

Synthesis, Raman Spectrum and Single-Crystal Structure of $\text{CaBa}_8[\text{CN}_2]_6\text{O}_2(\text{N}_{0.5}\text{H}_{0.5})$

Olaf Reckeweg^a, Armin Schulz^b and Francis J. DiSalvo^a

^a Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA

^b Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Reprint requests to Dr. Olaf Reckeweg. Fax: +1-607-255-4137. E-mail: olaf.reykjavik@gmx.de

Z. Naturforsch. **2013**, *68b*, 39–43 / DOI: 10.5560/ZNB.2013-2292

Received October 23, 2012

Colorless, transparent single crystals of $\text{CaBa}_8[\text{CN}_2]_6\text{O}_2(\text{N}_{0.5}\text{H}_{0.5})$ ($R\bar{3}$ (no. 148), $a = 996.94(4)$ and $c = 1803.18(8)$ pm, $Z = 3$) were obtained by the reaction of Ca_3N_2 , Ba_2N and NaHCN_2 (of which one of the latter two most likely was contaminated with some oxygen impurity) in arc-welded Nb ampoules at 1200 K. The title compound consists of distorted $(\text{H/N})\text{Ba}_6$ octahedra which share two of their opposite faces with OBa_4 tetrahedra interconnected by $[\text{N}=\text{C}=\text{N}]^{2-}$ units of $\text{Ca}(\text{N}=\text{C}=\text{N})_6$ octahedra with C=N bond lengths of 121.9(6) and 124.3(6) pm and with a bond angle deviating from linearity with $(\text{N}-\text{C}-\text{N}) = 175.9(5)^\circ$. A Raman spectrum obtained from the crystal used for the structure determination indicates the presence of the $[\text{N}=\text{C}=\text{N}]^{2-}$ unit.

Key words: Barium, Calcium, Carbodiimide, Cyanamide, Hydride, Nitride, Oxide, Raman Spectroscopy

Introduction

Serendipity played and plays many times a major role in solid-state chemistry since many new compounds obtained are unsought. Confessing that unwanted, but lucky circumstances influenced the synthesis of a new compound, has never really been wide spread, since it usually indicates some fault or mistake in the synthesis. Reactions with barium in metal ampoules are notorious for incorporating container material or other impurities from different sources to form unexpected products such as $\text{Ba}_9[\text{NbN}_4]_2\text{O}[\text{CN}_2]$ [1], $(\text{Ba}_6\text{N}_{5/6})_2[\text{NbN}_4][\text{CN}_2]_6$ [2] or the quaternary hydride oxide iodide $\text{Ba}_5\text{H}_2\text{O}_2\text{I}_4$ [3].

While exploring the Ca-Ba-CN₂-H system to obtain a compound such as $\text{CaBa}_9[\text{CN}_2]_4(\text{N}_{3.5}\text{H}_{1.5})$ (expected to be isopointal to $\text{Ba}_{10}[\text{BN}_2]_4(\text{F}_4\text{C})$, [4]), some oxygen impurity caused the formation of a few crystals of $\text{CaBa}_8[\text{CN}_2]_6\text{O}_2(\text{N}_{0.5}\text{H}_{0.5})$, which enabled us to determine its crystal structure and to record its Raman spectrum.

Experimental Section

Synthesis

All manipulations of reactants and products were performed in a glove box under purified argon unless stated otherwise. Orientated at the desired composition $\text{CaBa}_9[\text{CN}_2]_4(\text{N}_{3.5}\text{H}_{1.5})$ with an excess of Ba, N and H, 75 mg (0.5 mmol) Ca_3N_2 (Alfa Aesar, 99%), 290 mg (3.45 mmol) Ba_2N [obtained by the reaction of Ba (Strem, 99.9%) with nitrogen at 1100 K, rhombohedral, lattice constants (trigonal setting): $a = 402.8(3)$; $c = 2251(2)$ pm], and 320 mg (4.25 mmol) NaHCN_2 (Sigma-Aldrich, > 98%) were ground intimately in an agate mortar and arc-welded into a clean niobium container. The metal container was sealed in an evacuated silica tube. The tube was placed upright in a box furnace and heated to 1200 K within 12 h. After three days the furnace was switched off and allowed to cool to room temperature. The reaction produced mainly an X-ray-amorphous colorless powder with a few transparent crystals of the title compound, which are air and moisture sensitive.

