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Solvothermal Synthesis, Crystal Growth, and Structure Determination of Sodium and Potassium Guanidinate

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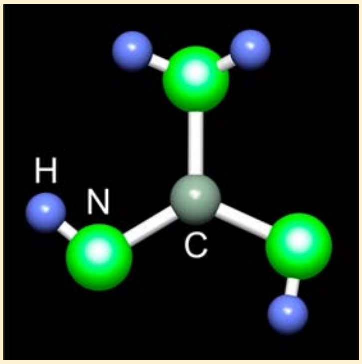
Supporting Information

ABSTRACT: Phase-pure $NaCN_3H_4$ and KCN_3H_4 were synthesized from molecular guanidine and elemental metal in liquid ammonia at room temperature and elevated pressure close to 10 atm. The crystal structures were determined at 100 K using single-crystal X-ray diffraction. Both compounds crystallize in the monoclinic system ($P2_1/c$, No. 14) but are far from being isotypical. $NaCN_3H_4$ (a = 7.9496(12) Å, b = 5.0328(8) Å, c = 9.3591(15) Å, β = 110.797(3)°, Z = 4) contains a tetrahedrally N-coordinated sodium cation while KCN_3H_4 (a = 7.1200(9) Å, b = 6.9385(9) Å, c = 30.404(4) Å, β = 94.626(2)°, Z = 16) features a very large c axis and a rather complicated packing of irregularly N-coordinated potassium cations. In the crystal structures, the guanidinate anions resemble the motif known from $RbCN_3H_4$, that is, with one elongated C−$^{(amino)}$N single bond and two shorter C−$^{(imino)}$N bonds (bond order = 1.5) although the orientation of one N−H bond differs in the guanidinate anion of $NaCN_3H_4$. Both crystal structures and infrared spectroscopy evidence the presence of hydrogen-bridging bonds, and the vibrational properties were analyzed by *ab initio* phonon calculations.



INTRODUCTION

Despite the fact that pure guanidine was synthesized by Strecker already in 1861,[1] it took another 148 years to eventually determine its crystal structure,[2] strangely enough. This finding is even more astonishing given the fact that guanidine plays a highly important role in biochemistry, as reflected from the vast number of biomolecules containing guanidine as their central subunit.[3] Within the field of coordination chemistry, a plethora of substituted guanidines and also negatively charged guanidinates is known.[4] In addition, diverse ligands incorporating the guanidine backbone are also used as building blocks in "supramolecular" chemistry.[5]

In the realm of solid-state chemistry, however, the synthesis and structural characterization of the first guanidine salt $RbCN_3H_4$ has only recently been achieved.[6] $RbCN_3H_4$ and also the here described $NaCN_3H_4$ and KCN_3H_4 are remarkable in that they contain the negatively charged, unsubstituted ("naked") *guanidinate* anion $CN_3H_4^-$, not the ubiquitous mesomerism-stabilized guanidinium cation $CN_3H_6^+$. The latter ion's high stability easily explains the strongly basic character of the neutral guanidine molecule, similar in strength to potassium hydroxide.

In fact, rubidium guanidinate could only be synthesized by a solid−solid reaction without any solvents through mixing powderous rubidium hydride and pure guanidine at room temperature, thereby yielding $RbCN_3H_4$ and gaseous hydrogen, the latter enhancing the reaction by entropic means. The crystal structure (orthorhombic, *Pnma*, Z = 4) was solved from well-resolved powder X-ray data together with first-principles calculations needed for localizing the otherwise invisible H atoms in the proximity of rubidium.[6]

Very unfortunately, the analogous reaction of potassium hydride and guanidine did not lead to any crystalline product. Because of that, an alternative route to crystalline potassium guanidinates by employing potassium *amide* as a necessary base was examined, following the ideal reaction:

$$KNH_{2(s)} + CN_3H_{5(s)} \rightarrow KCN_3H_{4(s)} + NH_{3(g)}$$

Although there is a reaction, its products were also amorphous or even pastelike, except for one occasion where a highly complicated powder diffractogram was found. Nonetheless, it was impossible to index or even solve the latter, but the later single-crystal study (see below) corroborated the successful synthesis of KCN_3H_4 and its phase-pure character.

