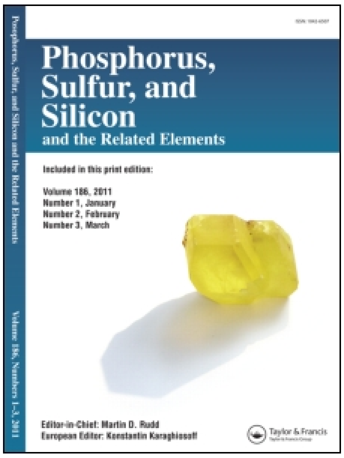

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Crystal Structures of Mono-, Di-, and Triaminoguanidinium Sulfate, as Well as Azidoformamidinium Sulfate: Important Precursors for Syntheses of Nitrogen Rich Ionic Compounds

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*Bis(1-aminoguanidinium) sulfate monohydrate ($AG_2SO_4 \cdots H_2O$, **1**), bis(1,3-diamino-guanidinium sulfate (DAG_2SO_4, **2**), bis(1,3,5-triaminoguanidinium) sulfate dihydrate ($TAG_2SO_4 \cdots 2H_2O$, **3**) and bis(azidoformamidinium) sulfate (AF_2SO_4, **5**) were synthesized and characterized by multinuclear NMR, IR, and Raman spectroscopy and elemental analysis. In the synthesis of **3**, double protonated triaminoguanidinium sulfate ($HTAGSO_4$, **4**) was obtained as a byproduct. The molecular structures of **1–5** in the crystalline state were determined by low-temperature single crystal X-ray diffraction. **1**: orthorhombic, Pnma, a = 6.7222 (8) Å, b = 14.153 (2) Å, c = 11.637 (1) Å, V = 1107.1(2) Å^3, Z = 4, $\rho_{calc.} = 1.586\ g\ cm^{-3}$, $R_1 = 0.0442$, $wR_2 = 0.1007$ (all data). **2**: hexagonal, $P6_122$, a,b = 6.6907 (1) Å, c = 43.4600 (8) Å, $\gamma = 120^\circ$, V = 1684.86 (5) Å^3, Z = 6, $\rho_{calc.} = 1.634\ g\ cm^{-3}$, $R_1 = 0.0321$, $wR_2 = 0.0714$ (all data). **3**: monoclinic, C2/c, a = 9.6174 (8) Å, b = 22.858 (1) Å, c = 6.7746 (5) Å, $\beta = 109.49$ (1), V = 1404.0 (4) Å^3, Z = 4, $\rho_{calc.} = 1.620\ g\ cm^{-3}$, $R_1 = 0.0292$, $wR_2 = 0.0781$ (all data). **4**: monoclini c, $P2_1/c$, a = 8.9998 (9), b = 6.3953 (6), c = 13.3148(12) Å, $\beta = 99.679$ (8), V = 755.44 (13) Å^3, Z = 4,*

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$\rho_{calc.} = 1.778\,g\,cm^{-3}$, $R_1 = 0.0305$, $wR_2 = 0.0809$ (all data); ***5****: orthorhombic, Pbca, $a = 11.3855\,(9)$, $b = 7.1032\,(6)$, $c = 12.807\,(1)$ Å, $V = 1035.74\,(14)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.720\,g\,cm^{-3}$, $R_1 = 0.0389$, $wR_2 = 0.0862$ (all data).*

Keywords Aminoguanidinium; azidoformamidinium; crystal structures; diaminoguanidinium; sulfates; triaminoguanidinium