Attempts to increase the yield by stoichiometric amounts of starting materials were not successful as yet since always

the binary oxides formed. The reductive reaction condition had to be maintained to obtain even a few crystals per experiment, but using Zn[CN₂] or Na₂[CN₂]₂ instead of NaHCN₂ as a source of hydrogen resulted in no crystals of the title compound at all.

Crystallographic studies

Samples of the reaction mixture were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene > 90%) for single-crystal selection under a polarization microscope, mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A stream of cold nitrogen ($T = 170(2)$ K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Intensity data were collected with a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized Mo K_α radiation ($\lambda = 71.073$ pm). The intensity data were manipulated with the program package [5] that came with the diffractometer. An empirical absorption correction was applied using SADABS [6]. The intensity data were evaluated,

and the input files for solving and refining the crystal structure were prepared by XPREP [7]. The program SHELXS-97 [8, 9] delivered with the help of Direct Methods the positions of Ca and Ba. O, C and N positions were apparent from the positions of highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares techniques with the use of SHELXL-97 [10, 11]. Only one electron density was apparent after these refinements, which was not unreasonably close to heavy atom positions. The bond lengths were with approximately 290 pm in a familiar range for an oxide, a nitride or a hydride anion. The octahedral coordination of this site is in accordance for nitride or hydride in an octahedral coordination by barium, while oxygen usually is surrounded in a tetrahedral fashion by barium atoms in similar compounds [1–3, 12–14]. Nevertheless, neither N nor O could be refined on this site with a full occupancy. Free refinement of the site occupation factor led to about 60% occupation of the position with O or N, but this did not concur with the electroneutrality of the compound demanded by its transparency and lack of color. Therefore, a split occupancy of this position with

Compound	CaBa ₈ [CN ₂] ₆ O ₂ (N _{0.5} H _{0.5})
M_r	404.21
Crystal color	transparent colorless
Crystal shape	square lath
Crystal size, mm ³	0.11 × 0.02 × 0.02
Crystal system	rhombohedral (trigonal setting)
Space group (no.), Z	$R\bar{3}$ (148), 3
Lattice parameters	
a , pm	996.94(4)
c , pm	1803.18(8)
V , Å ³	1552.06(11)
D_{calcd} , g cm ⁻³	4.55
$F(000)$, e ⁻	1824
μ , mm ⁻¹	15.2
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD
Radiation; λ , pm; monochromator	Mo K_α ; 71.073; graphite
Scan mode; T , K	φ - and ω -scans; 170(2)
$2\theta_{\text{max}}$, deg; ranges hkl	66.22; $-14 \rightarrow 9$, $-13 \rightarrow 15$, $-27 \rightarrow 27$
Data correction	LP, SADABS [6]
Transmission: min. / max.	0.5470 / 0.7465
Reflections: measured / unique	5018 / 1324
Unique reflections with $F_o > 4\sigma(F_o)$	1136
$R_{\text{int}} / R_\sigma$	0.0237 / 0.0211
Refined parameters	46
$R1^a / wR2^b / \text{GoF}^c$ (all refl.)	0.0314 / 0.0616 / 1.099
Factors x / y (weighting scheme) ^b	0.0206 / 38.08
Max. shift / esd, last refinement cycle	< 0.00005
$\Delta\rho_{\text{fin}}$ (max / min), e ⁻ Å ⁻³	2.73 (73 pm to Ba2) / -2.07 (59 pm to Ba2)
CSD number	425 124

Table 1. Summary of single-crystal X-ray diffraction structure determination data of CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}).

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ and x and y are constants adjusted by the program; ^c $\text{GoF} = S = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

Table 2. (a) Atomic coordinates and equivalent isotropic displacement parameters^a of CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}). (b) Anisotropic displacement parameters^a (pm²) of CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}).

