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Synthesis, Structure, and Properties of $SrC(NH)_3$, a Nitrogen-Based Carbonate Analogue with the Trinacria Motif

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Abstract: *Strontium guanidinate, $SrC(NH)_3$, the first compound with a doubly deprotonated guanidine unit, was synthesized from strontium and guanidine in liquid ammonia and characterized by X-ray and neutron diffraction, IR spectroscopy, and density-functional theory including harmonic phonon calculations. The compound crystallizes in the hexagonal space group $P6_3/m$, constitutes the nitrogen analogue of strontium carbonate, $SrCO_3$, and its structure follows a layered motif between Sr^{2+} ions and complex anions of the type $C(NH)_3^{2-}$; the anions adopt the peculiar trinacria shape. A comparison of theoretical phonons with experimental IR bands as well as quantum-chemical bonding analyses yield a first insight into bonding and packing of the formerly unknown anion in the crystal.*

Although nitrogen chemistry has been performed since antiquity, fundamental synthetic insights concerning inorganic nitrogen chemistry were compiled relatively late, for example, by Juza[1] for the solid amides in the 1960s. The last two decades, in particular, have witnessed enormous progress: representatives of the first generation of N-based compounds, with only metal besides nitrogen, already show fascinating properties, for example, the large groups of the solid nitrides[2] and pernitrides,[3] the azides,[4] and the diazenides.[5] N-based inorganic compounds of the second generation may be classified as those containing an additional non-metal atom, for example, the nitridoborates,[6] oxidonitrides,[7] or carbodiimides,[8] all of which gave rise to novel findings. Following our own contributions concerning (correlated) 3d carbodiimides with an NCN^{2-} unit, our interest has broadened to include a third class of complex N-based compounds which relate to the biomolecule guanidine, CN_3H_5, and which all exhibit a triangular motif with a central CN_3 core.

As early as 1861,[9] Strecker synthesized pure guanidine which is a strong organic base, comparable to KOH, but the first crystallographic data of guanidine in co-crystals were not obtained until 2007,[10] followed two years later by the crystal structure of pure guanidine,[11] and more recently by single-crystal neutron-diffraction data.[12] Because of its exceptional basicity, only substituted derivatives of guanidine or guanidinium cations were known until recently, but no anionic guanidinates of the type $[(NH_2)C(NH)_2]^-$. The year 2011 saw the first such guanidinate, namely $RbCN_3H_4$ (synthesized from guanidine and RbH),[13] followed by a series of related alkali-metal guanidinates.[14] The synthesis in liquid ammonia often leads to good single crystals.

In a 1922 contribution, Franklin mentioned[15] the doubly deprotonated guanidinate unit $[C(NH)_3]^{2-}$ but without convincing evidence, in particular without spectroscopic or structural proof. We have finally succeeded in quantitatively synthesizing such an anion in the alkaline-earth metal guanidinate $SrC(NH)_3$ and determining its crystal structure. The structure was approximately solved, despite the strong scattering power of Sr, from X-ray powder data, significantly improved by DFT calculations, and finally validated by means of highly resolved neutron diffraction (Figure 1).

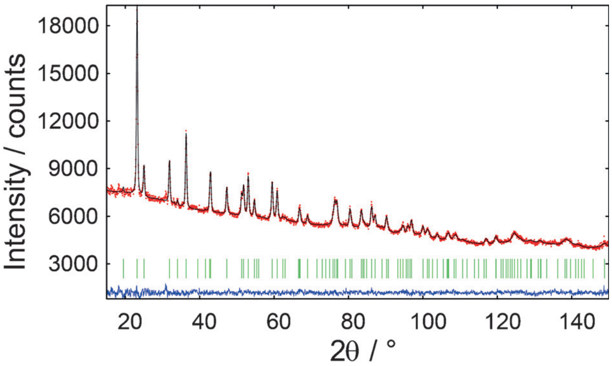

Figure 1. Observed (red), calculated (black) and difference intensities (blue) of the neutron Rietveld refinement of $SrC(NH)_3$ with the Bragg reflections in green.

$SrC(NH)_3$ crystallizes in the hexagonally primitive space group $P6_3/m$ (no. 176) with two formula units per unit cell (Figure 2, top). The Sr atoms sit along *c* with $z = 0$ and $^1/_2$ while the guanidinate anions adopt a layer-like motif at $z = {}^1/_4$ und $^3/_4$, thus alternating with the Sr partial structure. Six N atoms coordinate one Sr^{2+} ion with a distance of 2.669(8) Å resulting in an elongated octahedron such that there are *trans* face-sharing SrN_6 octahedra along *c*. As expected, the shortest Sr^{2+}–Sr^{2+} distance is 3.583(2) Å, far beyond the sum of the effective ionic radii for Sr^{2+} with sixfold coordination (1.18 Å).

