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Development of Metal Cyanurates: The Example of Barium Cyanurate (BCY)

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Metal cyanurate compounds were prepared by means of solid-state metathesis reactions between a metal halide and an alkali cyanurate. Following this procedure, a mixture of $BaCl_2$ and K(OCN) was heated in a fused silica tube at 575 °C to yield highly crystalline barium cyanurate. This reaction was analyzed by differential scanning calorimetry (DSC) measurements and involves a cyclotrimerization of cyanate ions to yield the cyclic cyanurate $(O_3C_3N_3)^{3-}$ ion. The crystal structure of $Ba_3(O_3C_3N_3)_2$ was refined by single-crystal X-ray diffraction, and the presence of cyanurate was verified by infrared spectroscopy.

Introduction

The discovery of new fields in chemistry is a great opportunity to satisfy the growing demand for new high-performance materials. For this goal, new research strategies and synthetic methods are needed. One consideration for the development of new compounds is the employment of diverse anions. On this basis, compounds with complex anions such as $[NBN]^{3-}$, $[NCN]^{2-}$, and $[OCN]^{-}$ have been prepared in our laboratory over the past few years. Most of these compounds were synthesized by solid-state metathesis (SSM) reactions.[1] A quite large number of boronitride (nitridoborate) compounds have been developed, including the dinitridoborate ion.[2] Unfortunately, many of them behave hygroscopically and require handling under an inert gas, although there are some interesting exceptions.

Many new inorganic carbodiimide (or cyanamide) compounds have been developed over the past decade.[3,4] Several of them are stable compounds and exhibit some exciting optical[4,5] and magnetic[6] properties. The dominant method of synthesis for most of these compounds has been SSM reactions.

This new or modified type of SSM reaction involves a soft ignition that propagates through the sample. This stage is supposed to involve the metathesis, which usually produces an X-ray-amorphous product plus the crystalline metathesis salt. A crystalline product is obtained after further heating by crystallization from a melt.[7] This type of reaction is different to the well-known highly exothermic SSM reaction that has been reported for the preparation of many nitride, carbide, or boride compounds, but fails for the preparation of thermally labile compounds.

Hence, moderate or less exothermic SSM reactions offer perspectives for the preparation of thermally labile compounds that are usually not accessible by classical solid-state reactions. After this method was successfully employed for preparations of boronitride and carbodiimide (cyanamide) compounds, its potential was recently demonstrated again in the attempt to prepare new cyanate or cyanurate compounds.

Cyanurates have been reported in the literature for more than one hundred years;[8,9] however, no such compound has been structurally characterized until $LiSr(O_3C_3N_3)$ and $Li_3Sr_2F(O_3C_3N_3)_2$ were reported very recently.[10] Both compounds were prepared by treating Li(OCN) with SrX_2 (X = Cl, F). On this basis, more cyanurate compounds would seem to be accessible in a straightforward manner.

In this work we describe the preparation, formation reaction, crystal structure, and electronic structure of barium cyanurate (BCY).

Results and Discussion

Synthesis

Inorganic cyanurates have been under discussion for decades but no example has been structurally verified until recently. It is clear that cyanurate may be either prepared by trimerization of $(OCN)^{-}$ ions, which is well-known in organic chemistry,[9] or from the trianion of cyanuric acid, which appears to be difficult to prepare, as has been shown in the past.[8,11]

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Our preparations were guided by the employment of SSM reactions in which a reactive alkali cyanurate is combined with a metal halide. Previously, the employment of Li(OCN) and $SrCl_2$ (and SrF_2) have yielded $LiSr(O_3C_3N_3)$ and $Li_3Sr_2F(O_3C_3N_3)_2$. From these reactions it became clear to us that the employment of Li(OCN) is limited, because it shows decomposition effects above 475 °C with the formation of carbonate as a decomposition product.[12] Therefore, we decided to explore the usage of K(OCN). A thermoanalytic study of K(OCN) performed in a differential thermal analysis (DTA) apparatus revealed a congruent melting at 329 °C upon heating (with a rate or 2 $K\,min^{-1}$). The melt remained stable at least up to 525 °C (Figure 1). Recrystallization upon cooling was observed at 329 °C. Hence, K(OCN) showed sufficiently good performance – even better than Li(OCN) – for employment in SSM reactions. K(OCN) was fully preserved after the DTA run as could be shown by powder XRD, which revealed no decomposition products.