Instead, we were inspired by the pioneering research by Franklin[7] who proposed the formation of $K_2CN_3H_3$ in liquid ammonia (in 1922 already!) but who could not provide unambiguous analytical or even structural information at that time. It was also Franklin who suggested that guanidine should act as an acid in that medium:

$$CN_3H_{5(solv)} + NH_{3(l)} \rightarrow CN_3H^-_{4(solv)} + NH^+_{4(solv)}$$

In order to determine the acidity of pure guanidine in liquid ammonia by experimental means, we have carefully explored various pNH_4^+-indicators as proposed by Jander,[8] but we were unable to corroborate guanidine's aforementioned acidity. We also note that Franklin already mentioned the reaction

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$$\mathrm{CN_3H_6{}^{+}{}_{(solv)} + NO_3{}^{-}{}_{(solv)} + 3K^{+}{}_{(solv)} + 3NH_2{}^{-}{}_{(solv)}}$$

$$\mathrm{\rightarrow K_2CN_3H_{3(s)} + K^{+}{}_{(solv)} + NO_3{}^{-}{}_{(solv)} + 2NH_{3(l)}}$$

thereby emphasizing the role of the strong base KNH_2 needed to deprotonate guanidine nitrate. Following Franklin's approach, we have now conducted new experiments in dry liquid ammonia but by utilizing molecular guanidine (instead of guanidinium nitrate) and elemental potassium (instead of potassium amide) as starting materials. In doing so, single-phase sodium and potassium guanidinate not only have been made but also were made in the form of single crystals.

■ EXPERIMENTAL SECTION

Due to the extreme sensitivity toward air and moisture, all experiments were carried out under dry argon. Pure guanidine was synthesized as described before[2] and further purified by sublimation at 50 °C and a pressure of approximately 6×10^{-2} mbar. At first, potassium amide was prepared in liquid ammonia as has been described by Juza and coworkers.[9] The white powder was characterized by powder X-ray diffraction. No impurities were detected. As said before, however, grinding of equimolar amounts of potassium amide and guanidine did not lead to crystalline products.

In a next step, a simpler one-pot synthesis in liquid ammonia was attempted by first transforming pure potassium *in situ* into highly reactive potassium amide. A 132.4 mg (3.39 mmol) portion of potassium and 200 mg (3.39 mmol) of guanidine were weighed in a steel autoclave. After evacuation, 3.5 mL (0.17 mol) of dry ammonia (99.999%) was condensed into the autoclave. The autoclave was then closed and stored at room temperature for two days. Under pressure, ammonia is easily liquefied, the necessary pressure being about 8.9 atm.[10] After opening, colorless plate-shaped single crystals were obtained. The reaction presumably proceeds in two steps:

$$\mathrm{K_{(s)} + NH_{3(l)} \rightarrow K^{+}{}_{(solv)} + NH_2{}^{-}{}_{(solv)} + 0.5H_{2(g)}}$$

$$\mathrm{CN_3H_{5(solv)} + K^{+}{}_{(solv)} + NH_2{}^{-}{}_{(solv)} \rightarrow KCN_3H_{4(s)} + NH_{3(l)}}$$

The synthesis of $NaCN_3H_4$ was attempted using the same reaction conditions. At first the synthesis did not lead to single crystals but to a phase-pure powder whose diffractogram was monoclinically indexed with the same lattice parameters as later found from single-crystal diffraction. Using considerably lower concentrations of the starting materials, that is, 17.2 mg (0.75 mmol) of sodium, 44.3 mg (0.75 mmol) of guanidine, and 3.5 mL (0.17 mol) of ammonia, colorless plate-shaped single crystals were also obtained in this case.

