A Metal Nitride Carbodiimide with a Stuffed Skutterudite-type Structure: Synthesis, Crystal Structure and IR Spectra of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$

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Coppery-red, transparent single crystals of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ ($Im\bar{3}$, no. 204, a = 1125.83(3) pm, Z = 2) are obtained by the reaction of Ba_2N and $ZnCN_2$ with the container walls of the arc-welded Nb ampoules at 1100 K. The title compound assumes a stuffed skutterudite-type structure in which edge-sharing ($Ba_6N_{5/6}$) octahedra form large voids which are occupied by either $[NbN_4]$ tetrahedra or by $[N{=}C{=}N]^{2-}$ units with symmetric C=N bond lengths of d = 121.8(6) pm but a bond angle deviating significantly from linearity ($\measuredangle$(N–C–N) = 175.3(9)°). The IR spectra corroborate this crystallographic result by the fact that *all* fundamental vibrations are visible in the IR spectrum [ν_1 = 1262 (symmetric stretching mode); ν_2 = 1957/2009 (antisymmetric stretching mode); ν_3 = 611/633/653 cm^{-1} (bending modes)], which is symmetry forbidden for $[N{=}C{=}N]^{2-}$ units having $D_{\infty h}$ symmetry but expected for the C_{2v} symmetry found in the title compound.

Key words: Barium, Carbodiimide, IR Spectroscopy, Niobium, Nitride, Skutterudite Structure, Structure Elucidation

Introduction

High-temperature syntheses employed in solid state chemistry often face a problem: the supposedly inert reaction container turns out to be more reactive than expected or wanted. A simple relation is found to be true: the higher the reaction temperature and the more reactive the reactants are, the more likely that the container material is also incorporated in the products. If binary alkaline earth metal subnitrides of the AE_2N type (AE = Ca, Sr, Sr/Ba and Ba) [1, 2] are employed as reactants, synthetic approaches become even more challenging. These compounds react rather readily even at r. t. with H_2, O_2 or X_2 (X = Cl, Br or I). Even among those subnitrides, Ba_2N stands out as especially reactive. One might take as an indicator that a good crystal structure refinement was not reported until recently [3].

Nevertheless, we used Ba_2N together with $ZnCN_2$ [4] as a starting material in an attempt to obtain $Ba_4N_2[CN_2]$ which we thought would be isotypic to $AE_4N_2[CN_2]$ (AE = Ca, Ca/Sr or Sr) [5 – 7], but instead the product incorporated traces of the supposedly inert container material to yield $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$.

Experimental Section

Synthesis

All manipulations of reactants and products were performed in a glove box under purified argon unless stated otherwise. 580 mg (3.45 mmol) Ba_2N (obtained by the reaction of Ba (99.9 %, dendritic, Strem) with nitrogen at 1100 K, rhombohedral, lattice constants (trigonal setting): a = 402.8(3); c = 2251(2) pm), and 106 mg (4.25 mmol) $ZnCN_2$ (obtained as described in [3] from $Zn(NO_3)_2 \cdot 6\,H_2O$ (Fluka, $\geq$ 99 %), H_2CN_2 (Aldrich, 99 %) and NaOH (Merck, *p.a.*), dried and degassed at 400 K under dynamic vacuum for 2 h) were mixed 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 1100 K within 12 h. After three days the furnace was switched off and allowed to cool to r. t. The reaction produced some droplets of a Ba-Zn alloy and transparent, copper-like red crystals of cubic $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ which are air and moisture sensitive.

Compound	$(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$
Space group, Z	$Im\bar{3}$ (No. 204), 2
Lattice parameter a, pm	1125.83(3)
Calc. density, g cm^{-3}	4.80
Crystal color / form	transparent red / rectangular plate
Crystal size, mm^3	$0.12 \times 0.10 \times 0.03$
Radiation; temperature, K	MoK_α (λ = 71,073 pm); 170(2)
Ranges, $2\theta_{max}$, deg, hkl	65.03; $-9 \rightarrow 16$, $-9 \rightarrow 17$, $-10 \rightarrow 16$
Distance detector-crystal, mm	41
Number of frames; exposure time, s	739; 20
Transmission min./max.	0.240/0.635
μ(MoK_α), mm^{-1}	16.67
Reflections measured/unique	5916/493
R_{int}	0.0321
Unique reflections with $F_o \geq 4\sigma(F_o)$	431
Refined parameters	24
Weight factors x/y	0/26.94
$R1/wR2$/GooF (all reflexions)[a]	0.0322/0.0461/1.154
Max. shift/esd, last refinement cycle	< 0.0005
Res. electron density: max./min., e Å^{-3}	1.61 (60 pm to Ba)/−1.79 (63 pm to Ba)

Table 1. Results of the X-ray single crystal structure determination on $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$.

