

Calcium Carbodiimide Compounds Revisited – Syntheses, Single Crystal Structure Determination and Vibrational Spectra of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, $\text{Ca}_4\text{N}_2[\text{CN}_2]$ and $\text{Ca}[\text{CN}_2]$

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Single crystals of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ (dark red needles, tetragonal, $P4_2/mmm$ (no. 136), $a = 1456.22(5)$, and $c = 361.86(2)$ pm, $Z = 2$), $\text{Ca}_4\text{N}_2[\text{CN}_2]$ (transparent yellow needles, orthorhombic, $Pnma$ (no. 62), $a = 1146.51(11)$, $b = 358.33(4)$, and $c = 1385.77(13)$ pm, $Z = 4$) and $\text{Ca}[\text{CN}_2]$ (transparent, colorless, triangular plates, rhombohedral, $R\bar{3}m$ (no. 166), $a = 369.00(3)$, and $c = 1477.5(3)$ pm, $Z = 3$) were obtained by the reaction of $\text{Na}_2[\text{CN}_2]$, CaCl_2 and Ca_3N_2 (if demanded by stoichiometry) in arc-welded Ta ampoules at temperatures between 1200–1400 K. Their crystal structures were re-determined by means of single crystal X-ray structure analyses. Additionally, the Raman spectra were recorded on these same single crystals, whereas the IR spectra were obtained with the KBr pellet technique. The title compounds exhibit characteristic features for carbodiimide units with $D_{\infty h}$ symmetry ($d(\text{C}-\text{N}) = 121.7\text{--}123.8$ pm and $\angle(\text{N}-\text{C}-\text{N}) = 180^\circ$). The vibrational frequencies of these units are in the expected range ($\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$: $\nu_s = 1230$, $\nu_s = 2008$; $\delta = 673/645/624$ cm^{-1} ; $\text{Ca}_4\text{N}_2[\text{CN}_2]$: $\nu_s = 1230$, $\nu_s = 1986$; $\delta = 672/647$ cm^{-1} ; $\text{Ca}[\text{CN}_2]$: $\nu_s = 1274$, $\nu_s = 2031$, $\delta = 668$ cm^{-1}). The structural results are more precise than the previously reported data, and with the newly attained Raman spectrum of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ we correct data reported earlier.

Key words: Calcium, Nitride, Carbodiimide, Cyanamide, Dinitridocarbonate, Crystal Structure, Raman Spectroscopy

Introduction

The renaissance of investigations on compounds containing the triatomic $[\text{CN}_2]^{2-}$ unit started in 1994 with a paper by Schnick *et al.* [1] reporting the first reliable structural and spectroscopic data for $\text{Mg}[\text{CN}_2]$, $\text{Sr}[\text{CN}_2]$, and $\text{Ba}[\text{CN}_2]$. Strangely enough, $\text{Ca}[\text{CN}_2]$ [2–5] as the archetype of this class of compounds was completely left out despite the fact that the most reliable structure determination dated back to 1962 [5], and no spectroscopic properties were known. A few years later, we found out by serendipity that ‘ Ca_{11}N_8 ’ [6] really is $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ [7] and showed on the same occasion the ‘high-temperature form of Ca_3N_2 ’ (which was also known as $\gamma\text{-Ca}_3\text{N}_2$) [8] to be $\text{Ca}_4\text{N}_2[\text{CN}_2]$ [9–10]. Since the crystallographic data were not completely reported by us and we found out about an error in our reading of the Raman spectrum of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, we report in this paper an alternative synthetic pathway (metathesis reaction) to obtain single crystalline material of

$\text{Ca}[\text{CN}_2]$, $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ together with the complete data of the single crystal structure determinations and of Raman and IR spectral analyses.

Experimental Section

Syntheses

All manipulations were performed in a glove box under purified argon unless stated otherwise. The starting materials consisted of CaCl_2 (Alfa Aesar, powder, ultradry, 99.99 %), Na_2CN_2 (Pfaltz & Baur, powder, 97 %, dried and degassed at 400 K under dynamic vacuum for 2 h; the major impurity was identified to be NaHCN_2 by its X-ray powder diffractogram) and thoroughly ground Ca_3N_2 (Alfa Aesar, pieces, 99 %). The reactions were designed to follow the equations (1)–(3).