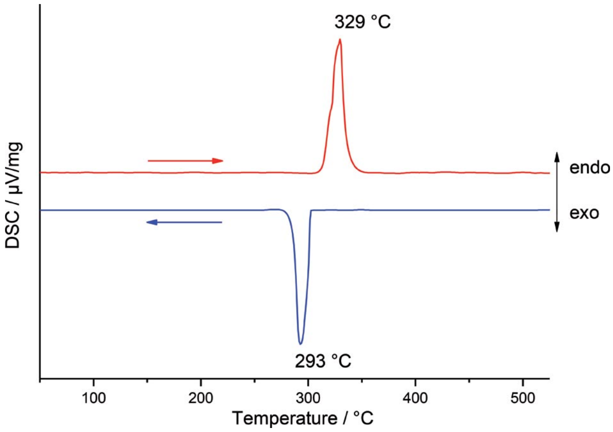

Figure 1. Differential thermal analysis of K(OCN) with melting (329 °C) and recrystallization (293 °C) peaks.

Thermal Analysis

The synthesis of BCY was performed by SSM reaction between $BaCl_2$ and K(OCN) in the molar ration 1:2 at 575 °C. The reaction is described by Equation (1). An excess of K(OCN) is advantageous to provide a flux medium in the reaction mixture, hence lowering the melting point of the mixture as well as facilitating the crystallization of the product. The formation reaction involves a cyclotrimerization of cyanate ions yielding cyanurate ions.

$$3\,BaCl_2 + 6\,K(OCN) \rightarrow Ba_3(O_3C_3N_3)_2 + 6\,KCl \tag{1}$$

We note here that an alternate description of reaction equivalents of $BaCl_2$ and 2 K(OCN) could be given to yield $Ba(OCN)_2$. However, we prefer the formula $Ba_3(O_3C_3N_3)_2$ to express the presence of cyanurate ions in the structure, in contrast to the yet unknown barium cyanate $[Ba(OCN)_2]$.[13]

The reaction given in Equation (1) was performed with a quantitative conversion rate, as indicated by powder XRD analysis displayed in Figure 2, and produced a highly crystalline product that was stable in air but started to decompose when treated with water. Single crystals were selected for an XRD crystal structure refinement. A comparison of the observed XRD powder pattern and a theoretical pattern calculated from single-crystal X-ray data is shown in Figure 2.

The course of the reaction between $BaCl_2$ and K(OCN) in a 1:3 molar ratio was investigated by thermal studies. Since K(OCN) melts near 329 °C, it appeared likely that it acted not only as a reactant but also as a melt flux. According to a differential scanning calorimetry (DSC) study, the reaction in Equation (1) readily proceeds in a small tem-

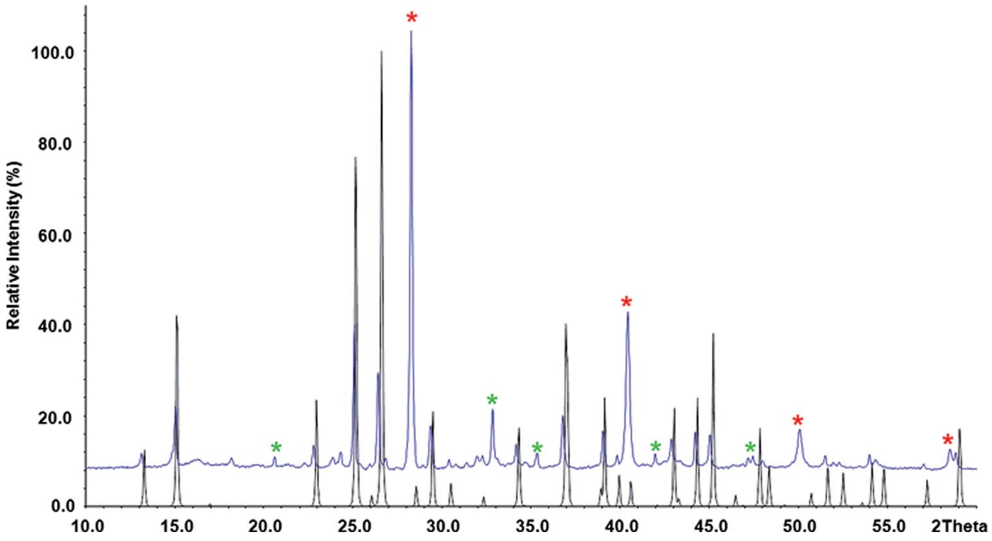

Figure 2. Observed powder pattern of $Ba_3(O_3C_3N_3)_2$ (blue) in comparison to the theoretical pattern calculated from single-crystal X-ray data (black). The stars mark reflections due to an excess amount of K(OCN) (green, PDF [8-471]) used in the reaction, and the metathesis salt KCl (red, PDF [41-1476]).

perature interval between 284 and 295 °C (Figure 3). The reaction can be assumed to be initiated by a coincidence of an exothermic ignition of the reaction and the melting of K(OCN). This is displayed in Figure 3 with the exothermic effect (Figure 3, peak 1; 284 °C onset, 315 °C offset) due to the ignition of the metathesis, which is superimposed by an endothermic effect (Figure 3, peak 2; 295 °C) caused by the melting of the mixture of starting materials. During this process the cyclotrimerization of cyanate ions into cyanurate is expected to take place before an endothermic effect in the DSC (Figure 3, peak 3; 338 °C) indicates the melting of the product mixture. Upon cooling, two exothermic effects represent the recrystallization of the reaction products (Figure 3, peak 4; 303 °C) and a mixture of K(OCN) and KCl (Figure 3, peak 5; 259 °C).