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP$ with $P = [(F_o^2) + 2F_c^2]/3$, GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, with n being the number of reflections and p being the number of parameters.

Atom	Wyckoff site	Site occupancy	x	y	z	U_{eq}[c] (pm^2)
Ba	24g	1	0	0.29063(3)	0.17955(3)	208(1)
Nb	2a	1	0	0	0	109(3)
C	12e	1	0.6545(6)	0	1/2	126(14)
N1	24g	1	0	0.1590(5)	0.6081(5)	284(13)
N2	16f	1/2	0.1002(6)	x	x	202(25)
N3	8c	0.417(35)	1/4	1/4	1/4	326(59)
P	24g	1	0	0.3539	0.1504	–
La	2a	1	0	0	0	–
Fe	8c	1	1/4	1/4	1/4	–
As	24g	1	0	0.35	0.15	–
Co	8c	1	1/4	1/4	1/4	–

Table 2. Crystal coordinates and equivalent isotropic displacement factors of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ and the crystal coordinates of $CoAs_3$ (skutterudite, $Im\bar{3}$, a = 819.7 pm)[a] and $LaFe_4P_{12}$ ($Im\bar{3}$, a = 783.16 pm)[b] for comparison.

[a] Ref. [14]; [b] ref. [15], [c] U_{eq} is defined as a third of the orthogonalized U_{ij} tensor.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	365(2)	134(2)	125(2)	17(1)	0	0
Nb	109(3)	U_{11}	U_{11}	0	0	0
C	59(30)	197(36)	124(32)	0	0	0
N1	458(36)	243(28)	151(25)	−4(22)	0	0
N2	202(25)	U_{11}	U_{11}	−33(28)	U_{23}	U_{23}
N3	326(59)	U_{11}	U_{11}	168(76)	U_{23}	U_{23}

Table 3. Anisotropic displacement factors U_{ij}[a] (pm^2) for $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$.

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

Crystallographic studies

Samples of the reaction product were removed from the glovebox in polybutene oil for single crystal selection. A suitable single crystal of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ was selected under a polarization microscope, mounted in a drop of polybutene oil sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen at 170(2) K froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The orientation matrix and the cubic cell constant were obtained by using APEX2 [8]. The program SAINT [9] was used to integrate the data. An empirical absorption correction was applied using SADABS [10]. The initial input file for solving the crystal structure was prepared by XPREP [11]. This program suggested the chi-

Table 4. Selected bond lengths (pm) and angles (deg) of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$. Partial occupancies are not considered for the multiplicities given here.

Atoms		Multiplicity	d	Atoms		Multiplicity	d
Ba –	N2	2 ×	258.2(5)	N1 –	C	1 ×	121.7(6)
	N1	1 ×	281.3(6)		Ba	1 ×	281.3(6)
	N1	2 ×	293.1(4)		Ba	2 ×	293.1(4)
	N3	2 ×	295.97(1)		Ba	2 ×	321.6(4)
	N1	2 ×	321.6(4)	N2 –	Nb	1 ×	195.3(12)
Nb –	N2	8 ×	195.3(12)		Ba	3 ×	258.2(5)
C –	N1	2 ×	121.8(6)	N3 –	Ba	6 ×	295.97(1)
∡(N–C–N)		1 ×	175.3(9)°				