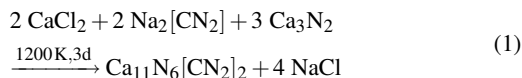
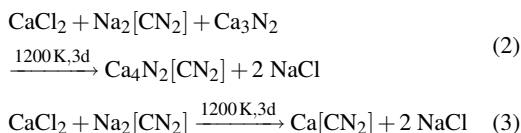


Table 1. Details of the X-ray single crystal structure determinations of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, $\text{Ca}_4\text{N}_2[\text{CN}_2]$, and $\text{Ca}[\text{CN}_2]$.

Compound	$\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$	$\text{Ca}_4\text{N}_2[\text{CN}_2]$	$\text{Ca}[\text{CN}_2]$
Space group (no.), Z	$P4_2/mmm$ (136), 2	$Pnma$ (62), 4	$R\bar{3}m$ (166), 3
CSD number	418944	418945	418451
Lattice parameter: a , pm	1456.22(5)	1146.51(11)	369.00(3)
b , pm	a	358.33(4)	a
c , pm	361.86(2)	1385.77(13)	1477.5(3)
Calculated density, g cm^{-3}	2.62	2.66	2.29
Crystal color	dark red	transparent yellow	transparent colorless
Crystal shape	needle	needle	triangular plate
Crystal size, mm^3	$0.12 \times 0.02 \times 0.02$	$0.12 \times 0.01 \times 0.01$	$0.12 \times 0.11 \times 0.04$
Diffractometer	Stoe IPDS II	Nonius Kappa CCD	Bruker X8 Apex II equipped with a 4 K. CCD
Radiation; monochromator	— $\text{MoK}\alpha$ ($\lambda = 71.073$ pm); graphite —		
Temperature, K	293(2)	293(2)	160(2)
Ranges, $2\theta_{\text{max}}$; h, k, l	52.73° ; $\pm 18, \pm 18, \pm 4$	52.66° ; $\pm 14, \pm 3, \pm 17$	73.20° ; $-5 \rightarrow 6, -5 \rightarrow 6, \pm 23$
Distance detector-crystal, mm	60	25	40
Number of frames	225	154	1078
Exposure time, s	300	38	10
Data correction	LP	LP	LP
μ , mm^{-1}	3.8	3.7	2.3
Measured reflections	5367	4835	713
Unique reflections	488	548	129
Unique reflections with $F_o \geq 4\sigma(F_o)$	380	404	128
R_{int}	0.128	0.138	0.029
Refined parameters	43	55	8
Weight factors x/y	0.0234 / 0.4174	0 / 5.3138	0.0155 / 0.2111
$R1^a$ / $wR2^b$ / GooF^c (all refls.)	0.0797 / 0.0767 / 1.227	0.0695 / 0.1007 / 1.156	0.0207 / 0.0444 / 1.193
Max. shift / esd, last refinement cycle	< 0.00005	< 0.00005	< 0.00005
Res. electron density: max. / min., e \AA^{-3}	0.80 (133 pm to N1) / −0.77 (197 pm to Ca4)	0.63 (133 pm to N1) / −0.66 (163 pm to Ca1)	0.43 (64 pm to N) −0.45 (71 pm to Ca)

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



The starting materials [$\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$: 222 mg (2 mmol) CaCl_2 , 450 mg (3.04 mmol) Ca_3N_2 and 172 mg (2 mmol) Na_2CN_2 ; $\text{Ca}_4\text{N}_2[\text{CN}_2]$: 222 mg (2 mmol) CaCl_2 , 300 mg (2.02 mmol) Ca_3N_2 and 172 mg (2 mmol) Na_2CN_2 ; $\text{Ca}[\text{CN}_2]$: 222 mg (2 mmol) CaCl_2 and 172 mg (2 mmol) Na_2CN_2] were ground together in an agate mortar and then arc-welded into clean Ta containers. The metal containers were sealed into evacuated silica tubes. The tubes were placed upright in a box furnace and heated to the appropriate temperature within 12 h. After 3 d the furnace was switched off and allowed to cool to r.t. Next to the desired products ($\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$: dark red needles; $\text{Ca}_4\text{N}_2[\text{CN}_2]$: transparent yellow needles; $\text{Ca}[\text{CN}_2]$: transparent, colorless, often triangular-shaped plates) the samples contained cube-shaped crystals of NaCl.

