Syntheses, Single-crystal Structure and Vibrational Spectra of $Ca_{15}(CBN)_6(C_2)_2H_2$

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, U. S. A.
[b] Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

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

Z. Naturforsch. **2011**, *66b,* 1092 – 1096; received October 8, 2011

Single crystals of $Ca_{15}(CBN)_6(C_2)_2H_2$ were obtained either by the reaction of stoichiometric amounts of graphite, hexagonal BN, and CaH_2 with an excess of distilled Ca, or by using graphite, boron powder, Ca_3N_2, and CaH_2 with an excess of distilled Ca. Both reactions took place in silica-jacketed Ta ampoules at 1400 K. Crystals of the title compound are transparent dark-red and isopointal to $Ca_{15}(CBN)_6(C_2)_2O$ adopting the cubic space group $Ia\bar{3}d$ (no. 230, $Z = 8$) with the cell parameter $a = 1653.30(17)$ pm. The vibrational spectra were recorded and are compared with IR and Raman data of isotypic compounds.

Key words: Acetylide, Calcium, CBN^{4-} Anion, Hydride, Structure Elucidation, Vibrational Spectra

Introduction

Recently we synthesized and characterized the compound $Ca_{15}(CBN)_6(C_2)_2F_2$ [1] which is isotypic to $Ca_{15}(CBN)_6(C_2)_2O$ [2]. As can be seen from this example, oxides and fluorides often show similar crystal chemical behavior when stabilized by a suitable host structure. Under such conditions, these two ions are exchangeable or sometimes share the same crystallographic positions. Since fluoride and hydride compounds such as $Ba_7Cl_2F_{12}$ [3] and $Sr_7H_{12}Cl_2$ [4] are also sometimes very similar in structure or even isotypic, we wanted to find out if the "$Ca_{15}(CBN)_6(C_2)_2$" structural frame can harbor hydride anions H^- instead of O^{2-} or F^-.

We present here the syntheses, the single-crystal structure determination and the vibrational spectra of $Ca_{15}(CBN)_6(C_2)_2H_2$.

Experimental Section

Synthesis

All manipulations were performed in a glove box under purified argon unless otherwise stated. The first synthesis employed a 2 : 30 : 20 : 12 molar ratio of CaH_2 (99 %, powder, Aldrich), Ca (99.99 %, distilled, dendritic pieces, Aldrich), graphite (99.999 % powder, 325 mesh, degassed at 670 K under dynamic vacuum for 2 h), and hexagonal BN (99+ %, powder, Strem, degassed at 670 K under dynamic vacuum for 2 h) with an overall mass of 475 mg. The second strategy employed a 6 : 25 : 50 : 30 : 15 molar ratio of CaH_2, Ca, graphite, B (Strem, crystalline, 99.5 %), and thoroughly ground Ca_3N_2 (Alfa Aesar, pieces, 99 %) with an overall mass of 885 mg. In both cases, the mixtures were intimately ground in an agate mortar and then arc-welded in a clean Ta container under argon with minimal air exposure. The metal container was then sealed into an evacuated silica tube. The tubes were placed upright in a box furnace and heated to 1400 K within 12 h. After 3 d reaction time the furnace was switched off and allowed to cool to r. t. In both cases, the product contained nearly exclusively transparent, dark-red crystals of the title compound and a surplus of unreacted Ca metal. The surplus Ca metal was found to be necessary since it serves as a flux and prevents the compound from losing Ca metal due to its relatively high vapor pressure at elevated temperatures. $Ca_{15}(CBN)_6(C_2)_2H_2$ decomposes within a few minutes when exposed to moist air.

Qualitative elemental analyses were performed on small samples (50 – 100 mg) of the product under normal atmosphere for carbon evolving as CO_2 probably stemming from the CBN^{4-} anion (to some of the product a drop of half-concentrated HCl was added and a drop of saturated $Ba(OH)_2$ solution at the end of a glass rod held over this quickly turned milky-white), for boron (Pt wire moistened with half concentrated H_2SO_4 and then covered with the decomposition product resulted in a green coloring of the hot Bunsen burner flame), hydrogen (a detergent-containing water-acetone mixture being placed on some portion of the sample, the resulting soap bubbles removed from the water-

Table 1. Summary of single-crystal X-ray diffraction structure determination data of $Ca_{15}(CBN)_6(C_2)_2H_2$.