Compound	Cubic lattice parameter *a* (pm)	*d*(C–N) (pm)	∠ (deg)	*d*(M–N) (pm)	Ref.
$Ba_9[NbN_4]_2O[CN_2]$	–	122.0/122.5	173.7	196.7	[17]
$Ba_8[WN_4][CN_2]_5$	–	121.5	175.2	186.1	[6, 16]
$(Ba_6N)_2[WN_4][CN_2]_6$	1121.9	122.9	171.2	189.1	[6, 16]
$(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$	1125.83(3)	121.8(6)	175.3(9)	195.3(12)	this work

Table 5. Synopsis of selected properties of compounds containing Ba, N, M (M = Nb, Mo or W) and the $[N{=}C{=}N]^{2-}$ unit.

ral space groups 197 and 199 as well as the centrosymmetric space group 204 as possible space groups in accord with the systematic absences. The *E* statistics showed a value of $|E^2 - 1| = 0.829$ and is therefore inconclusive (expected values: 0.968 for a centrosymmetric, 0.736 for a non-centrosymmetric structure). Satisfactory refinement was only achieved in the space groups 197 and 204, but the Flack parameter obtained during the refinement in the chiral space group 197 was 0.45(6). This is usually an indication for twinning or that the chosen space group is wrong. The refinement was not improved by introducing the twinning option into the calculations, and therefore the centrosymmetric space group $Im\bar{3}$ was used for all further calculations. The initial Ba and Nb positions were obtained by Direct Methods in SHELXS-97 [12], the C and N positions were apparent from the positions of highest electron density in the difference Fourier map resulting after the first refinement cycle by full-matrix least-squares techniques with the use of the SHELXL-97 [13]. Further final refinement cycles converged to a stable model for the crystal structure.

Additional crystallographic details are described in Table 1. Atomic coordinates and isotropic displacement coefficients are shown in Tables 2 and 3, and selected bond lengths and angles are listed in Table 4.

Further details of the crystal structure investigation can 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-416963.

IR Spectroscopy

The FT-IR spectrum was obtained with a Jasco FT-IR 600 spectrometer from pressed polyethylene pellets ($\nu < 400\ cm^{-1}$, Fig. 3a) and KBr pellets ($\nu > 400\ cm^{-1}$, Fig. 3b) which contained the powdered compound. A Raman spectrum could not be determined due to the strong absorption of the dark-red material.

Results and Discussion

Crystal structure

The crystal structure of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ is a variation of the stuffed skutterudite-type [14], such as $LaFe_4P_{12}$ [15], which is the archetype of a still growing class of compounds (Fig. 1). Edge-sharing, slightly tilted (FeP_6) units form a 3D network in which voids of different sizes are present. The largest void with an icosahedral environment is occupied by La. In the structure of the title compound, the 3D network is formed by edge-sharing ($Ba_6N_{5/6}$) octahedra with the partially occupied N3 site in their center (Fig. 2a). The icosahedrally coordinated void is occupied by isolated $[NbN_{8/2}]$ tetrahedra with the half occupied nitrogen position N2 (Fig. 2b), and the $[CN_2]$ units are harbored by the smaller voids (Fig. 2c). Following this, the original formula $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ can be rewritten as $[NbN_4](N_{10/6}Ba_{12})[CN_2]_6$ to show the parallels to $LaFe_4P_{12}$. This relation can also be seen if one looks at the crystal coordinates of $CoAs_3$, $LaFe_4P_{12}$ and $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ (Table 2).

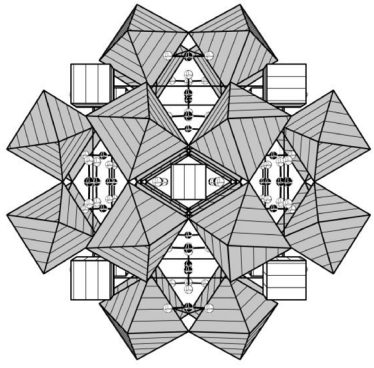

Fig. 1. A view parallel to the *a* axis of crystals of $(Ba_6N_{5/6})[NbN_4][CN_2]_6$. ($Ba_6N_{5/6}$) units are displayed as light grey, shaded octahedra, C as black and nitrogen as white ellipsoids at the 95 % probability level.