All three title compounds are moderately sensitive to normal atmosphere and decompose slowly.

Crystallographic studies

$\text{Ca}[\text{CN}_2]$: Samples of the reaction mixtures were removed from the glove box in polybutene oil (Aldrich, $M_n \sim 320$, isobutylene > 90 %) for single-crystal selection. Suitable single crystals of the respective compounds were 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 ($T = 160(2)$ K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture from 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 $\text{MoK}\alpha$ radiation ($\lambda = 71.073$ pm). All further data processing was performed with the Bruker SMART software [11].

Single crystals of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ were selected under a microscope in a glove box and sealed into glass capillaries. A suitable crystal of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ was mounted on a Stoe IPDS II while a specimen of $\text{Ca}_4\text{N}_2[\text{CN}_2]$ was centered on a Nonius Kappa CCD diffractometer. The quality of the respective crystals were checked, and a set

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ ($P4_2/mnm$), $\text{Ca}_4\text{N}_2[\text{CN}_2]$ ($Pnma$) and $\text{Ca}[\text{CN}_2]$ ($R\bar{3}m$).

Atom	W.-Site	x	y	z	U_{eq}
Ca1	2a	0	0	0	118(6)
Ca2	8i	0.29520(9)	0.52018(9)	0	103(4)
Ca3	4g	0.16733(10)	−x	0	133(5)
Ca4	8i	0.39460(10)	0.11703(10)	0	141(4)
N1	4f	0.4104(4)	x	0	102(17)
N2	8i	0.6897(4)	0.0283(4)	0	135(12)
N3	4g	0.2437(5)	x	0	329(25)
N4	4f	0.1245(4)	x	0	191(20)
C	4g	0.1846(5)	x	0	135(22)
Ca1	4c	0.61349(15)	1/4	0.32765(12)	89(6)
Ca2	4c	0.37966(16)	1/4	0.46003(12)	90(6)
Ca3	4c	0.87770(14)	1/4	0.61528(12)	99(6)
Ca4	4c	0.64096(15)	1/4	0.73977(12)	88(6)
N1	4c	0.2333(6)	1/4	0.3158(5)	99(20)
N2	4c	0.4989(6)	1/4	0.6176(5)	94(20)
N3	4c	0.7682(7)	1/4	0.4569(5)	178(23)
N4	4c	0.9544(7)	1/4	0.3703(6)	204(24)
C	4c	0.8611(8)	1/4	0.4137(6)	114(23)
Ca	12c	0	0	0	60(2)
C	18e	0	0	1/2	60(5)
N	36f	0	0	0.41677(11)	78(3)

Table 3. Anisotropic displacement parameters U_{ij}^a (pm^2) of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, $\text{Ca}_4\text{N}_2[\text{CN}_2]$, and $\text{Ca}[\text{CN}_2]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	109(9)	U_{11}	139(16)	0	0	4(10)
Ca2	110(7)	113(7)	86(7)	0	0	−12(5)
Ca3	157(7)	U_{11}	84(11)	0	0	62(8)
Ca4	161(8)	159(7)	103(7)	0	0	−58(5)
N1	133(24)	U_{11}	39(41)	0	0	−16(30)
N2	124(30)	149(30)	133(32)	0	0	−5(24)
N3	344(37)	U_{11}	299(62)	0	0	−163(48)
N4	186(28)	U_{11}	202(51)	0	0	−52(37)
C	137(30)	U_{11}	129(58)	0	0	15(39)
Ca1	92(9)	64(17)	111(9)	0	27(7)	0
Ca2	91(10)	97(16)	81(9)	0	−2(6)	0
Ca3	82(9)	113(16)	103(9)	0	−2(7)	0
Ca4	76(8)	83(16)	106(9)	0	−4(7)	0
N1	105(35)	97(65)	95(39)	0	−11(29)	0
N2	73(34)	114(64)	70(36)	0	−16(29)	0
N3	177(43)	217(72)	140(40)	0	10(32)	0
N4	139(41)	261(76)	212(43)	0	−2(34)	0
C	189(49)	16(72)	135(45)	0	−66(40)	0
Ca	60(2)	U_{11}	60(2)	0	0	$1/2 \times U_{11}$
C	42(7)	U_{11}	97(11)	0	0	21(4)
N	87(5)	U_{11}	60(7)	0	0	44(3)