Single-crystal X-ray diffraction intensities at T = 100 K were collected using a Bruker D8 goniometer (Incoatec microsource, multilayer optics, Mo Kα radiation, λ = 0.710 73 Å) equipped with a SMART APEX area detector. The temperature was controlled by an Oxford Cryostream 700 instrument. All intensity data were corrected for absorption by multiscan methods.[11] The crystal structures were solved by direct methods implemented in the SHELXS program and refined by full-matrix least-squares SHELXL procedures based on F^2 using all measured reflections.[12] All metal, nitrogen, and carbon atoms were refined with anisotropic displacement parameters. The high-resolution data allowed all hydrogen atoms to be located from the difference Fourier maps, and they were refined using a common isotropic displacement parameter and with a soft N–H bond-length restraint. More data on the crystal-structure determination are found in Table 1. Further details may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition number CSD-424644 for $NaCN_3H_4$ and CSD-424645 for KCN_3H_4.

Powder X-ray diffraction data were collected using a STOE STADI P diffractometer with strictly monochromatized Cu Kα_1 radiation and an image-plate detector. The samples were sealed in a glass capillary with a diameter of 0.3 mm. The measurement range was a wide 5–110° with a step size of 0.015° in 2Θ. The Rietveld refinements based on the single-crystal structure model were carried out with the FULLPROF package[13] and arrived at essentially the same results but with a significantly lower accuracy. Because all Bragg reflections were unambiguously assigned, the two powders can be considered phase-pure.

Table 1. Single-Crystal Data and Structure Refinement Details of $NaCN_3H_4$ and KCN_3H_4 at T = 100 K

	$NaCN_3H_4$	KCN_3H_4
fw (amu)	81.06	97.17
space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)
a (Å)	7.9496(12)	7.1200(9)
b (Å)	5.0328(8)	6.9385(9)
c (Å)	9.3591(15)	30.404(4)
β (deg)	110.797(3)	94.626(2)
V (Å^3)	350.0(5)	1497.1(3)
Z	4	16
ρ_{calcd} (g cm^{-3})	1.538	1.724
T (K)	100	100
cryst dimensions (mm^3)	0.10 × 0.10 × 0.08	0.20 × 0.15 × 0.07
radiation	Mo Kα, λ = 0.710 73 Å	Mo Kα, λ = 0.710 73 Å
μ(Mo Kα) (mm^{-1})	0.22	1.20
transm factors	0.9787–0.9829	0.7953–0.9207
2Θ limits, deg	5.48–52.86	5.38–53.12
data collected	$-9 \leq h \leq 9$	$-8 \leq h \leq 8$
	$-6 \leq k \leq 6$	$-8 \leq k \leq 8$
	$-11 \leq l \leq 11$	$-38 \leq l \leq 38$
no. refls collected/unique reflns	4256/716	17861/3115
no. variables/restraints	59/6	230/24
final R indices: R1/wR2 (all data)	0.0404/0.0781	0.0499/0.0967
GOF	1.117	0.974
largest difference peak/hole (e Å^{-3})	0.24/−0.20	0.47/−0.54

The infrared spectra of both compounds were measured using a Bruker ALPHA FT-IR-spectrometer with an ATR Platinum Diamond sample holder and a measurement range 400–4000 cm^{-1}. The spectrometer was placed inside a glovebox to prevent any moisture from getting into contact with the highly sensitive sodium and potassium guanidinate.