The stoichiometry, the structural motifs and the bond lengths found for the title compound are similar to those of comparable compounds such as $Ba_9[NbN_4]_2O[CN_2]$ [17], $Ba_8[MN_4][CN_2]_5$ [6, 16] and especially to $(Ba_6N)_2[MN_4][CN_2]_6$ (M = Mo or W) [6, 16] (Table 5), but as the structural description of the latter compounds is not complete yet we cannot compare the structures in detail. Nevertheless, the lattice parameters of the compounds crystallizing with cubic symmetry are very close to each other, the stoi-

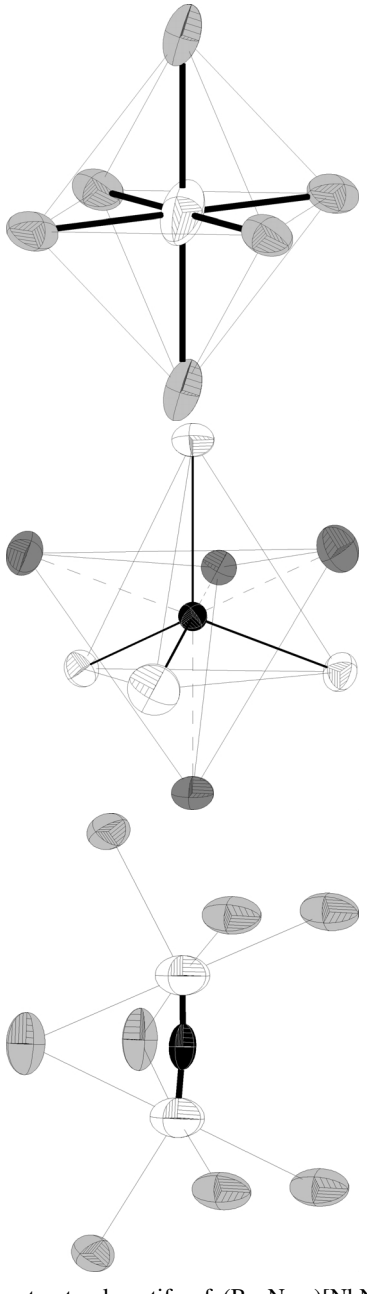

Fig. 2. The structural motifs of $(Ba_6N_{5/6})[NbN_4][CN_2]_6$: $(Ba_6N_{5/6})$ octahedron with partially occupied N3 position, isolated $[NbN_{8/2}]$ tetrahedron with disordered nitrogen N2 position as expressed by the colorings white and medium grey, and the $[N{=}C{=}N]^{2-}$ carbodiimide unit coordinated by Ba (always displayed as light grey ellipsoids at the 95 % probability level).

chiometry is nearly identical and the space groups are symmetry-related to each other. $(Ba_6N)_2[MN_4][CN_2]_6$ (M = Mo or W) with $Pn\bar{3}$ (no. 201) is a t2 subgroup to $Im\bar{3}$ (no. 204) of the title compound.

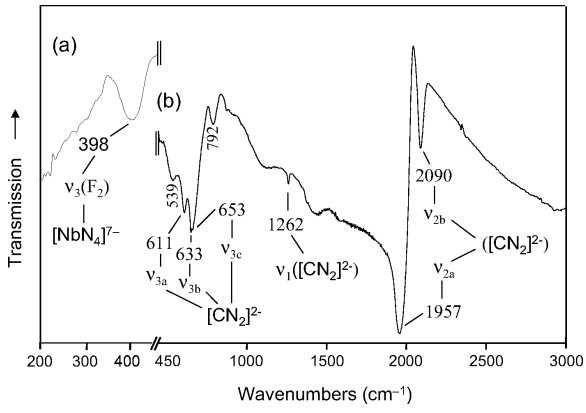

Fig. 3. IR spectrum of $(Ba_6N_{5/6})[NbN_4][CN_2]_6$.