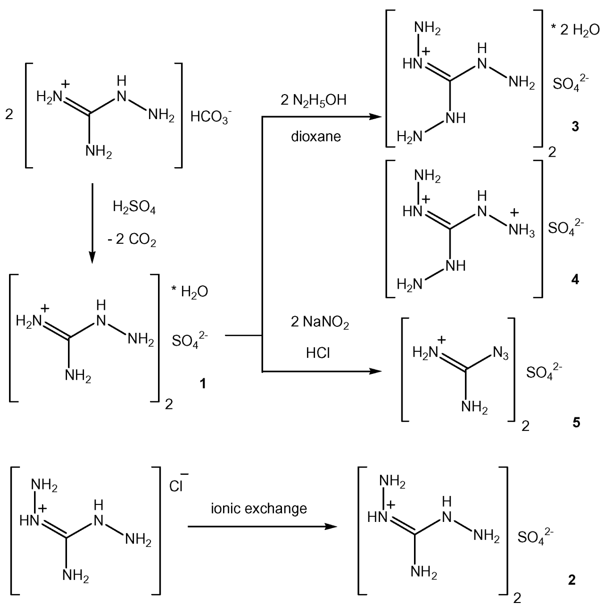
INTRODUCTION

Guanidine chemistry has extended over a period of more than 100 years, and many useful compounds have been identified. The spectrum of uses of these compounds is highly diverse, ranging from biologically active molecules to highly energetic materials, thus indicating the manifold usability of the guanidine moiety as building block.[1] The development of new high-energy-density materials (*HEDM*)[2] is an ongoing area of interest in our research group.[3] One approach is the synthesis of nitrogen-rich compounds, which deliver their energy due to their high heat of formation. In addition to the common ammonium and toxic hydrazinium cations, guanidinium derivatives are used as nitrogen-rich cations in energetic salts. High-energetic salts have the main advantages of often possessing a high thermal stability, a low vapor pressure, and higher densities, due to their lattice energies.[4] Many energetic nitrogen-rich guanidinium salts like guanidinium dinitramide,[5] aminoguanidinium dinitramide,[6] bisguanidinium dinitramide,[7] triaminoguanidinium dinitramide,[8] guanidinium 5,5′-azotetrazolates,[9] and bistetrazolylamines[10] were synthesized and characterized as energetic materials. Mostly the syntheses of these compounds proceed via metathesis reaction either using the precipitation of low-soluble silver chloride or compounds like barium sulfate. For the latter case, guanidinium sulfates can be used as the ideal starting materials. Guanidinium sulfate itself is commercially available and also its structure is described in the literature.[11] Also, the structure of zinc guanidinium sulfate was determined and discussed.[12] Here we present the synthesis and characterization of several further guanidinium sulfates with high nitrogen content by facile reactions that can be also performed in larger scales.

RESULTS AND DISCUSSION

Synthesis

The syntheses of *bis*(1-aminoguanidinium) sulfate monohydrate (**$AG_2SO_4 \cdots H_2O$**, **1**), *bis*(1,3-diaminoguanidinium) sulfate



SCHEME 1 Synthesis of guanidinium sulfates **1**–**5**.

(**DAG$_2$SO$_4$**, **2**), *bis*(1,3,5-triaminoguanidinium) sulfate dihydrate (**TAG$_2$SO$_4$**, **3**), and *bis*(azidoformamidinium) sulphate (**AF$_2$SO$_4$**, **5**) were performed according to Scheme 1. Aminoguanidinium bicarbonate is a cheap, commercially available starting material, which can be reacted with diluted mineral acids forming the corresponding aminoguanidinium salts. The reaction with half an equivalent of 1 M H_2SO_4 was performed in an open vessel for better CO_2 release. After evaporating of the water, the raw product is recrystallized from a hot ethanol/water (3:1) mixture yielding colorless single crystals of *bis*(1-aminoguanidinium) sulfate monohydrate (**1**). This can be transformed into *bis*(1,3,5-triaminoguanidinium) sulfate dihydrate (**4**) by the reaction with an excess of hydrazine hydrate in dioxane solution. The reaction progress can be controlled by the release of NH_3 gas using a bubble counter. Single crystals of **3** were obtained by recrystallization from a hot ethanol/water (4:1) mixture. A very small amount of the double-protonated triaminoguanidinium sulfate (HTAGSO$_4$, **4**) was detected using a microscope while picking a suitable crystal of **3** for X-ray diffraction. However, **4** can be synthesized selectively by the reaction of **3** with sulfuric acid. *bis*(Azidoformamidinium) sulfate (**5**) is obtained by the reaction of **1** with two equivalents of sodium nitrite and diluted hydrochloric acid at temperatures lower than 40°C. After evaporating the water at temperatures not higher than 70°C, (to avoid a ring closure reaction forming 5-aminotetrazole),[13] single crystals were also obtained from a ethanol/water (1:1) mixture.

Molecular Structures

The single crystal X-ray diffraction data of **1**, **4**, and **5** were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD detector. The data collection was undertaken using the CRYSALIS CCD software[14] and the data reduction was performed with the CRYSALIS RED software.[15] The data for compound **2** were collected on a Nonius Kappa CCD diffractometer under an N_2 stream. Data collection and reduction was done by the Bruker "Collect" and the "HKL Denzo and Scalepack" software.[16] The data for compound **3** were collected on a STOE IPDS diffractometer at 200 K. The structures were solved with SIR-92[17] (**1**, **5**), SIR-97[18] (**3**), and SHELXS-97[19] (**2**, **4**) and refined with SHELXL-97[20] implemented in the program package WinGX[21] and finally checked using PLATON.[22] Due to the chiral space group in the structure of **2** the "Friedel pairs" were merged. Selected data and parameters from the X-ray data collection and refinement are given in Table I. Further information regarding the crystal structure determination has been deposited with the Cambridge Crystallographic Data Centre[23] as supplementary publications CCDC 701148 (**1**), CCDC 701147 (**2**), CCDC 701146 (**3**), CCDC 701145 (**4**), and CCDC 701149 (**5**).