(a)	Wyckoff				U_{eq}
Atom	site	x	y	z	(pm ²)
Ca	3b	0	0	1/2	377(7)
Ba1	6c	0	0	0.30029(2)	111(1)
Ba2	18f	0.19915(3)	0.24836(3)	0.09849(1)	119(1)
O	6c	0	0	0.1629(3)	151(10)
N1	18f	0.3441(5)	0.0882(5)	0.05824(2)	169(7)
N2	18f	0.4711(5)	0.5627(5)	0.0891(2)	194(8)
C	18f	0.0027(5)	0.3950(5)	0.0715(2)	129(7)
N3 / H	3a	0	0	0	937(149)

^a U_{eq} is defined as one third of the orthogonalized U_{ij} tensors.

(b)						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	183(9)	212(10)	227(10)	-20(8)	44(8)	16(8)
Ba1	175(9)	191(9)	202(9)	0	37(7)	0
Ba2	180(3)	194(4)	238(4)	20(3)	28(3)	-29(3)
O	183(4)	144(4)	156(3)	16(3)	36(3)	-8(3)
N1	153(3)	171(4)	290(4)	49(3)	19(3)	-32(3)
N2	137(4)	187(4)	174(4)	8(3)	22(3)	13(3)
C	137(4)	187(4)	174(4)	8(3)	22(3)	13(3)
N3 / H	198(4)	187(4)	278(4)	-18(3)	44(3)	38(3)

^aThe anisotropic displacement factor takes the form: $U_{ij} = \exp[-2\pi^2(h^2a^*{}^2U_{11} + k^2b^*{}^2U_{22} + l^2c^*{}^2U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

N and H was refined leading to balanced charges following (Ca²⁺)(Ba²⁺)₈([CN₂]²⁻)₆(O²⁻)₂(N³⁻)_{0.5}(H⁻)_{0.5} and sensible coordination environments both for a nitride and a hydride anion in a Ba²⁺ octahedron. Doing further refinement cycles, the refinement converged and resulted in a stable model for the crystal structure. Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2. Table 3 displays selected interatomic distances and angles of the title compound.

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-karlsruhe.de/request_for_deposited_data.html), on quoting the depository number CSD-425124 for CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}).

Atoms	Multiplicity	d	Atoms	Multiplicity	d		
Ca-	N2	6 ×	251.8(6)	H/N3-	Ba2	6 ×	288.28(3)
O-	Ba1	1 ×	247.7(6)	O-	Ba2	3 ×	255.1(3)
C-	N1	1 ×	124.3(6)	C-	N2	1 ×	121.9(6)
∠(N=C=N)		1 ×	175.9(5)				

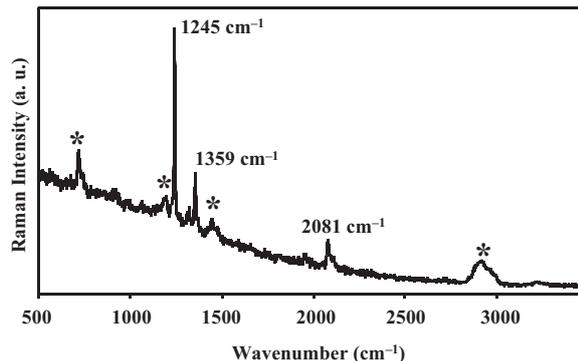


Fig. 1. Raman spectrum of CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}). Only background was observed in the region $\nu \geq 3500$ cm⁻¹. Asterisks indicate bands attributed to polybutene oil [15].

Raman spectroscopy

Raman investigations were performed on a microscope laser Raman spectrometer (Jobin Yvon, 4 mW, equipped with an HeNe laser with an excitation line at $\lambda = 632.817$ nm, 50 × magnification, samples in glass capillaries, 2 × 40 s accumulation time) on the very specimen used for the structure determination. The resulting Raman spectrum for CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}) is shown in Fig. 1, the exact frequencies and their assigned modes are listed in Table 4.