Because hydrogen bond lengths can not be determined with confidence by X-ray diffraction alone, more accurate H positions were gained from plane-wave density-functional theory (DFT). The latter procedure has recently been validated on the basis of highly accurate neutron diffraction data as a reference.[14] For $NaCN_3H_4$ and KCN_3H_4, we therefore optimized the hydrogen atomic positions using the VASP package[15] and the selective dynamics approach,[14] thus leaving the lattice parameters and the coordinates of the heavier atoms fixed at their experimental values, as done in previous studies.[6,14] To do so, a plane-wave basis set with a cutoff energy larger than 400 eV together with the PAW method[16] were chosen, employing the GGA parametrization by Perdew, Burke, and Ernzerhof[17] and 36 irreducible **k** points (e.g., for $NaCN_3H_4$) taken according to the recipe by Monkhorst and Pack.[18]

The phonon density-of-states was computed by the *ab initio* force-constant method[19] as implemented in the FROPHO code.[20,21] To obtain the Hellmann–Feynman forces[22,23] necessary for evaluating the dynamical matrix, a 2 × 4 × 2 supercell of the primitive cell was used. The forces were also calculated with VASP.

RESULTS AND DISCUSSION

The synthesis of sodium and potassium guanidinate may be understood as a room-temperature acid−base reaction in the nonaqueous solvent liquid ammonia. The stronger base NH_2^- generates the singly deprotonated guanidinate species which precipitates together with Na^+ or K^+ as their solubility product in $NH_{3(l)}$ is exceeded. It appears that the concentration of the starting materials is crucial for the crystal-growth velocity and the formation of either single crystals or powder samples. Despite the fact that sodium and potassium, as direct alkaline-metal neighbors, are expected to show a similar chemical behavior, the crystal structures of the two guanidinates adopting the same monoclinic space group $P2_1/c$ differ in many details, and they also differ from the one of $RbCN_3H_4$.

Starting with the crystal structure of sodium guanidinate, it is shown as a balls-and-sticks and also polyhedral plot in Figure 1 (top). There is a network of tetrahedrally coordinated Na^+ cations, and the four nearest Na−N bonds are between 2.38 and 2.48 Å. All important interatomic distances are found in Table 2. The NaN_4 tetrahedra are linked with each other through the guanidinate anions such that the sodium atoms alone exhibit the motif of a zigzag chain along *b*, with a nonbonding Na−Na distance of 3.50 Å. Not too surprisingly, Schwarzenbachs's method[24] of effective coordination numbers (ECoN) arrives at a value of 3.81 for Na, quite close to the naive value of 4. In addition, the calculation of an empirical bond-valence sum based on a standard distance of r_0 = 1.93 Å[25] yields 1.07 for Na^+, showing that the nearest Na−N bonds are well adjusted.

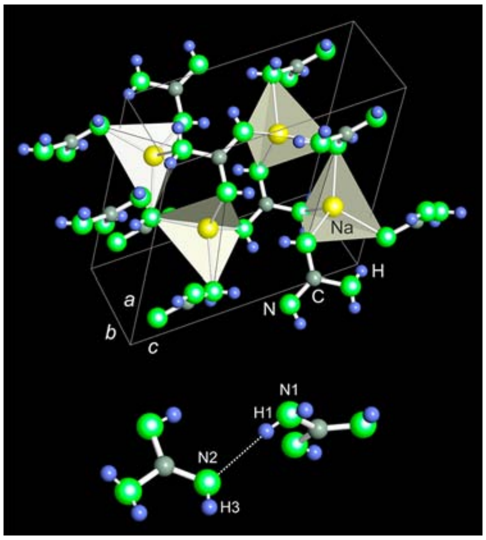

Figure 1. Perspective view[30] into the crystal structure of $NaCN_3H_4$ (top) and hydrogen-bond linkage of two adjacent guanidinate anions (bottom).

