found in TRIMEB. The $^1C_4$ form may be considered as a reaction intermediate because the O4(2)-O4(3)-O4(4) angle is 161.5° (Table 1)—instead of the average 128° in β-CD—and leads to an elliptical distortion of the macrocycle. Only a further slight rotation of the $^1C_4$ inverted glucose unit and revertion to the "normal" $^4C_1$ form would be required to complete the flip.

Thus far, the common property of all partially and fully methylated CDs crystallized from hot water is that water is not located in their molecular cavities. It seems that the expulsion of water molecules from the cavity is a major driving force for crystallization of these substances. "Empty" cavities can only be obtained if the cavity volumes are either greatly reduced or if the cavities are totally blocked. This principle requires different structural changes for CDs of different sizes, and is always associated with the inward rotation of two or three O6-methyl groups to close the cavities. Since the three permethylated CDs are of different size this closure requires different structural changes, and ranges from a simple tilting of glucose units to inversion of the chair form, and flipping by about 180°. As shown by a number of X-ray structure analyses this does not occur if a guest molecule is added that can fill the cavity.[15]

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[10] Crystal structure of TRIMEB (Cyclolab, Budapest; crystallized as the monohydrate at approximately 40 °C): Data collection and structure analysis were as for TRIMEG dihydrate. $C_{63}H_{112}O_{35} \cdot H_2O$, $M_r = 1445.5$, crystal dimensions $0.50 \times 0.25 \times 0.25$ mm^3, orthorhombic, space group $P2_12_12_1$ with $a = 14.823(5)$, $b = 19.382(3)$, $c = 26.534(5)$ Å, $V = 7623(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.259$ g cm^{-3}, 6225 unique reflections measured, 6214 observed with $I > 2\sigma(I)$. Methoxy groups are ordered. Water hydrogen atoms could not be located. $R = 0.053$, $R_W = 0.126$.[11]

[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101208. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] The angle O4($n+1$)-O4(n)-O4($n-1$) between the O4 atoms of consecutive glucose units is flexible, and allows some opening and closing. In α-CD the average angle is 120°, in β-CD it is 128°, and in γ-CD it is 135°.

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$Ca_5Cl_3(C_2)(CBC)$: A Compound with a Layer Structure and an Unusual Anion Combination**

Olaf Reckeweg and Hans-Jürgen Meyer*

Reports concerning "calcium monochloride"[1] inspired us some years ago to investigate reactions in and with melts of calcium chloride. The colorless "calcium monochloride" was found to be CaHCl,[2] the red one turned out to be $Ca_3Cl_2C_3$.[3] The synthetic potential of calcium chloride melts as a solvent for graphite or calcium metal is well known. When CaC_2 is dissolved in a melt of $CaCl_2$ the compound $Ca_3Cl_2C_3$ with the C_3^{4-} ion is formed. Reactions of calcium with certain combinations of the elements B, C, and N in calcium chloride melts yield compounds such as Ca_3Cl_2CBN with CBN^{4-} ions,[4] Ca_2ClBN_2,[5] and $Sr_3(BN_2)_2$[6] with BN_2^{3-} ions or the title compound $Ca_5Cl_3(C_2)(CBC)$.[7]

In attempts to synthesize "$Ca_4Cl_3BC_2$" with the help of a melt of calcium chloride, the new compound $Ca_5Cl_3(C_2)$(CBC) has been obtained which contains acetylide and dicarbidoborate ions. A characteristic feature of the structure of $Ca_5Cl_3(C_2)(CBC)$ is the puckered layers with the sequence Cl-Ca-Ca. The layered structure is reflected in the habitus of the crystals which occur as thin aggregates that are very often grown together. The C_2^{2-} and CBC^{5-} ions are sandwiched between double layers of calcium ions (Figure 1). The C_2^{2-} ions are coordinated by a distorted octahedron of Ca^{2+} ions.

