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Formation of Cocrystals between Alkali Triazine Tricarboxylates and Cyanuric Acid – Reactivity Considerations and Structural Characterization of the Adduct Phases $M_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (M = K, Rb)

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Keywords: Alkali metals; Carbon nitrides; Cocrystals; Crystal structure; *s*-Triazine

Abstract. The reactivity of cyanuric acid towards alkali triazine tricarboxylates was investigated and the first triazine-triazine adduct phases comprising alkali metal ions were synthesized and characterized by single-crystal X-ray diffraction and thermal analysis. An investigation of the reaction between the alkali triazine tricarboxylates $M_3[C_3N_3(CO_2)_3]\cdot xH_2O$ (M = Li, Na, K, Rb, Cs) and cyanuric acid showed that the degree of ion transfer from triazine tricarboxylate to cyanuric acid increases gradually from the lithium to the cesium salt reflecting an increasing basicity of the triazine tricarboxylates. The reaction of potassium and rubidium triazine tricarboxylate dihydrate with cyanuric yielded the novel co-crystals $K_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3a**) and $Rb_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3b**). In comparison to metal free triazine-triazine adduct phases in these compounds the assembly of molecules in the crystal is mainly determined by Coulomb interactions and only to a certain degree by hydrogen bonds and dispersive interactions. In the crystal the *s*-triazine units exhibit a layered structure with triazine tricarboxylate and isocyanuric acid being arranged in zigzag strands within the layers and stacked in columns perpendicular to the layers. Thermal analysis revealed a quite weak cohesion between triazine tricarboxylate and cyanuric acid upon heating.

Introduction

In the last decades the concept of crystal engineering for the rational design of new solid materials with desired physical and chemical properties has attracted considerable interest.[1] For the directed preparation of solids with specific architecture and properties a detailed understanding of the factors that affect the arrangement of molecular building blocks in the solid state is an indispensable prerequisite. The assembly of molecules and ions in the crystal is determined by several types of non covalent interactions such as hydrogen bonding, coordination interactions, or π–π stacking interactions.[1,2] In this regard we are especially interested in such non covalent interactions between molecular carbon nitride compounds. Even though recent research in the field of carbon nitrides is mainly focused on synthesis, characterization, and application of covalently bound frameworks[3] also several adduct phases, in which the cohesion between molecular carbon nitrides is solely achieved by various types of non covalent interactions, were investigated.[4–7] The most prominent example is probably the adduct between the *s*-triazine compounds melamine and cyanuric acid, in which the self-assembly of two molecules with a threefold symmetry leads to the formation of a highly symmetric rosette-like arrangement.[4,6] Further adduct phases of *s*-triazine (C_3N_3) and *s*-heptazine (C_6N_7) compounds were obtained from solutions comprising both building blocks[5] or under solvent free conditions as intermediates during the thermal condensation of *s*-triazine precursors.[7] However, to the best of our knowledge no structurally characterized compound is known so far, in which two different *s*-triazine molecules are present together with metal ions. In contrast to the above mentioned adduct phases in such systems not only hydrogen bonds and dispersive interactions but also Coulomb and coordination interactions will determine the assembly of molecules in the crystal.

In order to obtain a system, in which the effect of various types of non covalent interactions on the arrangement of *s*-triazine molecules as well as the mutual influence of these diverse types of interactions can be studied we tried to combine *s*-triazine based salts with further *s*-triazine compounds capable of metal coordination. For this purpose we used alkali triazine tricarboxylates $M_3[C_3N_3(CO_2)_3]$ (M = Li, Na, K, Rb, Cs), an interesting class of compounds that has been studied in detail only recently,[8,9] as molecular *s*-triazine based salts and cyanuric acid as further ligand (see Scheme 1). In this contribution the reactivity of different alkali triazine tricarboxylates (TTC) towards cyanuric acid is investigated and the synthesis and crystal structure of the co-crystals $K_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3a**) and $Rb_3[C_3N_3(CO_2)_3]$-$[C_3N_3O_3H_3]\cdot H_2O$ (**3b**) is presented. The influence of hydrogen bonding and π–π stacking interactions in comparison to Coulomb interactions on the arrangement of the *s*-triazine building blocks in these adduct phases is discussed and the strength of