AG_2SO_4

H_2O crystallizes in the orthorhombic crystal system in the space group *Pnma*. By including four molecular moieties in the unit cell, a density of 1.586 g cm^{-3} is calculated, which is the lowest observed in this work. The atoms S1, O1, O3, O4, H4a, and H4b lie on the special position $-x, {}^3\!/_3\ , -z$, representing a mirror along the *a*,c-plane. As expected and found in all structures discussed in this work, the sulfate anions are tetrahedral (O–S–O angles between 108.9 and 110.1°). The S–O bond lengths of all structures of **1–5** lie between 1.46 and 1.48 Å, which are typical values observed for the sulfate anion; e.g., in sodium[24] or potassium sulfate.[25] In general, the aminoguanidinium cations have geometries also found in aminoguanidinium chloride,[26] nitrate,[27] or perchlorate.[28] They are nearly planar (N1–C1–N3–N4 = 2.1(2)°), whereby three different C–N bond lengths are observed (C1–N1 = 1.335(3) Å, C1–N3 = 1.325(3) Å, and C1–N4 = 1.312(3) Å). These distances are considerably shorter than C–N single bonds (1.47 Å) but

TABLE I Crystallographic Data for Compounds 1–5

	1	2	3	4	5
Formula	$C_2H_{16}N_8O_5S$	$C_2H_{16}N_{10}O_4S$	$C_2H_{22}N_{12}O_6S$	$CH_{10}N_6O_4S$	$C_2H_8N_{10}O_4S$
Form. weight (g mol^{-1})	264.30	276.28	342.39	202.21	268.24
Crystal system	Orthorhombic	Hexagonal	Monoclinic	Monoclinic	Orthorhombic
Space group	*Pnma* (62)	$P6_122$ (178)	*C2/c* (15)	$P2_1/n$ (14)	*Pbcn* (60)
Color/habit	Colorless needles	Colorless prism	Colorless needles	Colorless rods	Colorless blocks
Size (mm)	0.25 × 0.32 × 0.24	0.04 × 0.12 × 0.17	0.20 × 0.29 × 0.38	0.10 × 0.10 × 0.14	0.22 × 0.31 × 0.35
a (Å)	6.7222 (8)	6.6907 (1)	9.6174 (8)	8.9998 (9)	11.3855 (9)
b (Å)	14.153 (2)	6.6907 (1)	22.858 (1)	6.3953 (6)	7.1032 (6)
c (Å)	11.637 (1)	43.4600 (8)	6.7746 (5)	13.315 (1)	12.807 (1)
α(°)	90	90	90	90	90
β (°)	90	90	109.490 (9)	99.679 (8)	90
γ(°)	90	120	90	90	90
V (Å^3)	1107.1 (2)	1684.86 (5)	1404.0 (2)	755.44 (13)	1035.7 (1)
Z	4	6	4	4	4
$\rho_{\text{calc.}}$ (g cm^{-3})	1.586	1.634	1.620	1.778	1.720
μ (mm^{-1})	0.319	0.317	0.285	0.422	0.342
F (000)	560	876	728	424	
$\lambda_{MoK\alpha}$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	200	200	200	200	200
Θ_{Min}, Θ_{Max} (°)	4.5, 26.3	3.5, 26.1	2.4, 27.9	4.4, 26.2	4.6, 26.0
Dataset	−8:5; −16:17; −14:13	−8:8; −8:8; −53:53	−12:12; −30:27; −8:8	−11:9; −7:7; −16:16	−14:14; −8:8; −15:15
Reflections collected	5486	8426	6062	3792	9576

(Continued on next page)

TABLE I Crystallographic Data for Compounds 1–5 *(Continued)*

	1	2	3	4	5
Independent reflections	1167	1102	1577	1513	1018
R_{int}	0.044	0.091	0.036	0.018	0.027
Observed reflections	1011	991	1383	1381	1006
No. parameters	114	120	140	149	94
R_1 (obs)	0.0405	0.0321	0.0292	0.0305	0.0389
wR_2 (all data)	0.0906	0.0714	0.0781	0.0809	0.0862
S	1.15	1.07	1.03	1.03	1.18
Resd. dens. (e Å^{-3})	−0.38, 0.24	−0.32, 0.25	−0.35, 0.25	−0.46, 0.23	−0.39, 0.22
Device type	Oxford Xcalibur3 CCD	Nonius Kappa CCD	Stoe IPDS	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SHELXS-97	SIR-97	SHELXS-97	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	Multi-scan	None	None	Multi-scan	Multi-scan
CCDC	701148	701147	701146	701145	701149