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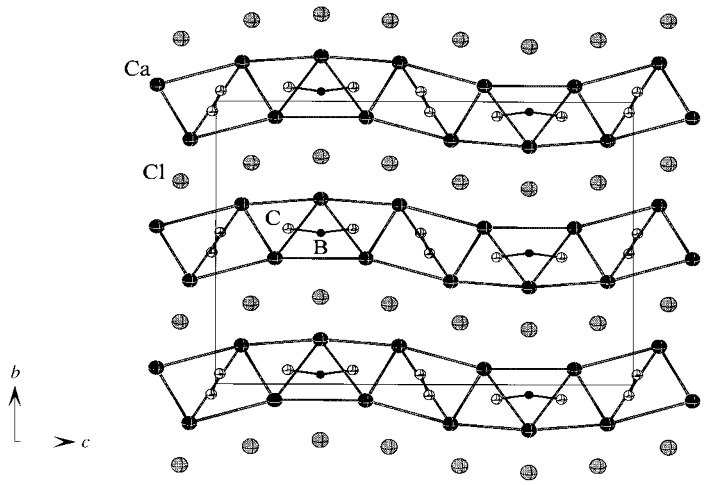

Figure 1. Projection of the structure of $Ca_5Cl_3(C_2)(CBC)$. The calcium ions are connected with lines to emphasize the double layers.

The initial results from the X-ray structure analysis reveal that the C_2^{2-} ion resides at the special position 8*f* (sited in the mirror plane at $x=0$) and has an extremely short C–C bond length of 108 pm. A similar short C–C bond length of 109.5 pm has been reported for $Ca_{15}(CBN)_6(C_2)_2O$.[8] In this case the short C–C bond length is explained by virtual shortening due to thermal motion or statistical displacement. One could think that for the observed shortening of the acetylide in $Ca_5Cl_3(C_2)(CBC)$ the same was true. The refinement of a split position (50% occupation of the general position 16*h*) results in a C–C bond length of 119(2) pm. This distance is in the range of the expected value for a C≡C triple bond (C–C bond length in CaC_2: 119(1) pm[9]). Therefore the virtual position of the C_2^{2-} ion in the mirror plane (1) is a superposition of the split position (2) (Figure 2).

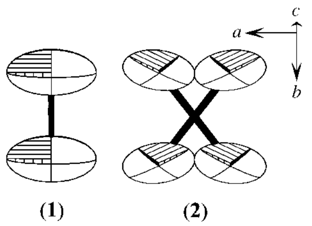

Figure 2. Virtual (1) and real position (2, split position) of the C_2^{2-} ion in $Ca_5Cl_3(C_2)(CBC)$.

Each BC_2^{5-} ion is surrounded by a bicapped trigonal prism of calcium ions. The boron atom is sited nearly in the middle of the prism. Each of the two carbon atoms of the BC_2 unit lie above a rectangular prismatic face that is capped by another calcium ion. Thus, the carbon atoms are coordinated by a nearly square pyramid of calcium ions. The double layers built up by calcium ions are interconnected by two crystallographically independent chloride ions. The Cl(1) ion is surrounded by a distorted tetrahedron of calcium ions ($\bar{d}=281.4$ pm) and the Cl(2) ion is coordinated by a strongly distorted octahedron of calcium ions ($\bar{d}=308.4$ pm).

A saltlike charge assignment leads to $(Ca^{2+})_5(Cl^-)_3(C_2^{2-})(BC_2^{5-})$. An indication for the saltlike character of this compound is the transparency of the orange-brown crystals, which are very sensitive to hydrolysis. The deviation of the C-B-C angle of the BC_2^{5-} unit (164.0(7)°) from linearity is very unusual. A linear arrangement would generally be expected for CO_2-like (isoelectronic) ions with 16 electrons, such as C_3^{4-}, CBN^{4-}, BN_2^{3-}, and BC_2^{5-}. The observed bent arrangement of such ions could be caused either by packing effects or by electronic effects.[10] The change of the energy levels and of the molecular orbitals of an isolated CBC fragment have been investigated as a function of the C-B-C angle.[11] The two extreme cases correspond formally to the linear arrangement of the atoms of a CO_2 molecule with 16 and of a bent SO_2 molecule (119°) with 18 valence electrons.

In compounds that contain triatomic anions the bond angle correlates with their charge. The change of the energy levels of an isolated (CBC) ion is shown as a function of its angle in the Walsh diagram in Figure 3. The degeneracy of the π levels vanishes for bent C-B-C arrangements. The change of the "π_g" (HOMO for BC_2^{5-}) and "π_u^*" energy levels (LUMO for BC_2^{5-}) becomes notable when the C-B-C angle deviates from 180°. As the bond angle decreases one of the "π_g" levels becomes more and more antibonding, while one of the other "π_u^*" levels becomes more and more bonding, which basically allows a transition from a 16-electron anion (BC_2^{5-}) to an 18-electron anion (BC_2^{7-}). An evident decrease of the HOMO–LUMO gap of an isolated BC_2^{5-} is observed when the C-B-C angle is smaller than about 160°.