Compound	$Ca_{15}(CBN)_6(C_2)_2H_2$
Crystal color	transparent red
Crystal shape	plate
Crystal size, mm^3	$0.08 \times 0.06 \times 0.02$
M_r	878.22
Crystal system	cubic
Space group (no.), Z	$Ia\bar{3}d$, (230), 8
Lattice parameters: a, pm	1653.30(17)
V, $Å^3$	4519.1(8)
D_{calcd}, $g\,cm^{-3}$	2.56
$F(000)$, e^-	3472
$\mu(MoK_\alpha)$, mm^{-1}	3.5
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD
Radiation, λ, pm; monochromator	MoK_α; 71.073; graphite
Scan mode; T, K	ϕ- and ω-scans; 173(2)
Ranges, $2\theta_{max}$, deg; h, k, l	60.91; $-15 \rightarrow 16$, $-11 \rightarrow 23$, $-22 \rightarrow 11$
Data correction	LP, SADABS [7]
Transmission: min. / max.	0.649 / 0.746
Reflections: measured / unique	4589 / 581
Unique reflections with $F_o \geq 4\sigma(F_o)$	479
R_{int} / R_σ	0.0446 / 0.0258
Refined parameters	31
$R1$[a] / $wR2$[b] / GoF[c] (all refl.)	0.0306 / 0.0461 / 1.093
Factors x / y (weighting scheme)[b]	0.0145 / 6.15
Max. shift/esd, last refinement cycle	< 0.00005
$\Delta\rho_{fin}$ (max, min), $e\,Å^{-3}$	0.36 (72 pm to C2) -0.34 (105 pm to Ca2)
CSD number	423519

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

acetone solution, and touched with a lighted splint for ignition) and for ammonia (a sample of the product put into Neßlers' reagent showed typical yellow-brown precipitating flakes). The tests were positive for the respective substance. The presence of Ca was indicated by its visible spectrum observed with the help of a hand-held spectrometer while some sample was sprinkled into the hot Bunsen burner flame. The acetylide moiety was clearly identified by its typical Raman spectrum (see below).

Experiments to obtain '$Ca_{15}(CBN)_6(C_2)_2Cl_2$' yielded mainly $Ca_3(CBN)Cl_2$ [5] in addition to some remaining starting materials.

Raman and IR spectroscopy

Single crystals of $Ca_{15}(CBN)_6(C_2)_2H_2$ sealed under a protective argon atmosphere in Mark capillaries were used for the Raman investigations (microscope laser Raman spectrometer: Jobin Yvon, 1 mW, excitation line at λ = 632.817 nm (HeNe laser), 20× magnification, 3600 s accumulation time, Fig. 1).

The IR spectrum (Fig. 1) was obtained with a Bruker AFS 66 FT-IR instrument with the KBr pellet technique (2 mg product being ground together with 400 mg dried KBr). The IR spectrum showed some absorptions typical for CO_2 in the region $1300 - 1600\ cm^{-1}$ (asymmetric stretching mode) since the measurements were performed in normal, but dry atmosphere.

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 cold stream of nitrogen (T = 173(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 MoK_α radiation (λ = 71.073 pm). The intensity data were manipulated with the program package [6] that came with the diffractometer. An empirical absorption correction was applied using SADABS [7]. The intensity data were evaluated, and the input files for solving and refining the crystal struc-

Table 2a. Atomic coordinates and equivalent isotropic displacement parameters[a] (pm^2) of $Ca_{15}(CBN)_6(C_2)_2H_2$.

Atom	Wyckoff site	x	y	z	U_{eq}
Ca1	96*h*	0.11937(2)	0.19791(2)	0.29811(2)	110(1)
Ca2	24*c*	$^1/_8$	0	$^1/_4$	99(2)
H	16*a*	0	0	0	284(40)
C1 / N1	96*h*	0.0229(1)	0.0805(1)	0.3304(1)	219(4)
B	48*g*	$^1/_8$	0.7202(1)	$^1/_4 - y$	233(8)
C2	32*e*	0.1057(1)	x	x	399(12)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors.

Table 2b. Anisotropic displacement parameters[a] (pm^2) of $Ca_{15}(CBN)_6(C_2)_2H_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	130(2)	95(2)	105(2)	4(1)	–1(1)	–13(1)
Ca2	88(3)	104(2)	U_{22}	–18(3)	0	0
C1 / N1	210(9)	203(9)	244(10)	–90(8)	130(9)	–87(8)
B	312(18)	194(10)	U_{22}	135(14)	187(12)	U_{13}
C2	399(12)	U_{11}	U_{11}	–92(11)	U_{23}	U_{23}

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

Table 3. Lattice parameters, selected bond lengths (pm), temperature (K) and angles (deg) of $Ca_{15}(CBN)_6(C_2)_2Y_2$ (Y = H, F or $O_{1/2}$). The bond length of the acetylide anion is geometrically corrected for its precession and given in italics.