IR Spectra

The vibrational spectroscopically relevant units in the title compound are discrete $[NbN_4]^{7-}$ and $[N{=}C{=}N]^{2-}$ moieties with idealized symmetry T_d and $D_{\infty h}$, respectively, for which the following fundamentals are expected:

$$\Gamma_{\mathrm{vib}}(D_{\infty h}) = \Sigma_{\mathrm{g}}(\nu_1,\mathrm{R}) + \Sigma_{\mathrm{u}}(\nu_2,\mathrm{IR}) + \Pi_{\mathrm{u}}(\nu_3,\mathrm{IR})$$

$$\Gamma_{\mathrm{vib}}(T_d) = \mathrm{A}_1(\nu_1,\mathrm{R}) + \mathrm{E}(\nu_2,\mathrm{R}) + 2\mathrm{F}_2(\nu_3,\nu_4;\,\mathrm{R},\mathrm{IR}).$$

In the crystalline state, the anions $[NbN_4]^{7-}$ and $[N{=}C{=}N]^{2-}$ occupy the sites $T_h/m\bar{3}$ and $C_{2v}/mm2$, meaning that the selection rules for the tetrahedral $[NbN_4]^{7-}$ units are holding also for the solid while the carbodiimide groups experience a symmetry reduction with respect to the free anion. The site symmetry C_{2v} predicts that the degeneracy for the deformation mode Π_{u} (ν_3) in $D_{\infty h}$ and mutual exclusion for g and u modes will be abolished, so that the stretching vibrations Σ_{g} (ν_1) and Σ_{u} (ν_3) become active, both in Raman and IR. Furthermore, the spectroscopic unit cell (primitive) contains one $[NbN_4]^{7-}$ but six $[N{=}C{=}N]^{2-}$ moieties whose dynamic coupling in the crystal may give rise to characteristic band splitting (factor group splitting).

The IR spectrum (Fig. 3) of the title compound can be discussed in terms of three well separated wave regions: $\nu = 150-400\,\mathrm{cm}^{-1}$, where the triply degenerate antisymmetric (Nb-N) stretch ν_3 (F_2) and the deformation mode ν_4 (F_2) for $[NbN_4]^{7-}$ are expected, and

ν = 600 – 700 cm^{-1}, in which [N=C=N]$^{2-}$ deformations are present, while the region $\nu > 1100$ cm^{-1} is clearly dominated by the [N=C=N]$^{2-}$ valence modes.

ν_3 (F_2) for [NbN_4]$^{7-}$ is not split but appears as a broad band at 398 cm^{-1} in the far IR (Fig. 3a). The broadness may arise from the disorder of the N2 ligands in the crystal structure. $\nu_4(F_2)$ is expected around 200 cm^{-1}, but the IR spectrum allows no clear assignment despite the presence of some weak bands in this region. Unfortunately, there are no vibrational data available on nitridoniobates(V) and niobates(V) with tetrahedral coordination, which would allow a reasonable spectral comparison and discussion.

In accordance with the predictions, all three modes of the carbodiimide group are observable in the IR sectrum (Fig. 3b). The degenerate mode $\prod_u$ (ν_3) was expected to split into two bands, but a triplet is observed instead at 611, 633 and 653 cm^{-1}, indicating the factor group splitting. For the same reason the antisymmetric mode Σ_u (ν_3) is also split and is registered as a pair of bands at 1957 and 2090 cm^{-1}. The symmetric stretching mode Σ_g (ν_1), which is strictly IR-forbidden for $D_{\infty h}$, becomes active due to the site symmetry C_{2v} and is recorded as a weak band at 1262 cm^{-1}. The bands at 539 and 792 cm^{-1} are definitely not fundamentals and are interpreted as lattice modes. The observed frequencies for the carbodiimide anion in the present work compare well with those previously reported [18].

Conclusion

(Ba_6N)$_2$[NbN_4][CN_2]$_6$ adopts a skutterudite-type structure and is probably symmetry-related to (Ba_6N)$_2$[MN_4][CN_2]$_6$ (M = Mo or W) [6, 17]. The results of the first detailed analysis of the IR spectrum of a Ba-M-N-CN_2 (M = Nb, Mo or W) compound are in good agreement with those of the X-ray single crystal investigations confirming that the structure of the title compound contains [NbN_4]$^{7-}$ and [N=C=N]$^{2-}$ as the characteristic anionic moieties. In accordance with the structural and optical results, the symmetry of the carbodiimide containing [CN_2]$^{2-}$ units is lowered from $D_{\infty h}$ to C_{2v} which is probably due to packing effects.

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