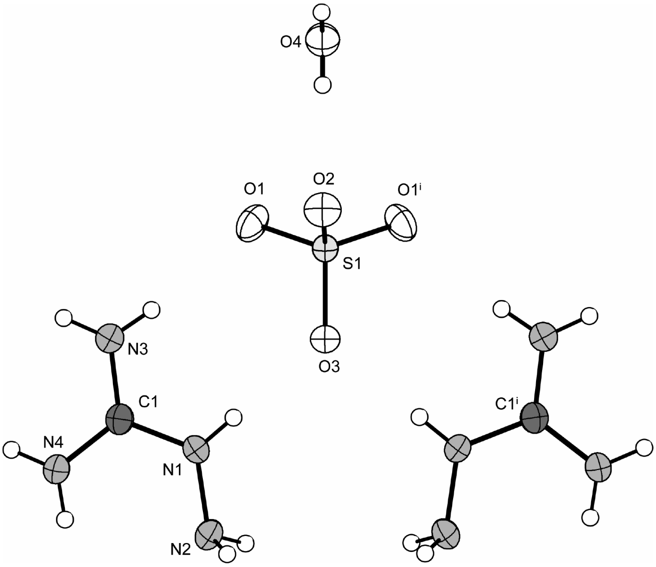


FIGURE 1 Molecular moiety of **1** H_2O. Thermal ellipsoids are drawn at the 50% probability level. (i) x, −0.5 − y, z.

significantly longer than C = N double bonds (1.22 Å)[29] and show explicitly the delocalization of the positive charge. However, the N1–N2 hydrazine bond length of 1.407(2) Å is found to be significantly longer (Figure 1).

The packing of **1** is strongly influenced by several strong hydrogen bonds involving all oxygen atoms of the sulfate anions. With this a wave-like pattern is formed, which can be seen in Figure 2 along the *c* axis.

DAG_2SO_4

DAG_2SO_4 crystallizes in the hexagonal space group $P6_122$ with six molecules in the unit cell (Figure 3). The sulfate anions are strongly disordered; therefore, the atom O2 was split into two positions. The geometry of the 1,3-diaminoguanidinium cations is comparable to that of, e.g., diamino-guanidinium azotetrazolate[9] and diaminoguanidinium 3-nitro-1,2,4-triazol-5-one.[30] The C–N bonds are in the same range as observed in **1** (C1–N1 = 1.329(2) Å, C1–N3 = 1.315(3) Å, and C1–N5 = 1.323(3) Å). Also, the hydrazine bonds are regulated and have distances of 1.406(2) Å (N1–N2) and 1.400(2) Å (N3–N4). The packing of **2** is shown in Figure 4. Again, the packing is characterized by several

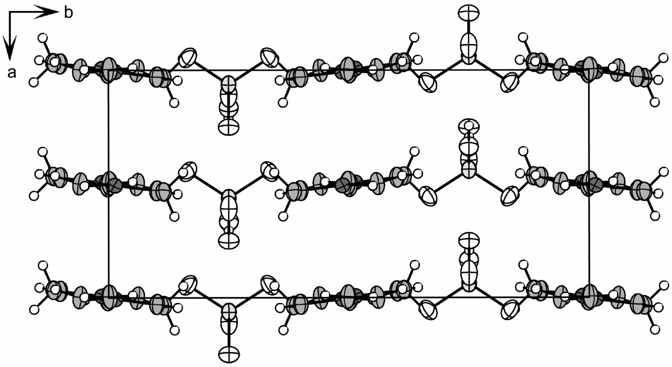


FIGURE 2 View of the unit cell of **1** along the *c* axis.

strong hydrogen bonds, mainly formed between the oxygen atoms of the sulfate anions and the nitrogen atoms of the cations.

TAG_2SO_4

$TAG_2SO_4 * 2\ H_2O$ crystallizes in the monoclinic space group *C*2/*c*, whereby four molecular moieties are found in the unit cell. The geometry of the cation is comparable to that observed for triaminoguanidinium chloride[31] and nitrate[32] in the literature. Again, the positive charge is delocalized, which can be seen by the similar C–N bond lengths (d(C1–N1) = 1.325(2) Å, d(C1–N3) = 1.333(2) Å, d(C1–N5) = 1.325(2) Å) building a planar fragment (Figure 5). The hydrazine bonds have similar lengths between 1.40 and 1.42 Å. Again, the packing is influenced by several N–H · · · O and N–H · · · N hydrogen bonds, resulting in a density of 1.620 g cm^{-3}.

