One more Compound Containing the CBN^{4-} Ion – Synthesis, Single-crystal Structure and Vibrational Spectra of $Ca_{15}(CBN)_6(C_2)_2F_2$

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Z. Naturforsch. **2010**, *65b,* 1409 – 1415; received September 6, 2010

Single crystals of $Ca_{15}(CBN)_6(C_2)_2F_2$ were obtained by the reaction of graphite, hexagonal BN and CaF_2 with an excess of distilled Ca metal in silica-jacketed Ta ampoules at 1300 K. The title compound is transparent red and crystallizes 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 $a = 1653.6(4)$ pm. Its vibrational spectra are compared with IR and Raman data of similar compounds from the literature and with the newly measured Raman spectra of $Ca_5(BC_2)(C_2)Cl_3$ and $Ca_9(BC_2)_2Cl_8$.

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

Introduction

The characterization and preparation of the first compound containing the CBN^{4-} ion by Meyer [1] was achieved nearly simultaneously to the theoretical prediction of its existence by Pyykkö *et al.* [2]. Following this very closely in time, some more compounds containing this specific anion were prepared and characterized, such as $Ca_3(CBN)Br_2$ and $Sr_3(CBN)Cl_2$ [3], or $Ca_{9+0.5x}(BN_2)_{6-x}(CBN)_x$ [4] and $Ca_{15}(CBN)_6(C_2)_2O$ [5].

We present here the synthesis, the single-crystal structure determination and the vibrational spectra of $Ca_{15}(CBN)_6(C_2)_2F_2$, one more member of this class of compounds. Additionally, we compare the vibrational data of related compounds obtained either from literature or from our own measurements.

Experimental Section

Synthesis

All manipulations were performed in a glove box under purified argon unless otherwise stated. 360 mg (9 mmol) Ca (99.99 %, distilled, dendritic pieces, Aldrich), 40 mg (0.51 mmol) CaF_2 (99.9 %, powder $<$ 5 microns), 75 mg (3.02 mmol) hexagonal BN (99+ %, powder, Strem, degassed at 670 K under dynamic vacuum for 2 h) and 70 mg (5.83 mmol) graphite (99.999 % powder, 325 mesh, degassed at 670 K under dynamic vacuum for 2 h) were arc-welded into a clean Ta container. The metal container was sealed into an evacuated silica tube. The tube was placed upright in a box furnace and heated to 1300 K within 12 h. After 2 d reaction time the furnace was switched off and allowed to cool to r. t. The product contained nearly exclusively transparent, dark-red crystals of the title compound and a surplus of unreacted Ca metal. This surplus metal was found to be necessary since it serves as a melt and prevents the compound from losing Ca metal due to the relatively high Ca vapor pressure at elevated temperatures. $Ca_{15}(CBN)_6(C_2)_2F_2$ decomposes in a few minutes when exposed to moist air.

Qualitative elemental analyses performed on small samples (50 – 100 mg) of the product under normal atmosphere for carbon (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 turned quickly milky-white), 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 Bunsenburner flame), fluoride (a few drops of half concentrated H_2SO_4 with a sample of the product in a small, dry glass tube showed the typical 'etching effect': the acid did not wet the glass after some time) and nitrogen (a sample of the product put into Neßlers' reagent showed typical yellow-brown precipitating flakes) were all positive for the respective element. The presence of Ca is indicated by its visible spectrum observed with the help of a hand-held spectrometer while some sample is sprinkled into the hot Bunsen burner flame, while the acetylide moiety was clearly identified by its typical Raman spectrum (see below).

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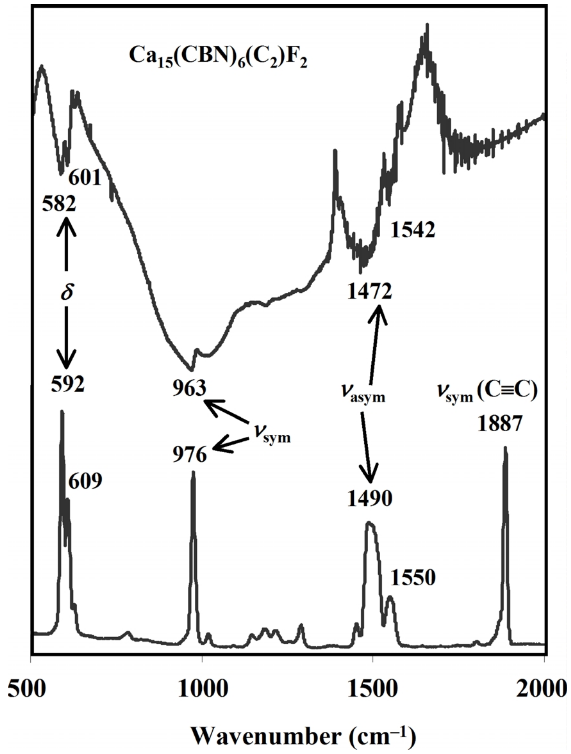

