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Rb₃[C₆N₇(NCN)₃] • 3 H₂O and Cs₃[C₆N₇(NCN)₃] • 3 H₂O – Synthesis, Crystal Structure and Thermal Behavior of two Novel Alkali Melonates

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Rb₃[C₆N₇(NCN)₃] · 3 H₂O and Cs₃[C₆N₇(NCN)₃] · 3 H₂O – Synthesis, Crystal Structure and Thermal Behavior of two Novel Alkali Melonates

Sophia J. Makowski and Wolfgang Schnick*

Keywords: Melonate salts; *s*-Heptazine; Tri-*s*-triazine; Crystal structure

Abstract. Rubidium melonate trihydrate Rb₃[C₆N₇(NCN)₃] · 3 H₂O and cesium melonate trihydrate Cs₃[C₆N₇(NCN)₃] · 3 H₂O were obtained by ion exchange reactions in aqueous solution. The structure of the cesium salt was determined by single-crystal X-ray diffraction (*Pna*2₁, *a* = 687.34(14), *b* = 2196.5(4), *c* = 1232.6(3) pm, *V* = 1860.9(7) · 10⁶ pm³, *Z* = 4, *T* = 200 K). The crystal structure of the isotopic rubidium salt was refined from X-ray powder diffraction data by the Rietveld method (*Pna*2₁, *a* = 674.48(2), *b* = 2146.4(1), *c* = 1207.5(1) pm, *V* = 1753.4(6) · 10⁶ pm³, *Z* = 4, *T* = 298 K). In the crystal structure planar melonate ions and alkali cations as well as water molecules are arranged in alternating layers. The melonate entities are interconnected by a dense hydrogen bonding network. Rb₃[C₆N₇(NCN)₃] · 3 H₂O and Cs₃[C₆N₇(NCN)₃] · 3 H₂O were investigated by FTIR spectroscopy, TG and DTA measurements.

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Introduction

The first report on potassium melonate dates back to 1835 when *Gmelin* obtained this compound as a by-product during the synthesis of potassium thiocyanate [1]. Although the structure of the melonate anion was already proposed correctly by *Pauling* and *Sturdivant* in 1937 [2], this prediction has been confirmed only recently. By employing the synthetic route that has already been described by *Liebig* and *Henneberg* [3,4], namely the reaction of melon [C₆N₇(NH)(NH₂)_n] in molten KSCN, *Kroke* et al. obtained a sample of potassium melonate pentahydrate K₃[C₆N₇(NCN)₃] · 5 H₂O suitable for X-ray crystal structure determination [5].

In the last two decades molecular carbon nitrides have attracted substantial attention as convenient materials for numerous technical applications, due to the high thermal and oxidation stability as well as the semiconducting properties of this class of materials. For instance, condensed carbon nitrides can serve as metal-free catalysts for Friedel Crafts reactions, CO₂ activation or hydrogen production from water [6-9] and several materials for electronic applications are based on carbon nitrides as well [10-12].

To be employed as precursors for condensed carbon nitride networks the salts of anions which contain only carbon and nitrogen in an alternating arrangement are of special interest. Known examples are the cyanides (CN)⁻, cyanamides or carbodiimides (NCN)²⁻, dicyanamides [N(CN)₂]⁻ and the tricyanomelaminates [C₃N₃(NCN)₃]³⁻, which have all been extensively investigated in the past [13-20]. The melonates [C₆N₇(NCN)₃]³⁻ can be seen as a further member of this group of carbon nitride anions, but only the respective potassium salts have been sufficiently characterized so far [5,21].

Due to the recent structural characterization of a number of two-dimensional carbon nitride networks [8,22-26] and theoretical calculations [27,28] it is assumed that a structure of g-C₃N₄ based on the *s*-heptazine core [C₆N₇] should be more stable than an analogous *s*-triazine-based [C₃N₃] network at moderate temperatures, whereas as distinctively higher temperatures a conversion of *s*-heptazine to *s*-triazine cycles occurs [21]. Against this background the melonates

[C₆N₇(NCN)₃]³⁻ represent an interesting new class of *s*-heptazine derivatives. Due to the high thermal stability of many *s*-heptazine-based compounds [29-31], the high nitrogen content and the alternating arrangement of carbon and nitrogen in the structure, the melonates are promising starting materials for the synthesis of condensed carbon nitrides at elevated temperatures.

In the present study we report on the synthesis, crystal structure determination and thermal behavior of two novel alkali melonates, thereby providing a further contribution to the systematic investigation of molecular carbon nitrides.

Results and Discussion

Crystal structure

The structures of Rb₃[C₆N₇(NCN)₃] · 3 H₂O **1** and Cs₃[C₆N₇(NCN)₃] · 3 H₂O **2** are isotopic. Both melonate salts crystallize in the orthorhombic space group *Pna*2₁ with four formula units in the unit cell. Crystallographic data and details of the structure refinement are summarized in Table 1. The crystal structure is built up of alkali ions M⁺, planar melonate anions [C₆N₇]³⁻ and crystal water molecules (cf. Figure 1).

