUN and GUP were experimentally determined using bomb calorimetry to be −1546 and −1510 cal g^{-1}, respectively. The energies of formation (ΔU_f) were back calculated from the ΔH_{comb} to be −4242 (GUN) and −2433 (GUP) kJ kg^{-1}. Using the molecular formula, density, and ΔU_f, the EXPLO5 computer code [20] can be used to calculate the detonation velocity (D) and pressure (P) of CHNO-based explosive materials. For GUN, moderate values for the detonation parameters were calculated ($D = 5734$ m s^{-1} and $P = 10.6$ GPa) comparable to those of tetranitromethane, for which $D = 5995$ m s^{-1} and $P = 13.4$ GPa. The low-oxygen content of GUN ($\Omega = -33.9\%$)* and relatively low performance of the standalone compound prompted us to calculate the performance of its mixtures with an oxidizer such as ammonium nitrate (AN) or ammonium dinitramide (ADN) in a neutral oxygen ratio. The results obtained are tabulated in Table 4. Both AN and ADN increase remarkably the detonation parameters of GUN (AN: $D = 7424$ m s^{-1}, and $P = 20.2$ GPa, ADN: $D = 8027$ m s^{-1}and $P = 24.8$ GPa) to values comparable to those calculated for formulations of TNT with AN ($\Omega = +0.2\%$) for which $D = 8087$ m s^{-1}, and $P = 25.4$ GPa.

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*Calculation of the oxygen balance: $\Omega(\%) = (\text{O} - 2\text{C} - \text{H}/2 - x\text{AO})1600/M$; where M is molecular mass.

In conclusion, two salts containing the planar guanylurea cation with nitrate (GUN) and perchlorate (GUP) anions were synthesized in high yields and fully characterized. In addition, the crystal structure of the perchlorate salt was solved. The compounds showed good thermal stabilities to above 200°C and no sensitivity to classical stimuli. The performance of the nitrate salt and that of mixtures with AN and ADN were assessed, showing good performances for formulations of GUN with ADN, which may make GUN of prospective interest in new environmentally friendly, insensitive explosive formulations.

SUPPORTING INFORMATION

Supporting information related to the crystallographic data is available from the first author (tmk@cup.uni-muenchen.de) on request.

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