The shape of the guanidinate anion in $NaCN_3H_4$, depicted in Figure 3a, is similar to what is known from the $RbCN_3H_4$ structure, but with one notable difference. The hydrogen atom H3, bonded to the N2 atom in the lower left part of the complex anion, points away from the related H4 atom such that the term "anti" for that particular H-atom conformation according to the nomenclature of organic chemistry[3] may be appropriate. In $RbCN_3H_4$ (and also in KCN_3H_4, see below), the conformation should then be designated as syn. The reason for the occurrence of the anti form immediately results from the H-bond connection of two neighboring guanidinate anions. As seen from the bottom of Figure 1, the complex anions form a one-dimensional chain along *c*, and the shortest N−N distance of 3.09 Å occurs between the $^{(amino)}$N1 atom and the $^{(imino)}$N2 atom. It seems as if the hydrogen bond involving the H1 atom requires a free coordination site at N2 and this, in turn, demands the anti position for the leftover H3 atom bonded to N2. The anti form also allows for a rather narrow N2−C1−N3 angle of 124°, see Figure 3a. In addition, both neighboring guanidinates are rotated against each other by approximately 83°. According to a recent theoretical study[26] conducted for the neutral parent compound guanidine, the strength of such 3.09 Å long amino−imino H-bond can be estimated to be around 20−30 kJ mol^{-1}.

Another interesting detail of the crystal structure of $NaCN_3H_4$ is that all amino nitrogen atoms point away from the sodium ions, and the first three Na−N bonds are formed by

Table 2. Metal−Nitrogen Distances in $NaCN_3H_4$ and KCN_3H_4 at T = 100 K[a]

Na1−	N3	2.384(2) Å	K1−	N11	2.798(3) Å	K2−	N12	2.791(3) Å
	N2	2.393(2) Å		N3	2.849(3) Å		N2	2.833(3) Å
	N3	2.413(2) Å		N6	2.877(3) Å		N3	2.913(3) Å
	N1	2.484(2) Å		N5	2.894(3) Å		N5	2.971(2) Å
	N1	*3.427(2)* Å		N8	2.963(3) Å		N11	2.983(3) Å
				N7	2.972(3) Å		N10	3.157(3) Å
				N4	*3.478(3)* Å		N12	3.175(3) Å
							N1	*3.679(3)* Å
			K3−	N1	2.911(3) Å	K4−	N8	2.705(3) Å
				N2	2.944(3) Å		N6	2.807(3) Å
				N3	2.986(3) Å		N9	2.839(3) Å
				N4	3.033(3) Å		N9	2.917(3) Å
				N10	3.042(3) Å		N6	3.097(3) Å
				N12	3.069(3) Å		*N5*	*3.411(3)* Å
				N5	3.128(3) Å			
				N11	3.281(3) Å			
				N1	3.292(3) Å			
				N6	*3.745(3)* Å			

[a] The last entry of each colum (in italics) indicates the first noncoordinating metal−nitrogen distance.

imino nitrogens, followed by a longer bond to an amino-nitrogen atom. This results in a "layered" structure in which two guanidinate layers are separated by a shortest interlayer imino–amino distance of 3.30 Å. The shortest amino–amino distance, however, is 3.41 Å.

With respect to the crystal structure of potassium guanidinate, its sheer complexity is rather astonishing. Figure 2 offers a perspective view into that structure by a simple balls-and-sticks representation but not a polyhedral one since highly symmetrical coordination polyhedra are not discernible throughout. There are four symmetry-independent potassium cations, coordinated by nearest-neighbor nitrogen atoms, just like before, with the shortest K–N bond distance starting at 2.71 Å. All important interatomic distances are given in Table 2. One may tentatively recognize a bond-length gap at around 3.4 Å, and up to this distance, naive counting of coordination numbers arrives at 6 (K1), 7 (K2), 9 (K3), and 5 (K4) nearest N neighbors, strangely enough. One is tempted to guess (see volume-chemistry discussion below, however) that the imperfect match of the size of K^+ to its guanidinate environment and the possibly rigid carbon–nitrogen backbone is responsible for the low symmetry of the entire packing and crystal structure. To proceed more quantitatively, Schwarzenbach's method[24] of calculating ECoNs was utilized, once again, and this yields ECoN = 5.2 (K1), 5.6 (K2), 7.2 (K3), and 3.8 (K4), but this also does not improve understanding. The calculation of empirical bond-valence sums using a scaling distance of r_0 = 2.26 Å,[25] however, results in empirical valences of 1.10 (K1), 1.08 (K2), 1.05 (K3), and 1.01 (K4). Clearly, the local K–N bonding is almost perfectly adjusted as well, despite our obvious inability to recognize polyhedral symmetry or, so to speak, structural beauty.