The bent cyanamide sidearms are orientated in such a way that the anion shows only minor deviations from the molecular symmetry C_{3h}. This resembles the orientation of the sidearms in K₃[C₆N₇(NCN)₃] · 5 H₂O and in the tricyanomelaminates Na₃[C₆N₉] · 3 H₂O and [C(NH₂)₃]₃[C₆N₉] · 2 H₂O [5,32,33] as well as in the related compound [C₆N₇](N₃)₃ [34], whereas in most tricyanomelaminates one sidearm is rotated by 180°, reducing the molecular symmetry to C_s.

Bond lengths and angles in **1** and **2** (cf. Table 2) are in accordance with the values reported for K₃[C₆N₇(NCN)₃] · 5 H₂O. As calculated by Zheng et al. [35] the cyanamide sidearms cause a widening of the adjacent angles and an elongation of the adjacent C-N bonds and hence a slight distortion of the *s*-heptazine core. The sidearms can be approximately accounted cyanamide groups -N-C≡N, as indicated by the terminal C-N bond lengths (117 pm) which correspond to triple bonds. However, the binding situation is described more accurately by taking a contribution of the resonant carbodiimide form -N=C=N into account as well [36-38]. The bonds between the *s*-heptazine core and the sidearms (C2/4/6-N8/10/12) as well as the next bonds within the sidearms (N8/10/12-C7/8/9) are significantly shorter (135–136 pm and 131–133 pm respectively) than the central C-N bonds of the *s*-heptazine core (141 pm). While the central bonds do not contribute to the aromatic system and can therefore be regarded as single bonds, the bond lengths C2/4/6-N8/10/12 and N8/10/12-C7/8/9 rather range between a single and a double bond (131–136 pm), denoting a delocalization of electron density from the sidearms into the *s*-heptazine core. Further indications for the superposition of several resonant structures are the slight bending of the sidearms and the distribution of electron density at the carbon atoms in the sidearms. While the ellipsoids at the nitrogen atoms are orientated perpendicular to the binding axes as expected due to vibrations of the sidearms, the ellipsoids at C7/8/9 are orientated parallel to the bond axes. Since these effects can be observed in numerous dicyanamides and tricyanomelaminates [32,33,39-42] they are assumed not to be artefacts, but a result of the superposition of the cyanamide and carbodiimide form.

In analogy to the crystal structure of K₃[C₆N₇(NCN)₃] · 5 H₂O the melonate ions, alkali cations and crystal water molecules are arranged in an AA'BB' type stacking pattern perpendicular to [100] (cf. Figure 2). Along [100] the melonate ions form columns in which the central N atoms (N1) of two anions of adjacent layers A and A' are situated exactly above each other. Around N1 the anions of two adjacent layers are rotated in the *bc*-plane by 28.3°. Within one layer two adjacent anions are tilted by an angle of 12.3° to each other. The sidearms are orientated clockwise in the A layers and counterclockwise in the A' layers. The interlayer distances of 338 pm (**1**) and 344 pm (**2**) are similar to the values typically found for other molecular *s*-heptazine derivatives [29,30,34,43-45] and for two-dimensional layered CN_x structures [8,25,26,46-48].

The layers of melonate ions are interconnected by hydrogen bonds of moderate strength (cf. Table 3, Figure 3) [49] with all hydrogen atoms of the crystal structure being part of the hydrogen bonding network. While in tricyanomelamine hydrates always at least one of the ring nitrogen atoms of the *s*-triazine core is involved in the hydrogen bonding network, in **1** and **2** only the nitrogen atoms of the sidearms are part of this network. The distinct disorder of one crystal water molecule (O2) may be explained with a merely loose bonding of the respective water molecule into the structure. The slight elongation of the adjacent hydrogen bond (O2-H4...N9) as compared to the remaining hydrogen bonds supports this assumption.

The Cs⁺ and Rb⁺ ions are coordinated by seven N and two or three O atoms, respectively, in the form of irregular polyhedrons. Each cation is coordinated by N atoms from four melonate anions of two adjacent columns with the distance to one column being remarkably shorter than to the other. As in potassium melonate both the N atoms in the sidearms and the peripheral N atoms in the *s*-heptazine core are involved in metal coordination (cf. Table 2). The M-O distances (283–371 pm (**1**) and 297–359 pm (**2**)) and the M-N distances (299–362 pm (**1**) and 317–360 pm (**2**)) are in accordance with the ionic radii sums [50] and are comparable to the values observed in other solids for the coordination of Rb⁺ and Cs⁺ by crystal water [40,51-54] and C-N ligands [40,52,55-57].