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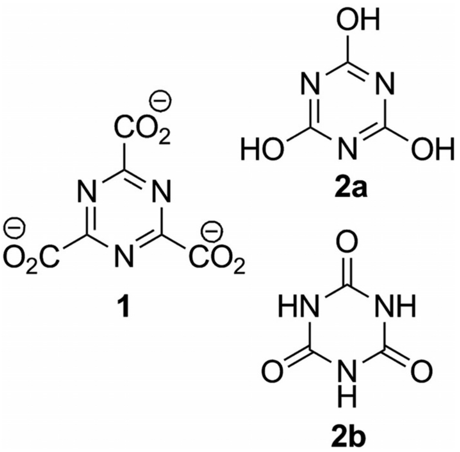
the cohesion by non covalent interactions is further examined by thermal analysis.



Scheme 1. Triazine tricarboxylate TTC (**1**), the enol form of cyanuric acid (**2a**) and its keto form isocyanuric acid **2b**.

Results and Discussion

Reactivity

The alkali triazine tricarboxylates $M_3[C_3N_3(CO_2)_3]\cdot xH_2O$ (M = Li, Na, K, Rb, Cs) (**1a–e**) were combined with cyanuric acid $C_3N_3O_3H_3$ (**2**) in an attempt to prepare metal comprising *s*-triazine adduct phases. Both starting materials represent *s*-triazine-based tridentate ligands with threefold symmetry and sufficient solubility in water. Aqueous solutions of the respective alkali triazine tricarboxylate and cyanuric acid were mixed and hold at room temperature until the evaporation of solvent caused the precipitation of the product. A characterization of the products by X-ray diffraction revealed a dependency of the reactivity on the alkali ions. For the combination of lithium and sodium triazine tricarboxylate with cyanuric acid no co-crystallization occurred but the starting materials crystallized separately. In the case of potassium and rubidium triazine tricarboxylate co-crystals with cyanuric acid were obtained but only the combination of potassium triazine tricarboxylate and cyanuric acid yielded a phase pure sample of the adduct $K_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (K-TTC-CA·H_2O) (**3a**). The reaction of rubidium triazine tricarboxylate with cyanuric acid resulted in a reaction mixture comprising single-crystals of the adduct $Rb_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (Rb-TTC-CA·H_2O) (**3b**), single-crystals of rubidium cyanurate and further unidentified phases. From the reaction product of cesium triazine tricarboxylate and cyanuric acid only cesium cyanurate could be isolated.

Hence from **1a** to **1e** the tendency of a transfer of the alkali ions from triazine tricarboxylate to cyanuric acid increases gradually. The lithium and sodium ions remain bound to triazine tricarboxylate, the potassium ions are coordinated by triazine tricarboxylate and cyanuric acid simultaneously, the rubidium ions are partially shared between both ligands and are partially transferred to cyanuric acid and the cesium ions are eventually completely transferred from triazine tricarboxylate to cyanuric acid. Aqueous solutions of **1d** and **1e** are basic enough to deprotonate cyanuric acid resulting in the formation of the alkali cyanurates $M_3[C_3N_3O_3]\cdot xH_2O$ (M = Rb, Cs). This observation is also in accordance with expectation due to the HSAB concept. Metal ions are coordinated by triazine tricarboxylate via two carboxylate groups and the intermediate nitrogen atom of the *s*-triazine ring. In contrast to these hard coordination sites the keto oxygen atoms of isocyanuric acid can be regarded as rather soft. The binding strength between the hard triazine tricarboxylate units and alkali metal ions decreases from hard Li^+ to soft Cs^+, whereas the trend is just vice versa for isocyanuric acid. The formation of co-crystals between triazine tricarboxylate and cyanuric acid can only be achieved for potassium and rubidium, where the coordination strength of both ligands for the respective metal cation is comparable.