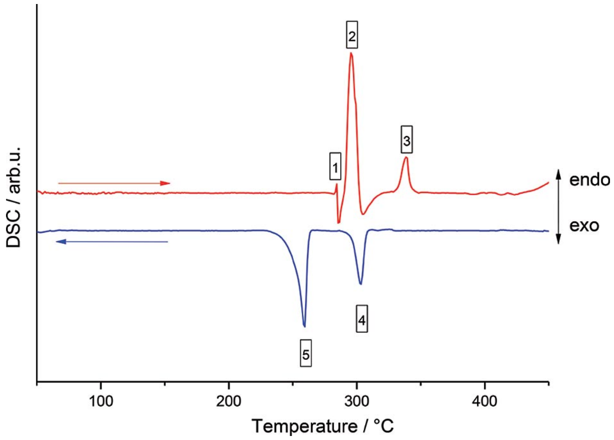

Figure 3. DSC of a 1:3 molar mixture of $BaCl_2$ and K(OCN).

The occurrence of the cyanate cyclotrimerization was investigated in more detail by interrupting the reaction just at the temperature observed for the exothermic ignition. At this stage SSM reactions (e.g., of carbodiimides) have always shown X-ray-amorphous products plus the metathesis salt,[7] and until now there has been no structural proof of the identity of a product that has been formed in the exothermic process. Hence, the trimerization reaction of $(OCN)^-$ can be studied in more detail on the basis of the DSC measurements. For this purpose, a (1:3 molar) sample mixture of $BaCl_2$ and K(OCN) was heated to 300 °C (heating rate 2 K min^{-1}) and then rapidly cooled. An infrared spectrum was recorded on this sample at room temperature. The vibration bands can be clearly assigned to stretching vibrations $\nu(C_3N_3)$ as well as bending vibrations $\delta(C_3N_3)$ characteristic of the cyanurate ion. These vibrations appeared to be similar to those of BCY samples that were prepared according to the reaction in Equation (1).

Crystal Structure

$Ba_3(O_3C_3N_3)_2$ (BCY) crystallizes in the trigonal space group $R\bar{3}c$ with six formula units (Table 4) and is isotypic with the structure of α-$Ba(B_2O_4)$, which contains the cyclic $(B_3O_6)^{3-}$ ion with three exocyclic oxygen atoms.[14] The crystal structure of BCY contains a cyanurate ion (Figure 4) that occupies general positions with its O, C, and N atoms (Table 1). The cyanurate ring is almost planar and shows an average angle between three adjacent atoms of 119.1°, which matches quite well with the corresponding angle reported for cyanuric acid (122.42°). The relatively large torsion angle of 3.88° (compared to 0.39° in cyanuric acid) might be caused by matrix effects.

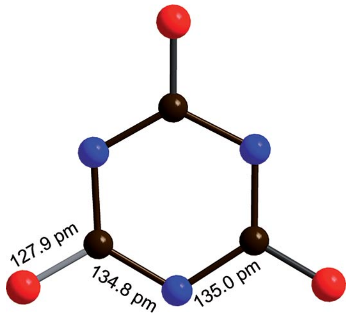

Figure 4. Cyanurate ion of BCY.

Table 1. Atom positions and isotropic displacement parameters [pm^2 × 10^{-1}] of $Ba_3(O_3C_3N_3)_2$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{eq}[a]
Ba1	12c	0	0	0.3511(1)	25(1)
Ba2	6a	0	0	1/4	27(1)
O1	36f	0.3976(8)	0.0707(8)	0.0370(1)	46(1)
N1	36f	0.1753(1)	0.2095(1)	0.0393(2)	36(1)
C1	36f	0.9669(1)	0.1680(1)	0.0388(2)	31(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. All atoms occupy 18b sites.