FTIR Spectroscopy

Rubidium- and cesium melonate trihydrate were analyzed by FTIR spectroscopy. The spectra are shown in Figure 5. The signal at 795 cm^{-1} can be attributed to the bending vibration of the *s*-heptazine core, the signals at $1418\text{--}1634\text{ cm}^{-1}$ to the stretching vibrations of the ring [58-60]. Additionally to these characteristic *s*-heptazine bands, signals of the $\text{C}\equiv\text{N}$ stretching vibrations of the cyanamide sidearms can be observed at $2140\text{--}2170\text{ cm}^{-1}$. Hence the presence of melonate units in the structure is clearly indicated by the FTIR spectra. In accordance with the crystal structure the $\text{C}\equiv\text{N}$ stretching signal shows splitting due to the slight variations in $\text{C}\equiv\text{N}$ bond lengths. The broad band at $3000\text{--}3600\text{ cm}^{-1}$ corresponds to the OH stretching vibrations. As expected the moderate strong hydrogen bonds cause a red-shift of the $\nu(\text{OH})$ stretching region to wavenumbers below 3600 cm^{-1} .

Thermal behavior

TG and DTA curves of **1** and **2** are displayed in Figure 6. In the temperature range between 65 and $150\text{ }^\circ\text{C}$ the melonates are dehydrated stepwise. The first crystal water molecule per formula unit is released below $90\text{ }^\circ\text{C}$ (mass loss *observed* $2.3/3.2\%$, *calculated* $2.4/3.0\%$), the remaining two water molecules at $90\text{--}150\text{ }^\circ\text{C}$ (mass loss *observed* $4.8/5.9\%$, *calculated* $4.9/6.0\%$). The dehydrated compounds remain thermally stable up to $500\text{ }^\circ\text{C}$; neither condensation nor decomposition processes seem to occur below this temperature. The onset of decomposition is accompanied by a sharp endothermic signal at around $570\text{ }^\circ\text{C}$ which might be caused by a melting or crosslinking reaction. Above $680\text{ }^\circ\text{C}$ the rapid mass loss indicates a complete decomposition of the samples. Hence the investigated melonates show a high thermal stability comparable to other *s*-heptazine-based compounds as melem, cyameluric acid or alkalicymelurates [29-31].

Conclusions

We have reported on the synthesis, crystal structure and thermal behavior of two novel alkali melonate salts, namely $\text{Rb}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3\text{ H}_2\text{O}$ and $\text{Cs}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3\text{ H}_2\text{O}$. The melonate ion comprises solely carbon and nitrogen in an alternating arrangement with a C/N ratio of 0.69 which is close to the theoretical value of 0.75 for *g*- C_3N_4 . Hence the melonates represent an interesting group of molecular carbon nitrides but only the potassium salts have been characterized in detail so far. This study has expanded the investigations of melonate salts to two new compounds, providing a further insight into the structural and thermal properties of this class of molecular carbon nitrides. The presented crystal structures are isotopic and resemble that of $\text{K}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 5\text{ H}_2\text{O}$ with the arrangement of melonate ions and alkali cations in alternating layers. Both melonate salts exhibit a high thermal stability as characteristic for *s*-heptazine based compounds and no remarkable effect of the respective cation on the thermal behavior could be observed.

Experimental Section

Syntheses

Melon was synthesized in preparative amounts according to [31] by heating commercially available melamine (Fluka, purum) in an open porcelain crucible at $490\text{ }^\circ\text{C}$ for 4 days.

Potassium melonate pentahydrate was prepared according to the method described by Kroke et al. [5]. 10.0 g (49.7 mmol) melon were added in small portions to a melt of 20.0 g (206 mmol) KSCN (Acros, $\geq 99\%$). After heating for 1 h the reaction was quenched and the obtained yellow solid was dissolved in 100 ml boiling H_2O and filtered. While cooling down to room temperature a yellow solid crystallized from the filtrate. The raw product was recrystallized from water three times for purification. After drying at $75\text{ }^\circ\text{C}$ 8.32 g (16.7 mmol , 34%) of potassium melonate pentahydrate were obtained as colorless needles.

Rubidium and cesium melonate trihydrate were prepared by ion exchange in aqueous solution at room temperature. Onto a column containing 55 ml of a strongly acidic ion exchange resin (Amberlyst 15, Fluka) with an ion exchange capacity of 1.8 mmol ml^{-1} a solution of 1.00 g (2.01 mmol , 0.02 M) $\text{K}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 5\text{ H}_2\text{O}$ was poured. The eluate, containing *in situ* generated hydromelononic acid, was dropped into an aqueous solution of 924 mg (4.00 mmol , 0.04 M) Rb_2CO_3 (Merck) or 3.26 g Cs_2CO_3 (10.0 mmol , 0.2 M , Merck), respectively. After removing the solvent by vacuum evaporation a white solid was obtained which was elutriated in 20 ml H_2O , filtered and recrystallized twice from water. 878 mg (1.62 mmol , 81%) **1** and 1.10 g (1.48 mmol , 74%) **2** were obtained as colorless needles.

