

# Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] – Synthesis, Crystal Structure and Raman Spectrum

Olaf Reckeweg and Francis J. DiSalvo

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

Reprint requests to Dr. O. Reckeweg. E-mail: olaf.reykjavik@gmx.de

Z. Naturforsch. **58b**, 201–204 (2003); received October 11, 2002

Red transparent single crystals of Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] were synthesised by the reaction of BaO coated Ba metal, C and Nb powder in arc-welded Nb ampoules at 1300 K. The title compound was characterised by X-ray single crystal diffraction (*P* $\bar{1}$ , *a* = 799.05(2), *b* = 962.61(2) and *c* = 1264.38(4) pm;  $\alpha$  = 75.859(1),  $\beta$  = 85.745(1) and  $\gamma$  = 87.8621(8)°; *Z* = 2) and Raman spectroscopy ( $\nu_{\text{sym}}$  = 1234 and  $\delta$  = 632/658/668 cm<sup>−1</sup>). It now seems likely that a nitride-azide compound we previously reported, Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>], does not exist, but is in fact the title compound.

**Key words:** Cyanamide, Nitride, Structure Elucidation

## Introduction

In nitride chemistry quite a few compounds of unusual stoichiometry have aroused interest and discussion. Unusual or non-integer oxidation states, as in *e.g.* Ae<sub>2</sub>N (Ae = Ca, Sr, Ba) [1], SrN [2], Sr<sub>4</sub>N<sub>3</sub> [3], SrN<sub>2</sub> [2], BaN<sub>2</sub> [4], Ba<sub>3</sub>N [5] and Ca<sub>11</sub>N<sub>8</sub> [6], or synthetic methods that result in compounds containing structural elements that are likely to be unstable under the reaction conditions, as in Cs<sub>11</sub>(WN<sub>2.5</sub>O<sub>1.5</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> [7] or Ba<sub>9</sub>[MN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>] (*M* = Nb or Ta) [8,9] are interesting examples. Recent studies support the existence of the subnitrides Ae<sub>2</sub>N and of N<sub>2</sub><sup>2−</sup> containing Sr-N and Ba-N compounds, but we found that ‘Ca<sub>11</sub>N<sub>8</sub>’ was in fact Ca<sub>11</sub>N<sub>6</sub>(CN<sub>2</sub>)<sub>2</sub> [10]. In the latter case, carbon impurities in the reaction mixture are responsible for the formation of the nitride-cyanamide. This finding explained away the apparent difficulty of the incomplete reduction of nitrogen that would result from the stoichiometry of ‘Ca<sub>11</sub>N<sub>8</sub>’, since no N—N bonding was apparent.

For Ba<sub>9</sub>[MN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>] (*M* = Nb or Ta) the ‘normal’ oxidation states (Ba<sup>2+</sup>, *M*<sup>5+</sup>, N<sub>3</sub><sup>3−</sup>, N<sub>3</sub><sup>−</sup>) balance nicely to zero. However, the yield in synthesizing both compounds was quite low. For the Ta compound quenching was an important factor in the synthesis, while the Nb compound was cooled down to room temperature over 8 days. Also, since azides are generally stable at atmospheric pressure only to 550–660 K, it was surprising to see the presence of azide in a compound synthesized at a few tens of bars and at temperature be-

tween 1123–1223 K. The only similar case reported is Cs<sub>11</sub>(WN<sub>2.5</sub>O<sub>1.5</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> [7] which was synthesised at *T* = 893 K in an autoclave at elevated pressures under ammonothermal conditions. The presence of azide in that oxy-nitride seems more plausible.

We present here the synthesis, crystal structure and Raman spectrum of Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] and we conclude that our previous report of a nitride-azide, Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>], is incorrect.

