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Ca₁₁N₆(CN)₂ and Ca₄N₂(CN)₂: The True Nature of an “Unusual Binary Nitride” Is Finally Revealed**

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The compound reported in the literature as the “electron deficient, binary nitride Ca₁₁N₈” has been an object of discussion for many years.^[1] Both its electronic and crystal structure are not yet fully understood. The only reported structure determination of “Ca₁₁N₈” is based solely on X-ray crystallographic methods.^[1] Because of their similar X-ray scattering factors, boron, carbon, nitrogen, and oxygen are often hard to distinguish with X-ray methods. It has been suggested^[2] an oxygen contamination during the reaction led to the ionic compound (Ca²⁺)₁₁(N³⁻)₆(O²⁻)₂ and the net electrical neutrality simplifies the electronic situation. However, this model requires an unusual coordination sphere for one of the nitrogen atoms. The average Ca–N interatomic distance in “Ca₁₁N₈” is 248 pm for N1 (numbering after ref. [1]) and 242 pm for N2 (both in a distorted octahedral environment), but 263 pm (two 250 pm bonds and one 290 pm bond) for N3 (247 pm with coordination number six in Ca₃N₂^[3]). For this unusual nitrogen (or oxygen) coordination

sphere, or for the even more exceptional electron-deficient binary nitride, no satisfying explanation had been found yet.

While we were pursuing research in the ternary system Ca–Cu–N, a reaction of Ca₃N₂, Cu₃N, and NaN₃ in a stainless steel ampoule yielded metallic copper and two different kinds of crystals. Both crystals appeared as very fine needles, one being a yellow-green color and transparent, the other being dark red, nearly black, but also transparent if intensely illuminated. Both crystals are air and moisture sensitive.

Single crystal X-ray structure analysis showed surprising results.^[4] The crystal structure of the dark-red crystals has a striking resemblance to the one reported for “Ca₁₁N₈”. The crystallographic data (*P*4₂*nm* (No. 102), *a* = 1445(2) pm, and *c* = 360(1) pm for “Ca₁₁N₈”, compared to *P*4₂*mm* (No. 136), *a* = 1452.3(2) pm, and *c* = 360.83(4) pm for the dark-red crystals) and the coordinates of almost all atoms of “Ca₁₁N₈” and our compound are closely related to each other (see Figure 1). The only difference (except the missing mirror plane ⊥ *c* in “Ca₁₁N₈”) is, instead of the single (and already under doubt) nitrogen atom on the N3 position of “Ca₁₁N₈”, our data showed a triatomic unit with three crystallographically independent sites. Refinements with nitrogen atoms on all three sites showed a very large atomic displacement factor for the middle nitrogen atom. Refining a carbon atom for this position instead of a nitrogen atom decreased both *R* values

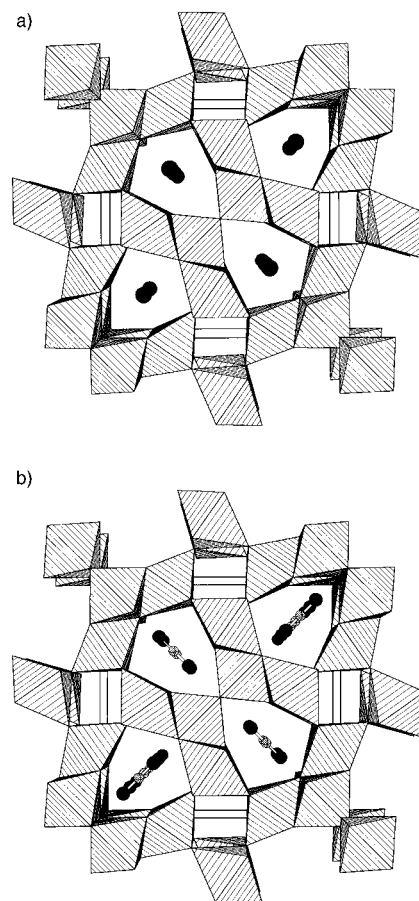


Figure 1. Comparison of the structures of a) “Ca₁₁N₈” and b) **1**. The views parallel to the *c* axes are shown. The distorted Ca₆N octahedra are displayed as hatched polyhedra, nitrogen atoms as black circles, carbon atoms as gray spheres.

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significantly ($\approx 0.5\%$), the thermal displacement factors became reasonable, and the bond angle and the bond distances were in a range known for cyanamide ions (Table 1). Instead of “ Ca_{11}N_8 ”, we found the red crystals to be $\text{Ca}_{11}\text{N}_6(\text{CN}_2)_2$ (**1**).