Elemental analysis (wt. %): (**1**) N 24.62 (calc. 24.51), C 14.54 (calc. 14.55), H 0.88 (calc. 0.81); (**2**) N 30.08 (calc. 30.32), C 17.76 (calc. 18.00), H 1.11 (calc. 1.01).

X-ray Structure Determination

Single-crystal X-ray diffraction data of $\text{Cs}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3\text{ H}_2\text{O}$ were collected at 200 K on a Kappa CCD diffractometer using monochromated Mo- K_α radiation ($\lambda = 71.073\text{ pm}$). The diffraction intensities were scaled using the SCALEPACK software package [61]

and an additional adsorption correction was applied employing the program SADABS [62]. The crystal structure was solved by direct methods using the software package SHELXS-97 [63] and refined against F^2 by applying the full-matrix least-squares method (SHELXL-97) [64]. 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.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-420601.

A powdered sample of $\text{Rb}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ was enclosed in a glass capillary of diameter 0.1 mm. A powder X-ray diffraction pattern was registered in Debye-Scherrer geometry on a STOE Stadi P powder diffractometer using Ge(111) monochromated $\text{Cu-K}\alpha_1$ radiation ($\lambda = 154.06 \text{ pm}$). The Rietveld refinement of the data was performed with the software package TOPAS [65] using the lattice parameters and the atomic coordinates of $\text{Cs}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ as starting values. The melonate ions were fixed as rigid bodies and only the translation and rotation of these fragments was refined but not the bond lengths and angles within these entities. The result of the Rietveld refinement is given in Figure 4.

FT-Infrared Spectroscopy

FTIR spectra were recorded at room temperature on a Spektrum BX II FTIR spectrometer (Perkin Elmer) equipped with a DuraSampler diamond ATR device. The spectra were measured between 600 and 4000 cm^{-1} at ambient conditions.

Thermal Analysis

Thermoanalytical measurements were performed with a Thermoanalyzer TG-DTA92 (Setaram) under inert atmosphere (He). The alkali melonates were heated in alumina crucibles from room temperature to $750 \text{ }^\circ\text{C}$ with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$.

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Figure 1. Representation of one formula unit of $\text{M}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ ($\text{M} = \text{Rb}, \text{Cs}$). Thermal ellipsoids (except for H) are drawn at the 50 % probability level.

Figure 2. Crystal structure of $\text{M}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ ($\text{M} = \text{Rb}, \text{Cs}$), representing the layered structure with a AA'BB' type stacking pattern. Thermal ellipsoids (except for H) are drawn at the 50 % probability level.

Figure 3. Hydrogen bonding interactions in $\text{M}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ ($\text{M} = \text{Rb}, \text{Cs}$). Thermal ellipsoids (except for H) are drawn at the 50 % probability level.

Figure 4. Observed (crosses) and calculated (line) X-ray powder diffraction patterns as well as difference profile of the Rietveld refinement of $\text{Rb}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$. ($\lambda = 154.06 \text{ pm}$, $T = 298 \text{ K}$).

Figure 5. FTIR spectra of $\text{Rb}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ (top) and $\text{Cs}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$ (bottom).

Figure 6. TG and DTA curves of **1** and **2**, recorded with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. Top: $\text{Rb}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$; bottom: $\text{Cs}_3[\text{C}_6\text{N}_7(\text{NCN})_3] \cdot 3 \text{H}_2\text{O}$.

Table 1. Crystallographic data and details of the structure refinement for $M_3[C_6N_7(NCN)_3] \cdot 3 H_2O$ ($M = Rb, Cs$).

	Rb ₃ [C ₉ N ₁₃] · 3 H ₂ O	Cs ₃ [C ₉ N ₁₃] · 3 H ₂ O
molar mass / g mol ⁻¹	600.64	743.00
crystal system		orthorhombic
space group		<i>Pna</i> 2 ₁ (no. 33)
T / K	298	200
diffractometer	Stoe STADI P	Nonius Kappa-CCD
	powder diffr.	single-crystal diffr.
radiation, λ / pm	Cu-K _{α1} , 154.06	Mo-K _α , 71.073
a / pm	674.5(10)	687.34(14)
b / pm	2146.3 (3)	2196.5(4)
c / pm	1207.4(2)	1232.6(3)
V / 10 ⁶ pm ³	1747.9 (4)	1860.9(7)
Z	4	4
calc. density / g cm ⁻³	2.259	2.652
diffraction range	2.50° ≤ θ ≤ 25.05°	3.13° ≤ θ ≤ 27.49°
GooF	1.093	1.053
final R indices		R1 = 0.0238
[I > 2σ(I)]		wR2 = 0.0421 ^[a]
final R indices	wRp = 0.04392	R1 = 0.0305
(all data)	Rp = 0.03451	wR2 = 0.0440 ^[a]
Durbin-Watson statistics	1.357	
crystal size / mm ³		0.67 x 0.06 x 0.03
abs. coeff. / mm ⁻¹		5.890
absorption correction		multi scan
min./max. trans. ratio		0.486/0.838
index range		-8 ≤ h ≤ 8
		-28 ≤ k ≤ 28
		-16 ≤ l ≤ 15
param. / restraints		272 / 7
total no. of reflect.		31599
no. of ind. reflect.		4247
no. of obs. reflect.		3856
min./max. residual elec. dens. / 10 ⁶ pm ³		-0.754/ +0.829