Crystal Structure

Potassium triazine tricarboxylate isocyanuric acid hydrate $K_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3a**) crystallizes in the triclinic space group $P\bar{1}$ and rubidium triazine tricarboxylate isocyanuric acid hydrate $Rb_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3b**) in the monoclinic space group $P2_1/c$. Crystallographic data and details of the structure refinements are summarized in Table 1. In both compounds the alkali ions are coordinated by triazine tricarboxylate and cyanuric acid simultaneously. Cyanuric acid is present in its keto form isocyanuric acid thereby providing three carbonyl groups as coordination sites, whereas the nitrogen atoms of the triazine ring are protonated and hence do not participate in metal coordination. Each triazine tricarboxylate unit coordinates three K^+ or Rb^+ atoms, respectively, via two carboxylate groups and the intermediate *s*-triazine nitrogen atom as in the respective triazine tricarboxylate salts. The coordination sphere is completed by the carboxyl groups of other triazine tricarboxylates and the oxygen atoms of isocyanuric acid and water molecules amounting to coordination numbers of 5–8 for **3a** and 7–9 for **3b**. The M–O distances (K: 258–295 pm, Rb: 276–364 pm) are comparable with the distances observed in the respective triazine tricarboxylate salts[9] and are in accordance with the ionic radii sums.[10] On contrast the M–N distances (K: 281–290 pm, Rb: 301–303 pm) are on average 5 pm longer than in the triazine tricarboxylate salts, indicating a less tighter binding of the alkali ions to the triazine core as can be expected due to the additional coordination by isocyanuric acid. Both adduct phases form layered structures typically for *s*-triazine systems (cf. Figure 1). The interlayer distances amount to 355 pm in **3a** and 360 pm in **3b** and hence are slightly larger than in the respective triazine tricarboxylate salts. Hydrogen bonds are mainly present within the layers and especially in **3b** only to a small amount also between the layers. As illustrated in Figure 2 each two isocyanuric acid (CA) units are interconnected by a double N–H···O hydrogen bridge. Additionally, each CA entity forms a strong hydrogen bond to a carboxylate group of triazine tricarboxylate (TTC). Further hydrogen bonding interactions connect crystal water molecules with both CA and TTC units with all hydrogen atoms of H_2O

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Table 1. Crystallographic data and details of the structure refinement for $K_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3a**) and $Rb_3[C_3N_3(CO_2)_3][C_3N_3O_3H_3]\cdot H_2O$ (**3b**).

	3a	**3b**
Molar mass /g·mol^{-1}	474.49	613.58
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
T /K	293	293
Diffractometer	Nonius Kappa-CCD	Nonius Kappa-CCD
Radiation, λ /pm	Mo-K_α, 71.073	Mo-K_α, 71.073
a /pm	709.66(14)	720.01(14)
b /pm	964.97(19)	3756.4(8)
c /pm	1279.1(3)	1256.9(3)
α /°	75.83(3)	90
β /°	75.38(3)	101.81(3)
γ /°	70.88(3)	90
V /10^6·pm^3	788.1(3)	3327.5(11)
Z	2	4
Calculated density /g·cm^{-3}	1.911	2.450
Crystal size /mm	$0.33 \times 0.23 \times 0.20$	$0.27 \times 0.13 \times 0.11$
Absorption coefficient /mm^{-1}	0.930	8.859
$F(000)$	450	2336
Absorption correction	none	multi-scan
Min. / max. transmission		0.1889 / 0.3084
Diffraction range	$3.23° \leq \theta \leq 34.41°$	$3.18° \leq \theta \leq 26.42°$
index range	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$	$-7 \leq h \leq 8$, $-46 \leq k \leq 45$, $-15 \leq l \leq 15$
Parameters / restraints	271 / 5	517 / 4
Total no. of reflections	11999	44111
No. of independent reflections	6608	6796
No. of observed reflections	5053	5128
Min. / max. residual electron density / e·10^{-6}·pm^{-3}	–0.472 / +0.563	–2.026 / +0.849
GooF	0.935	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.1008^{a)}$	$R_1 = 0.0473$, $wR_2 = 0.1195^{b)}$
Final R indices (all data)	$R_1 = 0.0570$, $wR_2 = 0.1123^{a)}$	$R_1 = 0.0712$, $wR_2 = 0.1318^{b)}$

a) $w = [\sigma^2(F_o^2) + (0.0483P)^2 + 0.5488P]^{-1}$, with $P = (F_0^2 + 2F_c^2)/3$. b) $w = [\sigma^2(F_o^2) + (0.0606P)^2 + 14.1010P]^{-1}$, with $P = (F_0^2 + 2F_c^2)/3$.