By having a view along the *c* axis the typical arrangement of *C*2/*c* structures can be detected. The cations are formed in shifted layers orthogonal to the *c* axis. The water molecules are located within these

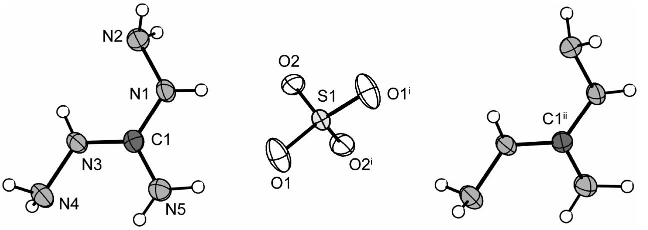


FIGURE 3 Molecular moiety of **2**. Thermal ellipsoids are drawn at the 50% probability level. (i) x, 2 + x − y, 1/6 − z, (ii) −1 + y, 1 − x + y, −1/6 + z.

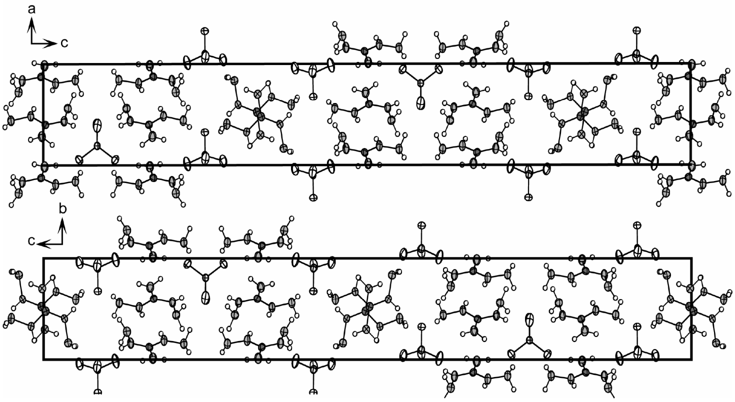


FIGURE 4 View of the unit cell along the *b* (top) and the *a* axis (below).

layers, whereas the sulfate anions act as cross-linkers between the layers (Figure 6).

The molecular moiety of **HTAGSO$_4$**, which crystallizes in the monoclinic space group $P2_1/n$, is depicted in Figure 7. The density of 1.778 g cm^{-3} is the highest observed in this work. The second protonation takes place at one of the outer NH$_2$ groups. This causes an elongation ($\sim$ 0.03 Å) of the corresponding C1–N1 bond. However, the N–N bonds are all in the same range. In contrast to the geometry in **3**, the cation is not planar, whereby especially the NH$_3$ group is bent (torsion angle N3–C1–N1–N2 = −29.6(2)°).

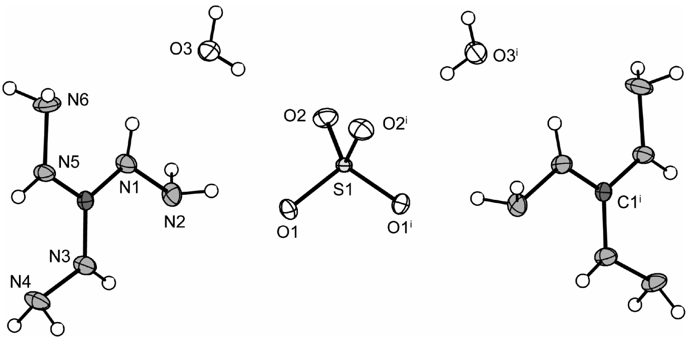


FIGURE 5 Molecular moiety of **3**. Thermal ellipsoids are drawn at the 50% probability level. (i) 1 − x, y, −0.5 − z.

