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Synthesis, single-crystal structure determination and Raman spectra of the tricyanomelaminates $NaA_5[C_6N_9]_2 \cdot 4\ H_2O$ (A = Rb, Cs)

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Abstract: Transparent colorless crystals of $NaA_5[C_6N_9]_2 \cdot 4\ H_2O$ (A = Rb, Cs) were obtained by blending aqueous solutions of $Na_3[C_6N_9]$ and RbF or CsF, respectively, and subsequent evaporation of the water under ambient conditions. Both compounds crystallize in the space group $P2_1/m$ (no. 11) with the cell parameters a = 815.56(16), b = 1637.7(4) and c = 1036.4(3) pm, and β = 110.738(12)° for $NaRb_5[C_6N_9]_2 \cdot 4\ H_2O$ and a = 843.32(6), b = 1708.47(11) and c = 1052.42(7) pm, and β = 112.034(2)° for $NaCs_5[C_6N_9]_2 \cdot 4\ H_2O$, respectively. Raman spectra of the title compounds complement our results.

Keywords: alkali metal; cesium; Raman spectra; rubidium; sodium; tricyanomelaminate.

1 Introduction

The compound $Na_3[C_6N_9] \cdot 3\ H_2O$, a water-soluble salt containing the tricyanomelaminate anion (called from now on [TCM]) has been known since 1938 [1]. Unfortunately, next to a short sketch of the synthesis (spontaneous trimerization of sodium dicyanamide (dca), $Na[N(CN)_2]$, in aqueous solution) only the lattice parameters, the symmetry and some thoughts concerning the possible crystallographic positions are given. Some 60 years later [2], Schnick et al. reported an alternative synthesis (heat induced trimerization of anhydrous Na[dca] and subsequent recrystallization in aqueous solution) and performed a complete structure analysis on single crystals. Additionally, IR spectra and DSC/TG data were collected. Based on these results, Schnick et al. expanded the knowledge about this class of compounds by synthesizing the anhydrous alkali metal salts A_3[TCM] (A = Na [3], K and Rb [4]) and some of the hydrated species with the stoichiometries $A_3[TCM] \cdot H_2O$ (A = K and Rb) [5] and $Rb[H_2C_6N_9] \cdot ½\ H_2O$ [6] which were also structurally characterized including a study of their thermal behavior. Li_3[TCM] has been synthesized [7, 8], but no structural information is reported, while the cesium salt is only mentioned as unpublished results (ref. [6] in ref. [9]).

While attempting to synthesize Cs_3[TCM] by a metathesis reactions in aqueous solution, we serendipitously found crystals of $NaCs_5[TCM]_2 \cdot 4\ H_2O$. In follow-up experiments we were able to reproduce our results and to also synthesize $NaRb_5[TCM]_2 \cdot 4\ H_2O$. We report here the results of the single-crystal structure determination and the Raman spectra of both compounds and compare them with literature data.

2 Experimental section

2.1 Synthesis

All manipulations were performed under normal atmospheric conditions. Na_3[TCM] was obtained by sealing gram portions of Na[dca] (Alfa Aesar, 96 %) under vacuum in silica tubes and heating the container up to 500 °C with subsequent annealing at this temperature for 6 h. The thus obtained Na_3[TCM] was dissolved with the respective alkali metal fluoride (Aldrich, 99 %) in a stoichiometric ratio of 2:5 (overall mass: 0.5 g) in 10 mL deionized, boiling water. The water was allowed to evaporate at r.t. leaving small cubes of NaF and brick-like cuboids of the title compounds behind.

An analog approach to synthesize $NaK_5[TCM]_2 \cdot 4\ H_2O$ or similar mixed alkali metal compounds has been unsuccessful so far.

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2.2 Crystallographic studies

Crystals of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$ were selected by their habit and immersed in polybutene oil (Aldrich, M_n ~ 320, isobutylene > 90 %) for single-crystal selection under a polarization microscope. Single crystals were mounted in a drop of polybutene sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen (T = 223(2) K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Intensity data were collected with a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The intensity data were manipulated with the program package [10] that came with the diffractometer. An empirical absorption correction was applied using SADABS [11]. The program SHELXS-97 [12, 13] found the positions of the respective alkali metal(s) with the help of Direct Methods. The positions of the carbon and nitrogen atoms and of carbon, nitrogen and oxygen atoms, respectively, were apparent from the positions of the highest electron density on the difference Fourier maps resulting from the first refinement cycles by full-matrix least-squares calculations on F^2 with SHELXL-97 [14, 15]. The positions of the hydrogen atoms could not be found and refined reliably. Doing further refinement cycles with all atoms being refined unrestrained the refinement converged and resulted in stable models for the respective crystal structure. Crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2 for $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and in Table 3 for $NaCs_5[TCM]_2 \cdot 4\ H_2O$. Table 4 displays selected interatomic distances and angles of the title compounds.