The average C–N bond length in the cyanurate ion of BCY (135 pm) is only slightly shorter than the one reported for solid cyanuric acid (136 pm), in which three hydrogen atoms are located at the nitrogen atoms. Both bond lengths are relatively close to the value expected for a C–N double bond (130 pm) rather than for a C–N single bond (147 pm). The average C–O bond in BCY [127.9(8) pm] is longer than the value found in solid cyanuric acid (121 pm), which is close to the expected value for a C–O double bond (122 pm) (Figure 4).[15] Terminal oxygen atoms in the structure of BCY play a dominant role in the connectivity with surrounding cations, as will be shown later.

These findings suggest that the three negative charges of the cyanurate ion are partially located on the terminal oxygen atoms, but some delocalization of negative charge throughout the ring can be assumed.

The $(O_3C_3N_3)^{3-}$ ring, displayed in Figure 4 is located perpendicular to the threefold rotation axis. The presence of this large planar ion introduces a layered character into the crystal structure (Figure 5).

The in-plane arrangement of cyanurate ions follows the motif of a closest-packed layer, as displayed in Figure 6, with barium ions situated above and below.

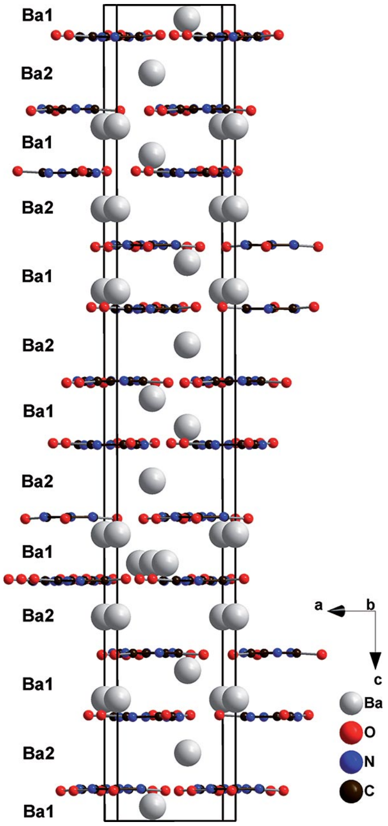

Figure 5. Unit cell of $Ba_3(O_3C_3N_3)_2$ projected along the *b* axis emphasizing the alternating sequence of Ba1 and Ba2 ions along the *c* axis.

A sequence of twelve identical cyanurate layers that are shifted differently within the *ab* plane makes up for the long *c* axis of the unit cell. Barium ions occupy two distinct positions in the structure of BCY. They alternate in interlayer spaces created by the arrangement of cyanurate ions (Figure 5). Both barium ions have sixfold coordination environments with oxygen atoms of six surrounding cyanurate ions. Ba1 is situated on a threefold axis that has a distorted trigonal-antiprismatic environment with two distinct Ba1–O distances at 276.8(5) pm (3×) and 288.2(5) pm (3×) (Table 2). Moreover, there are three nitrogen contacts [d_{N1-Ba1} = 297.1(6) pm] that may be included in the coordination environment to result in a ninefold coordination for Ba1. Ba2 is situated on a threefold inversion axis, surrounded in a trigonal-prismatic fashion by six oxygen atoms with Ba2–O distances of 264.0(5) pm (6×), as shown in Figure 7.

Table 2. Selected bond lengths [pm], multiplicities (*n*×), and angles [°] in the structure of $Ba_3(O_3C_3N_3)_2$.

Ba1–O1	276.8(5) (3×), 288.2(5) (3×)
Ba2–O1	264.0(5) (6×)
Ba1–N1	297.1(6) (3×)
O1–C1	127.9(8)
C1–N1	134.8(1), 1.35(1)
C1–N1–C1	115.9(6)
N1–C1–N1	124.1(6)
O1–C1–N1	116.4(7), 119.6(7)

