Synthesis and Crystal Structure Determination of a Guanidine Adduct of Sodium Guanidinate, $NaCN_3H_4(CN_3H_5)_2$

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Well-grown single crystals of $NaCN_3H_4(CN_3H_5)_2$ were synthesized from guanidine and sodium hydride. The new compound crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with Z = 4 and a = 6.2007(4), b = 9.6261(8), c = 15.7630(11) Å and β = 93.783(3)° at 293 K. The asymmetric unit comprises two sodium cations on special positions, one guanidinate anion and two symmetry-independent guanidine molecules. The structure is built up from columns of face-sharing NaN_6 octahedra oriented along the crystallographic a axis. The coordinating organic ligand anions and molecules are connected by hydrogen bonds from amino H atoms to imino N atoms to generate a tube-like motif. These tubes are then linked by two more hydrogen bonds to form a three-dimensional network.

Key words: Guanidinate, Guanidine Adduct, Sodium, Crystal Structure, Hydrogen Bonds

Introduction

Although guanidine, $(NH_2)_2C{=}NH$, was first synthesized in 1861 [1], the elucidation of its crystal structure was accomplished not earlier than 2009 [2]. Guanidine is an important molecule in both organic and inorganic chemistry. Its very strong basic character (pK_B = 0.4) [3] explains why a large number of salts containing a guanidinium cation $[(NH_2)_3C]^+$ are known. On the other hand, salts containing an unsubstituted, negatively charged guanidinate anion are almost non-existent. Only one study, by Franklin in 1922, postulated such compounds, but their amorphous nature did not allow for structure determination [4].

Recently we presented the first fully characterized guanidinate compound, $RbCN_3H_4$ [5]. We now report on the synthesis and structure determination of a guanidine adduct of sodium guanidinate, $NaCN_3H_4(CN_3H_5)_2$, the second example of this new class of compounds and the first one characterized by single-crystal X-ray diffraction.

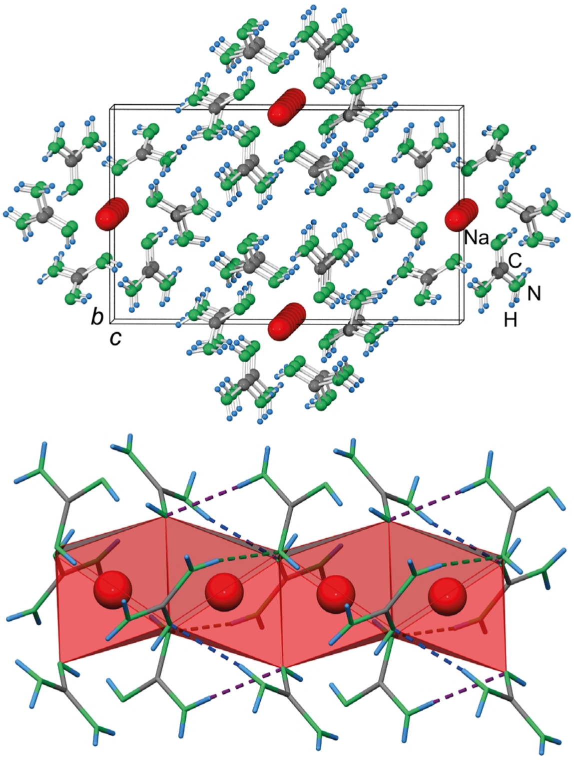

Fig. 1 (color online). Perspective view into the crystal structure of $NaCN_3H_4(CN_3H_5)_2$ along the a axis (top) and projection of the coordination around the sodium cations (bottom).

Results and Discussion

$NaCN_3H_4(CN_3H_5)_2$ is a highly moisture-sensitive compound and melts without decomposition at approx. 50 ℃. Further heating to *ca.* 140 ℃ results in the formation of Na_2NCN. An analogous reaction was also observed for $RbCN_3H_4$. $NaCN_3H_4(CN_3H_5)_2$ crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with four formula units per cell, as depicted in the upper part of Fig. 1. The asymmetric unit comprises two sodium cations on special positions, one guanidinate anion and two guanidine molecules. All spatial and atomic displacement parameters are given in Table 1.