Results and Discussion

Optical spectra

A typical band for the symmetric stretching mode of the [CN₂]²⁻ unit is observed with $\nu_s = 1245$ cm⁻¹, and for its antisymmetric stretching mode at $\nu_{as} = 2081$ cm⁻¹. As also noted in the Raman spectrum of BaCN₂ [12], the bending mode δ could not be observed, but the overtone at $2\delta = 1359$ cm⁻¹ was clearly visible in the expected range. Some other bands can be attributed to the polybutene oil [15].

The Raman spectrum of the title compound compares not only well with that of similar compounds such as BaCN₂ [12], Ba₉[NbN₄]₂O[CN₂] [1] or (Ba₆N_{5/6})₂[NbN₄][CN₂]₆ [2], but also with those

Table 3. Selected bond lengths (pm) and angles (deg) of (CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5})).

Table 4. Synopsis of selected barium compounds containing a [CN₂]²⁻ unit. Selected bond lengths (pm), angles (deg), Raman and IR (in italics) bands (cm⁻¹) are given. Bold print indicates the strongest intensity. A band without the wavenumber given in the respective paper is labeled 'N. N.'.

	CaBa ₈ [CN ₂] ₆ O ₂ (N _{1.5} H _{1.5})	Ba ₉ [NbN ₄] ₂ O[CN ₂] [1]	(Ba ₆ N _{5/6}) ₂ [NbN ₄][CN ₂] ₆ [2]	BaCN ₂ [12]
<i>d</i> (C=N)	121.9(6) / 124.3(6)	122.0(20) / 122.5(19)	121.8(6) / 121.8(6)	119.2(11) / 119.2(11)
<i>∠</i> (N=C=N)	175.9(5)	173.7(15)	175.3(9)	177.2(18)
<i>v</i> _s	1245	1234	1262	1238
<i>v</i> _{as}	2081	–	1957 / 2090	1947 / N. N.
<i>δ</i>	–	632 / 658 / 668	611 / 633 / 653	662 / 673
2 <i>δ</i>	1359	1312 / 1343	–	N. N.

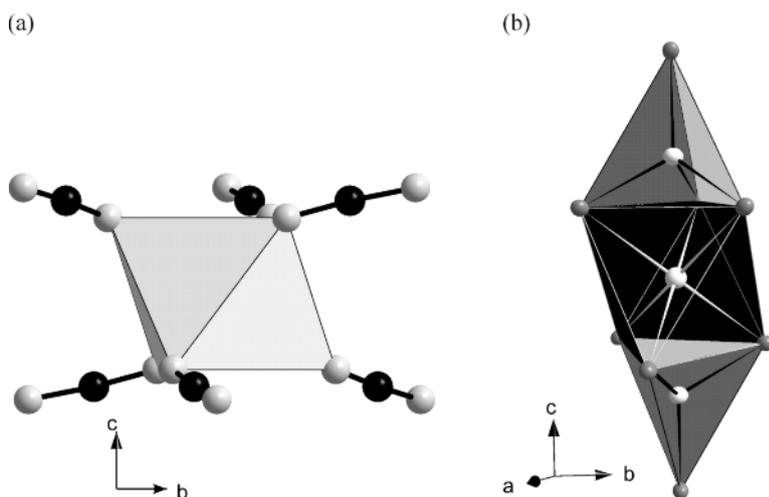


Fig. 2. (a) A Ca(N=C=N)₆ octahedron is displayed as a white polyhedron. Carbon is displayed as full black, nitrogen as full light-grey spheres. (b) A (H/N3)Ba₆ octahedron is shown as an open black polyhedron and OBa₄ as an open light-grey tetrahedron. Ba is displayed as light-grey, and the centering O and N3/H atoms are drawn as white spheres. Coordinating [CN₂]²⁻ units are omitted for clarity.

of other carbodiimide compounds previously reported [16].