being involved in the hydrogen bonding network. Hydrogen bonds in **3a** and **3b** can be classified as medium strong with donor-acceptor distances of 267–299 pm (**3a**) and 264–301 pm (**3b**) and donor-hydrogen-acceptor angles of 121–166° (**3a**) and 113–173° (**3b**) (see Table 2).[11]

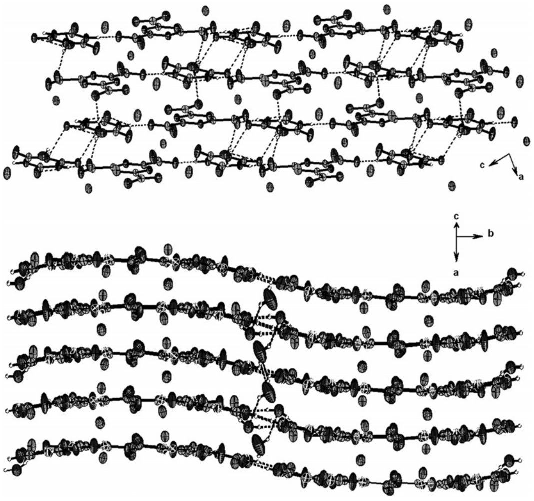

Figure 1. Layered structures of K-TTC-CA·H_2O (**3a**) (top) and Rb-TTC-CA·H_2O (**3b**) (bottom). Dashed lines represent hydrogen bonds. Thermal ellipsoids (except for hydrogen) are drawn at the 50 % probability level.

The ligands triazine tricarboxylate and isocyanuric acid are stacked in columns perpendicular to [100] (cf. Figure 3). In **3b** these columns form single zigzag strands along *c*, whereas the crystal structure of **3b** comprises double strands along *c* which surround hexangular voids that are filled with crystal water molecules and rubidium ions. The remaining rubidium ions in **3b** and all potassium ions in **3a** are located between the zigzag strands of ligands forming corrugated bands. The composition of the columns is different for both adduct phases. In **3a** only one type of columns is present, in which triazine tricarboxylate TTC and isocyanuric acid CA units are alternately stacked with a partial overlap of the *s*-triazine cores. In contrast in **3b** the columns comprise either TTC or CA and show a complete overlap of the *s*-triazine cores (cf. Figure 4). Hence in **3b** the two ligands TTC and CA are merely connected via shared metal coordination and hydrogen bonds, whereas in **3a** additionally weak dispersive interactions between the *s*-triazine cores of both ligands are present. Interestingly, in the metal free adduct melamine·cyanuric acid M·CA an alternative assembly M–CA–M–CA is the most stable stacking arrangement,[6] whereas in **3a** and **3b** a homogeneous CA–CA and TTC–TTC stacking is preferred to an alternating TTC–CA–TTC–CA stacking as the varying degrees of overlap show. The observation that homogeneous CA–CA stacks are favored over CA–TTC stacks in **3a** and **3b** but not over CA–M stacks in M·CA might be explained by the influence of the rather strong

