

Ammonothermal Synthesis, Crystal Structure, and Vibrational Properties of the Doubly Deprotonated Calcium Guanidinate, $\text{CaC}(\text{NH})_3$

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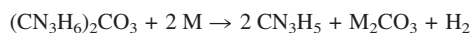
Dedicated to Professor Dr. Hans-Jörg Deiseroth on the Occasion of his 75th Birthday

Abstract. We report the synthesis of the doubly deprotonated calcium guanidinate, $\text{CaC}(\text{NH})_3$, from liquid ammonia and its crystal structure as determined from powder X-ray and neutron diffraction, and confirmed using CNH elemental analysis and infrared (IR) spectroscopy data. $\text{CaC}(\text{NH})_3$ crystallizes in the hexagonal system with space group

$P6_3/m$ (no. 176) with $Z = 2$ and $a = 5.2666(13) \text{ \AA}$, $c = 6.5881(6) \text{ \AA}$ and $V = 158.25(4) \text{ \AA}^3$. We also compare the structural similarities and differences of this phase with the isotypical strontium and ytterbium compounds.

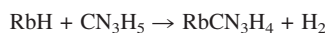
Introduction

Guanidine is a molecular compound that can either be classified as being organic or inorganic in nature. It is one of the strongest bases with a $\text{p}K_{\text{B}}$ value of 0.4.^[1] *Strecker* first synthesized guanidine in 1861 by isolating guanine from bird's droppings (feces).^[2] Today, the synthesis is carried out either using guanidine carbonate or guanidine chloride with an alkali metal in liquid ammonia, followed by removal of the ammonia and subsequent sublimation of molecular guanidine at 50 °C to separate it from the alkaline chloride or carbonate.^[3]

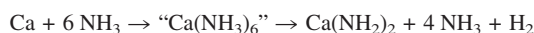
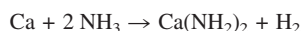


So far, the known metal guanidates with a negatively charged guanidine anion have been synthesized in two ways: a one-pot synthesis by combining an alkali (Li, Na, K, Cs), alkaline-earth (Ba, Sr), or lanthanide (Yb, Eu) metal and guanidine in an autoclave and using ammonia as the reaction medium, thereby often reaching single crystals. The other, even

simpler method is a solid-solid reaction using a metal hydride and guanidine without ammonia, as was the pioneering case for synthesizing RbCN_3H_4 .^[4]



In this work, calcium guanidinate was made from calcium amide and guanidine. This approach assumes a reaction taking place in three steps. First, the alkali metal dissolves in ammonia to form a cation, indicated by a color change of the solution due to solvated electrons.^[5] Second, the cation reacts with ammonia to form the metal amide which, third, reacts with guanidine.^[6] We here used the same synthetic technique for calcium guanidinate starting from calcium amide at 50 °C, and it was *Juza* and *Schumacher* who first reported an X-ray crystallographic study of the latter phase in 1963.^[7] Calcium amide can also be synthesized in two ways; either by reacting calcium metal with liquid ammonia under pressure at room temperature or by reacting calcium metal with gaseous ammonia at 0 °C to form a material dubbed “ $\text{Ca}(\text{NH}_3)_6$ ”, which then decomposes at room temperature to form calcium amide.^[8]



Herein we employed the first method by reacting calcium metal with liquid ammonia in steel autoclaves at 20 °C for 7 days. Residual ammonia was then released by a Schlenk line leaving a white powder which was confirmed using XRD analysis to be $\text{Ca}(\text{NH}_2)_2$.

This very approach is advantageous because a one-pot synthesis starting from equimolar amounts of calcium metal and guanidine even at different temperatures (25–60 °C) leads to amorphous products and, eventually, to the formation of calcium amide. Reacting equimolar amounts of calcium amide and guanidine at 50 °C, however, directly yields crystalline $\text{CaC}(\text{NH})_3$. Thus, this synthetic approach follows the prior work on 4f guanidates as given by *Görne* et al.^[5,8]