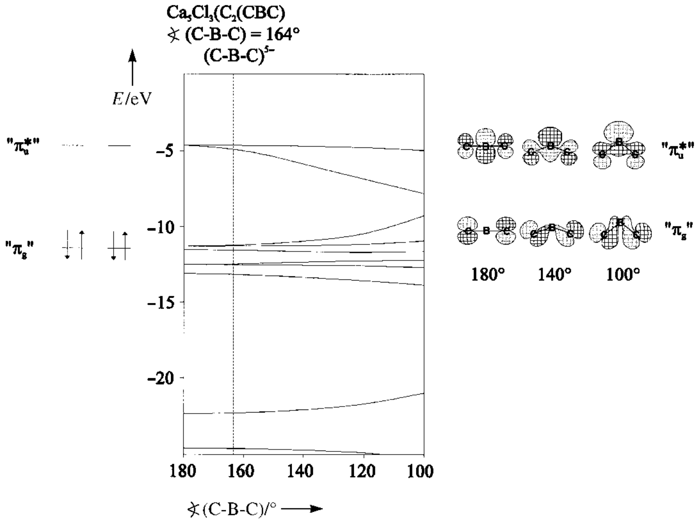

Figure 3. The change of the MO energy levels for an isolated (CBC) unit is shown from a linear (CBC) unit to a bent one (B–C bond length: 144 pm). For a CBC^{5-} ion the "π_g" orbitals and for a CBC^{7-} ion the "π_u^*" orbitals are occupied with two electrons each. Orbital combinations for the C-B-C angles 180°, 140°, and 100° are displayed. The order of the energy levels is given in reference [10].

Covalent d-p(π*) interactions have to be considered, however, in compounds of d or f metals with (CBC) ions. The simultaneous occupation of d-"π_u*" orbital combinations is sometimes regarded as "π* → d backbonding".[12] An analogous bonding behavior with d-p(π*) interactions is known from metal acetylides $Ln^{(3+)}C_2$ of the trivalent lanthanoids (= Ln). In alkaline earth metal acetylides (e.g. CaC_2) the "π*" orbitals are unoccupied which is the reason for the shorter C–C bond lengths compared to $Ln^{(3+)}C_2$.

When d-p(π*) interactions are present in compounds containing d and f metals, ionic charges can hardly be addressed to the di- or triatomic anions. The compound Sc_2BC_2 with linear $(CBC)^{5-}$ ions has been assigned as $(Sc^{3+})_2(BC_2^{5-})(e^-)$.[13] In $La_9Br_6(CBC)_3$ the C-B-C bond angle is 148° and the charges have formally been assigned as $(La^{3+})_9(Br^-)_6(CBC^{7-})_3$.[14] So the bent CBC^{7-} ions are isoelectronic to SO_2 with respect to the valence shell.

The example of $Ca_5Cl_3(C_2)(CBC)$ demonstrates very clearly that the observed C-B-C bond angle of the CBC ion (164.0(7)°, Table 1) is not a reliable proof for its ionic charge. The compound is saltlike (transparent, orange-brown crystal plates) and can be considered as $(Ca^{2+})_5(Cl^-)_3(C_2^{2-})(CBC^{5-})$. A bent C_3^{4-} ion (bond angle: 169°), which is isoelectronic with CBC^{5-}, has already been characterized in the compound $Ca_3Cl_2C_3$. Although the degeneracy of the π levels is broken up by the nonlinearity of such triatomic anions, there is no real change in energy for these levels at bond angles between 180 and 160° (Figure 3). Therefore the nonlinearity of triatomic anions in these saltlike compounds may not be viewed as a consequence of an electronic stabilization but from the dense packed matrix of the ions in the structure.

Table 1. Comparison of compounds containing BC_2 anions.