$$^{[a]} \omega = [\sigma^2(F_0^2) + (0.0180P)^2 + 0.3839P]^{-1}, \text{ with } P = (F_0^2 + 2 F_c^2)/3$$

Table 2. Selected bond lengths (in pm) and angles (in deg) in $M_3[C_6N_7(NCN)_3] \cdot 3 H_2O$ ($M = Rb, Cs$), standard deviations in parentheses. M-N and M-O distances are given for both compounds, the bond lengths and angles within the melonate entities correspond to the single-crystal data of 2.

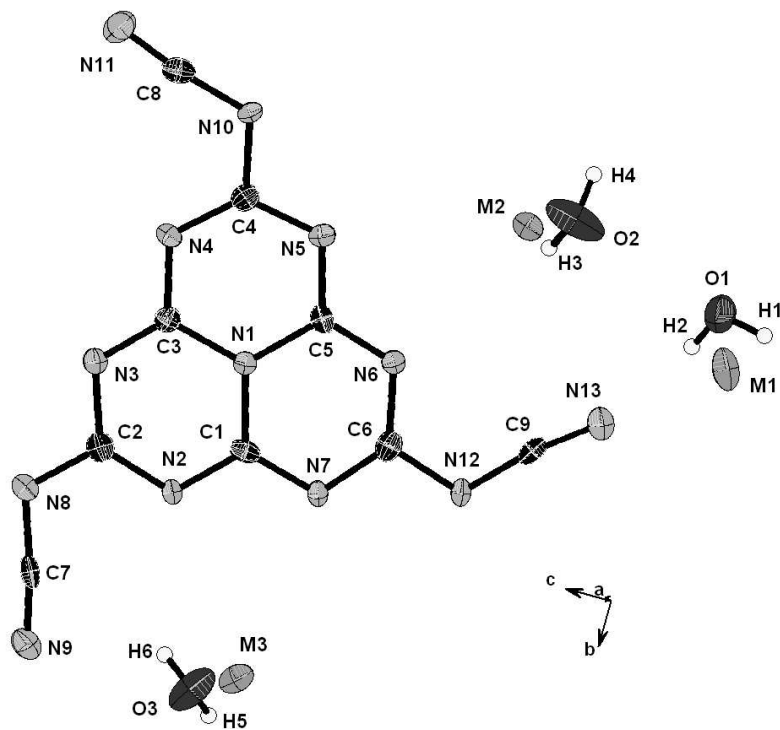
Cs1 - N3	354.0(3)	Cs3 - N5	356.3(3)	N2 - C1 - N1	119.2(4)
Rb1 - N3	338.5(9)	Rb3 - N5	339.0(5)	N2 - C1 - N7	120.3(4)
Cs1 - N3	359.7(3)	Cs3 - N7	332.5(3)	N7 - C1 - N1	120.5(4)
Rb1 - N3	347.0(9)	Rb3 - N7	322.1(5)	N2 - C2 - N3	125.4(4)
Cs1 - N4	323.9(4)	Cs3 - N9	335.6(4)	N2 - C2 - N8	119.6(4)
Rb1 - N4	311.0(12)	Rb3 - N9	310.7(11)	N8 - C2 - N3	115.0(4)
Cs1 - N8	324.0(3)	Cs3 - N9	346.9(4)	N3 - C3 - N1	120.4(4)
Rb1 - N8	315.5(8)	Rb3 - N9	361.8(12)	N3 - C3 - N4	121.1(4)
Cs1 - N11	331.2(4)	Cs3 - N10	324.7(3)	N4 - C3 - N1	118.5(4)
Rb1 - N11	321.2(6)	Rb3 - N10	310.9(9)	N4 - C4 - N5	127.1(4)
Cs1 - N13	316.5(4)	Cs3 - N11	322.7(4)	N4 - C4 - N10	119.8(4)
Rb1 - N13	291.6(9)	Rb3 - N11	305.6(8)	N10 - C4 - N5	113.1(4)
Cs1 - N13	331.3(4)	Cs3 - O1	336.9(4)	N5 - C5 - N1	119.8(4)
Rb1 - N13	325.3(8)	Rb3 - O1	316.9(4)	N6 - C5 - N1	119.6(4)
Cs1 - O1	358.7(5)	Cs3 - O3	297.4(4)	N6 - C5 - N5	120.7(4)
Rb1 - O1	370.9(6)	Rb3 - O3	283.4(6)	N6 - C6 - N7	126.7(4)
Cs1 - O2	336.8(6)	N1 - C1	140.8(5)	N6 - C6 - N12	119.8(4)
Rb1 - O2	325.9(11)	N1 - C3	140.6(5)	N12 - C6 - N7	113.6(4)
Cs2 - N5	336.9(3)	N1 - C5	140.6(5)	N9 - C7 - N8	174.0(5)
Rb2 - N5	322.7(11)	N2 - C1	131.8(5)	N11 - C8 - N10	174.1(5)
Cs2 - N6	318.0(3)	N2 - C2	134.2(5)	N13 - C9 - N12	171.7(4)
Rb2 - N6	298.6(6)	N3 - C2	137.5(5)	C3 - N1 - C1	119.6(3)
Cs2 - N7	335.5(3)	N3 - C3	131.9(5)	C5 - N1 - C1	119.6(3)
Rb2 - N7	327.0(8)	N4 - C3	133.4(5)	C5 - N1 - C3	120.8(3)
Cs2 - N9	317.5(4)	N4 - C4	134.3(5)	C1 - N2 - C2	118.7(4)
Rb2 - N9	307.0(5)	N5 - C4	136.4(5)	C3 - N3 - C2	116.7(4)
Cs2 - N11	350.9(4)	N5 - C5	132.8(5)	C3 - N4 - C4	117.6(4)
Rb2 - N11	355.1(5)	N6 - C5	132.5(5)	C5 - N5 - C4	116.2(4)
Cs2 - N12	334.8(3)	N6 - C6	134.8(6)	C5 - N6 - C6	117.7(4)
Rb2 - N12	327.0(6)	N7 - C1	133.3(5)	C1 - N7 - C6	116.0(4)
Cs2 - N13	347.7(4)	N7 - C6	136.3(5)	C7 - N8 - C2	115.2(4)
Rb2 - N13	340.3(8)	N8 - C2	134.7(5)	C8 - N10 - C4	117.4(4)
Cs2 - O1	335.8(4)	N8 - C7	133.4(5)	C9 - N12 - C6	116.8(3)
Rb2 - O1	305.9(11)	N9 - C7	114.5(5)		
Cs2 - O2	305.0(4)	N10 - C4	135.5(5)		
Rb2 - O2	321.2(7)	N10 - C8	131.8(6)		
Cs2 - O3	345.8(4)	N11 - C8	115.8(6)		
Rb2 - O3	339.3(10)	N12 - C6	135.6(5)		
Cs3 - N2	323.3(3)	N12 - C9	131.4(5)		
Rb3 - N2	311.4(7)	N13 - C9	116.3(5)		