## Experimental Section

Due to the air and moisture sensitivity of educts and products, all manipulations were carried out in a glove box under permanently purified and monitored argon. The starting materials 1350 mg of Ba (rod, purity: 99% (metals base), Aldrich, coated with an oxide layer), 5 mg of carbon (Strem, powder, 99.999%), 40 mg of Nb (Strem, powder, 99.8%) and 65 mg of NaN<sub>3</sub> (99%, powder, Aldrich, degassed at 400 K under dynamic vacuum for 2 h) were sealed into a clean niobium container by arc-welding. The metal container was fused into an evacuated silica tube. The tube was placed in a box furnace and heated to 1300 K within 12 h. After 48 h the furnace was switched off and allowed to cool to room temperature. This procedure produced transparent, red crystals of Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] ‘floating’ on the top of and imbedded in the solidified Ba/Na melt. Only a few specimens could be chipped from the metal surface. Variations of the starting stoichiometry and of the reaction parameters did not produce single-phase material. The phase only formed if the reaction mixture stayed metal rich and oxygen and carbon deficient; it never formed if either oxygen or carbon were rigorously excluded.

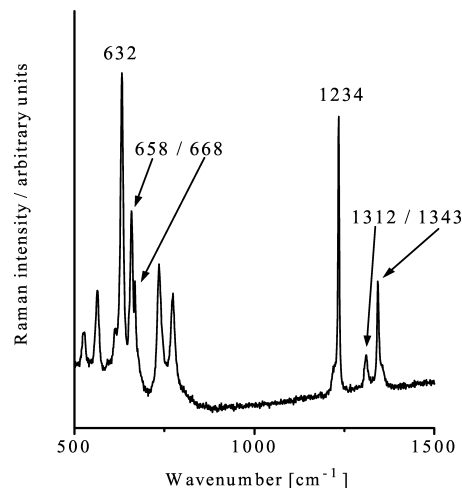
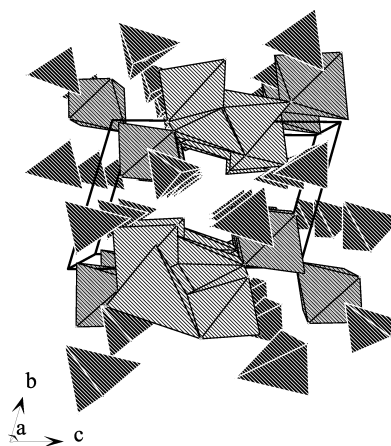
Table 1. X-ray single crystal structure determination on Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>].

Space group, <i>Z</i>	<i>P</i> $\bar{1}$ , 2
CSD-No.	412664
Lattice constants / pm	799.05(2), 962.61(2), 1264.38(4)
°	75.859(1), 85.745(1), 87.8621(8)
Calc. density / gcm <sup>-3</sup>	5.616
Crystal colour	transparent red
Crystal form	plate
Crystal size / mm <sup>3</sup>	0.12 × 0.10 × 0.03
Diffractometer	Bruker Smart CCD
Radiation, monochromator, temperature / K	Mo-K $\alpha$ ( $\lambda$ = 71,073 pm), graphite, 293(2)
Ranges / $2\theta_{\max}$ ; <i>h</i> , <i>k</i> , <i>l</i>	56.56°; $\pm 10$ , $\pm 12$ , $-16 \rightarrow 13$
Distance detector-crystal / mm	50
Increment $\Delta\phi$ / °	0.3
Exposure time / s	30
Absorptions corrections	LP, SADABS
Min. / max. transmission	0.130734 / 0.703992
$\mu$ / mm <sup>-1</sup>	19.69
Measured reflections	8946
Unique reflections	4275
Unique reflections	4081
$F_o > 4\sigma(F_o)$	
<i>R</i> <sub>int</sub>	0.0386
Refined Parameter	209
<i>R</i> 1, <i>wR</i> 2, GooF (all Refl.)	0.0602, 0.1699, 1.131
Max. shift / esd, last refinement cycle	< 0.0005
Res. electron density: max, min	3.88, -3.49 e <sup>-</sup> / Å <sup>3</sup> , 94, 98 pm from Ba

### X-ray and Raman Investigations

Single crystals of the red transparent product were selected under a microscope in a glove box and sealed into glass capillaries. A suitable crystal was mounted on a Bruker Smart CCD diffractometer (293 K, Mo-K $\alpha$ ,  $\lambda$  = 71.073 pm) and a full data set was collected. The crystal structure solution and refinement were performed with the SHELXTL program package [11] in the centrosymmetric space group *P* $\bar{1}$ . All atoms were refined anisotropically. Selected results of the measurement and structure refinement are displayed in Tables 1–3. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666, e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412664.

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 Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] is shown in Fig. 1.