The molar volume of $SrC(NH)_3$ is $52.6\,cm^3\,mol^{-1}$, and subtracting the Sr^{2+} increment[16] leaves a value of $41.6\,cm^3\,mol^{-1}$ for the anionic unit which positions

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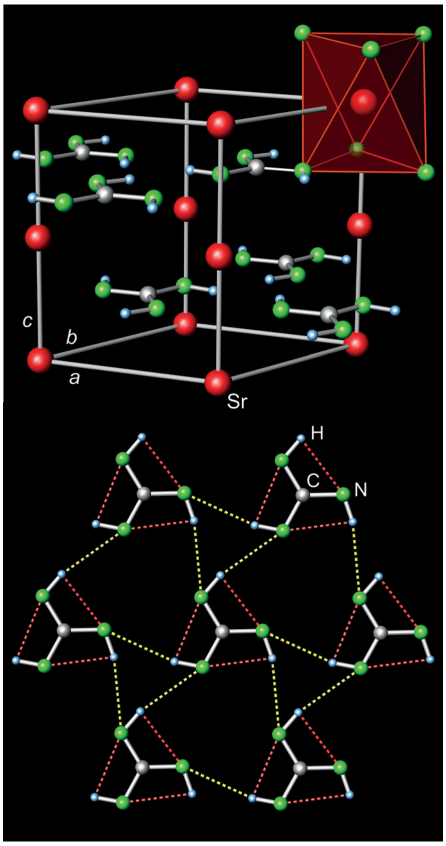

Figure 2. top: Perspective view into the crystal structure of $SrC(NH)_3$ with distorted octahedral coordination around Sr^{2+}; bottom: layer of guanidinate anions with the trinacria motif and H contacts of intermolecular (yellow) and intramolecular (red) nature.

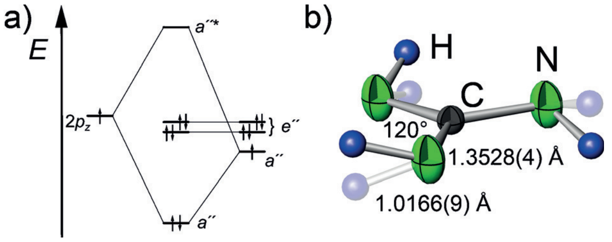

Figure 3. a) Qualitative MO diagram of the $2p_z$ orbital of C and the ligand group orbital (LGO) built from the $2p_z$ orbitals of the N_3 fragment. One π molecular orbital delocalized over all four atoms leads to C–N bonds with a π bond order of $^1/_3$. The MO resembles that of the isoelectronic NO_3^- ion.[18] b) ORTEP representation of the guanidine trinacria based on neutron data with thermal ellipsoids set at 50% probability. H lies above or below the mirror plane with equal occupancies.

$[C(NH)_3]^{2-}$ in the middle of all guanidinates investigated to date. The CN_3 core of the complex anion is fully planar within experimental resolution, and the entire anion reflects the predicted[17] C_{3h} symmetry with a trinacria motif (Figure 2, bottom). The symmetry determines the N-C-N bond angle to be exactly 120°, and there is also only one short C–N and one short N–H bond. The C–N distance of 1.3528(4) Å lies between those in rubidium guanidinate (1.33 and 1.39 Å)[14b] and in pure guanidine (1.30 and 1.37 Å).[12] We note that guanidine, $(NH_2)_2CNH$, contains bond orders of one and two while the bond orders of $[(NH_2)C(NH)_2]^-$ are one and one-and-a-half. The bond length of $[C(NH)_3]^{2-}$, however, clearly results from a bond order of $1^1/_3$ (Figure 3a), that is, the sum of a regular σ bond between C and N and another π bond fully delocalized over the C–N triangle. The N–H bond at 1.0166(9) Å compares well with the typical values, for example, those in $RbCN_3H_4$ (1.02–1.03 Å) and in guanidine itself (1.00–1.03 Å). Interestingly, the H atom must slightly (0.3 Å) shift away from the mirror plane to allow for a chemically sensible single-bond distance such that, within a centrosymmetric description (paraelectric phase), H lies either above or below (50% each) the CN_3 plane (Figure 3b). Despite incoherent scattering it was possible to arrive at a satisfactory refinement of the moderately anisotropic (C, N) and isotropic (H) displacement parameters by means of the neutron Rietveld technique which forms the basis of our structural model.