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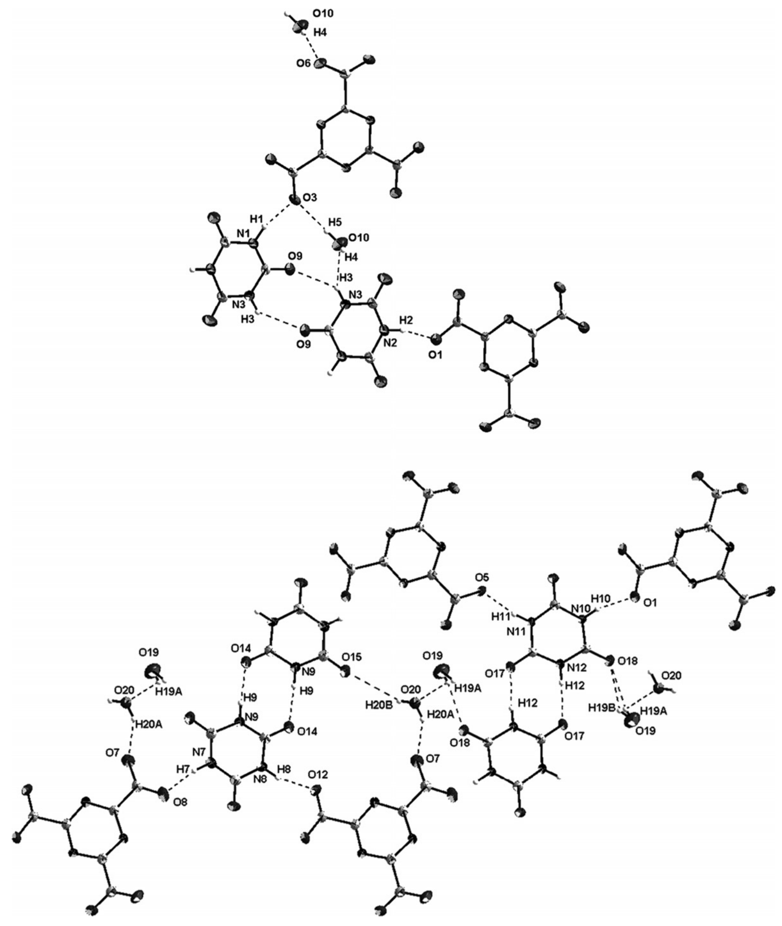

Figure 2. Hydrogen bonding interactions in K-TTC-CA·H_2O (**3a**) (top) and Rb-TTC-CA·H_2O (**3b**) (bottom). Thermal ellipsoids (except for hydrogen) are drawn at the 50 % probability level.

Table 2. Donor-acceptor distances and donor-hydrogen-acceptor angles /pm, ° for the hydrogen bonding network in K-TTC-CA·H_2O (**3a**) and Rb-TTC-CA·H_2O (**3b**).

D–H···A	D···A	<D–H···A
K-TTC-CA·H_2O (**3a**)		
N1–H1···O3	264.6	165.11
N2–H2···O1	266.9	165.61
N3–H3···O10	294.3	151.06
N3–H3···O9	298.5	120.55
O10–H4···O6	276.7	151.79
O10–H5···O3	288.9	153.75
Rb-TTC-CA·H_2O (**3b**)		
N7–H7···O8	264.1	167.17
N8–H8···O12	266.2	161.79
N9–H9···O14	279.2	172.98
N10–H10···O1	265.5	164.76
N11–H11···O5	266.4	170.48
N12–H12···O17	282.0	172.96
O19–H19A···O18	286.1	124.91
O19–H19A···O20	300.2	120.89
O19–H19B···O18	286.1	118.41
O20–H20A···O7	268.7	140.79
O20–H20B···O20	300.6	112.73

Coulomb interactions in **3a** and **3b** impeding a complete overlap of TTC and CA. In contrast to metal free triazine–triazine adduct phases, where π–π stacking interactions – next to strong hydrogen bonds – are essentially determining the arrangement of molecules in the crystal these interactions become less important in the presence of strong Coulomb interactions.

Thermal Behavior

The thermal behavior of the adduct phase K-TTC-CA·H_2O (**3a**) was compared with that of the starting materials K-TTC·2H_2O (**1c**) and cyanuric acid (**2**) (see Figure 5). The potassium salt **1c** is dehydrated below 200 °C and starts to decompose around 350 °C. Cyanuric acid **2** completely transforms into gaseous isocyanic acid HNCO around 400 °C.[12] TG and DTA curves of the adduct phase **3a** show a release of crystal water at low temperatures and subsequent a slow decomposition of the dehydrated compound starting around 200 °C. Hence the adduct phase **3a** exhibits a lower thermal stability than its components. The main mass loss occurs stepwise between 320 and 420 °C accompanied by three exothermic signals in the DTA curve. Two of these signals closely match the decomposition temperatures of K-TTC·2H_2O (**1c**) and cyanuric acid (**2**). This indicates that the cohesion between the ligands TTC and CA seems to be broken up while heating, so that the thermal decomposition of the two individual compounds TTC and CA can be observed.