Fig. 1. Raman Spectrum of Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>]. Only background was observed in the region  $\nu \geq 1500$  cm<sup>-1</sup>.Fig. 2. A view of the crystal structure of Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] along the *a* axis. [NbN<sub>4</sub>] tetrahedra are dark, [O]Ba<sub>6</sub> grey, and [CN<sub>2</sub>]Ba<sub>8</sub> light grey.

### Crystal structure

The crystal structure of Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] (Fig. 2) is complex. Isolated [O]Ba<sub>6</sub> octahedra (displayed grey) and the corner sharing irregular [(CN<sub>2</sub>)Ba<sub>8</sub>] polyhedra form layers which are interconnected by isolated [NbN<sub>4</sub>] tetrahedra. The plate-like shape of the single crystals mirrors this structure as well.

### Results and Discussion

A structural model obtained from good or even only satisfying X-ray intensity data with good R-factors is usually basically correct. However, attempts to distinguish light atoms such as Li, B, C, N or O from

Table 2. Synopsis of the atomic coordinates and equivalent isotropic displacement parameters. The sites in question are indicated by fat print.

Atoms	Ba <sub>9</sub> [NbN <sub>4</sub> ] <sub>2</sub> O[CN <sub>2</sub> ]				Ba <sub>9</sub> [NbN <sub>4</sub> ] <sub>2</sub> N[N <sub>3</sub> ] [8]			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq.</sub> / pm <sup>2</sup>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq.</sub> / pm <sup>2</sup>
Ba1	0.49899(9)	0.31945(8)	0.42230(6)	118(2)	0.4988(1)	0.3196(1)	0.42215(7)	<sup>1)</sup>
Ba2	0.47012(9)	0.62095(8)	0.12854(6)	105(2)	0.4703(1)	0.6208(1)	0.12846(7)	<sup>1)</sup>
Ba3	0.03510(9)	0.23790(8)	0.38089(6)	118(2)	0.0351(1)	0.2379(1)	0.38091(7)	<sup>1)</sup>
Ba4	0.25395(10)	0.01183(8)	0.00079(6)	145(2)	0.2540(1)	0.0118(1)	0.00081(7)	<sup>1)</sup>
Ba5	0.17110(9)	0.58099(8)	0.38259(7)	144(2)	0.1713(1)	0.5810(1)	0.38265(8)	<sup>1)</sup>
Ba6	0.46041(9)	0.93080(8)	0.27289(6)	117(2)	0.4604(1)	0.9309(1)	0.27294(7)	<sup>1)</sup>
Ba7	0.01663(9)	0.07013(8)	0.72210(6)	120(2)	0.0165(1)	0.0701(1)	0.72210(7)	<sup>1)</sup>
Ba8	0.00760(9)	0.38354(8)	0.89276(6)	118(2)	0.0077(1)	0.3835(1)	0.89294(8)	<sup>1)</sup>
Ba9	0.26977(9)	0.70884(8)	0.83987(6)	115(2)	0.2696(1)	0.7088(1)	0.83999(7)	<sup>1)</sup>
Nb1	0.26877(13)	0.29598(11)	0.12001(9)	77(2)	0.2689(2)	0.2960(2)	0.1201(1)	<sup>1)</sup>
Nb2	0.27046(13)	0.36469(11)	0.66376(9)	77(2)	0.2703(2)	0.3648(1)	0.6638(1)	<sup>1)</sup>
N1	0.1947(14)	0.5475(12)	0.6982(10)	162(22)	0.193(2)	0.548(1)	0.699(1)	170(30)
N2	0.2940(16)	0.3656(13)	0.2519(9)	188(24)	0.295(2)	0.363(1)	0.253(1)	170(30)
N3	0.0584(14)	0.1909(12)	0.1247(11)	171(23)	0.059(2)	0.191(2)	0.125(1)	210(30)
O / N4	<b>0.21572(11)</b>	<b>0.7983(10)</b>	<b>0.1793(8)</b>	<b>165(19)</b>	<b>0.216(2)</b>	<b>0.799(1)</b>	<b>0.180(1)</b>	<b>50(30)</b>
N5	0.1476(13)	0.3254(13)	0.5469(9)	132(20)	0.145(2)	0.327(1)	0.545(1)	150(30)
N6	0.2416(15)	0.2046(12)	0.7965(9)	143(21)	0.244(2)	0.205(1)	0.794(1)	110(30)
N7	0.4944(14)	0.6315(12)	0.3781(9)	134(20)	0.493(2)	0.633(1)	0.377(1)	150(30)
N8	0.2608(14)	0.4679(11)	0.0037(9)	128(21)	0.261(2)	0.468(1)	0.002(1)	140(30)
N9	0.4604(14)	0.1684(12)	0.0835(9)	122(20)	0.457(2)	0.168(2)	0.083(1)	210(30)
N10	0.2137(17)	0.9435(15)	0.4445(10)	252(28)	0.211(2)	0.944(2)	0.444(1)	250(30)
N11	0.3031(14)	0.9254(12)	0.6280(10)	155(22)	0.300(2)	0.927(2)	0.629(1)	200(30)
C / N12	<b>0.2621(15)</b>	<b>0.9409(14)</b>	<b>0.5342(12)</b>	<b>148(25)</b>	<b>0.260(2)</b>	<b>0.944(2)</b>	<b>0.532(1)</b>	<b>370(40)</b>