The sodium cations form “chains” along the a axis. Each Na^+ is octahedrally coordinated by six imino

Table 1. Spatial and atomic displacement parameters for $NaCN_3H_4(CN_3H_5)_2$ at r. t. (U_{eq} for Na, C and N, and U_{iso} for H), grouped into molecular entities. The Na atoms are on special Wyckoff positions 2*b* (Na1) and 2*c* (Na2) whereas all other atoms are on 4*e*.

Atom	x	y	z	U_{eq}/U_{iso} ($Å^2$)
Na1	$1/2$	$1/2$	0	0.0340(3)
Na2	0	$1/2$	0	0.0328(3)
C1	0.2652(3)	0.5099(2)	−0.19560(13)	0.0299(5)
N1	0.2495(3)	0.57551(19)	−0.12481(12)	0.0339(4)
N2	0.3994(4)	0.5445(3)	−0.25709(16)	0.0469(6)
N3	0.1518(4)	0.3905(2)	−0.21199(14)	0.0393(5)
H1	0.328(5)	0.647(3)	−0.1244(16)	0.052(8)
H2	0.473(5)	0.615(3)	−0.2468(18)	0.060(9)
H2′	0.388(5)	0.499(3)	−0.3019(18)	0.060(9)
H3	0.107(4)	0.376(3)	−0.2668(17)	0.057(8)
H3′	0.053(4)	0.382(2)	−0.1789(16)	0.040(7)
C2	0.2883(3)	0.7645(2)	0.10604(12)	0.0285(4)
N4	0.2546(3)	0.63112(19)	0.10345(12)	0.0332(4)
N5	0.4479(4)	0.8292(2)	0.15248(13)	0.0424(5)
N6	0.1541(4)	0.8492(2)	0.05926(15)	0.0464(6)
H4	0.334(4)	0.590(2)	0.1392(15)	0.035(7)
H5	0.542(4)	0.780(3)	0.1772(15)	0.042(8)
H5′	0.467(5)	0.917(3)	0.1439(17)	0.053(8)
H6	0.037(5)	0.816(3)	0.0311(17)	0.060(9)
H6′	0.176(4)	0.938(2)	0.0607(13)	0.032(6)
C3	0.3101(3)	0.2172(2)	0.08902(13)	0.0283(4)
N7	0.2515(3)	0.28760(19)	0.01893(11)	0.0333(4)
N8	0.1946(5)	0.2480(3)	0.15774(16)	0.0723(10)
N9	0.4653(4)	0.1256(2)	0.10519(14)	0.0430(5)
H7	0.325(4)	0.260(2)	−0.0188(13)	0.027(6)
H8	0.216(5)	0.202(3)	0.1958(17)	0.045(8)
H8′	0.084(5)	0.304(3)	0.1508(16)	0.056(8)
H9	0.526(4)	0.118(3)	0.0659(16)	0.040(8)

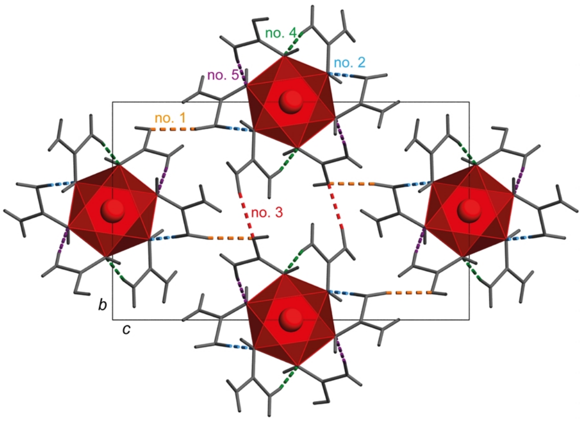

Fig. 2 (color online). H bonding network in the crystal structure of $NaCN_3H_4(CN_3H_5)_2$. H bonds no. 2, 4 and 5 connect the coordinating organic ligands to tubes along the *a* axis. H bonds no. 1 and 3 connect the tubes to form a three-dimensional network.

Table 2. Hydrogen bonds (Å, deg) in the crystal structure of $NaCN_3H_4(CN_3H_5)_2$.