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Results and Discussion

The white product was crystalline, visible from microcrystals seen in a microscope mounted into the glovebox. The air- and moisture-sensitive sample was filled and sealed into a 0.5 mm glass capillary. X-ray powder diffraction patterns were recorded at room temperature and indexed with the DICVOL04 algorithm^[9] as provided in the WINXPOW suite.^[10] A hexagonal cell was found with $a = 5.295(6)$ Å, $c = 6.627(3)$ Å, and $V = 160.9(3)$ Å³, very similar to YbC(NH)₃ with the same metric and space-group symmetry $P6_3/m$ (no. 176). Hence, YbC(NH)₃ served as the structural model in the Rietveld refinement performed using GSAS II.^[11] All N–C–N planes, N–C–N angles, and C–N bond lengths were restrained to sensible values as known from the literature,^[12] just like for the U_{iso} parameters. In order to allow for greater accuracy and also locate the exact positions of the hydrogen atoms, neutron powder-diffraction data were collected on the POWGEN neutron powder diffractometer in the Oak Ridge National Laboratory. These data were also refined using GSAS II (Figure 1) without restraining the N–H bond lengths and arrived at $R_F = 0.113$, $R_p = 0.014$, $R_B = 0.019$.

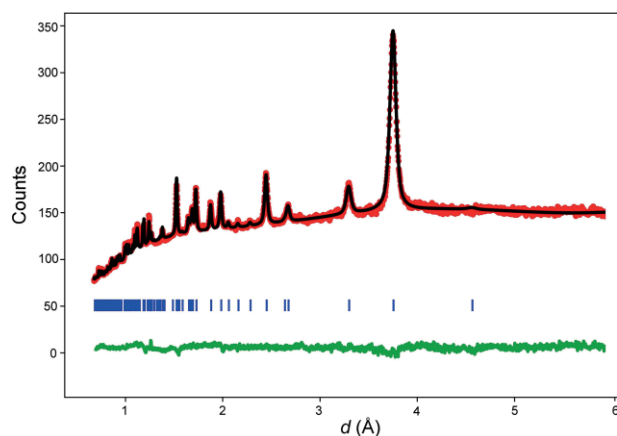


Figure 1. Rietveld refinement of the neutron powder diffraction pattern of CaC(NH)₃ at 298 K; collected pattern in red, calculated in black, difference plot in green, Bragg peaks in blue below.

As alluded to already, CaC(NH)₃ crystallizes in space group $P6_3/m$ with two formula units per cell and is isostructural to YbC(NH)₃ (Table 1). Ca occupies the high-symmetry Wyckoff positions $2b$ while C and N atoms go on $2c$ and $6h$, respectively (Table 2). Each calcium is coordinated by six nitrogen atoms with Ca–N = 2.514(9) Å building a distorted octahedron, whereas the nitrogen atoms are also connected to a central carbon atom at an angle of 120°, hence forming a trinacria-shaped guanidinate unit^[5] [the term *trinacria* (“three pointed”)

Table 2. Atomic positions and displacement parameters of CaC(NH)₃; all positions are fully occupied except hydrogen with a site-occupation factor of 0.5.

Atom	Wyckoff position	x	y	z	$U_{\text{eq}}/U_{\text{iso}}^* / \text{Å}^2$
Ca	$2b$	0	0	$\frac{1}{2}$	0.0102(12)
C	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.0168(4)
N	$6h$	0.6031(9)	0.692(5)	$\frac{1}{4}$	0.0162(5)
H	$12i$	0.5845(19)	0.4954(17)	0.2896(9)	0.0100(14) *

Table 1. Crystallographic data comparing CaC(NH)₃, YbC(NH)₃, and SrC(NH)₃.

Formula	CaC(NH) ₃	YbC(NH) ₃	SrC(NH) ₃
Formula weight / g·mol ⁻¹	97.134	230.10	144.676
Radiation	Neutron TOF	Cu- K_{α}	Neutron TOF
a / Å	5.2666(13)	5.2596(2)	5.3029(15)
c / Å	6.5881(6)	6.6704(2)	7.166(3)
V / Å ³	158.25(4)	159.81(1)	174.52(12)

relates to the Greek name of the island of Sicily, the trinacria motif also being found on its flag].

As regards the C–N bond lengths, they are 1.359(17) Å in CaC(NH)₃ and 1.373(5) and 1.3528(4) Å in YbC(NH)₃ and SrC(NH)₃, respectively. Not too surprisingly, the N–H bond lengths in CaC(NH)₃ and isostructural YbC(NH)₃ and SrC(NH)₃ are quite similar, 1.006(18) vs. 1.024 Å (computed) and 1.0166(9) Å, and in order to yield a regular N–H single bond, the hydrogen atoms are located above and below the mirror plane, on the low-symmetry position $12i$ with half occupancy in CaC(NH)₃ and SrC(NH)₃ but within the mirror plane, on position $6h$, as has been computed by DFT for YbC(NH)₃.^[5] The split position of hydrogen is visible both from Figure 2 and Figure 3. It is important to note that all atoms were refined anisotropically apart from the hydrogen atom, which was refined isotropically such as to derive a statistically meaningful hydrogen position.