Fig. 1. Raman and IR spectrum of $Ca_{15}(CBN)_6(C_2)_2F_2$. On the vertical axis, Raman intensity and IR transmission are displayed in arbitrary units. All numbers are given in cm^{-1}.

Raman and IR spectroscopy

Single crystals of $Ca_{15}(CBN)_6(C_2)_2F_2$ 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 (also Fig. 1) was obtained with a Bruker AFS 66 FT-IR instrument with the KBr pellet technique (2 mg product were ground together with 400 mg thoroughly dried KBr). The IR spectrum shows absorptions typical for CO_2 (around 2350 cm^{-1} for the symmetric and in the region between 1300 – 1500 cm^{-1} for the asymmetric stretching mode) since the measurements were performed in normal, but dry atmosphere due to the set-up of the instrument used.

For comparison, the Raman spectra of the compounds $Ca_5(BC_2)(C_2)Cl_3$ [6] and $Ca_9(BC_2)_2Cl_8$ [7] were recorded on single crystals in Mark capillaries sealed under a protective argon atmosphere (microscope laser Raman spectrometer: Jobin Yvon, 4 mW, excitation line at λ = 632.817 nm (HeNe laser), 100× magnification, 6 × 30 s accumulation time) since these had not been reported yet (Fig. 2).

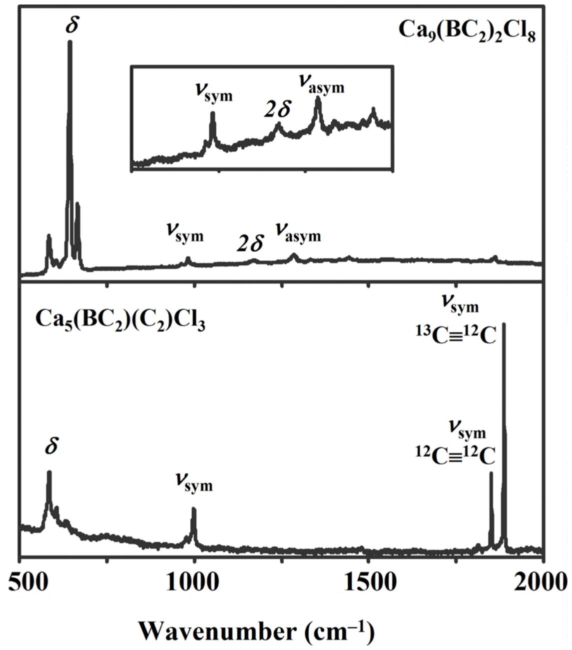

Fig. 2. Raman spectra of $Ca_5(BC_2)(C_2)Cl_3$ (bottom) and of $Ca_9(BC_2)_2Cl_8$ (top). Raman intensity is displayed on the vertical axis in arbitrary units. For $Ca_9(BC_2)_2Cl_8$, an inset from 750 to 1500 cm^{-1} is shown with different scaling of the Raman intensity to emphasize observed Raman modes with low intensities.

The valence force constants were calculated according to the method of Siebert [19] if the necessary data were known. The results are displayed in Table 1.

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. A suitable single crystal was selected 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. 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 respective lattice parameters were obtained by using APEX2 [20]. The internal R value of R_{int} = 0.097 is relatively high. In the SHELXL-97 manual [21] it is pointed out that generally R_{int} should be below 0.1 for a correct assignment. It also has to be taken into account that many symmetry-equivalent reflections have to be merged for this high-symmetry cubic Laue group. Therefore, R_{int}

Table 1. Structural and optical properties of compounds containing selected di- and triatomic moieties consisting of atoms of the second period. Raman data are given in bold. Underlined figures were obtained in the frame of this work.