Table 1. Spectroscopic^[a, b] and X-ray data of alkaline earth cyanamides.

Compound	$\tilde{\nu}_s$ [cm ⁻¹]	$\tilde{\nu}_{as}$ [cm ⁻¹]	δ [cm ⁻¹]	$d(\text{C}=\text{N})$ [pm]	\angle [°]	Ref.
MgCN ₂	1301	2114	681	124.8(2)	180.00(8)	[5]
CaCN ₂	—	—	—	122.4(16)	180	[6]
SrCN ₂	1251	1989	663	122.8(10)	178.8(9)	[5]
		2023	677	122.2(11)		
BaCN ₂	1238	1947	662	119.2(11)	177.2(18)	[5]
			673			
CaCN ₂ ^[c]	1271	2033	670	—	—	
1 , $\text{Ca}_{11}\text{N}_6(\text{CN}_2)_2$	1263	2008	652	119.3(24)	180.0(14)	own data
			646	123.8(24)		
2 , $\text{Ca}_4\text{N}_2(\text{CN}_2)_2$	1228	1988	672	121.9(12)	179.7(10)	
			647	124.1(13)		

[a] Raman measurements were performed on powdered samples (CaCN_2 and **2**) and on selected crystals (**1**) with a Dilor spectrometer (Aerotech, HeNe laser of $\lambda = 632.8$ nm). All samples sealed airtight in thin-walled glass capillaries. [b] IR measurements were performed with a Mattson Polaris FT-IR spectrometer (KBr pellets). [c] CaCN_2 has been prepared by the reaction of Ca_3N_2 , C, and NaN_3 in silica-jacketed niobium ampoules at 1200 K (1 d.). The X-ray powder diagram could be indexed on the base of the reported^[6] rhombohedral structure (hexagonal, $a = 369.5(1)$ and $c = 1476.7(5)$ pm).

The yellow-green crystals turned out to be the structurally related compound $\text{Ca}_4\text{N}_2(\text{CN}_2)_2$ (**2**, Figure 2), in which a slightly different combination of the same structural elements

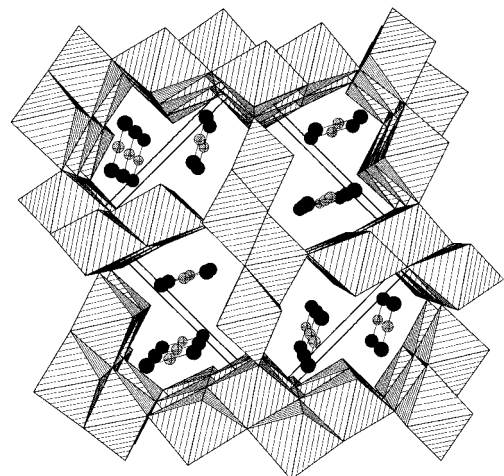


Figure 2. The structure of **2**. A view parallel to the b axis is shown. The distorted Ca_4N octahedra are displayed as hatched polyhedra, nitrogen atoms are displayed as black circles, carbon atoms as gray spheres.

occur as in **1**. Both compounds can be described as open three-dimensional frameworks formed by linking distorted NCa_6 octahedra through shared edges and corners. The CN_2^{2-} guest species are hosted in channels along $[001]$ in **1** and along $[010]$ in **2**.

To confirm the structures obtained by X-ray crystallographic methods, we pursued further experiments. Syntheses

repeated with carbon (as graphite) added in stoichiometric amounts led to high yields ($> 90\%$) of both compounds. With samples obtained this way we confirmed the single crystal data (through single crystal X-ray structure analysis), the unit cell dimensions (by means of indexing the X-ray powder patterns), and the nature of the triatomic unit (through Raman and IR measurements, Table 1). Compounds **1** and **2** can be considered as ionic compounds formulated as $(\text{Ca}^{2+})_{11}(\text{N}^{3-})_6(\text{CN}_2^{2-})_2$ and $(\text{Ca}^{2+})_4(\text{N}^{3-})_2(\text{CN}_2^{2-})$, respectively, as indicated by the bonding distances and angles of their CN_2^{2-} ions.