<sup>1)</sup> Not reported.Table 3. Synopsis of barium compounds containing tri-atomic anions. Fat print indicates the strongest intensity, all wavenumbers are given in cm<sup>-1</sup>.

	Ba <sub>9</sub> [NbN <sub>4</sub> ] <sub>2</sub> O[CN <sub>2</sub> ]	BaCN <sub>2</sub> [1]	Ba(N <sub>3</sub> ) <sub>2</sub> [14]
d(Ba-N) / pm	122.0(20) / 122.5(19)	119.2(11)	117.7(8) / 116.8(7) 117.0(8) / 118.1(8)
∠ (X-Y-Z) / deg.	173.7(15)	177.2(18)	179.2(8) 178.9(6)
<i>V</i> <sub>sym.</sub>	1234	1238	1347 / <b>1363</b>
<i>V</i> <sub>asym.</sub>	not measured.	1947	2123 / <b>2087</b> / 2069
δ	<b>632</b> / 658 / 668	<b>662</b> / 673	628 / <b>634</b> / 647
2δ	1312 / <b>1343</b>	–	–
Lattice vibrations	528 / <b>564</b>	–	–
Not assigned	<b>735</b> / 774	–	–

each other in the presence of heavy, strongly scattering atoms (*e.g.*, barium and niobium) is sometimes next to impossible if one relies exclusively on X-ray data. Applying no other analytical methods may lead to incorrect conclusions.

Following our synthetic method, we can not say much about the yield since most of the crystals seem

to be embedded into the metallic matrix. The few crystals we could chip from the surface of the solidified bulk were not sufficient for a detailed chemical analysis, but we were not able to produce any crystals of the title compound without deliberately adding oxygen and carbon ‘impurities’.

The X-ray single crystal data make it clear that the compound is at least isotypic, if not identical to the one we reported in literature as Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>] [8] (Table 2) since all the crystallographic data of our compound and the ones reported in literature are identical within the standard deviations. Nevertheless, a close examination of the results of the X-ray single crystal structure analysis is yielding some hints and indications favoring our model. Basically all structural parameters, crystal coordinates and *R*-values obtained from the refinement of the X-ray data as Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] or Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>] are the same. But there are two exceptions: the equivalent isotropic displacement parameters for the positions make the difference between the two models, C *vs.* N4 and O *vs.* N12. The values obtained for C and O (148(25) and 165(19) pm<sup>2</sup>, respectively) in the

Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] model are in the expected range (126–250 pm<sup>2</sup>) set by the other light atoms, while a refinement as nitrogen in the Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>N[N<sub>3</sub>] model brings N4 to the top of this range and N12 much below the expected value (234(27) and 78(18) pm<sup>2</sup>, respectively). More circumstantial evidence is found if one compares the C—N bond length and the N—C—N bond angle of the triatomic unit with the range of bond lengths and bond angles reported for cyanamides and azides (Table 3). With very few exceptions azides have the tendency to be very close to D<sub>∞h</sub> with bond lengths ranging from 116.0 to 121.5 pm, while cyanamides differ sometimes considerably from the D<sub>∞h</sub> symmetry due to bond angle deviations from 180° and unsymmetrical bond lengths which range from 119.2 to 130.0 pm. Due to the overlap of the ranges and to the usually large standard deviations for both figures, no certainty is here to find as well.