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})	f (N cm^{-1})	Ref.
CaC_2	120	–	–	–	–	–	–	**1860** **1871**	$\underline{\mathbf{12.2}}$ $\underline{\mathbf{12.4}}$	[8]
$Ca_3(BN_2)_2$	–	–	131.7	180	582/625 602	1680/1760	1107	–	8.3	[4, 9]
$Ca_{10}(BN_2)_4(CBN_2)_2$	–	135.2	135.2	180	565	1587/1631 1701/1780	–	–	–	[4]
$Ca_2(BN_2)Cl$	–	–	132.4/134.6	177.2	–	–	–	–	–	[10, 11]
			132.9/133.2	176.5	586/628 616/647	1683/1743	1058	–	$\underline{7.9}$	
$Ca_3(C_3)Cl_2$	134.6	–	–	169.0	**644**	1660	**1159**	–	$\underline{8.0}$	[12, 13]
Sc_3C_4	134.2	–	–	175.8	–	–	–	–	–	[14]
$Mg_2(C_3)$	133.2	–	–	180	–	–	–	–	–	[15]
$Mg_3(BN_2)N$	–	–	136.5	180	563/608	1711/1770	**1058**	–	$\underline{8.0}$	[16, 17]
$Al_3(BC_2)C$	–	144	–	180	735	1580	**1041**	–	6.6	[18]
$Ca_3(CBN)Cl_2$	–	144.3	137.9	175.6	594/602 627	1516/1567		–	–	[1, 13]
					594/607 **590/604**	**1525/1576**	**997**		5.0/8.0 $\underline{\mathbf{6.1/6.9}}$	
$Ca_3(CBN)Br_2$	–	–	–	–	605	1490	–	–	–	[3]
$Sr_3(CBN)Cl_2$	–	143.6	139.3	168.5	607	1500	–	–	–	[3]
$Ca_9(BC_2)_2Cl_8$	–	145.2	–	161.5	$\underline{\mathbf{585/605}}$ $\underline{\mathbf{645/667}}$	$\underline{\mathbf{1446}}$	$\underline{\mathbf{984}}$	–	$\underline{\mathbf{5.6}}$	[7]
$Ca_5(BC_2)(C_2)Cl_3$	119.3 (109)	143.7	–	164.0	$\underline{\mathbf{587/606}}$ $\underline{\mathbf{634/663}}$	–	$\underline{\mathbf{999}}$	–	–	[6]
								$\underline{\mathbf{1851/1887}}$	$\underline{\mathbf{12.6}}$	
$Ca_{15}(CBN)_6(C_2)_2O$	121 (109.5)	140.8	140.8	178.2	580/602	1471/1538	966	–	$\underline{5.5/6.2}$ $\underline{5.9/6.6}$	[5]
$Ca_{15}(CBN)_6(C_2)_2F_2$	$\underline{120}$ $\underline{(109)}$	$\underline{141.7}$	$\underline{141.7}$	$\underline{178.5}$	$\underline{582/601}$	$\underline{1472/1542}$	$\underline{963}$	–	$\underline{5.5/6.2}$ $\underline{5.9/6.6}$	
					$\underline{\mathbf{592/609}}$	$\underline{\mathbf{1490/1550}}$	$\underline{\mathbf{976}}$		$\underline{\mathbf{5.7/6.3}}$ $\underline{\mathbf{6.0/6.7}}$	
								$\underline{\mathbf{1887}}$	$\underline{\mathbf{12.6}}$	

is in the acceptable range. The program SAINT [22] was used to integrate the data. An empirical absorption correction was applied using SADABS [23]. The initial input file was prepared by XPREP [24]. The crystallographic coordinates of $Ca_{15}(CBN)_6(C_2)_2O$ [5] transformed with STRUCTURE TIDY [25, 26] were used as a starting model, but owing to the different charges of O^{2-} and F^- the model we employed had a site occupation factor of 100 % on the $16a$ site. This model was refined by full-matrix least-squares techniques with the use of SHELXL-97 [21] and converged to a stable structure. The residual electron densities are low at 0.38 e Å^{-3} (109 pm to N1) and -0.46 e Å^{-3} (40 pm to F). Additional crystallographic details are described in Table 2. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 3, Table 4 displays the anisotropic displacement parameters.

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-422011 for $Ca_{15}(CBN)_6(C_2)_2F_2$.

Results and Discussion

Optical spectra

The IR spectrum of the title compound is, as expected, nearly identical to the one reported for $Ca_{15}(CBN)_6(C_2)_2O$ [5]. The observed modes in the Raman spectrum differ by approximately 10 – 15 cm^{-1}

Table 2. Summary of X-ray single-crystal structure determination data on $Ca_{15}(CBN)_6(C_2)_2F_2$.