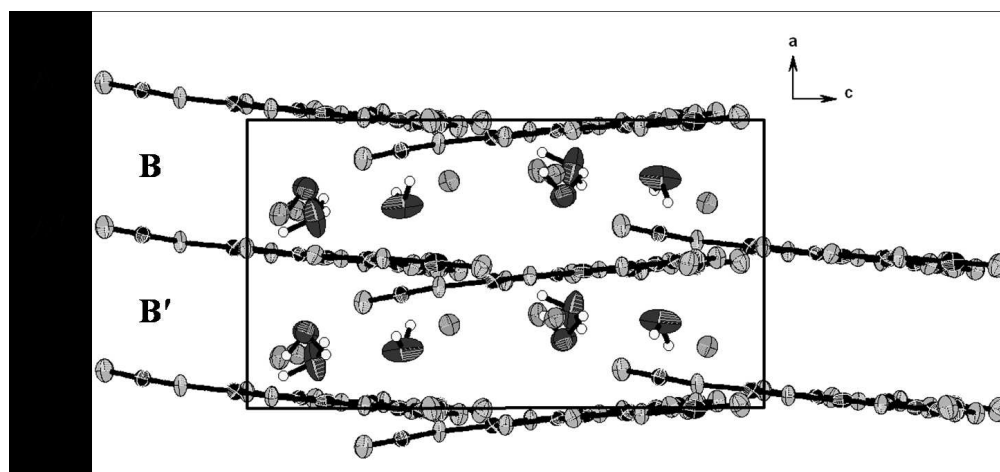
Table 3. Donor-acceptor distances and donor-hydrogen-acceptor angles (in pm / deg) for the hydrogen bonding network in $Cs_3[C_6N_7(NCN)_3] \cdot 3 H_2O$.