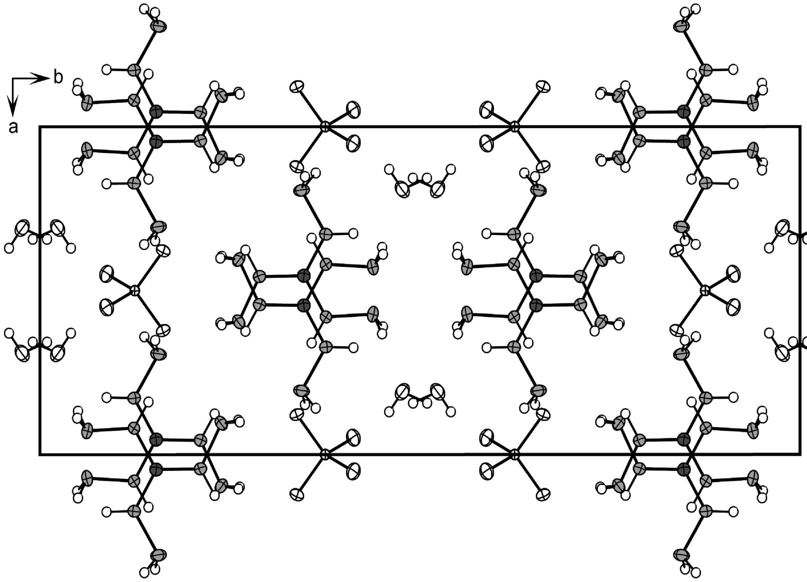


FIGURE 6 View of the unit cell of compound **3** along the *c* axis.

AF_2SO_4

AF_2SO_4 crystallizes in the orthorhombic space group *Pbcn* with eight formula moieties in the unit cell and the highest density of 1.720 g cm^{-3} observed for the mono-protonated guanidinium cations in this work

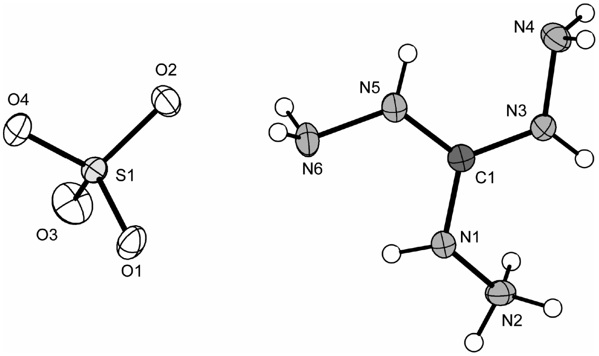


FIGURE 7 Molecular moiety of **4**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å): N1–C1 = 1.358 (2), C1–N3 = 1.321 (2), C1–N5 = 1.323 (2), N1–N2 = 1.426 (2), N3–N4 = 1.418 (2), N5–N6 = 1.415 (2).

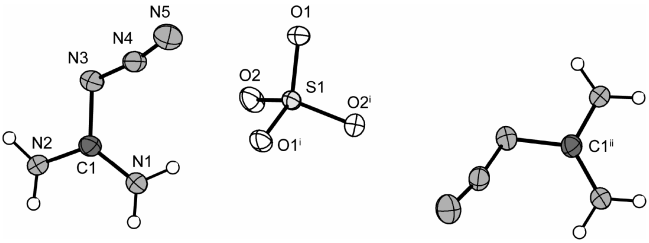


FIGURE 8 Molecular moiety of **5**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances (Å): C1–N1 = 1.317 (3), C1–N2 = 1.302 (2), C1–N3 = 1.398 (2), N3–N4 = 1.268 (2), N4–N5 = 1.112 (2). (i) 1 − x, y, 0.5 − z, (ii) 0.5 + x, −0.5 + y, 0.5 − z.

(Figure 8). The azidoformamidinium moiety is not planar (torsion angle N4–N3–C1–N1 = 15.3(3)°) and the azide has a N1–N2–N3 angle of 170.5(2)°, which is quite common for covalent azide groups and can be explained by hyperconjugation effects.[33] The NH_2 groups are in plane with the carbon atom, displaying a N1–C1–N2 angle of 124.0(2)°. The C−N distances and intramolecular angles are similar to those of azidoformamidinium chloride[34] and highly explosive azidoformamidinium perchlorate.[28] A good vibrational spectroscopy discussion of azidoformamidinium salts can be found in the literature.[35] The packing of **5** is also characterized by a three-dimensional network (Figure 9), whereby several strong hydrogen bonds are formed by the nitrogen atoms N1 and N2. The azide nitrogen atoms do not participate in any hydrogen bonds.

EXPERIMENTAL

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics) if not stated otherwise. 1-Aminoguanidine bicarbonate was purchased from Aldrich. 1,3-Diaminoguanidinium chloride was purchased from Acros Organics. Melting points were measured with a Linseis PT 10 DSC,[36] using heating rates of 5 degrees/min^{-1}. ^{1}H and ^{13}C spectra were recorded with a Jeol EX 400 or a Jeol Eclipse 400 instrument. All chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C). 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.