Residue	No.	D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
#1	1	$N3\text{-}H3\cdots N9^{i}$	0.90(3)	2.15(3)	3.037(3)	170(2)
	2	$N3\text{-}H3'\cdots N4^{ii}$	0.83(3)	2.32(3)	3.145(3)	172(2)
#2	3	$N5\text{-}H5'\cdots N9^{iii}$	0.86(3)	2.10(3)	2.953(3)	169(3)
	4	$N6\text{-}H6\cdots N7^{iv}$	0.88(3)	2.15(3)	3.028(3)	170(3)
#3	5	$N8\text{-}H8'\cdots N1^{iv}$	0.88(3)	2.38(3)	3.248(4)	171(3)

Symmetry codes: ^{i} $x-1/2, 1/2-y, z-1/2$; ^{ii} $-x, 1-y, -z$; ^{iii} $x, 1+y, z$; ^{iv} $-x, 1-y, -z$.

Table 3. Selected bond lengths and angles (Å, deg) of the guanidine molecule at 270 K [2] and in the guanidinate anion found in $RbCN_3H_4$ at 10 K [5]. Because the N–H bond lengths in $RbCN_3H_4$ were determined from electronic structure calculations, they do not suffer from the typical underestimation of H bonds in X-ray crystal structure analyses.

	CN_3H_5 [2]	$CN_3H_4^-$ [5]
C–NH_2	1.346 – 1.371	1.439(12)
C–NH	1.287 – 1.292	1.320(7)
N–H(amino)	0.83 – 0.89	1.028
N–H(imino)	0.84 – 0.89	1.033
H_2N–C–NH_2	114.6 – 115.5	–
HN–C–NH	–	128.7(3)
HN–C–NH_2	118.9 – 125.6	115.6(2)

Table 4. Crystal data and structure refinement details for $NaCN_3H_4(CN_3H_5)_2$.

Unit cell dimension	
a, Å	6.2007(4)
b, Å	9.6261(8)
c, Å	15.7630(11)
β, deg	93.783(3)
Volume, $Å^3$	938.82(12)
Z	4
Crystal size, mm^3	$0.4 \times 0.15 \times 0.12$
θ range for data collection, deg	2.48 to 30.83
Limiting indices	$-8 \le h \le 8, -13 \le k \le 13,$ $-13 \le l \le 22$
Reflections collected / unique	7294 /2707
Goodness-of-fit	1.032
Final R indices: R_1 / wR_2 (all data)	0.0621 / 0.1442
Largest difference peak / hole, e $Å^{-3}$	0.30 / −0.21

N atoms. The Na–N distances scatter between 2.53 and 2.68 Å and are very similar, even though two of the imino N atoms belong to the guanidinate anions and four to the guanidine molecules. The octahedra around Na^+ are linked to each other by sharing faces along the *a* axis, giving an $Na^+ \cdots Na^+$ distance of 3.10 Å. The coordination is depicted in the lower part of Fig. 1.

Regarding the entire crystal structure, the guanidine molecules and the guanidinate anion are connected *via* a total of five N–H···N hydrogen bonds, each from an amino H atom to an imino N atom. N9, the second imino N atom in the guanidinate anion and the only imino group not involved in metal coordination, represents the most efficient H acceptor. All relevant dis-