D-H...A	D...A	<D-H...A
O1-H1...N8	290.0	162.03
O1-H2...N13	290.8	168.63
O2-H3...N12	288.3	161.14
O2-H4...N9	314.3	141.43
O2-H4...O3	321.4	131.74
O3-H5...N11	284.1	166.27
O3-H6...N10	293.3	169.91

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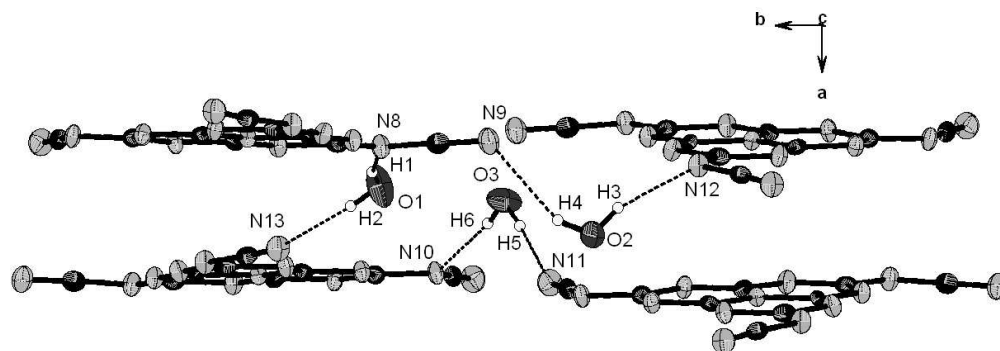
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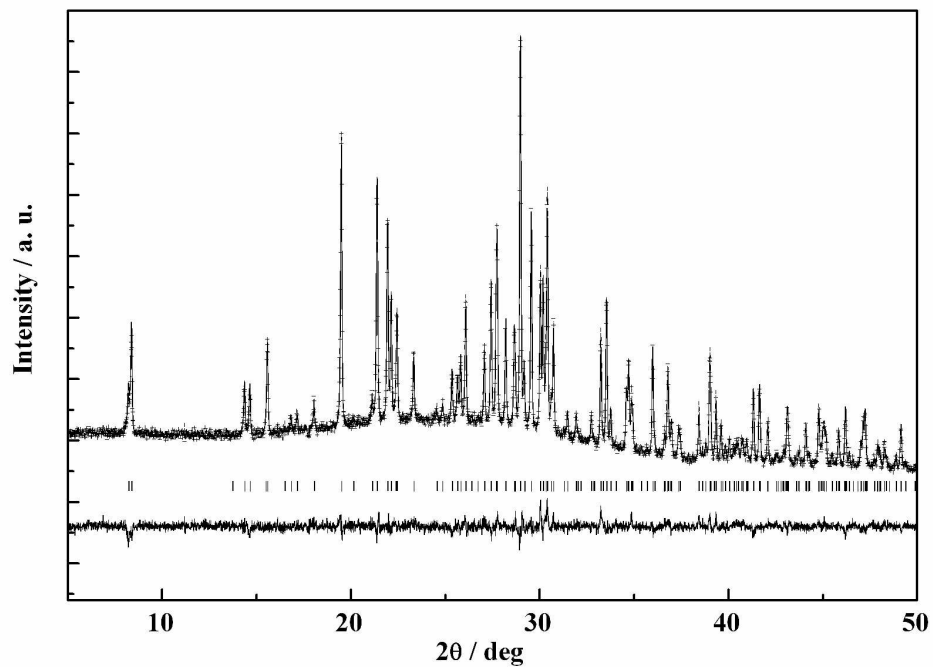


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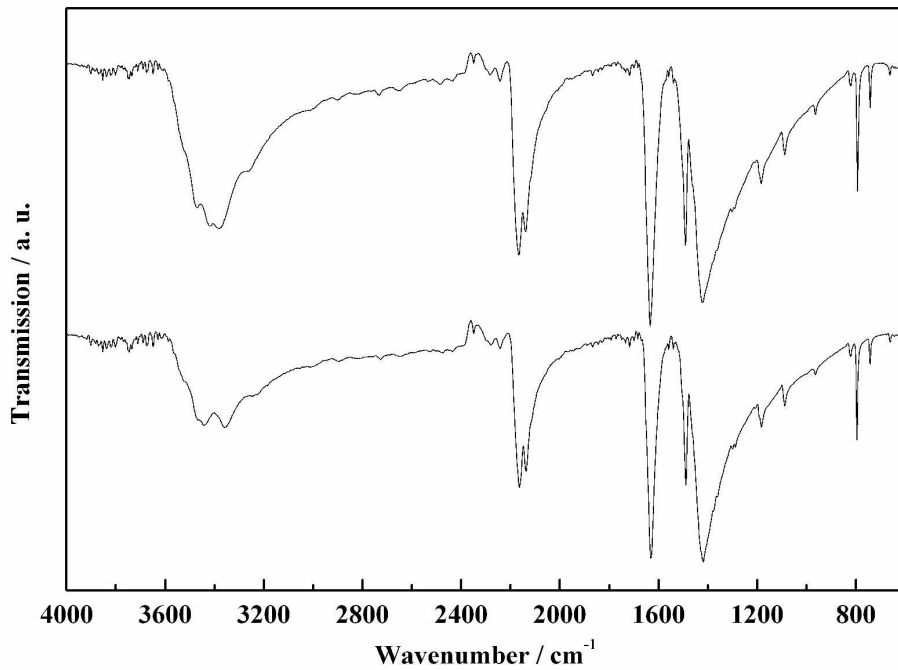