Some questions remain. One question asks how did we (or Laurent et al.^[1]) incorporate the carbon into the reactions that first yielded the compounds? The most probable explanation is that carbon leached out of the reaction container. Repeated reactions in niobium (instead of stainless steel) ampoules with the same batch of starting materials did not produce either of the two compounds described above. Another question concerns the nature of “ Ca_{11}N_8 ”. The most simple explanation is very often the best, and sometimes even the correct explanation. We feel confident that the most simple explanation, backed up by X-ray and spectroscopic data, is that “ Ca_{11}N_8 ” really is $\text{Ca}_{11}\text{N}_6(\text{CN}_2)_2$.^[7]

Experimental Section

All reagents and reaction containers were handled in a glove box under dry Ar. All reactions were performed with about 0.5 g educt mass, and all syntheses took place at 1300 K (2 d) and the heating and cooling rates were 100 K h^{-1} .

Single crystals of both compounds have first been obtained by the reaction of equimolar amounts of Ca_3N_2 (Ca: Strem, 99.99%, crystalline, dendritic; treated with dry, flowing N_2 at 1300 K for 8 h; product purity checked by its X-ray powder pattern), Cu_3N (Alfa, 99.5%), and NaN_3 (Aldrich, 99%; kept for two days at 400 K before use) in a silica jacketed, cleaned stainless steel ampoule.

Bulk material and single crystals suitable for X-ray analysis were obtained by the reaction of appropriate amounts of Ca_3N_2 , C (Strem, 99.999%, graphite powder; degassed for one day at 700 K under dynamic vacuum) and NaN_3 in cleaned, arc-welded silica-jacketed Nb container (Plansee, Germany, 99.99%). The excess sodium can be removed by vacuum sublimation at 600 K or by washing with liquid, anhydrous ammonia. Microcrystalline materials were also obtained by the reaction of appropriate amounts of Ca_3N_2 and C in alumina boats under a flow of dry N_2 .

Samples of **1** always contained traces of **2**, and vice versa for samples of **2**. Additionally some Ca_3N_2 was identified as an impurity (the impurities were identified by their X-ray powder patterns or by their Raman or IR spectra).

Ca and C were found by microprobe analysis (JEOL 8900, standardless, qualitative mode) of single crystals and of bulk material of both compounds.

On all samples of **2**, Raman and IR spectroscopy confirmed the presence of CN_2^{2-} . IR spectra of **1** are easily observed, but the Raman measurements worked only moderately well, probably due to the strong absorbance of the material, as indicated by its dark red color.

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[4] Crystal structure analysis data: **1**: Dark red needles; $0.01 \times 0.01 \times 0.15$ mm³; tetragonal; $P4_2/mmm$ (No. 136); $Z=2$; $T=293(2)$ K; $a=1452.32(16)$, $c=360.83(6)$ pm (powder data: $a=1452.9(2)$, $c=360.9(1)$ pm); $V=761.1 \times 10^6$ pm³; $2\theta_{\max}=44^\circ$, $\text{MoK}\alpha$ ($\lambda=71.073$ pm); graphite monochromator, Bruker Smart CCD (ω -scan); 1777 measured reflections, 292 reflections unique; $R_{\text{int}}=0.099$; LP correction; no other absorption correction applied; SHELXTL-5.03 (structure solution: direct methods; structure refinement: full-matrix least-squares on $|F^2|$); 39 parameters (all atoms refined anisotropically except N4 and C); max./min. residual electron density: $0.77/-0.73$ e Å⁻³; $R1=0.061/0.088$, $wR2=0.123/0.136$, $\text{GooF}=1.21/1.16$ (for $233 F_o > 4\sigma(F_o)$ /all 292 unique reflections). **2**: Yellow-green transparent needles; $0.03 \times 0.03 \times 0.15$ mm³; orthorhombic; $Pnma$ (No. 62); $Z=4$; $T=293(2)$ K; $a=1143.9(2)$, $b=357.72(7)$, $c=1384.4(3)$ pm (powder data: $a=1145.8(2)$, $b=358.5(1)$, $c=1386.4(3)$ pm); $V=566.5 \times 10^6$ pm³; $2\theta_{\max}=46.7^\circ$, $\text{MoK}\alpha$ ($\lambda=71.073$ pm); graphite monochromator, Bruker Smart CCD (ω -scan); 2271 measured reflections, 478 unique reflections; $R_{\text{int}}=0.085$; LP correction; no other absorption correction applied; SHELXTL-5.03 (structure solution: direct methods; structure refinement: full-matrix least-squares on F^2); 47 parameters (all atoms except C refined anisotropically); max./min. residual electron density: $0.88/-0.72$ e Å⁻³, $R1=0.056/0.085$, $wR2=0.115/0.126$, $\text{GooF}=1.23/1.12$ (for $344 F_o > 4\sigma(F_o)$ /all 478 unique reflections). Further details of the crystal structure investigations may 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 numbers CSD-410825 (Ca₄N₂(CN₂)) and CSD-410862 (Ca₁₁N₆(CN₂)).