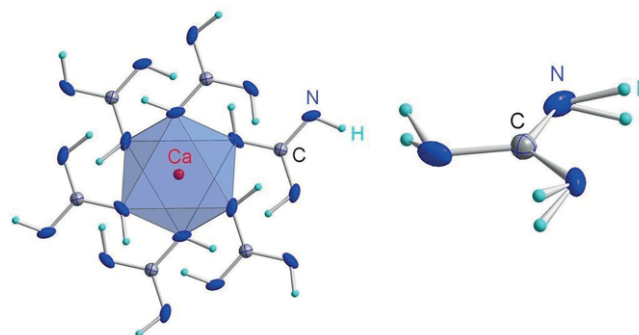


Figure 2. Coordination polyhedron (left) of calcium in CaC(NH)₃ and shape (right) of the C(NH)₃²⁻ anion showing partially occupied hydrogen positions.

An ATR-IR spectrum (thereby excluding any water signals) of pure CaC(NH)₃ was recorded under argon atmosphere at room temperature to further check the reliability of the structural results as shown in Figure 4. To validate the measured IR spectrum, the spectrum was theoretically simulated based on DFT-derived phonons, depicted in blue color. The vibrational

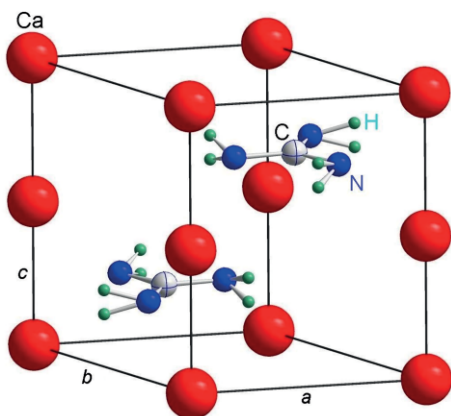


Figure 3. The unit cell of $\text{CaC}(\text{NH}_3)_3$.

bands of the N–H and C–N groups are listed in Table 3, and the experimentally observed and theoretically predicted IR data match each other well, with only small deviations. The IR band at 1593 cm^{-1} is a $\nu_s(\text{N-H})$ vibration from a side phase, which could be identified as the singly deprotonated (amorphous, hence not seen in diffraction) calcium guanidinate, $\text{Ca}(\text{CN}_3\text{H}_4)_2$.

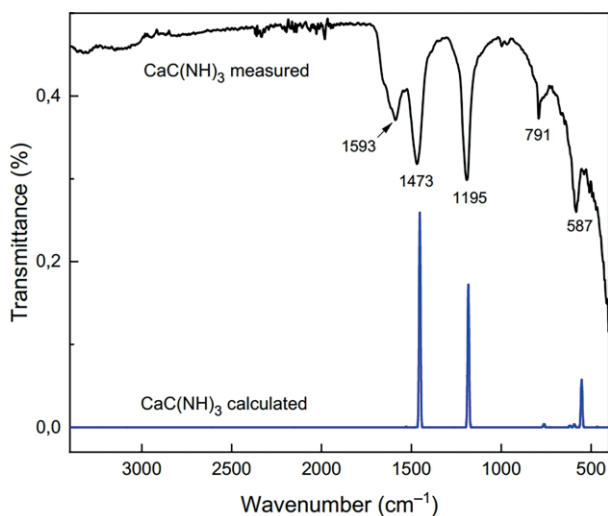


Figure 4. Infrared spectrum of $\text{CaC}(\text{NH}_3)_3$ measured at 293 K (black) together with the theoretical density of phonon states from DFT calculations (blue).

Table 3. Assignment of the vibrational bands of $\text{CaC}(\text{NH}_3)_3$ as obtained using DFT calculations.