Compound	$Ca_{15}(CBN)_6(C_2)_2F_2$
CSD number	422011
M_r	908.22
Crystal color	transparent red
Crystal shape	irregular block
Crystal size, mm^3	$0.11 \times 0.10 \times 0.09$
Crystal system	cubic
Space group (no.), Z	$Ia\bar{3}d$, (230), 8
Lattice parameters: a, pm	1653.6(4)
V, Å^3	4521.4(17)
D_{calcd}, g cm^{-3}	2.67
F(000), e$^-$	3600
μ, 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-scans; 173(2)
$2\theta_{max}$-Range, deg	52.66
h,k,l-Range	± 15, $-4 \rightarrow 20$, $-13 \rightarrow 11$
Data correction	LP, SADABS [23]
Transmission: min. / max.	0.587 / 0.747
Reflections: measured / unique	3744 / 391
Unique reflections with $F_o \geq 4\sigma(F_o)$	277
R_{int}/R_σ	0.0970 / 0.0537
Refined Parameters	32
$R1^a$ / $wR2^b$ / GooF^c (all refl.)	0.0664 / 0.0776 / 1.076
Factors x / y (weighting scheme)^b	0.0224 / 24.285
Max. shift/esd, last refinement cycle	< 0.00005
$\Delta\rho_{fin}$ (max / min), e$^-$ Å^{-3}	0.38 (109 pm to N1) / -0.46 (40 pm to F)

[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] 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 refined parameters.

Table 3. Atomic coordinates and equivalent isotropic displacement parameters^a of $Ca_{15}(CBN)_6(C_2)_2F_2$.

Atom	W. position	x	y	z	U_{eq} (pm^2)
Ca1	96h	0.11921(6)	0.19797(6)	0.29810(6)	127(3)
Ca2	24c	1/8	0	1/4	111(4)
F	16a	0	0	0	263(17)
C1 / N1	96h	0.0231(3)	0.0806(3)	0.3306(3)	246(12)
B	48g	1/8	0.7205(4)	$1/4 - y$	267(24)
C2	32e	0.1060(3)	x	x	407(31)

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

Table 4. Anisotropic displacement parameters^a (pm^2) of $Ca_{15}(CBN)_6(C_2)_2F_2$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca1	142(6)	109(5)	114(5)	6(4)	$-2(4)$	$-12(4)$
Ca2	93(10)	120(6)	U_{22}	$-3(9)$	0	0
F	263(17)	U_{11}	U_{11}	49(22)	U_{23}	U_{23}
C1/N1	205(28)	249(30)	284(32)	$-107(25)$	162(24)	$-100(23)$
B	349(55)	226(31)	U_{22}	163(40)	198(35)	U_{13}
C2	407(31)	407(31)	407(31)	$-121(25)$	U_{23}	U_{23}

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

from the values observed in the IR spectrum. The observed spectra are in good ageement with those reported for other acetylide containing Ca compounds (Table 1) with respect to wavenumbers at which the active modes are observed and also with respect to the resulting valence force constant f calculated according to the method of Siebert [19]. The B=N force constants of compounds containing $(BN_2)^{3-}$ and the C=C force constants of $Ca_3(C_3)Cl_2$ are found to be in the same range (around 8.0 N cm^{-1}) whereas the B=C force constant around 6.0 N cm^{-1} is somewhat weaker, and the one for the acetylide anion is stronger as expected for a triple bond (12.0 N cm^{-1}). For $(CBN)^{4-}$ compounds, the calculated valence force constants f(C=B) are with 5.5 – 6.1 N cm^{-1} in the same range as found for $[BC_2]^{5-}$ compounds, but the B=N bond seems to be weakened as indicated by f(B=N) values between 6.1 – 6.9 N cm^{-1}.

The Raman spectrum of the extremely bent $(BC_2)^{5-}$ anion in $Ca_9(BC_2)_2Cl_8$ [7] with C_{2v} symmetry and the Raman as well as the IR spectrum of the $(CBN)^{4-}$ anion with $C_{\infty v}$ symmetry observed in $Ca_{15}(CBN)_6(C_2)_2F_2$ exhibit all three modes ν_{sym}, ν_{asym} and δ (the modes are – not in accordance with the real symmetry – named in analogy to triatomic moieties with $D_{\infty v}$ symmetry) expected for a triatomic unit due to the decrease in symmetry. It is noteworthy that the antisymmetric stretching mode was not observed in the Raman spectrum of the compound $Ca_5(BC_2)(C_2)Cl_3$ [6] despite its similarity to $Ca_9(BC_2)_2Cl_8$ [7] regarding the symmetry and coordination of the $(BC_2)^{5-}$ moiety. The only difference is the bending angle of the anion, which at 161.5° for $Ca_9(BC_2)_2Cl_8$ deviates more from linearity than the angle of 164.0° for $Ca_5(BC_2)(C_2)Cl_3$ and therefore might be the reason for the different behavior.