Within the layer of the guanidinate units there is a remarkable and as yet unknown N–H···N motif which suggest two different types of hydrogen bonds (Figure 2, bottom). On the one hand, there is a relatively long H···N distance, 2.59(3) Å, of intermolecular type (yellow dashes in Figure 2), significantly longer than the proton–acceptor distance of 1.96–2.35 Å in pure guanidine[12] or in $RbCN_3H_4$ with 2.01 Å.[13] Additionally, there is a shorter intramolecular H···N distance of 2.36(4) Å because an H atom of the guanidinate binds back (red dashes in Figure 2) to another N atom of the same complex anion. We will touch upon the latter “bond” in just a moment.

Clearly, the displacement of the H atoms above and below the mirror plane allows for two different conformational isomers of $[C(NH)_3]^{2-}$ in which either three or two H atoms remain on one side. Given a long-range order in the crystal, a ferroelectric material is conceivable, but at room temperature we do not find any evidence for second-harmonic generation as found in $NaNO_2$.[19] It is possible to imagine an ordered arrangement of the H atoms and loss of centrosymmetry below some Curie temperature T_C but, again, there is no evidence for a phase transition between room temperature and 15 K from X-ray data. Moreover, theory shows that there is absolutely no reason to expect any structural order for the different conformational isomers: two plausible and likewise ordered centrosymmetric models (Figure 4) only result in marginal energy differences ($<1\,kJ\,mol^{-1}$), even with different DFT functionals including dispersion corrections. Apparently, the individual conformational isomers are fully disordered.

With regard to dynamics, the IR data of $SrC(NH)_3$ as given in Figure 5 can be easily assigned by means of the theoretical phonon spectrum based on electronic-structure calculations (PBE + D3) in terms of the various IR- (Table 1) and Raman-active vibrational modes. Most striking is the typical C–N vibrational range between 600 and 1500 cm^{-1} which we already know from the related alkali-metal guanidinates.[13,14]

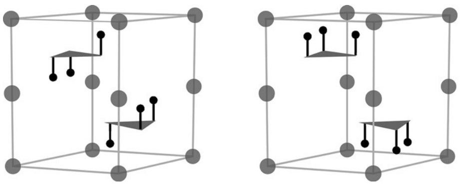

Figure 4. Schematic representation of two centrosymmetric structure models of $SrC(NH)_3$ based on acentric guanidinate conformational isomers.

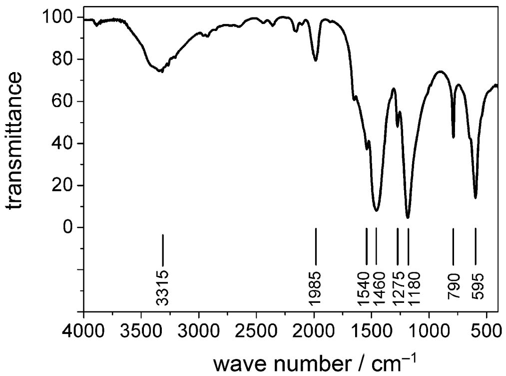

Figure 5. IR spectrum of $SrC(NH)_3$ between 4000 and 400 cm^{-1}.

Table 1: Assignment of the vibrational types to the positions of the IR bands.

Wave number	Vibrational type
ca. 3300 cm^{-1}	ν(N-H)
ca. 1450 cm^{-1}	ν(C-N) and δ(N-H)
1300–1150 cm^{-1}	ν(C-N) and δ(N-H)
ca. 760 cm^{-1}	C inversion through CN_3 plane
670–590 cm^{-1}	ν(C-N) and δ(N-H)

To quantify the suspected hydrogen bonds, COHP analyses[20] were carried out on the basis of the experimental structure for H···N. As expected, only minute covalent contributions of less than $-5\ kJ\,mol^{-1}$ are found (calculated as part of the band-structure energy = ICOHP) for the very long intermolecular H···N distance. For the shorter intramolecular H···N distance, however, the ICOHP is already in the slightly repulsive range; that bond does not exist. We have recently demonstrated how to quantify the covalency of hydrogen bonds from first principles using COHP analyses, and strongly covalent hydrogen bonds typically show up with ICOHP values of more than $-100\ kJ\,mol^{-1}$.[21] Evidently, the crystal structure of $SrC(NH)_3$ is not held together by significant hydrogen bonds but by ionic forces. The classically covalent bonds within the anion are strong, with ICOHP values of around $-440\ kJ\,mol^{-1}$ for the N−H and $-650\ kJ\,mol^{-1}$ for the C−N bond.