Compound	∢(C-B-C) [°]	d(B-C) [pm]	Formal charge	Ref.
$(Ca^{2+})_5(Cl^-)_3(C_2^{2-})(BC_2^{5-})$	164.0(7)	143.7(6)	− 5	
$(Al^{3+})_3(C^{4-})(BC_2^{5-})$	180	144	− 5	[15]
$(Sc^{3+})_2(BC_2^{5-})(e^-)$	180	148.4	− 5	[13]
$(La^{3+})_9(Br^-)_6(BC_2^{7-})_3$	148	149	− 7	[14]
$(La^{3+})_9(Br^-)_5(BC_2^{7-})_3(e^-)$	141(3) 151(3)	152(2)/154(2) 151(2)	− 7	[16]

As expected the B–C bond lengths of CBC^{5-} ions in the saltlike compounds $Al_3C(CBC)$[14] and $Ca_5Cl_3(C_2)(CBC)$ are in good agreement (Table 1). For all compounds with partially occupied "π_u^*" orbitals longer B–C distances have been reported (Table 1).

^{13}C MAS NMR investigations on samples of $Ca_5Cl_3(C_2)(CBC)$ gave two signals with isotropic chemical shifts of $\delta = 185(1)$ and $199(1)$ (integration ratio: 1:1.04). The isotropic chemical shift could be assigned based on ^{13}C MAS NMR measurements on MC_2 (M = Ca, Sr, Ba, Table 2). Another indication supporting the assignment is the broadening of the signal base observed at $\delta = 185$. This broadening is due to the B–C coupling.

Raman spectra of single crystals and of powdered samples of $Ca_5Cl_3(C_2)(CBC)$ showed signals at 1885 cm^{-1} and at 1495 cm^{-1}. The first signal was assigned to the symmetric C–C stretching vibration (Table 2).

Experimentals Section

All manipulations were performed under the strict exclusion of oxygen and moisture in an argon-filled glove-box (M. Braun, Garching).

In an experiment to synthesize "$Ca_4Cl_3BC_2$" a few thin, orange-brown, transparent, rectangular platelets of the title compounds were found in the product mixture. $Ca_5Cl_3(C_2)(CBC)$ can be synthesized in quantitative yield by the reaction of stoichiometric amounts of Ca, $CaCl_2$, B, and graphite.

Table 2. Spectroscopic data of alkaline earth metal carbides.

Compound	$\delta(^{13}C)$[a] [ppm]	$\tilde{\nu}_{sym}$[b] [cm^{-1}]
CaC_2	200(5),[17] 206.2,[18] 199(1)[c]	1870[c]
SrC_2	212(3),[17] 213(1)[c]	1847,[18] 1850[c]
BaC_2	229(2),[17] 232,[18] 229(1)[c]	1831[18]
$Ca_5Cl_3(C_2)(CBC)$	185(1) (BC_2^{5-}), 199(1) (C_2^{2-})[c]	1495 (not assigned), 1885 (C_2^{2-})[c]

[a] NMR measurements have been performed with a Bruker MS200 or a Bruker ASX300 at a rotation frequency of 10 kHz. [b] Raman measurements have been performed with a Bruker FT-IR spectrometer IFS66V (FT-Raman module RFA106, Raman microscope, primary light source: 1064 Nd-YAG-Laser, (Adlas)). [c] Own measurements.

The pure compound was synthesized from Ca (280.6 mg, 7 mmol; ABCR, 99.99 %), B (21.7 mg, 2 mmol; ABCR, 99.7 %), graphite (96.1 mg, 8 mmol; Merck, "Reinst", degased for 4 h at 670 K under vacuum conditions) and $CaCl_2$ (333 mg, 3 mmol; Strem, 99.99 %, dried 4 h at 670 K under flowing HCl). The starting materials were heated in arc-welded, silica-jacketed tantalum ampoules at a heating rate of 10 Kh^{-1} to 1170 K and kept for at least four days at this temperature. The oven was cooled down to room temperature at a cooling rate of 10 Kh^{-1} (the obtained products were pure with respect to X-ray powder diffraction, but with ^{13}C MAS NMR and Raman spectroscopy traces of $Ca_3Cl_2C_3$ were detected). A single crystal obtained by the described method was chosen under a microscope in a glove-box and sealed in a Mark capillary.

A sample of $Ca_5Cl_3(C_2)(CBC)$ for the ^{13}C MAS NMR spectroscopy was synthesized by the same route, but approximately 10 % of the employed graphite was substituted by ^{13}C (99 %, amorphous, Chemotrade).

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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-406847.