Further details of the crystal structure investigation(s) may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; E-mail:

Table 1: Summary of single-crystal X-ray diffraction structure determination data of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$.

Compound	$NaRb_5[C_6N_9]_2 \cdot 4\ H_2O$	$NaCs_5[C_6N_9]_2 \cdot 4\ H_2O$
M_r	918.7	1155.9
Crystal color	Transparent colorless	Transparent colorless
Crystal shape	Irregular thin plate	Irregular plate
Crystal size, mm³	0.07×0.06×0.03	0.12×0.10×0.07
Crystal system	Monoclinic	Monoclinic
Space group (no.); Z	$P2_1/m$ (11); 2	$P2_1/m$ (11); 2
Lattice parameters:		
a, pm	815.56(16)	843.32(6)
b, pm	1637.4(4)	1708.47(11)
c, pm	1036.4(3)	1052.42(7)
β, deg	110.738(12)	112.034(2)
V, Å³	1294.6(5)	1405.56(16)
D_{calcd}, g cm⁻³	2.36	2.73
F(000), e⁻	868	1048
μ, mm⁻¹	9.5	6.5
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD	
Radiation; λ, pm; monochromator	MoK_α; 71.073; graphite	
Scan mode; T, K	ϕ and ω scans; 223(2)	
Ranges		
$2\theta_{max}$, deg	61.11	66.31
h, k, l	−11 → 10, −23 → 23, −14 → 13	−12 → 11, −25 → 26, −15 → 16
Data correction	Lp, SADABS [11]	
Transmission: min./max.	0.597/0.746	0.566/0.747
Reflections: measured/unique	15881/4033	21977/5498
Unique reflections: $F_o > 4s(F_o)$	2631	4491
R_{int}/R_σ	0.0566/0.0607	0.0327/0.0313
Refined parameters	203	203
$R1^a/wR2^b$/GoF^c (all refl.)	0.0729/0.0914/0.972	0.0398/0.0712/1.022
Factors x/y (weighting scheme)^b	0.041/0	0.0359/0
Max. shift, esd, last refinement cycle	<0.0001	<0.0002
$\Delta\rho_{fin}$ (max, min), e⁻ Å⁻³	1.41 (97 pm to H11), −0.93 (192 pm to N11)	2.53 (143 pm to H11), −0.88 (145 pm to Cs4)
CSD number	430375	430376

$^aR1 = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$; $^bwR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, where $P = [(F_o^2) + 2F_c^2]/3$ and x and y are constants adjusted by the program; ^{c}GoF(S) $= [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, with n being the number of reflections and p being the number of refined parameters.

Table 2: Atomic coordinates and equivalent isotropic displacement parameters[a] of $NaRb_5[TCM]_2 \cdot 4\ H_2O$.