But where does the strange layer-like structure of $SrC(NH)_3$ originate from? Let us perform a thought experiment in which we replace the CO_3^{2-} of the known $SrCO_3$ structure[22] (*Pnma*) by the isoelectronic $[C(NH)_3]^{2-}$ anion: as expected, such a hypothetical $SrC(NH)_3$ structure ($Pna2_1$) is energetically less favorable than the experimental one,[23] and the molar volume inflates by almost $12\ cm^3\,mol^{-1}$; in particular, there is a considerable stretching of *a* because of the sterically significant H atoms. If $SrCO_3$ is computationally optimized in the experimental $SrC(NH)_3$ structure and compared with the real $SrCO_3$ structure, however, then the lattice parameters shrink just a little,[24] and taking the experimental structure, $SrC(NH)_3$ is only $4\ cm^3\,mol^{-1}$ more spacious than the carbonate! Clearly, there are steric but no electronic reasons for the preference of the $SrC(NH)_3$ structure because it allows for a relatively efficient packing of the bulky anion.[25]

To summarize, the first guanidinate with a doubly deprotonated guanidine unit combined with Sr^{2+} has been synthesized and characterized, thereby paving the way for other guanidinates of the divalent metals. The complex anion exhibits the trinacria motif. The results of neutron diffraction also evidence that, in principle, $C(NH)_3^{2-}$ comes with two different conformational isomers but there is no sign for any (ferroelectric) order as yet. The layered crystal structure is not a product of hydrogen bonds, which are quite insignificant in nature, but rather results from a favorable packing of the salt-like compound.

Experimental Section

Equimolar amounts of elemental strontium and pure guanidine were weighed in an argon-filled glove box and put into a steel autoclave which was evacuated and filled with condensing ammonia. The autoclave was then mildly heated for several days. The resulting white powder was finally removed under protective gas and analyzed.

The diffraction data of several reaction batches allowed for a comparative analysis and assignment of the reflections as regards target and side phase. At room temperature $SrC(NH)_3$ was indexed in the hexagonally primitive system and solved using direct methods[26] almost completely (Sr, C, N) based on X-ray powder data. The H atoms were roughly positioned according to earlier ab initio gas-phase calculations[17] and subsequently optimized using solid-state DFT total-energy calculations which lead to a slight twist of the guanidinate unit. The structural model was then refined against SPODI neutron data[27] ($\lambda = 1.5484$ Å, $T = 293$ K) and fully confirmed. The Rietveld refinement was conducted by means of the FullProf2000[28] computer program and a pseudo-Voigt profile function (Figure 1).

Crystal data of $SrC(NH)_3$: $M_r = 144.675$; space group $P6_3/m$ (no. 176); $a = b = 5.3029(15)$, $c = 7.166(3)$ Å, $V = 174.51(10)$ Å^3; $Z = 2$; $R_p = 0.0133$; $R_{wp} = 0.0159$; $R_{Bragg} = 0.0498$; Sr on 2*b*; C on 2*c*; N on 6*h* with $x = 0.5925(5)$, $y = 0.6750(7)$; H on 12*i* with $x = 0.5543(12)$, $y = 0.4760(15)$, $z = 0.2924(12)$. The standard deviations of the lattice parameters were corrected according to Pawley's formula. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-429498.

The IR spectrum was measured in a KBr pellet at room temperature using a Nicolet Avatar 360 FT-IR spectrometer. A temperature-resolved X-ray powder diffraction analysis showed that $SrC(NH)_3$ decays to strontium carbodiimide at about 130 °C.

All quantum-chemical structure optimizations were performed with VASP 5.3.5[29] using the PBE functional and the Projector-Augmented Wave (PAW) method,[30] additionally the VASP-implemented “D3” dispersion correction[31] and, as an alternative, the M06L functional[32] for the centric structure models (Figure 4). The cutoff criterion for the plane-wave kinetic energy was 500 eV, the convergence criterion for the electronic optimization at least 10^{-6} eV, and the force criterion for the structure optimization at least 5×10^{-3} eV Å^{-1}. Subsequently, harmonic phonons were calculated using Phonopy[33] while maintaining the experimental space group. In this case, the convergence criterion for structural optimization was 10^{-5} eV but 10^{-7} eV for the electronic energy. Projected Crystal Orbital Hamilton Population (COHP) analyses[20a] were carried out using the Lobster[20] computer program based on the PBE wave function. As for CuN_3 already, we utilized a special basis set fitted to PAW atomic functions.[4c]

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[23] The lattice parameters of the optimized structures on the PBE+D3 level widen from $a=6.048\rightarrow7.445$ Å, $b=5.149\rightarrow5.261$ Å and $c=8.463\rightarrow8.709$ Å.

[24] The shrinkage arrives at $a=5.335\rightarrow5.177$ Å and $c=7.169\rightarrow7.010$ Å.

[25] Compared to the isoelectronic carbonate CO_3^{2-} anion, the guanidinate $C(NH)_3^{2-}$ anion is always larger, and a comparison between the known alkali-metal guanidinates with the isoelectronic hydrogen carbonates yields the same tendency.

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