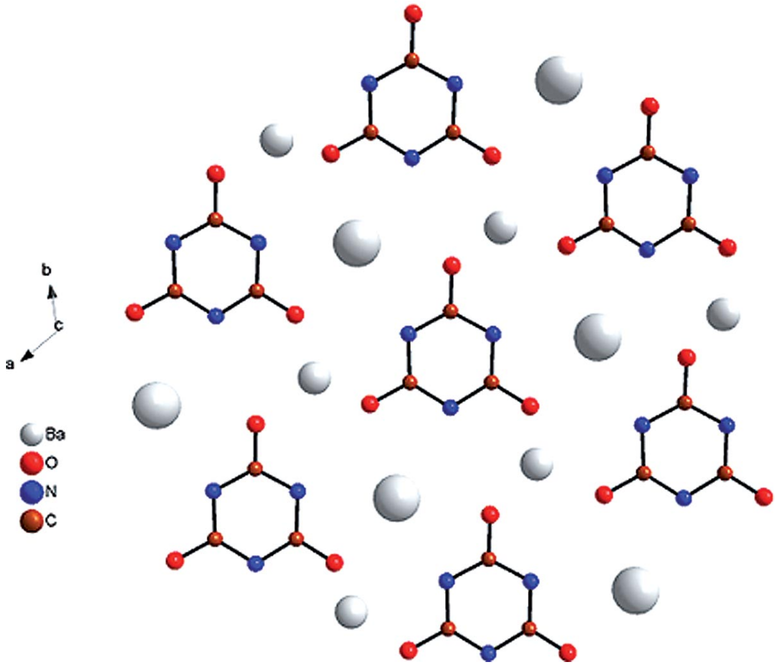

Figure 6. Motif of a closest-packed layer of $(O_3C_3N_3)^{3-}$ ions in the structure of $Ba_3(O_3C_3N_3)_2$ with barium ions above (large gray) and below (small gray) the layer.

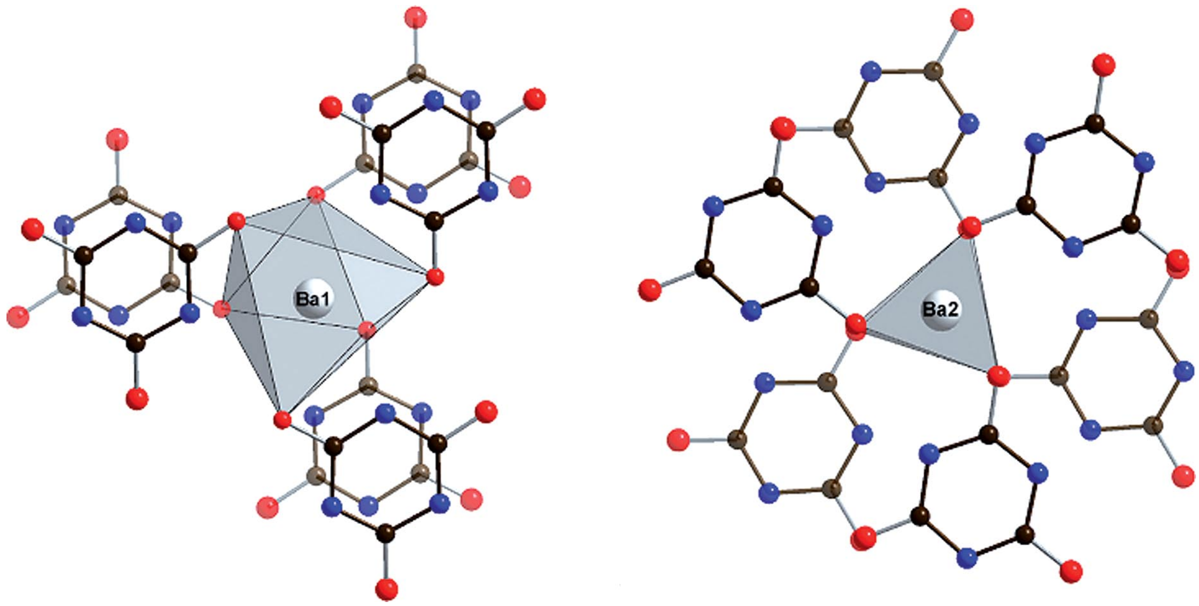

Figure 7. Perspective view of the structure of $Ba_3(O_3C_3N_3)_2$ showing the sixfold coordination environment of barium ions by oxygen atoms. Ba1 (left) exhibits a trigonal-antiprismatic environment, and Ba2 (right) is coordinated in a trigonal-prismatic manner.

MO Calculations

The cyanurate ion corresponds to a minimum of D_{3h} symmetry at the BBLYP/6-311+G* level of theory with C–N distances of 136.7 pm and C–O distances of 128.1 pm. Computation of the harmonic vibrational frequencies gives a very strong band at 1394 cm^{-1} (E′, I = 7428 $km\,mol^{-1}$) and weaker ones at 1408 cm^{-1} (E′, I = 454 $km\,mol^{-1}$) and 1128 cm^{-1} (E′, I = 65 $km\,mol^{-1}$) that correspond to CN stretching vibrations $\nu(C_3N_3)$. The out-of-plane bending vibration $\delta_{oop}(C_3N_3)$ is at 833 cm^{-1} (A_2'', I = 129 $km\,mol^{-1}$), whereas the in-plane bending vibration $\delta_{ip}(C_3N_3)$ is at 574 cm^{-1} (E′, I = 47 $km\,mol^{-1}$).

The electronic configuration involves six occupied π orbitals that result from the bonding and antibonding combination of the three p lone pairs of the oxygen atoms and the three π orbitals of the heterocycle (see Figures 8 and 9).