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

of intensity data was collected for $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ [7] and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ at r. t. The following processing of the intensity data was performed with the software package that came with the respective diffractometer [12, 13].

Atoms	Multiplicity	d
Ca1 – N4	2×	256.3(9)
N1	4×	258.5(6)
Ca2 – N1	1×	231.7(1)
N2	2×	247.6(4)
N3	2×	263.6(1)
Ca3 – N1	2×	241.6(5)
N4	2×	257.5(8)
N2	2×	290.4(6)
Ca4 – N2	2×	237.8(4)
N2	1×	244.7(6)
N4	1×	286.9(2)
C – N3	1×	121.7(14)
N4	1×	123.8(13)
$\angle(\text{N}–\text{C}–\text{N})$	1×	180.0(11)
Ca1 – N2	2×	233.4(4)
N1	1×	241.6(7)
N3	1×	252.1(8)
Ca2 – N2	2×	251.1(5)
N2	1×	257.7(7)
N1	1×	261.0(7)
N3	2×	272.2(6)
Ca3 – N1	2×	239.7(5)
N3	1×	252.9(8)
N4	2×	263.7(6)
Ca4 – N2	1×	234.9(7)
N1	2×	242.5(5)
N4	2×	277.1(6)
C – N3	1×	122.2(12)
N4	1×	122.8(12)
$\angle(\text{N}–\text{C}–\text{N})$	1×	180.0(10)
Ca – N	6×	246.14(8)
C – N	2×	123.0(2)
$\angle(\text{N}–\text{C}–\text{N})$	1×	180 ^a

Table 4. Selected bond lengths (pm) and angles (deg) of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, $\text{Ca}_4\text{N}_2[\text{CN}_2]$, and $\text{Ca}[\text{CN}_2]$.

^a Angle fixed, linearity set by symmetry.

For all three compounds, the intensity data were corrected for Lorentz and polarization effects, but since all compounds are poor X-ray absorbers, no absorption correction was applied. The crystallographic coordinates of $\text{Ca}[\text{CN}_2]$ [5], $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ [7] and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ [7], respectively, were used as starting models which were refined by full-matrix least-squares techniques with SHELXL-97 [14]. The refinements converged and resulted in stable models for the crystal structures of $\text{Ca}[\text{CN}_2]$, $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ or $\text{Ca}_4\text{N}_2[\text{CN}_2]$ corroborating the previous models. Additional crystallographic details are summarized in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2, and Table 3 displays the anisotropic displacement parameters. Selected bond lengths and angles are listed in Table 4.

Further details of the crystal structure investigations 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 deposition number CSD-418944 for $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, CSD-418945 for $\text{Ca}_4\text{N}_2[\text{CN}_2]$ and CSD-418451 for $\text{Ca}[\text{CN}_2]$.