Crystal structure

The crystal structure is isopointal to that of $Ca_{15}(CBN)_6(C_2)_2O$ [5] with the only difference that the 16a site of the former compound is only occupied to 50 % by oxide anions whereas the same site of the title compound is occupied to 100 % by fluoride anions which balance the charges to neutrality according to the formula $(Ca^{2+})_{15}(CBN^{4-})_6(C_2{}^{2-})_2(F^-)_2$. As described in detail for $Ca_{15}(CBN)_6(C_2)_2O$ [5], the structure resembles the garnet structure and is

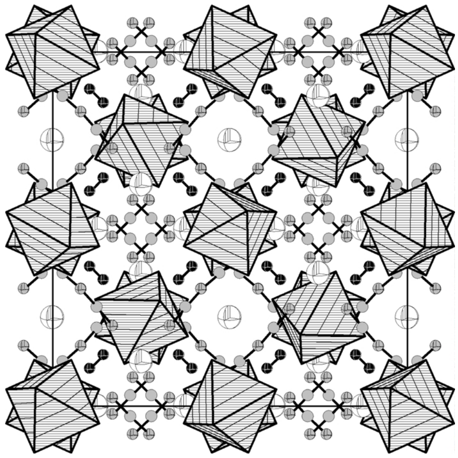

Fig. 3. Non-perspective view of the unit cell of $Ca_{15}(CBN)_6(C_2)_2F_2$ parallel to one of the symmetry-equivalent crystallographic axes. $[FCa1_6]$ octahedra are displayed white-hatched. Ca2 are shown as white-hatched octands, C1/N1 as light-grey hatched octands, B as light-grey spheres and C as black, white-hatched octands. C1/N1–B and C–C bonds are displayed as thick black lines. No displacement ellipsoids are used for clarity.

rather complex as demonstrated by the non-perspective (Fig. 3) view of the unit cell. The coordination geometry of the anions shows similarities to that in other alkaline earth metal compounds. The fluoride anion is coordinated by six Ca cations in nearly perfect octahedral fashion (Fig. 4a), which is not unusual. The C1/N1 end atoms of the nearly linear $(CBN)^{4-}$ ion are each surrounded by five metal ions in the form of a tetragonal pyramid with the square bases orientated to each other in an antiprismatic fashion (Fig. 4b). For comparison, the linear $(BN_2)^{3-}$ anion in $Ca_3(BN_2)_2$ [4] is coordinated in a similar way, but the bases are orientated to each other in a prismatic way. If the anions are more bent as in $Ca_3(C_3)Cl_2$ [12], $Ca_5(BC_2)(C_2)Cl_3$ [6] or $Ca_9(BC_2)_2Cl_8$ [7] (Table 1), the coordination sphere resembles very closely a bicapped trigonal prism. The possibility has already been discussed (*e. g.* for $(CN_2)^{2-}$ [27] or for $(BC_2)^{5-}$ [6]) that coordinative needs are responsible for the bending angle of the respective triatomic moiety, which does not take too much of an energetic effort and is possibly due to the low bending constants. The bending of the triatomic unit does not alter the bond lengths much as can be seen for the $(BN_2)^{3-}$ and the $(BC_2)^{5-}$ anions (Table 1). The observed C1/N1–B distance of 141.7 pm is an average of the B=N and B=C bond lengths due to the symmetry equivalence of the atoms C1 and N1 and is close to the 140.8 pm found in $Ca_{15}(CBN)_6(C_2)_2O$ [5]. The average bond length in $Ca_3[CBN]Cl_3$ [1] is 141.1 pm, which is in good accordance with the average of the B=N bond lengths in $(BN_2)^{3-}$ anions and B=C bond lengths in $(BC_2)^{5-}$ (139 pm). The acetylide anion is surrounded by a tri-