A set of degenerate π orbitals (π_5 and π_6) are the highest occupied molecular orbitals (HOMO). These have one nodal plane that bisects the six-membered ring and an antibonding interaction with the O(p) orbitals.

The corresponding MOs with a bonding interaction between the ring π orbitals and the O(p) orbitals are lower in energy (π_2 and π_3). In addition, there is one π orbital (π_1) without a nodal plane and small coefficients of O(p), whereas the antibonding combination of the ring π orbital and the in-phase O(p) comprises π_4 (see Figures 8 and 9).

These MOs resemble those of benzene, but include in addition contributions of the π lone pairs of the oxygen atoms. Natural population analysis[16] arrives at a charge of –0.89 on O, –0.83 on N, and +0.72 on C.

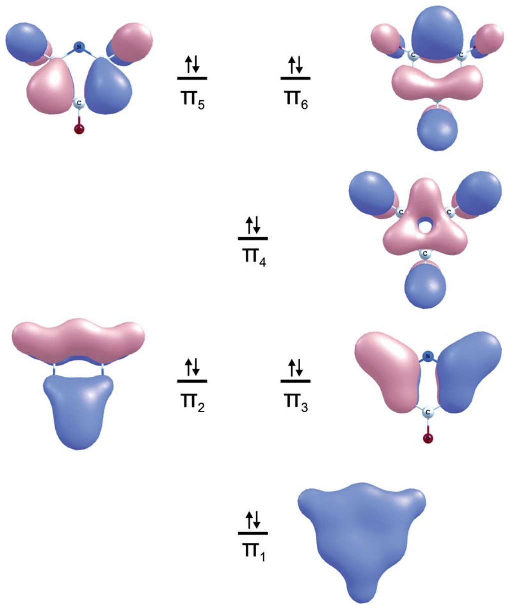

Figure 8. The π molecular orbitals of the cyanurate anion as computed at the B3LYP/6-311+G* level of theory.

Infrared Spectroscopy

An infrared spectrum of BCY was recorded between 4000 and 400 cm^{-1}. Stretching vibrations $\nu(C_3N_3)$ are to be found between 1060 and 1411 cm^{-1}; bending vibrations $\delta_{oop}(C_3N_3)$ are at 830–860 cm^{-1} and $\delta_{ip}(C_3N_3)$ at 590 cm^{-1}.[9,17] Some vibration bands corresponding to the $(OCN)^-$ ion are also present in the spectrum owing to the

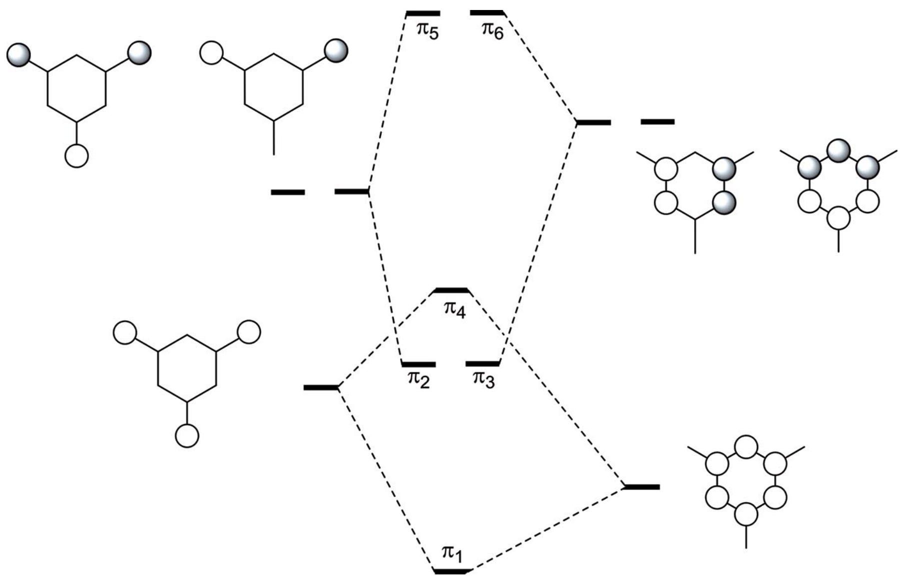

Figure 9. Schematic orbital interaction diagram of the cyanurate anion (not drawn to scale).

excess amount of K(OCN) used in the reaction. The fingerprint region of the IR spectrum of $Ba_3(O_3C_3N_3)_2$ is displayed in Figure 10; the assignment of the vibrational bands is shown in Table 3.