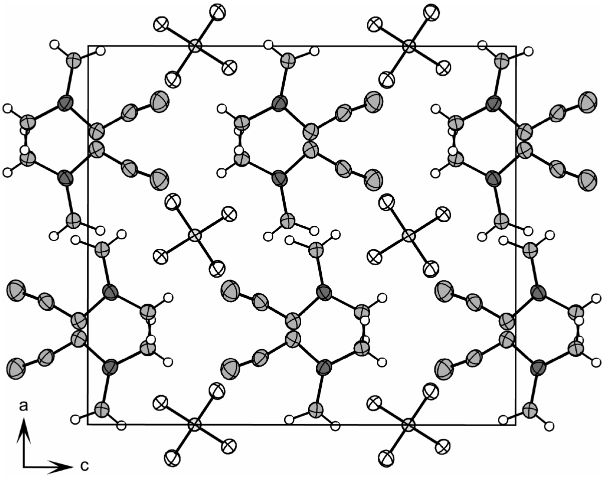


FIGURE 9 View of the unit cell along the *c* axis. Selected hydrogen bonds: N1–H1B ··· O1 (0.85 (3), 1.98 (3), 2.829 (2) Å, 172 (2)°); N2–H2B ··· O1 (0.86 (3), 1.94 (3), 2.795 (2) Å, 174 (2)°); N2–H2A ··· O2 (0.84 (2), 1.98 (2), 2.827 (2) Å, 175 (2)°); N1–H1A ··· O2 (0.82 (3), 2.15 (3), 2.962 (2) Å, 171 (2)°).

bis(1-Aminoguanidinium) Sulfate Monohydrate (1)

Aminoguanidinium bicarbonate (13.61 g, 0.1 mol) was neutralized with 50 mL (0.05 mol) of a 1 M H_2SO_4 solution. The mixture was warmed briefly to 80°C to increase the rate of CO_2 formation. After evaporation of the aqueous solution, the residue was recrystallized from an EtOH/water (3:1) mixture, whereby **1** was obtained as colorless needles suitable for XRD (11.5 g, 82%). mp 206°C (DSC, 5°/min); IR (KBr, cm^{-1}): $\tilde{\nu} = 3452$ (s), 3365 (s), 3349 (s), 3297 (s), 2929 (w), 1672 (s), 1655 (vs), 1570 (w), 1530 (w), 1420 (m), 1384 (w), 1317 (w), 1208 (m), 1121 (s), 988 (m), 724 (w), 617 (m), 503 (m), 479 (m); Raman (200 mW, 25°C, cm^{-1}): $\tilde{\nu} = 3250$ (8), 3203 (7), 1674 (5), 1612 (6), 1090 (6), 986 (100), 649 (8), 614 (6), 559 (6), 512 (9), 447 (16), 340 (8), 167 (9); ^1H NMR (*d*6-DMSO): $\delta = 8.51$ (s, 1*H*, N*H*), 7.04 (s, 4*H*, NH_2), 4.20 (s, 2*H*, NH_2), 3.40 (s, 2*H*, H_2O); ^{13}C NMR (*d*6-DMSO): $\delta = 159.3$ (*C*); Anal. Calcd for $C_2H_{16}N_8O_5S$ (264.27): C, 9.09; H, 6.10; N, 42.40. Found: C, 9.14; H, 6.29; N, 42.02%.

bis(1,3-Diaminoguanidinium) Sulfate (2)

A strong basic anionic-exchanger in Cl^- -form (Lewatit, M 5080, Merck) was loaded three times with an almost saturated aqueous Na_2SO_4 solution. A concentrated solution of diaminoguanidinium chloride (1.26 g, 0.01 mol) in 5 mL of water was exchanged once and the column was washed with water. After evaporation of the solvent and recrystallization from a small amount of water, **2** (1.24 g, 95%) was obtained as colorless prismatic crystals. mp 228°C (DSC, 5°/min); IR (KBr, cm^{-1}): $\tilde{\nu} = 3433$ (m), 3401 (m), 3289 (s), 2973 (m), 2881 (m), 2083 (w), 1679 (s), 1629 (m), 1581 (w), 1511 (w), 1456 (w), 1392 (w), 1356 (w), 1211 (m), 1111 (s), 1024 (m), 975 (m), 962 (m), 696 (w), 662 (w), 617 (m); Raman (200 mW, 25°C, cm^{-1}): $\tilde{\nu} = 3327$ (9), 3290 (10), 1702 (5), 1642 (5), 1203 (7), 1136 (4), 977 (100), 928 (20), 669 (7), 608 (8), 554 (14), 457 (11), 439 (9), 367 (8), 273 (7), 132 (5); ^{1}H NMR (*d*6-DMSO): $\delta = 8.74$ (s, 2*H*, N*H*), 7.28 (s, 2*H*, NH_2) 4.67 (s, 4*H*, NH_2); ^{13}C NMR (*d*6-DMSO): $\delta =$ 160.4 (*C*); Anal. Calcd for $C_2H_{16}N_{10}O_4S$ (276.28): C, 8.69; H, 5.84; N, 50.70. Found: C, 8.79; H, 5.85; N 50.09%.