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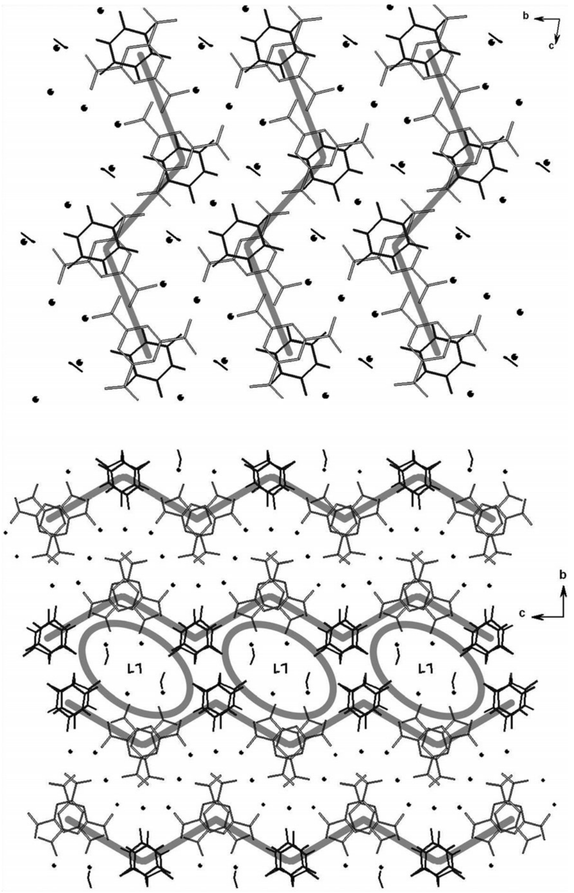

Figure 3. Crystal structures of the adduct phases K-TTC-CA·H_2O (**3a**) (top) and Rb-TTC-CA·H_2O (**3b**) (bottom), representing the arrangement of triazine tricarboxylate and cyanuric acid rods in zigzag strands and the formation of voids between two double strands in **3b**. Triazine tricarboxylate units are displayed in light gray and isocyanuric acid units in dark gray.

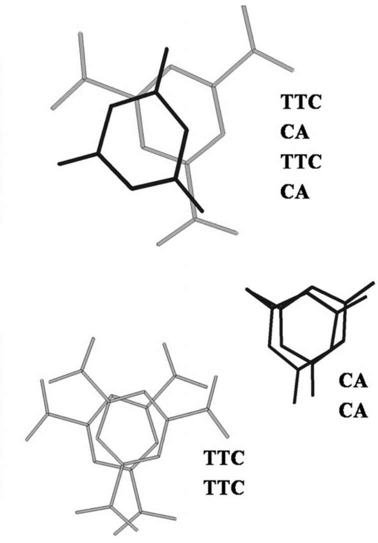

Figure 4. Stacking of the ligands triazine tricarboxylate (TTC) and cyanuric acid (CA) in the adduct phases K-TTC-CA·H_2O (**3a**) (top) and Rb-TTC-CA·H_2O (**3b**) (bottom). Triazine tricarboxylate units are displayed in light gray and isocyanuric acid units in dark gray.

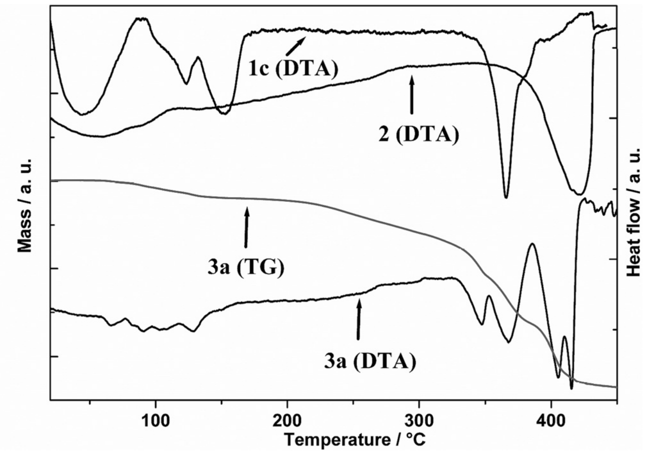

Figure 5. DTA curves (black) of K-TTC·$2H_2O$ (**1c**), cyanuric acid (**2**) and K-TTC-CA·H_2O (**3a**) and TG curve (gray) of K-TTC-CA·H_2O (**3a**), recorded with a heating rate of 5 K·min^{-1}.