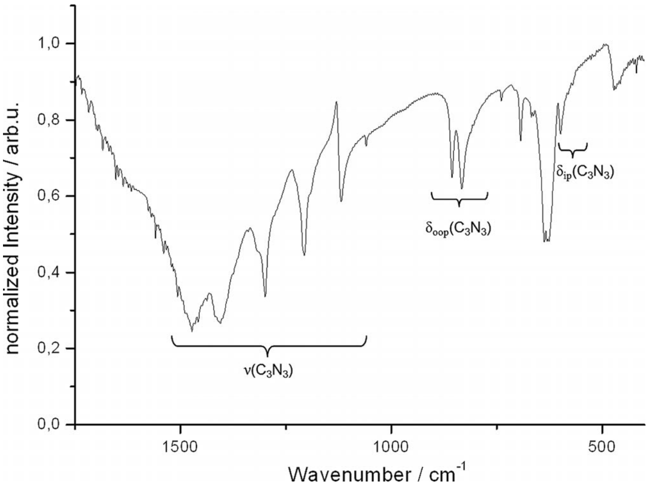

Figure 10. Fingerprint region of the IR spectrum of $Ba_3(O_3C_3N_3)_2$.

Table 3. Vibrational frequencies [cm^{-1}] of $Ba_3(O_3C_3N_3)_2$.

$\delta_{ip}(C_3N_3)$	590
$\delta_{oop}(C_3N_3)$	830–860
$\nu(BaO)$	693
$\nu(C_3N_3)$	1060–1411
$\delta(C{=}O)$	620

Conclusion

The novel compound $Ba_3(O_3C_3N_3)_2$ (BCY) was synthesized by means of a solid-state metathesis reaction and represents the first binary cyanurate. The crystal structure of BCY was refined isotypically to the structure of α-$Ba(B_2O_4)$ (α-BBO) in which the smaller $(O_3C_3N_3)^{3-}$ ion is substituted by $(O_3B_3O_3)^{3-}$.

The reaction performs well in its own K(OCN) flux as we have shown in DSC studies of the reaction. The reaction starts with a soft ignition near the melting point of K(OCN) to produce an X-ray-amorphous material. Similar reactions were previously reported by us with $Li_2(CN_2)$ to yield carbodiimide compounds. In the case of K(OCN), a trimerization takes place during the reaction to yield the cyclic $(O_3C_3N_3)^{3-}$ ion. The formation of this ion at about 300 °C just after the ignition process of the reaction was demonstrated by infrared spectroscopy. This confirms one of our previous assumptions for SSM reactions. The ignition involves the metathesis reaction and the following melting process serves to generate a highly crystalline powder of the product.

Experimental Section

Preparations: K(OCN) was prepared by heating a mixture of urea (>99% Merck) and $K_2(CO_3)$ (99%, Merck) in a 2.5:1 ratio (total mass ca. 2.5 g) in a corundum vessel. The mixture was slowly heated to 100 °C and remained at this temperature for 3 h. Then the mixture was slowly heated to 130 °C (decomposition of urea) within 30 min, where it remained for 30 min, followed by slow heating to 275 °C, where it remained for about 30 min to get rid of decomposition products of urea (biuret) before it was cooled to room temperature. Commercial $BaCl_2$ (anhydrous, Th. Goldschmidt A.-G., Essen) was dried under vacuum at 150 °C for 2 h. Both starting materials, $BaCl_2$ and K(OCN), were identified as single-phase materials according to powder X-ray diffraction (XRD). All procedures of the preparation including the mixing of starting materials and loading of silica tubes were performed in a glovebox under dry argon. $Ba_3(O_3C_3N_3)_2$ (BCY) was prepared from a carefully ground mixture of $BaCl_2$ with an excess amount of K(OCN) following a 1:3 molar ratio. This mixture was fused into a silica ampoule under vacuum, heated to 575 °C within about 4 h, and kept at this temperature for 48 h before it was cooled to room temperature with the natural cooling rate of the furnace. The ampoules were opened in air and the crystalline product was inspected by XRD. Powder XRD patterns indicated high conversion rates of reactions by showing only reflections of the product (BCY), the metathesis salt (KCl), and K(OCN), which was used in an excess amount as a flux medium. The crystal structure of $Ba_3(O_3C_3N_3)_2$ was refined by single-crystal XRD.

Thermal Analysis: Differential thermal analyses (DTA) were performed with a Netzsch Jupiter, STA 449 F3 apparatus. Samples were fused into homemade silica containers with typical total masses of 100 mg. Measurements of K(OCN) were performed between room temperature and 525 °C with heating and cooling rates of 2 K min^{-1}. DSC measurements were also performed with a Netzsch Jupiter, STA 449 F3 apparatus. Samples with typical total masses of 30 mg were enclosed into gold-plated stainless steel containers. Measurements were performed under argon between room temperature and 475 °C with a heating and cooling rate of 2 K min^{-1}.