Vibration	Measured / cm^{-1}	Calculated / cm^{-1}
$\nu_s, \delta_{\text{sciss}}(\text{N-H})$	1473	1453
$\delta_{\text{rock}}(\text{N-H})$	1195	1183
$\delta_{\text{twist}}(\text{N-H})$	791	762
$\delta_{\text{rock}}(\text{C-N}), \delta_{\text{rock}}(\text{N-H})$	587	553

Conclusions

An ammonothermal reaction was used to synthesize doubly deprotonated calcium guanidinate, $\text{CaC}(\text{NH}_3)_3$, by reacting cal-

cium amide with guanidine in a 1:1 molar ratio at $50\text{ }^\circ\text{C}$. Structure solution was done using X-ray and neutron powder diffraction. $\text{CaC}(\text{NH}_3)_3$ crystallizes isostructurally with $\text{SrC}(\text{NH}_3)_3$ and is close to $\text{YbC}(\text{NH}_3)_3$, the only difference stemming from the hydrogen position of the latter phase. In all three compounds, the guanidinate anion is made up of a N–C–N (bond angle = 120°) triangle with N–H and C–N bonds of similar lengths.

Experimental Section

CN_3H_5 was prepared in a one-pot synthesis by reacting equimolar guanidium carbonate, $(\text{CN}_3\text{H}_6)_2\text{CO}_3$ (Aldrich, 99%), with the alkali metal potassium (Alfa, 99.95%) together with 20 cm^3 of dry ammonia in a stainless-steel autoclave. After heating at $50\text{ }^\circ\text{C}$ for 7 d, the autoclave was cooled to room temperature within 1 d, then the NH_3 was released via the Schlenk line leaving a mixture of CN_3H_5 and K_2CO_3 , which was separated via sublimation. The sublimation vessel was held at $50\text{ }^\circ\text{C}$ in an oil bath for 7 d under reflux to give colorless, phase-pure powder as a sublimate. Simultaneously, moisture-sensitive Ca metal was deposited into an autoclave in the glovebox. Afterwards, 10 mL of dry NH_3 was condensed into the autoclave, and the reaction was left to proceed for 7 d at room temperature. NH_3 was removed via a Schlenk line leaving behind a white powder which was identified using PXRD as calcium amide. The highly moisture-sensitive CN_3H_5 (61.5 mg) and $\text{Ca}(\text{NH}_2)_2$ (50.4 mg) were weighed in the glovebox in a 1:1 molar ratio under Ar and transferred into a steel autoclave. The Schlenk line was evacuated for 15 min before 10 cm^3 of dried NH_3 was condensed (Linde, 99.999%, without further purification). The reaction was left to proceed for another 7 d at $50\text{ }^\circ\text{C}$, then the autoclave was cooled to room temperature. NH_3 was released via a Schlenk line. The phase-pure $\text{CaC}(\text{NH}_3)_3$ product with a yield of around 70% was identified by powder XRD, recorded at room temperature on a STOE STADI-P diffractometer using $\text{Cu-K}\alpha_1$ radiation. The measurement covered a range of $7\text{--}90^\circ$ in 2θ with step sizes of 0.015° .

Neutron powder-diffraction data were collected on the POWGEN diffractometer in the Oak Ridge National Laboratory. A total of 195 reflections were measured and their profiles refined using a Von Dreele–Jorgensen–Windsor function and the background subtracted using a 15-terms Chebyshev model, as provided by the GSAS II suite.^[11]

Infrared (IR) data of $\text{CaC}(\text{NH}_3)_3$ data were obtained at room temperature using a Bruker ALPHA FT-IR spectrometer placed in an argon-filled glove box and equipped with an ATR Platinum Diamond sample holder with a measurement range of $4000\text{--}400\text{ cm}^{-1}$.

Density-functional theory calculations were done utilizing the Vienna *ab initio* simulation package (VASP)^[13] with plane wave basis sets (kinetic-energy cutoff of 500 eV) and the exchange-correlation functional of Perdew, Burke and Ernzerhof.^[14] Van der Waals-like interactions were accounted by the D3 method with Becke–Johnson damping.^[15] Phonon properties were obtained by the small displacement approach as implemented in Phonopy.^[16] The infrared spectrum was derived using a customized python script.^[17]

Further details of 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, <http://www.fiz-karlsruhe.de/request> for deposited data. html) on quoting the depository number CSD-1976422.

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Keywords: Guanidinate; Calcium; Synthesis; Density-functional calculations (DFT); Liquid ammonia

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