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“Amphiphilic” Cleavage of γ -Stannyl Ketones with ATPH/RLi: Application to Enone Fragmentation by the Conjugate Addition–Cleavage Sequence**

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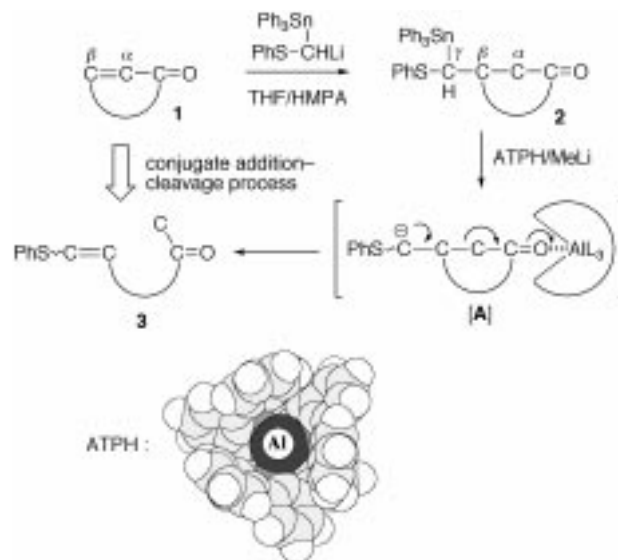
Despite the availability of many carbon–carbon bond forming reactions, including ring closures in organic synthesis, less attention has been paid so far to the corresponding reverse processes, that is, the selective ring cleavage of carbon–carbon bonds.^[1,2] Although it is not of synthetic importance, the McLafferty rearrangement of the C_α – C_β bond of aliphatic carbonyl compounds, as determined by mass spectrometry, is a typical example of such a reaction.^[3]

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The previously known ring-cleavage reactions can be divided into two classes depending on the mode of activation.^[1] Most involve base- or acid-promoted fragmentation by activating either electrofugal or nucleofugal moieties, respectively.^[4] The other, less general type of fragmentation is realized by the intramolecular push–pull effect of the electrofugal and nucleofugal parts,^[2c] as exemplified by retro-aldol reactions.

Here we report a conceptually new, “amphiphilic” cleavage reaction of the C_α – C_β bonds of γ -stannyl ketones **2**, leading to compounds of type **3** (Scheme 1). In combination with the



Scheme 1. Conjugate addition and amphiphilic cleavage of enone **1** with ATPH/MeLi leading to ketone **3**. L = 2,6-diphenylphenoxy.

conjugate addition of α -stannyl carbanion to enone **1**, this approach constitutes a novel two-step conjugate addition–cleavage sequence. The new fragmentation is interpretable as the nucleophilic attack of the electrofugal carbanion part to an electrophilically activated carbonyl moiety (in this respect, “amphiphilic” means electrophilically activated nucleophilic), and it should be categorized into a third, yet unexplored class of fragmentation. The success of this amphiphilic cleavage highly relies on the effective use of a combined Lewis acid/base system consisting of aluminum tris(2,6-diphenylphenoxy) (ATPH) and MeLi,^[5] thereby allowing the appropriate push–pull relay of the electrofugal and nucleofugal moieties in the key intermediate [A].

The requisite conjugate adduct, 3-[triphenylstannyl(phenylsulfanyl)methyl]cyclohexanone (**4**) can be readily prepared by treatment of cyclohexenone with triphenylstannyl(phenylsulfanyl)methyl lithium—generated from triphenylstannyl(phenylsulfanyl)methane with lithium diisopropylamide (LDA) in THF^[6]—in the presence of hexamethyl phosphoramide (HMPA) at -78°C . Complexation of **4** with ATPH (1.1 equiv) in toluene/diethyl ether at -78°C and subsequent addition of MeLi (3 equiv) afforded cleanly 7-phenylsulfanyl-6-hepten-2-one (**5**) as a product of C_α – C_β bond cleavage in 96% yield ($Z:E=1.3:1$; Table 1, entry 1). The push–pull effect of γ -lithio ketones by complexation with Lewis acidic ATPH is crucial for effecting the smooth C_α – C_β