X-ray Crystallography: A single crystal of $Ba_3(O_3C_3N_3)_2$ (BCY) was measured with a single-crystal X-ray diffractometer (STOE-IPDS) at room temperature (T = 293 K) using Mo-K_α radiation (λ = 0.71073 Å). The structure refinement and solution were performed with direct methods (SHELXS) and least-squares refinements on F^2 (SHELXL).[18] The crystal structure of BCY was refined on a transparent single crystal (ca. 0.08 × 0.08 × 0.06 mm) within the range Θ = 3.06–26.04°. A total number of 5715 collected reflections was corrected for Lorentz and polarization effects (STOE IPDS Software) and reduced to 389 independent reflections (R_{int} = 0.0701). Some results and final R values for BCY are shown in Table 4. The atom positions of BCY are given in Table 1. Selected bond lengths and angles of BCY are collected in Table 2. Further details of the crystal structure investigations may be obtained from the 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-426619 (BCY). Reaction products were inspected by powder XRD with a Stadi-P (STOE, Darmstadt) powder diffractometer with germanium-monochromated Cu-$K_{\alpha 1}$ radiation. The powder pattern recorded for the reported reaction indicates high conversion rates by showing reflections that belong to BCY, the co-produced metathesis salt (KCl), and K(OCN), which was used in an excess amount as a flux medium. The powder pattern of BCY was indexed with a trigonal unit cell and the following parameters: a = 708.4(3) pm, c = 4026(1) pm, β = 120°, V = 1750.0(1) Å^3.

Table 4. Crystal data and structure-refinement parameters of $Ba_3(O_3C_3N_3)_2$.

Formula	$Ba_3(O_3C_3N_3)_2$
Formula mass [g mol^{-1}]	664.14
T [K]	293(2)
Wavelength [pm]	71.073
Crystal system	trigonal
Space group	$R\bar{3}c$ (no. 167)
a [pm]	707.0(2)
b [pm]	707.0(2)
c [pm]	3995(2)
V [nm^3]	1.730(1)
Z	6
$D_{\text{cacld.}}$ [g cm^{-3}]	3.826
μ [mm^{-1}]	10.175
F(000)	1764
Crystal size [mm]	0.08 × 0.08 × 0.06
θ range for data collection [°]	3.06–26.04
Index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-48 \le l \le 49$
Reflections collected	5715
Independent reflections	389 (R_{int} = 0.0701)
Completeness for Θ = 26.04° [%]	100
Refinement method	full-matrix least squares on F^2
Data/parameters	389/33
Goodness-of-fit on F^2	1.149
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0354, wR_2 = 0.1224
R indices (all data)	R_1 = 0.0381, wR_2 = 0.1246
Largest diff. peak/hole [e Å^3]	1.901/–1.721

Computational Details: The cyanurate ion was investigated by using hybrid density functional theory (B3LYP)[19] in conjunction with a 6-311+G* basis set[20] as implemented in Gaussian 09.[21] As multiply charged anions are unstable towards loss of electrons in the gas phase, the computations simulated a water solution with the help of a polarizable continuum model.[22]

Infrared Spectra: Vibrational spectra were recorded with a Bruker Tensor 27 FTIR spectrometer within the range of 400–4000 cm^{-1} by using KBr pellets.

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Barium Cyanurate

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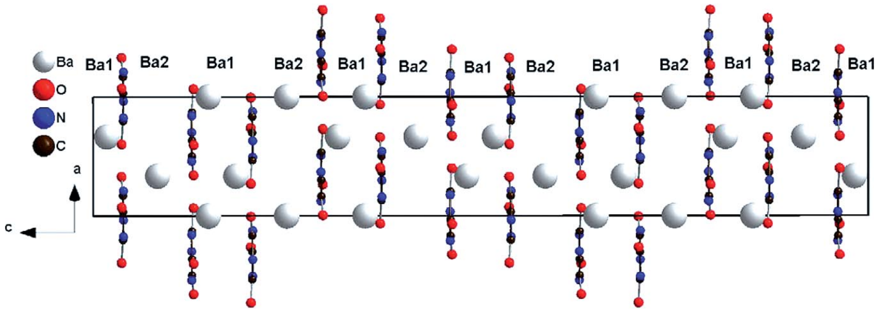
Development of Metal Cyanurates: The Example of Barium Cyanurate (BCY)

Keywords: Cyanurates / Barium / Metathesis / Solid-state reactions / Density functional calculations



The binary metal cyanurate $Ba_3(O_3C_3N_3)_2$ was synthesized by a solid-state metathesis reaction, and the nature of the cyanurate ion was examined by density functional methods.