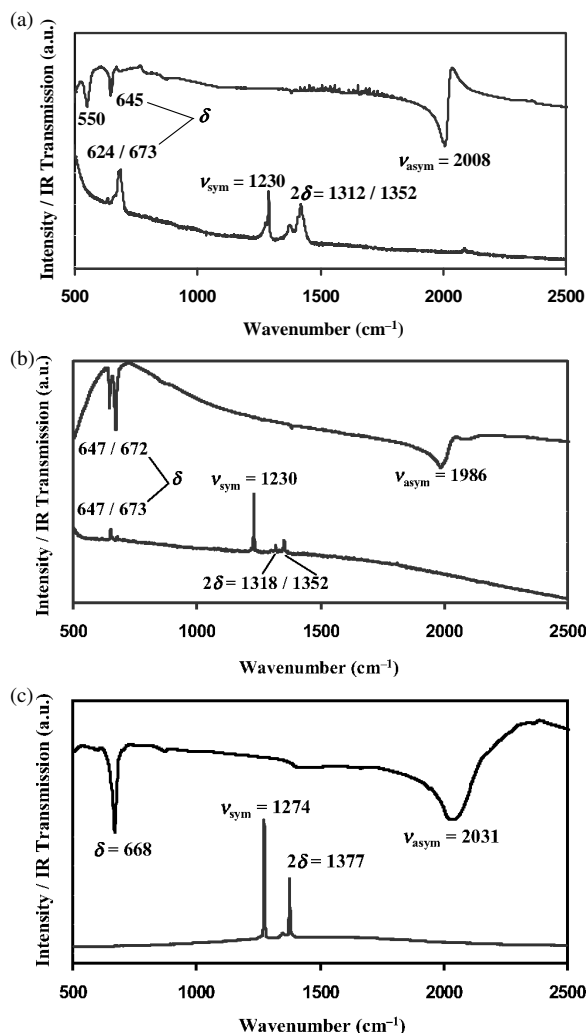


Fig. 1. Raman and IR spectra of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ (a), $\text{Ca}_4\text{N}_2[\text{CN}_2]$ (b), $\text{Ca}[\text{CN}_2]$ (c) (for details, see text).

Vibrational spectroscopy

The crystals used for the single crystal structure refinements were washed with hexane and sealed in Lindemann capillaries under an Ar atmosphere. The Raman investigations were performed on a microscope laser Raman spectrometer from Jobin Yvon (4 mW, excitation line at $\lambda = 632.817$ nm (HeNe laser), 20 \times magnification, 3 \times 60 s accumulation time).

IR investigations of all three title compounds and for ‘ Ca_3N_2 ’ were done with a Bruker AFS 66 FT-IR spectrometer. About 1–5 mg of the respective product was ground in an agate mortar with 450–500 mg of thoroughly dried KBr and pressed into a pellet. The results of the optical measurements are displayed in Fig. 1.

Results and Discussion

Crystal structures

The crystal structures of the title compounds can be seen as part of the pseudo-binary system Ca_3N_2 - CaCN_2 . The crystal structure of Ca_3N_2 is well-known [9] and can be described as an ordered defect variant of the CaF_2 type with $\text{Ca}_3^{[4t]}\text{N}_2^{[6o]}$ (Fig. 2a). Since the typical coordination environment of nitrogen consists of six Ca contacts, the coordination of the cations are not well met with this structure. The crystal structure of $\text{Ca}[\text{CN}_2]$ is adopted by many ternary carbodiimides containing divalent cations such as Mg^{2+} [1], Sr^{2+} [15], Mn^{2+} [16] or Cd^{2+} [17]. In these compounds, the M^{2+} cations form a cubic close packing. The coordination can be expressed as $\text{Ca}^{[6o]}[\text{C}^{[2i]}\text{N}^{[4t]}_2]$ (Fig. 2d). This geometry is closer to the typical coordination requirements of each ion. This is also mirrored by the increased stability of $\text{Ca}[\text{CN}_2]$ compared to Ca_3N_2 against air and moisture. $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ can structurally and chemically be seen as calcium nitride compounds with an increasing $\text{Ca}[\text{CN}_2]$ fraction.