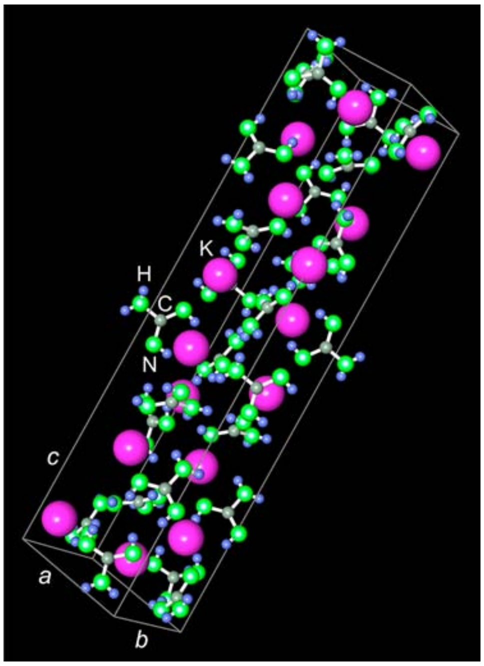

Figure 2. Perspective view[30] into the crystal structure of KCN_3H_4.

While the shortest amino–imino H-bridging bonds in $NaCN_3H_4$ comprise a one-dimensional guanidinate chain (see above), the guanidinate anions in KCN_3H_4 are arranged in *dimers* such that two H-bonds are formed between two molecules (not shown for reasons of brevity). For example, one H-bonded dimer is characterized by $^{(\text{imino})}$N5–$^{(\text{amino})}$N10 = 2.99 Å and $^{(\text{imino})}$N11–$^{(\text{amino})}$N4 = 3.14 Å. Two other dimers are more regular in that their bond lengths arrive at $^{(\text{imino})}$N2–$^{(\text{amino})}$N1 = $^{(\text{imino})}$N12–$^{(\text{amino})}$N10 = 3.07 Å.

As regards the four crystallographically independent guanidinate anions of KCN_3H_4, Figure 3b–e gives an overview of their shapes, the various intermolecular bond lengths, and the corresponding angles. For convenience, we also include the guanidinate anion of $NaCN_3H_4$ in the discussion. Just like in $RbCN_3H_4$, there is an obvious difference between the perpendicular and wider C–$^{(\text{amino})}$N single bonds (1.40 ± 0.01 Å) and the two shorter C–$^{(\text{imino})}$N bonds (1.33 ± 0.01 Å) at the bottom of the complex anions because the shortening reflects the higher bond order (1.5) of the latter. Nonetheless, the differentiation is not as distinct as in the case of $RbCN_3H_4$ (1.44 and 1.30 Å), whose bond lengths were derived from less accurate powder data in the presence of the heavy scatterer rubidium. We thus consider the single-crystal bond distances found here far more reliable. Because the N–H bond lengths mirror the typical X-ray underestimation (0.81–0.92 Å), we also offer more accurate DFT-derived H positions and bond lengths as Supporting Information. Since all four (b–e) guanidinates adopt the syn conformation, their lower N–C–N angles are relatively wide, namely 130 ± 1°.