Hosted anion Y			H^-	F^- [1]	$(O^{2-})_{1/2}$ [2]
lattice parameter			1653.3(2)	1653.6(4)	1656.84(9)
temperature			173	173	293
Atoms		Multiplicity	*d*	*d*	*d*
Y–	Ca1	6×	245.73(4)	246.0(1)	246.61(4)
C1/N1–	B	1×	141.4(2)	141.7(6)	141.4(2)
	Ca1	1×	250.2(2)	250.1(5)	250.7(2)
	Ca2	1×	252.8(2)	252.8(5)	253.7(2)
	Ca1	1×	256.8(2)	256.5(5)	257.1(2)
	Ca1	1×	256.9(2)	256.5(5)	257.3(2)
	Ca1	1×	269.0(2)	268.9(9)	271.2(2)
C2–	C2	1×	110.8(8)	109(2)	109.5(5)
	C2	*1*×	*[123]*	*[120]*	*[121]*
	Ca1	3×	272.4(3)	273.0(6)	273.6(3)
	Ca2	3×	297.47(8)	297.4(2)	298.0(2)
B–	C1/N1	2×	141.4(2)	141.7(6)	140.8(3)
	Ca1	2×	276.2(2)	275.6(5)	276.3(2)
	Ca2	2×	287.1(3)	287.6(7)	287.9(2)
∠(N1–B–C)		1×	178.1(3)	178.5(8)	178.2(5)

ture were prepared by XPREP [8]. The atomic coordinates of $Ca_{15}(CBN)_6(C_2)_2F_2$ [1] were used as starting models which were refined by full-matrix least-squares techniques with the use of SHELXL-97 [9]. H^- scattering factors were modeled using those of He [10] as performed before [11]. The residual electron densities are low at 0.36 e^- Å^{-3} (72 pm to C2) and −0.34 e^- Å^{-3} (105 pm to Ca2). 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 and its fluoride and oxide analog.

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-423519 for $Ca_{15}(CBN)_6(C_2)_2H_2$.

Results and Discussion

Optical spectra

The Raman and IR spectra of the title compound are, as expected when considering the close geometric analogies, nearly identical to those of $Ca_{15}(CBN)_6(C_2)_2O$ [2] or $Ca_{15}(CBN)_6(C_2)_2F_2$ [1] (Fig. 1). The observed spectra are in good agreement with those reported for other acetylide-containing Ca compounds (Table 4).

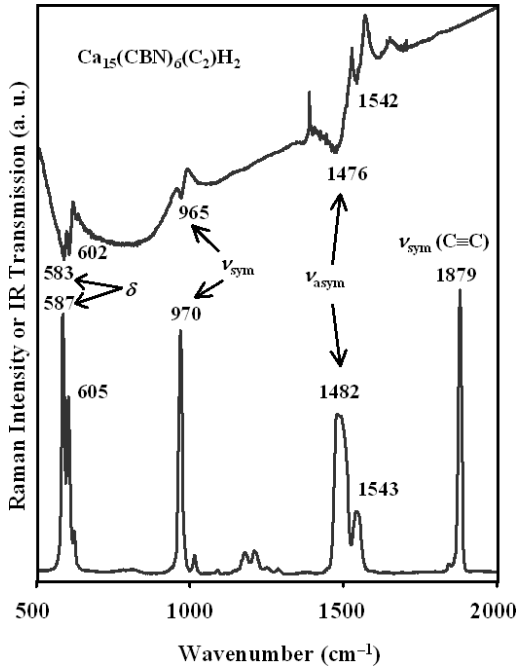

Fig. 1. Raman and IR spectrum of $Ca_{15}(CBN)_6(C_2)_2H_2$. On the vertical axis, Raman intensities and IR transmissions are displayed in arbitrary units. All numbers are given in cm^{-1}.