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Self-Assembling Sieves[**]

Tomas Szabo, Brendan M. O'Leary, and
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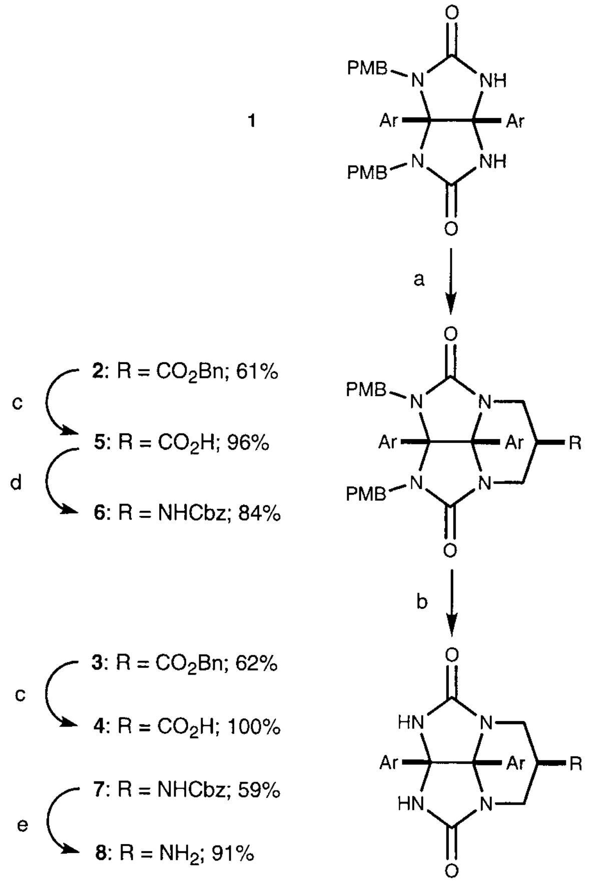
"Molecule within molecule"[1] complexes have been useful in stabilizing reactive intermediates,[2] defining new forms of stereoisomerism,[3] and accelerating Diels–Alder reactions.[4] Other applications await the availability of diverse sizes and shapes for selective and reversible encapsulation. We describe here a modular approach that gives access to some of the largest hydrogen-bonded capsules (≈0.5 nm^3) reported to date. These modules promise versatility in the assembly of many new structures using diverse molecular scaffolds.

The modules are based on the glycoluril system, a structure that provides both molecular curvature and a richness of hydrogen-bonding sites (Scheme 1). Alkylation of the unprotected face of **1**[5] with benzyl 2-(bromomethyl)acrylate[6] gives the tricyclic structure **2** featuring the equatorial ester as the major product. The fused six-membered ring contributes to the overall rigidity of the glycoluril unit and offers an attachment point for coupling to appropriate spacer units. Two deprotection steps then yield acid module **4**, suitable for condensation with amine- or alcohol-bearing spacers. Alternatively, subjecting acid **5** to a modified Curtius rearrangement[7] followed by deprotection affords amine module **8** for use with spacers containing carboxylic or sulfonic acids.



Scheme 1. Synthesis of glycoluril building blocks **4** and **8**. a) Benzyl 2-(bromomethyl)acrylate, Cs_2CO_3, MeCN, reflux, 3 h; b) CAN, MeCN/H_2O (5/1), RT, 24 h; c) H_2, Pd/C, EtOH, 3 h; d) DPPA, PhMe, RT, 30 min; then BnOH, reflux, 2 h; e) H_2, Pd/C, EtOH/EtOAc/AcOH (49/49/2), 3 h. Ar = 4-*n*-heptylphenyl, PMB = 4-methoxybenzyl, Cbz = phenylmethoxycarbonyl; CAN = ceric ammonium nitrate, DPPA = diphenylphosphoryl azide.

Our initial efforts focused on D_{3d}-symmetric capsules assembled through a seam of twelve hydrogen bonds. The hexa-substituted spacers **9**[8] and **10**[9] (Scheme 2) were expected to provide a geared arrangement[10] of substituents around the benzene ring and present all three modules on one side of the spacer. Condensation of triamine **9** with acid module **4** gave monomer **11** in 68% yield, while coupling triacid **10** with amine module **8** gave a 49% yield of monomer **12**, differing from **11** only by the "direction" of the amide linkage.[11]

Both systems gave tell-tale signs of exclusive dimerization as indicated by far downfield shifts for the glycoluril N–H resonances and sharp, first-order signals for the remaining

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