Crystal structure

The crystal structure of the title compounds consists of two more or less isolated components connected by bent [CN₂]²⁻ units as identified by their typical Raman emissions (see Table 4). The more simple moiety is a distorted Ca(N=C=N)₆ octahedron (Fig. 2a) with *d*(Ca–N) = 251.8(6) as a typical Ca–N distance for calcium in an octahedral coordination by nitride anions (*e. g.*, 259.2(2) pm [17] or 261.3(2) pm [18] in CaMg₂N₂). The more complex polyhedron is an also distorted (H/N3)Ba₆ octahedron which shares two opposite faces with OBa₄ tetrahedra (Fig. 2b) exhibiting Ba–O distances (247.7–251.1 pm) in the same range as found in such geometries frequently (248.7–255.5 pm) [3, 13, 14]. The central Ba₆ octahedron with the split H/N3 occupancy shows an atomic distance of *d*(Ba–H/N3) = 288.28(3) pm which is in

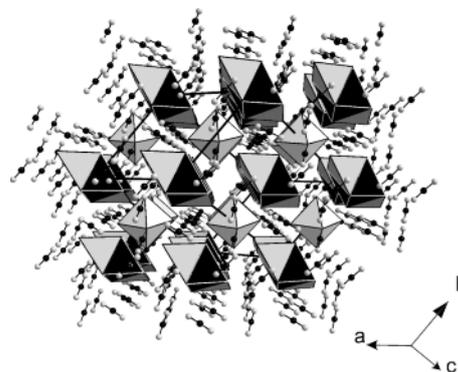


Fig. 3. Perspective view along [111]. The same color code as in Figs. 2a and b, the Ba atoms at the corners of the polyhedron displayed in Fig. 2b are not shown for clarity.

a similar range as the sum of the ionic radii according to Shannon [19] with 275 (Ba–N) and 281 pm (Ba–H). The fact that the observed atomic distance is somewhat longer than the one expected might be an explanation for the large displacement factor observed for this site, because the anions rattle in a coordina-

tion sphere slightly too large for qualifying as a perfect environment. The [(BaOBa₃(H/N₃)Ba₃OBa)] moieties are stapled along [111] and connected *via* bridging Ca(N=C=N)₆ octahedra (Fig. 3).

Conclusion

While exploring the Ca-Ba-CN₂-H system, instead of the target product CaBa₉[CN₂]₄(N_{3.5}H_{1.5})

the new compound CaBa₈[CN₂]₆O₂(N_{0.5}H_{0.5}) was obtained by serendipitous incorporation of oxygen (most likely from the very oxophilic educt Ba₂N or not completely solvent-free NaHCN₂) and characterized *via* single-crystal X-ray diffraction and Raman spectroscopy on the same crystal. All bond lengths, bond angles and Raman frequencies obtained are in a reasonable range when compared to literature data.

-
- [1] O. Reckeweg, F. J. DiSalvo, *Z. Naturforsch.* **2003**, *58b*, 201–204.
- [2] O. Reckeweg, M. Somer, F. J. DiSalvo, *Z. Naturforsch.* **2007**, *62b*, 1246–1250.
- [3] O. Reckeweg, F. J. DiSalvo, *Z. Naturforsch.* **2011**, *66b*, 21–26.
- [4] F. E. Rohrer, Doctoral Thesis, Eidgenössische Technische Hochschule, Zürich **1997**.
- [5] APEX2 (version 1.22), SAINT PLUS, Software for the CCD system, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2004**.
- [6] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.
- [7] XPREP (version 6.14), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2003**.
- [8] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **199**.
- [9] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.
- [10] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **199**.
- [11] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.
- [12] U. Berger, W. Schnick, *J. Alloys Compd.* **1994**, *206*, 179–184.
- [13] O. Reckeweg, F. J. DiSalvo, *Z. Naturforsch.* **2008**, *63b*, 519–524.
- [14] O. Reckeweg, F. J. DiSalvo, *Z. Naturforsch.* **2011**, *66b*, 1000–1004.
- [15] Y. Dong, F. J. DiSalvo, *J. Solid State Chem.* **2006**, *179*, 1363–1368.
- [16] O. Reckeweg, A. Simon, *Z. Naturforsch.* **2003**, *58b*, 1097–1104.
- [17] V. Schulz-Coulon, W. Schnick, *Z. Naturforsch.* **1995**, *50b*, 619–622.
- [18] O. Reckeweg, F. J. DiSalvo, *Z. Anorg. Allg. Chem.* **2001**, *627*, 371–377.
- [19] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751–767.