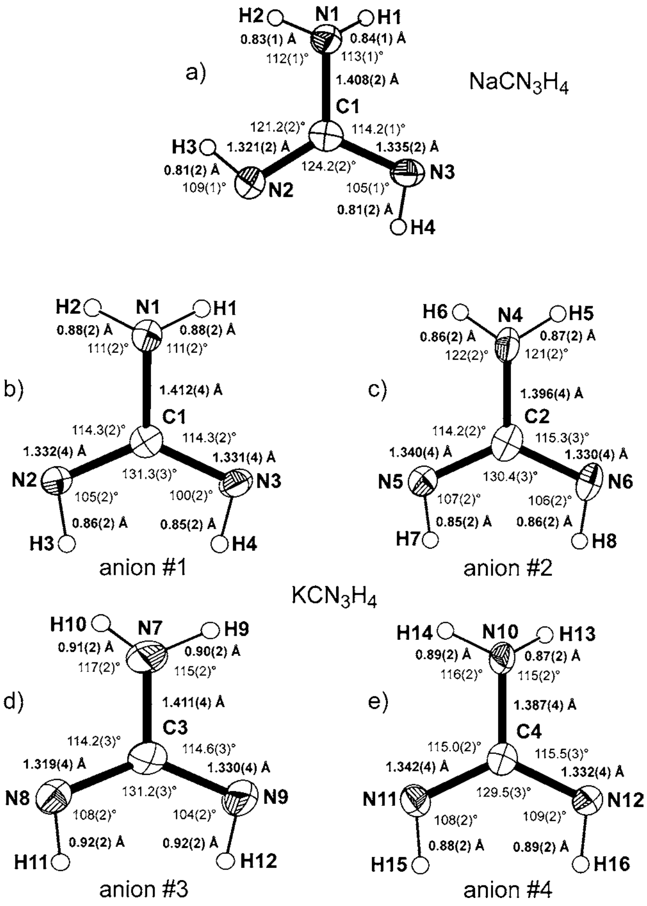

Figure 3. ORTEP[31] plots at the 70% probability level of the different guanidinate anions in (a) $NaCN_3H_4$ and (b–e) KCN_3H_4 at T = 100 K. The H atoms are drawn as spheres of arbitrary size.

Although the four symmetry-inequivalent guanidinates of KCN_3H_4 do not possess a crystallographic mirror plane through the central C–$^{(\text{amino})}$N single bond, their point-group symmetries are close to C_{2v} but only if one were to neglect the small pyramidalization of the upper $^{\text{(amino)}}$N atoms. For the guanidinate anion of $NaCN_3H_4$, the anti conformation of H3 destroys one (approximate) mirror plane and also the (approximate) 2-fold axis such that the point-group would be close to C_s (only if neglecting the nonplanarity around the $^{\text{(amino)}}$N1 atom). Nonetheless, the central CN_3 cores of all guanidinate anions are perfectly planar, as previously observed in the $RbCN_3H_4$ structure.[6] A list of experimental (XRD) and theoretical (DFT) amino H−N−H angles is also provided as Supporting Information.

The infrared spectra of both compounds are shown in Figure 4. To ease interpretation, the phonon DOS values were calculated from first principles as described[27] and then used to assign the vibrations. At first glance both spectra look quite similar, especially in the C−N vibrational range from 800 to 1700 cm^{-1}, which is well understandable by the fact that all anions incorporate the same carbon−nitrogen backbone. In addition, the IR data of KCN_3H_4 feature fine structures of the absorption bands in that range, which is not too surprising since the crystal structure is composed of *four* crystallographically independent guanidinate anions with slightly different bond lengths and angles. In the area of the N−H absorption bands between 3000 and 3500 cm^{-1}, both spectra feature a rather broad signal around 3100 cm^{-1} due to the presence of hydrogen bonds,[28] but the spectrum of KCN_3H_4 also contains a few rather sharp absorption bands (e.g., at 3429 cm^{-1}).