But we can present some hard, experimental data which settles the case and supports our

Ba<sub>9</sub>[NbN<sub>4</sub>]<sub>2</sub>O[CN<sub>2</sub>] model. The symmetric stretching mode  $\nu_{\text{sym}}$  is a very good tool to distinguish between azides and cyanamides. The highest observed frequency for cyanamides is  $\nu_{\text{sym}} = 1301 \text{ cm}^{-1}$  for MgCN<sub>2</sub> [12] while for azides the symmetric stretching modes are found well above that number.  $\alpha\text{-Hg(N}_3)_2$  [13] is as far as we know the only exception to this rule ( $\nu_{\text{sym}} = 1275/1285 \text{ cm}^{-1}$ ). Raman measurements are sufficiently reliable and precise so that our experimentally obtained value for the symmetric stretching mode  $\nu_{\text{sym}} = 1234 \text{ cm}^{-1}$  (Fig. 2, Table 3) and the comparison with BaCN<sub>2</sub> [12] and Ba(N<sub>3</sub>)<sub>2</sub> [14] leaves no doubt about the correctness of our model and that azides obtained at relatively high temperatures and ambient pressures hardly exist.

#### Acknowledgement

We would like to thank Dr. H. Vogt (Max-Planck-Institut für Festkörperforschung) for the Raman measurement.

- 
- |  |  |
|--|--|
| <p>[1] E.g.: O. Reckeweg, F. J. DiSalvo, <i>Solid State Sci.</i> <b>5</b>, 575 (2002); and references therein.</p> <p>[2] G. Auffermann, Y. Prots, R. Kniep, <i>Angew. Chem.</i> <b>113</b>, 565 (2001); <i>Angew. Chem. Int. Ed.</i> <b>40</b>, 547 (2001).</p> <p>[3] Y. Prots, G. Auffermann, M. Tovar, R. Kniep, <i>Angew. Chem.</i> <b>114</b>, 2392 (2002); <i>Angew. Chem. Int. Ed.</i> <b>41</b>, 2288 (2002).</p> <p>[4] G. V. Vajenine, G. Auffermann, Y. Prots, W. Schnelle, R. K. Kremer, A. Simon, R. Kniep, <i>Inorg. Chem.</i> <b>40</b>, 4866 (2001).</p> <p>[5] U. Steinbrenner, P. Adler, W. Hölle, A. Simon, <i>J. Phys. Chem. Solids</i> <b>59</b>, 1527 (1998); U. Steinbrenner, A. Simon, <i>Z. Anorg. Allg. Chem.</i> <b>624</b>, 228 (1998).</p> <p>[6] Y. Laurent, J. Lang, M. Th. Le Bihan, <i>Acta Crystallogr.</i> <b>B25</b>, 199 (1969).</p> | <p>[7] H. Stegen, H. Jacobs, <i>Z. Anorg. Allg. Chem.</i> <b>625</b>, 1093 (1999).</p> <p>[8] S. J. Clarke, F. J. DiSalvo, <i>Z. Kristallogr.</i> <b>212</b>, 309 (1997).</p> <p>[9] P. Höhn, R. Kniep, J. Maier, <i>Angew. Chem.</i> <b>105</b>, 1409 (1993); <i>Angew. Chem. Int. Ed.</i> <b>32</b>, 1350 (1993).</p> <p>[10] O. Reckeweg, F. J. DiSalvo, <i>Angew. Chem.</i> <b>110</b>, 397 (2000); <i>Angew. Chem. Int. Ed.</i> <b>39</b>, 412 (2000).</p> <p>[11] Program SHELXTL: G. M. Sheldrick, Göttingen (1997).</p> <p>[12] U. Berger, W. Schnick, <i>J. Alloys Comp.</i> <b>206</b>, 179 (1996).</p> <p>[13] U. Müller, <i>Z. Anorg. Allg. Chem.</i> <b>399</b>, 183, (1973); D. Seybold, K. Dehnicke, <i>Z. Anorg. Allg. Chem.</i> <b>361</b>, 277 (1968).</p> <p>[14] O. Reckeweg, A. Simon, unpublished results.</p> |
|--|--|