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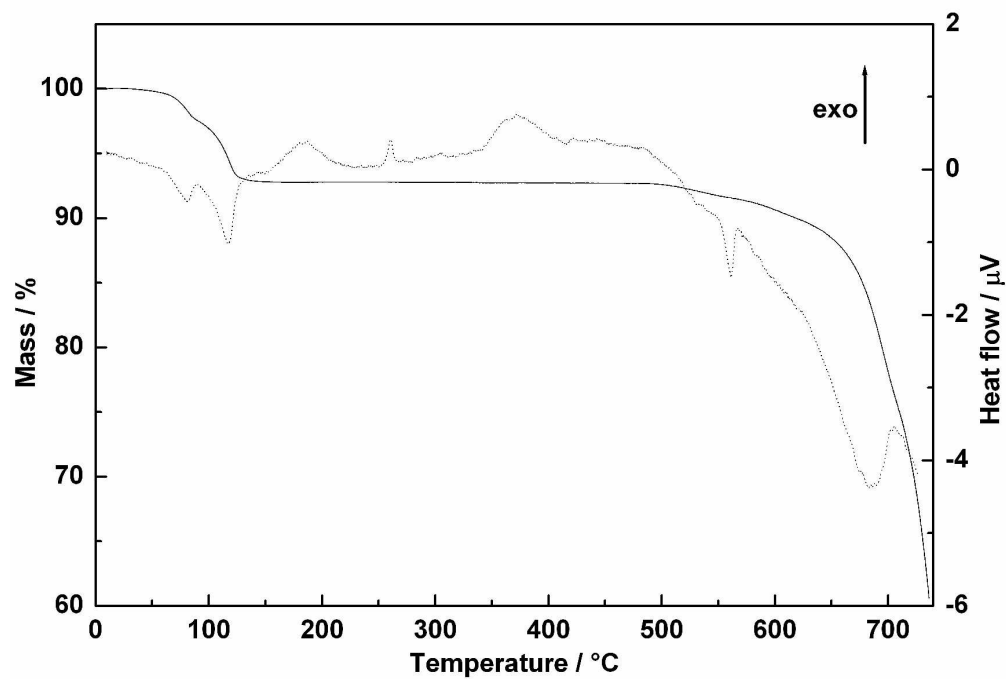


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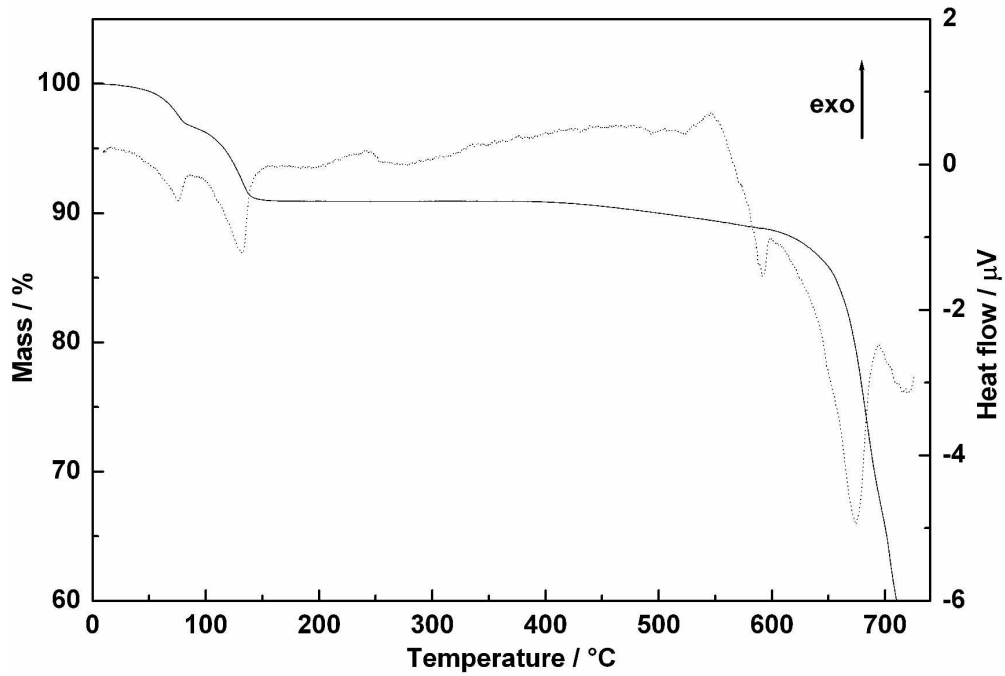


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