According to this view, the 3D structure of Ca_3N_2 is broken up into the open channel structures of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ before the 2D structure of $\text{Ca}[\text{CN}_2]$ is assumed. This can also be seen by the Ca and N coordination found in these two compounds. In $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ or – to emphasize the stoichiometry – $(\text{Ca}_3\text{N}_2)_3(\text{Ca}[\text{CN}_2]_2)$, all nitrogen atoms not within bonding distance to carbon are coordinated by a distorted octahedron of Ca atoms while the nitrogen atoms in the carbodiimide unit are surrounded by four Ca atoms and – of course – by one carbon atom. The coordination number of the Ca by N averages to 4.9 and ranges from 4 to 6. A similar picture can be seen for $\text{Ca}_4\text{N}_2[\text{CN}_2]$ or $(\text{Ca}_3\text{N}_2)(\text{Ca}[\text{CN}_2])$, but here the Ca_3N_2 : $\text{Ca}[\text{CN}_2]$ ratio is decreased to 1 : 1 compared to 3 : 2 in $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$. We also find in $\text{Ca}_4\text{N}_2[\text{CN}_2]$ that all nitrogen atoms not within bonding distance to carbon are coordinated by distorted octahedra of Ca atoms while the nitrogen atoms in the carbodiimide unit are surrounded by four Ca atoms and by one C atom. The average coordination number of Ca by N in $\text{Ca}_4\text{N}_2[\text{CN}_2]$ increases not significantly to 5.0 and still ranges from 4 to 6. The coordination of the $[\text{CN}_2]^{2-}$ moiety is more open to one side since the channels start to break down if one considers the transition being made from Ca_3N_2 to $\text{Ca}[\text{CN}_2]$.