Crystal structure

The crystal structure is isopointal to $Ca_{15}(CBN)_6(C_2)_2O$ [2] or isotypic to $Ca_{15}(CBN)_6(C_2)_2F_2$ [1]. In the title compound the charges are balanced to neutrality according to the formula $(Ca^{2+})_{15}(CBN^{4-})_6(C_2^{2-})_2(H^-)_2$. As described in detail for $Ca_{15}(CBN)_6(C_2)_2O$ [5], the structure resembles the garnet structure and is rather complex (Fig. 2). The structure of these three compounds is nearly identical within three times the estimated standard deviations and considering deviations due to the different temperatures of the measurements (Table 3). These similarities are also found for the coordination of the 16*a* position occupied either to 50 % by oxide or to 100 % by fluoride or hydride anions, respectively. The ions on this position are coordinated by six Ca cations in a nearly perfect octahedral fashion, and the interatomic distances in the three compounds are quite close to each other. The ionic radii of the oxide and the fluoride anions are quite close to each other with 140 and 133 pm [14], but the ionic radii or the incremental volumes strongly depend on the counter ions [15]. Since the three isotypic compounds show nearly identical structural features, the host structure seems to stabilize these three 'small' an-

Table 4. Structural and vibrational properties of compounds containing acetylide or/and CBN^{4-} moieties. Raman data are given in bold.

Compound	d(C≡C) (pm)	d(C=B) (pm)	d(B=N) (pm)	∠ (deg)	δ (cm^{-1})	ν_{as} (cm^{-1})	ν_{sym} (cm^{-1})	ν_{sym}(C≡C) (cm^{-1})	Ref.
CaC_2	120	–	–	–	–	–	–	**1860** **1871**	[12]
$Ca_3(CBN)Cl_2$	–	144.3	137.9	175.6	**594/607** **590/604**	**1525/1576**	**997**	–	[5, 13]
$Ca_{15}(CBN)_6(C_2)_2O$	121 (109.5)	140.8	140.8	178.2	580/602	1471/1538	966	–	[2]
$Ca_{15}(CBN)_6(C_2)_2F_2$	120 (109)	141.7	141.7	178.5	582/601 **592/609**	1472/1542 **1490/1550**	963 **976**	– **1887**	[1]
$Ca_{15}(CBN)_6(C_2)_2H_2$	123 (110.8)	141.4	141.4	178.1	583/602 **587/605**	1476/1542 **1482/1543**	965 **970**	– **1879** ($^{12}C{\equiv}^{12}C$)	this work

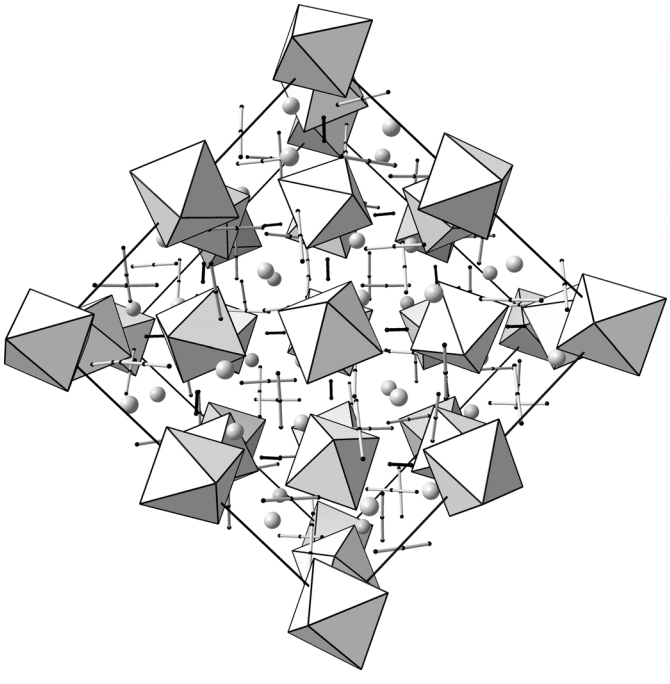

Fig. 2. Perspective view of the unit cell of $Ca_{15}(CBN)_6(C_2)_2H_2$ parallel to one of the symmetry-equivalent crystallographic axes. [$HCa1_6$] octahedra are displayed white-to-grey. Ca2 are shown as white-hatched octands, C1/N1, B and C2 are shown as small black spheres connected either by grey or black bonds, respectively. No displacement ellipsoids are used for clarity.

ions regardless of their actual size. However, chloride anions appear to be too large for the structure with its limited flexibility.

Conclusion

The compound $Ca_{15}(CBN)_6(C_2)_2H_2$ was synthesized and characterized by single-crystal X-ray methods and both Raman and IR spectroscopy. The atomic positions, interatomic distances and vibrational frequencies are very similar to those of the isopointal compound $Ca_{15}(CBN)_6(C_2)_2O$ [2] and to the isotypic compound $Ca_{15}(CBN)_6(C_2)_2F_2$ [1].

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