Conclusions

We have reported on the synthesis, crystal structure, and thermal behavior of two co-crystals of alkali triazine tricarboxylates and isocyanuric acid. $M_3[C_3N_3(CO_2)_3]$-$[C_3N_3O_3H_3]$·H_2O (M = K, Rb) represent the first examples of metal containing adduct phases between two different *s*-triazine molecules. This demonstrates a further possibility to construct layered *s*-triazine materials by combining diverse *s*-triazine ligands in a single compound. It was discussed how the formation of such co-crystals depends on the relative coordination strength of both ligands for the respective metal cation. Furthermore, the role of different types of non covalent interactions on the assembly of molecules and ions in the crystal was investigated and compared to metal free triazine–triazine adduct phases. These findings add to a deeper understanding of the factors that determine the assembly of different *s*-triazine molecules in the solid state and might contribute to a rational preparation of specific carbon nitride materials by crystal engineering in the future.

Experimental Section

Syntheses

The alkali triazine tricarboxylates **1a**–**e** were synthesized according to the procedure described for the potassium salt by saponification of the respective triethyl ester.[13] To prepare the ester dry HCl was piped through ethyl cyanoformate (20.0 g, 202 mmol, Aldrich, 99 %) in argon until the trimerization product started to precipitate. After cooling the reaction to 4 °C overnight the product was filtered, washed with cold water, and dried at 75 °C. Small amounts of the triethyl ester (250 mg, 0.85 mmol) were treated with 10 mL of a 1 M aqueous solution of *M*OH (ABCR, 99 %, *M* = Li, Na, K, Rb, Cs). The reaction was stirred at room temperature until the ester was completely dissolved. Afterwards, 200 mL ethanol was poured into the solution to precipitate the alkali salts. The products were filtered, washed with ethanol, and dried at 75 °C.

To prepare the adduct phases **3a** and **3b** equimolar amounts (0.15 mmol) of cyanuric acid **2** (20.0 mg, Aldrich, ≥ 98 %) and potas-

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sium or rubidium triazine tricarboxylate **1c** (56.3 mg) and **1d** (77.9 mg), respectively, were dissolved in water (50 mL) and mixed for 48 h at room temperature. By slow evaporation of the solvent at room temperature the product **3a** in the form of colorless block-like crystals or a mixture of several phases containing single-crystals of **3b** were obtained.

Elemental analysis for **3a**: N 15.16 (calcd. 17.71), C 20.83 (calcd. 22.78), H 1.41 (calcd. 1.06) %.

X-ray Structure Determination

Single-crystal X-ray diffraction data of **3a** and **3b** were collected with a Kappa CCD diffractometer (293 K, Mo-K_α radiation, λ = 71.073 pm). The diffraction intensities were scaled using the SCALEPACK software package.[14] For **3a** no additional absorption correction was applied and for **3b** an absorption correction was performed using the program SADABS.[15] The crystal structures were solved by direct methods using the software package SHELXS-97 and refined against F^2 by applying the full-matrix least-squares method (SHELXL-97).[16] The hydrogen positions could be determined from difference Fourier syntheses and were refined isotropically using restraints for oxygen-hydrogen distances. All non-hydrogen atoms were refined anisotropically.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-834102 and CCDC-834103 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

General Techniques

Powder X-ray diffraction data were collected in transmission geometry with a Huber G670 Guinier Imaging Plate diffractometer (Cu-K_α radiation, λ = 154.06 pm) and analyzed with the software WinXPOW.[17] Thermoanalytical measurements were performed in an inert atmosphere (He) with a Thermoanalyzer TG-DTA92 (Setaram). The samples were heated in an alumina crucible from room temperature to 450 °C with a heating rate of 5 K·min^{-1}. Elemental analyses for C, H, and N were performed with the elemental analyzer systems Vario EL and Vario Micro (Elementar Analysensysteme GmbH).

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