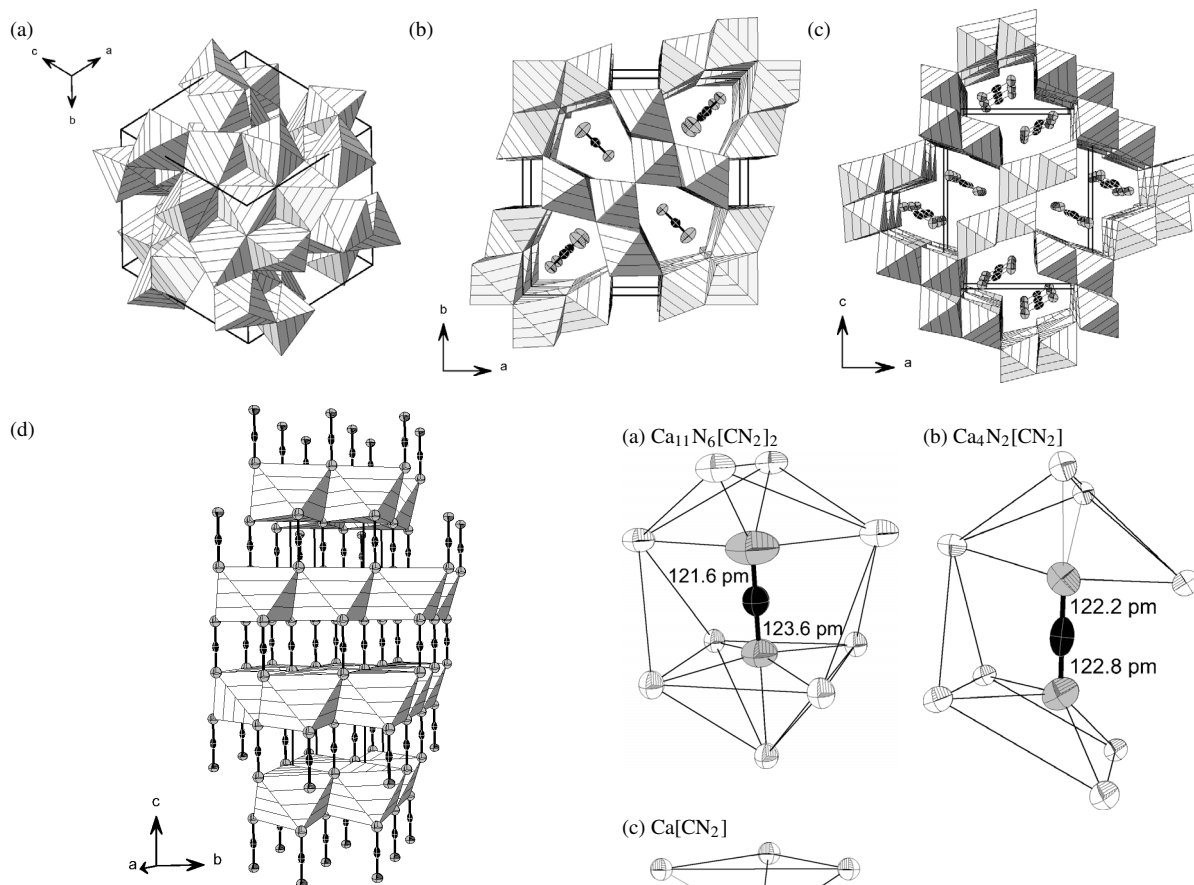


Fig. 2. Perspective view of the unit cells of Ca_3N_2 (a), $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ (b), $\text{Ca}_4\text{N}_2[\text{CN}_2]$ (c), and $\text{Ca}[\text{CN}_2]$ (d). The coordination octahedra about isolated N^{3-} are drawn as grey, hatched octahedra, C and N are displayed as crossed light grey, black and white circles, respectively. Displacement ellipsoids are drawn at the 95 % probability level.

In Fig. 2 this view is emphasized by displaying all compounds with $[\text{NCA}_6]$ octahedra, while Fig. 3 shows the different coordination environments of the triatomic $[\text{CN}_2]^{2-}$ unit which basically all show the carbodiimide structure with $D_{\infty h}$ symmetry within one standard deviation despite the unsymmetrical coordination environment found in $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and $\text{Ca}_4\text{N}_2[\text{CN}_2]$.

Vibrational spectra

The IR and Raman spectra show the fundamental vibrations expected for a $[\text{CN}_2]^{2-}$ unit with $D_{\infty h}$ symmetry [18]. Since the C–N distances are equal within the accuracy of the measurements, and the N–C–N angles show no significant deviations from linearity, the sin-

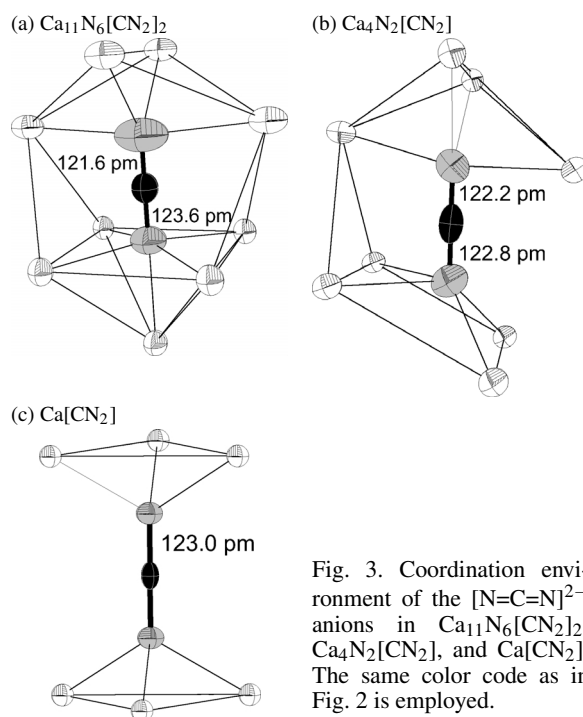


Fig. 3. Coordination environment of the $[\text{N}=\text{C}=\text{N}]^{2-}$ anions in $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, $\text{Ca}_4\text{N}_2[\text{CN}_2]$, and $\text{Ca}[\text{CN}_2]$. The same color code as in Fig. 2 is employed.

gle crystal structure analyses and the vibrational spectra are consistent.

The symmetric stretching mode for $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ reported by us in a previous paper [7] turned out to be wrong. In the course of our previous research, we used samples which obviously were not clean with respect to reaction by-products. This time the Raman measurement was done on single crystals cleaned thoroughly with *n*-hexane before the measurement.