bis(1,3,5-Triaminoguanidinium) Sulfate Dihydrate (3)

a) Bis(aminoguanidinium)sulfate monohydrate (2.82 g, 10.0 mmol) suspended in 50 mL of methanol was treated with hydrazine hydrate (1.24 mL, 25.0 mmol) and heated under reflux for 4 h. After removing the solvent, the residue was recrystallized two times from an MeOH/H_2O (1:3) mixture, whereby **3** (1.74 g, 51%) was obtained as colorless needles.

b) A strong basic anionic-interchanger in Cl^- -form (Lewatit, M 5080, Merck) was loaded three times with an almost saturated aqueous Na_2SO_4 solution. A concentrated solution of 1,3-diaminoguanidinium chloride (1.26 g, 0.01 mol) in 5 mL water was exchanged once and the column was washed with water. After evaporation of the solvent and recrystallization from MeOH/H_2O, **3** (1.24 g, 95%) was obtained as colorless prismatic crystals. mp 173°C (DSC, 5°/min); IR (KBr, cm^{-1}): $\tilde{\nu} = 3444$ (m), 3320 (s), 3210 (s), 3105 (m), 2749 (w), 2059 (w), 1684 (s), 1615 (m), 1381 (w), 1332 (m), 1128 (m), 952 (s), 742 (w), 638 (m), 612 (m); Raman (200 mW, 25°C, cm^{-1}): $\tilde{\nu} = 3321$ (100), 3238 (80), 1777 (12), 1680 (46), 1557 (14), 1438 (17), 1327 (56), 1186 (26), 1139 (55), 1186 (26), 1139 (55), 974 (26), 937 (18), 880 (84), 715 (24), 639 (53), 398 (60), 336 (33), 322 (31), 252 (29), 145 (73); ^{1}H NMR (*d*6-DMSO): $\delta = 4.48$ (s, 6H, NH_2), 8.59 (s, 3*H*, N*H*); ^{13}C NMR (*d*6-DMSO): $\delta = 159.6$ (*C*), Anal. Calcd for $C_2H_{22}N_{12}O_6S$ (342.34): C, 7.02; H, 6.48; N, 49.10. Found: C, 7.31; H, 6.50; N, 48.99%.

bis(Azidoformamidinium) Sulfate (5)

bis(Aminoguanidinium) sulfate (26.4 g, 100 mmol) was dissolved in 200 mL of 1 N hydrochloric acid. To this solution, 50 mL of a sodium nitrite (14.0 g, 200 mmol) solution was added slowly while keeping the temperature below 40°C. Afterwards, urea (200 mg) was added and the solvent was evaporated. The raw product was recrystallized from a hot water/ethanol 1:1 mixture yielding colorless crystals (22.8 g, 85%). mp 154°C (DSC, 5°/min); IR (KBr, cm^{-1}): $\tilde{\nu} = 3219$ (s), 3113 (s), 2990 (s), 2810 (m), 2180 (vs), 2113 (w), 1709 (s), 1602 (m), 1489 (s), 1423 (m), 1226 (s), 1152 (m), 1132 (m), 1083 (vs), 902 (w), 757 (m), 710 (m), 605 (m), 536 (w), 520 (w); Raman (200 mW, 25°C, cm^{-1}): $\tilde{\nu} = 3073$ (6), 2178 (57), 2114 (14), 1607 (4), 1485 (14), 1225 (17), 1151 (30), 1127 (13), 1083 (12), 979 (100) 905 (58), 714 (23), 653 (13), 614 (12), 520 (26), 489 (11), 474 (9), 431 (11), 231 (30); ^{1}H NMR (*d*6-DMSO, 25°C): $\delta = 6.42$ (s, 4*H*, NH_2); ^{13}C NMR (d_6-DMSO): $\delta = 159.5$ (*C*); Anal. Calcd for $C_2H_8N_{10}O_4S$ (268.21): C, 8.96; H, 3.01; N, 52.22. Found: C, 9.18; H, 3.04; N, 52.21%.

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