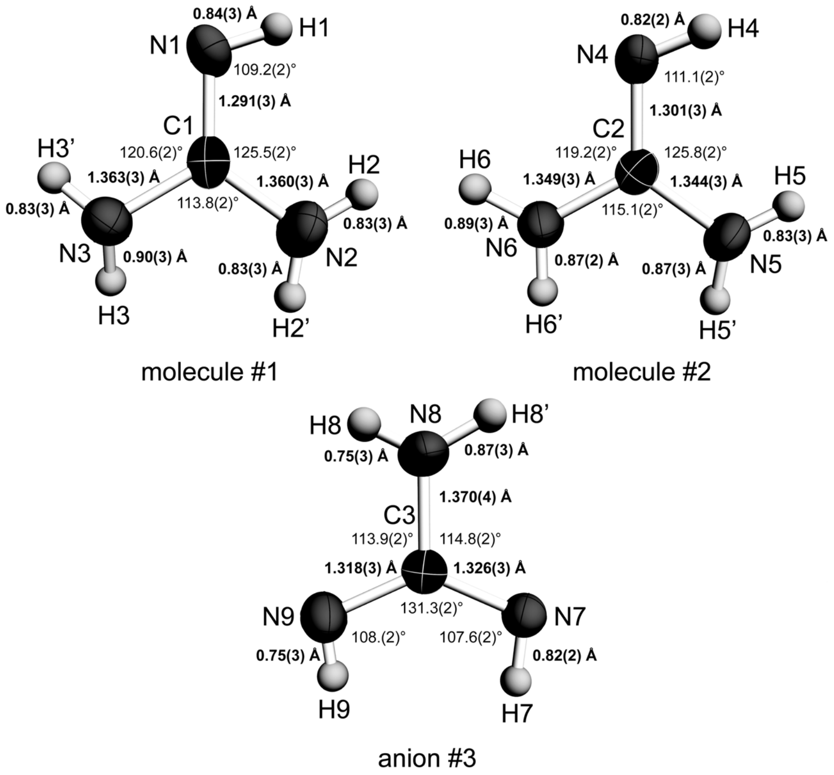

Fig. 3. Displacement ellipsoid plots of the guanidine molecules #1 and #2 and the guanidinate anion #3. C and N atoms are displayed with 50 % probability and H atoms as spheres of arbitrary size.

tances and angles are listed in Table 2, and a schematic drawing is shown in Fig. 2. Hydrogen bonds no. 2, 4, and 5 connect the coordinating molecules around one sodium "chain", forming tubes along the *a* axis. Two more hydrogen bonds (no. 1 and 3), from an amino H atom of a guanidine molecule to the imino N9 atom of the guanidinate anion, connect the tubes with each other to form a three-dimensional network. Based on their length and the negative charge on the acceptor N9 atom, we suggest that the bonds no. 1 and 3 are the strongest ones.

Fig. 3 depicts the guanidinate anion and the two symmetry-independent guanidine molecules in greater detail. For comparison, Table 3 gives the corresponding bond lengths and angles found in pure guanidine [2] and in the guanidinate anion of $RbCN_3H_4$ [5]. The bond lengths and angles of the two guanidine molecules (#1, #2) just reproduce those observed in pure guanidine. The C3–N8 bond in the guanidinate anion is shorter in $NaCN_3H_4(CN_3H_5)_2$ than in $RbCN_3H_4$. This is easily explained by the fact that the bond lengths in $RbCN_3H_4$ were observed at 10 K. For pure guanidine it was already shown that the shrinkage of the intramolecular distances with increasing temperature is due to thermal motion [2]. H8 and H8′ are not involved in any short H bonds and, therefore, the amino group of the guanidinate anion is more mobile. This is also seen in the displacement parameters (Table 1), where N8 has the largest U_{eq} compared to all other atoms. The C3–N9 and C3–N7 bonds do not exhibit such behavior, and the distances observed in $NaCN_3H_4(CN_3H_5)_2$ at r. t. and in $RbCN_3H_4$ at 10 K are almost the same. This is because N7 coordinates to the Na cation, and N9 is involved in two strong hydrogen bonds, in both cases suppressing the thermal motion.

Conclusion

$NaCN_3H_4(CN_3H_5)_2$ represents the second representative of the new class of guanidinate compounds, and it is the first one characterized by single-crystal X-ray diffraction. It is fortunate to have the single crystals available because – in contrast to $RbCN_3H_4$ – the determination of the hydrogen positions in this complex structure would have been difficult with electronic structure calculations alone. Furthermore, the coexistence of guanidine anions and guanidine molecules in the same crystal structure suggests that this structure may represent the first example of a larger class of compounds which combine design elements of inorganic salts with those of hydrogen-bonded molecular solids.

Experimental Section

$NaCN_3H_4(CN_3H_5)_2$ was synthesized by mixing guanidine and sodium hydride in a 3 : 1 ratio under a protective argon atmosphere and carefully heating the mixture to 50 °C. A substantial gas evolution indicated the start of the reaction which led to the title compound in practically quantitative yield:

$$3\,(NH_2)_2C{=}NH_{(s)} + NaH_{(s)} \longrightarrow NaCN_3H_4(CN_3H_5)_{2(s)} + H_{2(g)}$$

At 50 °C the product melts but after cooling to r. t. colorless single crystals appear. X-Ray intensities were collected using a Bruker D8 goniometer equipped with a SMART APEX CCD detector (MoK_α radiation). The structure was then solved by Direct Methods (SHELXS-97) [6] and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) [6]. The unit cell dimensions were taken from powder X-ray diffraction data. All carbon, nitrogen and sodium atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map, and their coordinates and isotropic displacement parameters were refined freely. Geometry calculations were performed with the program PLATON [7]. Details about the structure determination are given in Table 4.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-423132.

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