Discussion

$\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ was first mistaken as ' Ca_{11}N_8 ' [6]. Only small amounts of carbon need to be incorporated,

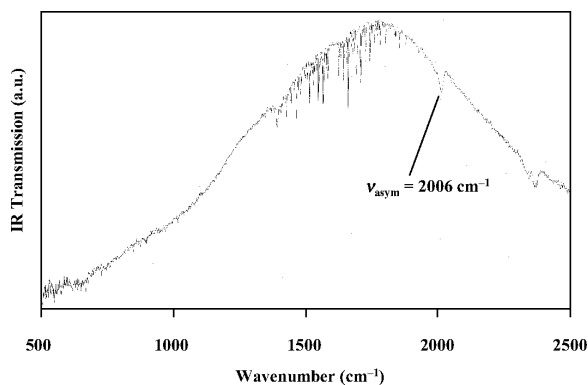
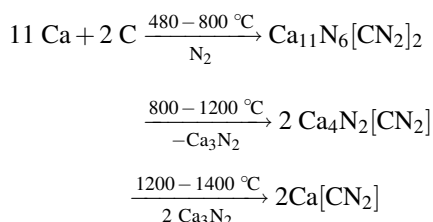


Fig. 4. IR spectrum of 'pure' Ca_3N_2 which shows clearly the asymmetric stretching mode (at 2006 cm^{-1}) of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$.

e. g. from CaCO_3 formed on the surface of the Ca metal used as an educt or by residues of carbon from the synthesis of the metal by electrolysis between carbon electrodes. If such a contaminated Ca metal is used for the synthesis of Ca_3N_2 , small amounts of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ are formed which are hard to detect by X-ray methods or by chemical analyses. We took an IR spectrum (KBr pellet technique) of such a 'pure' (according to powder X-ray diffraction) Ca_3N_2 sample and found despite strong absorption of the main compound and some CO_2 interferences the asymmetric stretching vibration of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ with $\nu_{\text{asym}} = 2006\text{ cm}^{-1}$ (Fig. 4). By heating this 'pure' Ca_3N_2 under flow-through conditions, $\text{Ca}_4\text{N}_2[\text{CN}_2]$ forms and sublimates away. Going to even higher temperatures, $\text{Ca}[\text{CN}_2]$ is finally formed. For flow-through reactions with N_2 this can be put in some simple scheme:



The formation of the compounds seems to be enhanced by the increasing vapor pressure of Ca_3N_2 with increasing temperature. Small amounts of carbon impurities and relatively low reaction temperatures are sufficient to form the compound, but if the reaction temperature chosen is too low, the crystallinity of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ is poor. If the reaction temperature is increased to improve the crystal quality, $\text{Ca}_4\text{N}_2[\text{CN}_2]$ formation begins. Another problem arises from the needle shape in which most crystals of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and also of $\text{Ca}_4\text{N}_2[\text{CN}_2]$ are formed. This needle shape of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ is not unexpected considering the crystal structure of these compounds.

Conclusion

The compounds $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$, $\text{Ca}_4\text{N}_2[\text{CN}_2]$ and $\text{Ca}[\text{CN}_2]$ were synthesized in good yields by $\text{Na}_2[\text{CN}_2]_2$ metathesis reactions with CaCl_2 which is an alternative to the methods employing $\text{Li}_2[\text{CN}_2]$ [19] or $\text{Zn}[\text{CN}_2]$ [20]. Complete structural characterization of $\text{Ca}_{11}\text{N}_6[\text{CN}_2]_2$ and $\text{Ca}_4\text{N}_2[\text{CN}_2]$ is reported for the first time. Especially in the case of $\text{Ca}[\text{CN}_2]$ data of higher precision are provided.

The title compounds show the typical geometrical features of carbodiimide $[\text{CN}_2]^{2-}$ units with $D_{\infty h}$ symmetry. The vibrational spectroscopy data yielded symmetric and asymmetric stretching modes as well as the bending modes which are in the expected range [18]. The previously reported symmetric stretching mode has been corrected.

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