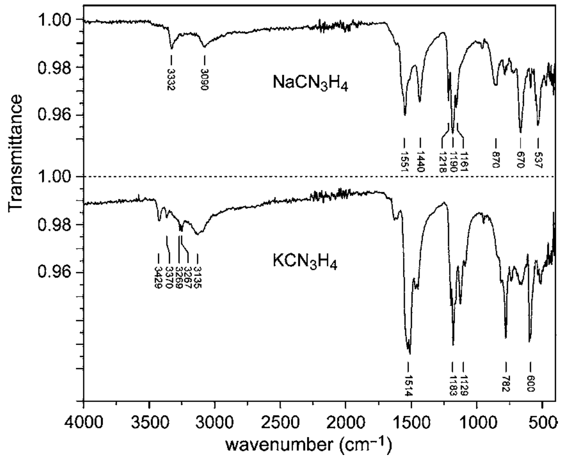

Figure 4. Infrared spectra of $NaCN_3H_4$ (top) and KCN_3H_4 (bottom) taken at room temperature.

The theoretical phonon DOS immediately confirms the low-energy region to represent the C−N vibrations. In addition, the N−H absorption bands (3000−3500 cm^{-1}) of $NaCN_3H_4$ may be analyzed in greater detail by visual inspection of the simulated phonons. Starting from the highest wavenumbers, the first N−H vibrations are torsional vibrations of the amino groups, $^{\text{(amino)}}\delta$, followed by stretching vibrations of the amino−imino groups, $^{\text{(amino-imino)}}\nu$. At lower energies, there is a combination of amino−imino rocking vibrations, $^{\text{(amino-imino)}}\delta$, whereas the lowest-energy N−H vibrations are found for the imino groups and possess torsional character, $^{\text{(imino)}}\delta$. Moving images of these four characteristic phonons at the Γ point of reciprocal space are provided as Supporting Information. In the structurally more complex phase KCN_3H_4, the vibrations follow essentially the same course, namely $^{\text{(amino)}}\delta/^{\text{(amino-imino)}}\nu/^{\text{(amino-imino)}}\delta/^{\text{(imino)}}\delta$, while moving down in energy.

A look into the volume chemistry[29] of the two guanidinate anions offers a surprising finding. We first recall that molecular guanidine CN_3H_5 has a molar volume of 46 cm^3 mol^{-1}[12] while the guanidinate anion in $RbCN_3H_4$ corresponds to a smaller molar volume of only 36 cm^3 mol^{-1}.[6] The here described guanidinate anions arrive at 47 cm^3 mol^{-1} for the sodium compound and 41 cm^3 mol^{-1} for the potassium compound. Thus, the beautifully symmetric structure of $NaCN_3H_4$, with almost perfectly tetrahedral Na−N coordination, is the *least* effectively packed metal guanidinate discovered so far. The aesthetically less pleasing structure of KCN_3H_4, with essentially no symmetry left at the four symmetry-inequivalent potassium ions, is more efficient in terms of volume. Still, the packing of $RbCN_3H_4$, with a 9-fold N-coordination of the voluminous rubidium cation, is the densest of all three.

CONCLUSION

Single crystals of $NaCN_3H_4$ and KCN_3H_4 have been synthesized from molecular guanidine and sodium (potassium) amide in liquid nitrogen. Both compounds crystallize in the monoclinic system but with unique crystal structures. Na is tetrahedrally coordinated by N atoms while the four K atoms experience highly irregular N coordinations. The shape of the guanidinate anions resembles the one known from $RbCN_3H_4$, with the exception of the $CN_3H_4^-$ unit in $NaCN_3H_4$ which adopts an anti conformation with respect to one $^{\text{(imino)}}$N-bonded H atom. Hydrogen bonds are apparent from the crystal-structure determination as well as from vibrational spectroscopy.

ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, DFT-optimized positions of all H atoms and their corrected N−H bond lengths in the crystal structures of $NaCN_3H_4$ and KCN_3H_4, experimental and theoretical amino H−N−H angles, as well as movies of the N−H vibrations in $NaCN_3H_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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