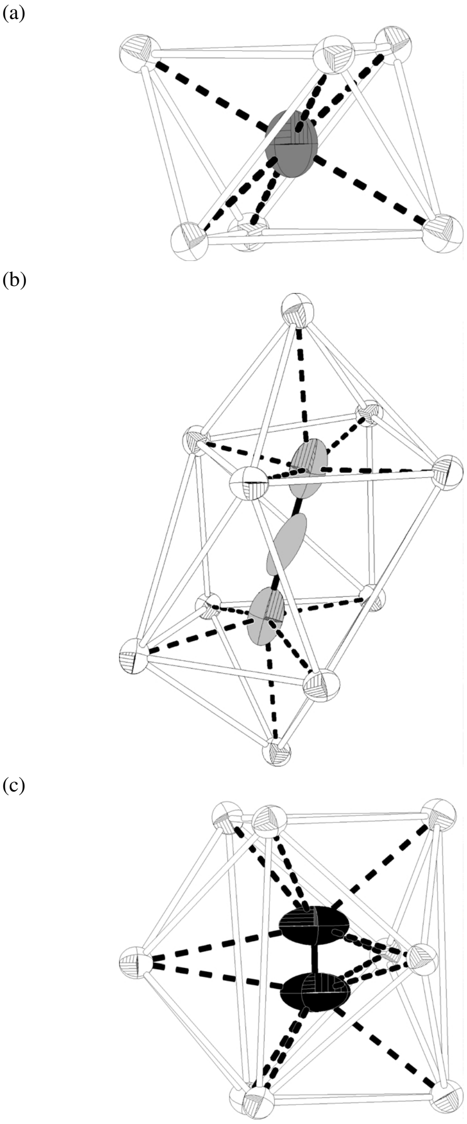

Fig. 4. Coordination of the fluoride anion (a), the $(CBN)^{4-}$ anion (b), and the C_2^{2-} anion (c) by Ca cations. Fluoride is displayed as dark-grey octand, Ca are as white octands. Bonds between anions and Ca cations are shown as dotted black lines, virtual Ca-Ca contacts as empty thick lines to emphasize the coordination of the central atom. Otherwise, the color codes are the same as in Fig. 3. The displacement ellipsoids are drawn at the 90 % probability level.

Table 5. Selected bond lengths (pm) and angles (deg) of $Ca_{15}(CBN)_6(C_2)_2F_2$. For the acetylide anion, the bond length geometrically corrected for the precession is given in italics.

Atoms		Multiplicity	*d*
F–	Ca1	6×	246.0(1)
C1/N1–	B	1×	141.7(6)
	Ca1	1×	250.1(5)
	Ca2	a×	252.8(5)
	Ca1	2×	256.5(5)
	Ca1	1×	268.9(9)
C2–	C2	1×	109(2) *[120]*
	Ca1	3×	273.0(6)
	Ca2	3×	297.4(2)
B–	C1/N1	2×	141.7(6)
	Ca1	2×	275.6(5)
	Ca2	2×	287.6(7)
∡(N1–B–C)		1×	178.5(8)

capped trigonal prism of calcium cations (Fig. 4c) as observed for $C_2{}^{2-}$ in $Ca_5(BC_2)(C_2)Cl_3$ [6]. However, in CaC_2 [8] six Ca^{2+} surround the acetylide anion forming an octahedra are squashed along the tetragonal axis but with similar bond lengths (1 × 260 and 4 × 281.3 pm in CaC_2 compared to 3 × 273.0 and 3 × 297.4 pm in the title compound). In Table 5 the distances are given for one C atom only. The carbon-carbon distance of 109 pm seems to be unrealistically short and is probably due to a precession motion which is averaged by X-ray methods as observed with $Ca_5(BC_2)(C_2)Cl_3$ [6] and $Ca_{15}(CBN)_6(C_2)_2O$ [5]. Correcting the bond length by geometric calculations, the resulting bond length of the diatomic oscillator is close to 120 pm.

Conclusion

The compound $Ca_{15}(CBN)_6(C_2)_2F_2$ has been synthesized and characterized by X-ray single-crystal methods and both Raman and IR spectroscopy. The measured atomic positions are very similar to those of the isopointal compound $Ca_{15}(CBN)_6(C_2)_2O$ [5]. Similarly, the observed bond lengths and optical data are quite close to those observed for other compounds containing similar ions.

Raman data of the related compounds $Ca_5(BC_2)(C_2)Cl_3$ and $Ca_9(BC_2)_2Cl_8$ complete the picture of the 'averaged' $(CBN)^{4-}$ anion with symmetry-equivalent C1 and N1 positions, a slightly weakened B=N bond and a more or less freely rotating acetylide anion.

Acknowledgement

Thanks are due to Dr. E. B. Lobkovsky (Cornell University, Ithaca, NY, USA) for the use of his diffractometer.

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