Atom	Wyckoff site	x	y	z	U_{eq} (pm^2)[a]
Rb1	2*e*	0.47146(7)	¼	0.02090(6)	286(1)
Rb2	2*e*	0.14802(6)	¼	0.51012(6)	273(1)
Rb3	2*d*	½	½	0	287(1)
Rb4	4*f*	0.23267(4)	0.50508(2)	0.43935(4)	270(1)
Na	2*e*	0.5963(3)	¼	0.4449(2)	240(5)
N1	4*f*	0.2295(4)	0.6347(2)	−0.0350(3)	207(7)
N2	4*f*	0.0782(4)	0.3763(2)	0.0804(3)	249(7)
N3	4*f*	0.1246(4)	0.6261(2)	0.1528(3)	201(6)
C1	4*f*	0.2537(4)	0.6341(2)	0.1006(4)	190(7)
N11	4*f*	0.5768(4)	0.3565(2)	−0.1834(3)	234(7)
C12	4*f*	0.4629(4)	0.6408(2)	0.3168(4)	199(8)
N13	4*f*	0.4863(4)	0.3602(2)	0.5618(3)	259(7)
C2	4*f*	0.0614(4)	0.6291(2)	−0.1212(4)	206(8)
N21	4*f*	−0.0244(4)	0.3708(2)	0.2603(3)	257(7)
C22	4*f*	−0.1617(5)	0.3638(2)	0.2973(3)	228(8)
N23	4*f*	0.2743(4)	0.6436(2)	0.6584(4)	317(8)
C3	4*f*	0.0392(4)	0.3794(2)	−0.0576(4)	223(8)
N31	4*f*	0.1801(4)	0.3875(2)	−0.0987(3)	267(7)
C32	4*f*	−0.1458(4)	0.5996(2)	0.2314(4)	219(8)
N33	4*f*	0.1313(4)	0.4134(2)	0.6550(4)	295(8)
O1	2*e*	−0.1307(5)	¼	0.6403(4)	296(10)
H11[b]	2*e*	−0.195(10)	¼	0.559(9)	740[c]
H12[b]	2*e*	−0.121(11)	¼	0.707(8)	740[c]
O2	2*e*	0.3204(5)	¼	0.2558(5)	345(10)
H21[b]	4*f*	0.267(7)	0.289(3)	0.211(5)	863[c]
O3	4*f*	0.3998(4)	0.4524(2)	0.2407(3)	356(8)
H31[b]	4*f*	0.466(8)	0.419(4)	0.272(6)	891[c]
H32[b]	4*f*	0.284(7)	0.428(4)	0.182(6)	891[c]

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors; [b] Site occupancy was restrained to $^2/_3$; [c] The isotropic displacement factor of the hydrogen atom was constrained to the equivalent displacement factor of oxygen as the last unconstrained atom as suggested in ref. [13].

Table 3: Atomic coordinates and equivalent isotropic displacement parameters[a] of $NaCs_5[TCM]_2 \cdot 4\ H_2O$.

Atom	Wyckoff site	x	y	z	U_{eq} (pm^2)[a]
Cs1	2*e*	0.47125(3)	¼	0.02091(3)	248(1)
Cs2	2*e*	0.15772(3)	¼	0.52806(2)	242(1)
Cs3	2*d*	½	½	0	278(1)
Cs4	4*f*	0.23247(2)	0.50395(1)	0.44584(2)	258(1)
Na	2*e*	0.6023(2)	¼	0.4503(2)	246(3)
N1	4*f*	0.2252(3)	0.6367(1)	−0.0386(2)	202(5)
N2	4*f*	0.0747(3)	0.3731(1)	0.0910(2)	228(5)
N3	4*f*	0.1215(3)	0.6286(1)	0.1433(2)	186(4)
C1	4*f*	0.2485(3)	0.6364(2)	0.0952(3)	177(5)
N11	4*f*	0.5853(3)	0.3567(1)	−0.1812(2)	216(5)
C12	4*f*	0.4507(3)	0.6423(2)	0.3141(3)	183(5)
N13	4*f*	0.5011(3)	0.3574(1)	0.5672(2)	239(5)
C2	4*f*	0.0616(4)	0.6326(2)	−0.1270(3)	202(5)
N21	4*f*	−0.0281(3)	0.3660(1)	0.2653(2)	242(5)
C22	4*f*	−0.1643(4)	0.3578(2)	0.2971(3)	239(6)
N23	4*f*	0.2728(4)	0.6502(2)	0.6616(3)	334(6)
C3	4*f*	0.0380(3)	0.3767(2)	−0.0458(3)	195(5)
N31	4*f*	0.1761(3)	0.3855(2)	−0.0828(2)	257(5)
C32	4*f*	−0.1453(3)	0.6012(2)	0.2125(3)	224(5)
N33	4*f*	0.1385(3)	0.4133(2)	0.6773(3)	296(6)
O1	2*e*	−0.1333(4)	¼	0.6521(3)	283(7)
H11[b]	2*e*	−0.200(9)	¼	0.589(7)	708[c]
H12[b]	2*e*	−0.114(10)	¼	0.710(7)	708[c]
O2	2*e*	0.3155(4)	¼	0.2700(3)	304(7)
H21[b]	4*f*	0.269(6)	0.280(2)	0.233(4)	761[c]
O3	4*f*	0.4051(3)	0.4446(2)	0.2480(3)	360(6)
H31[b]	4*f*	0.491(7)	0.408(3)	0.293(5)	900[c]
H32[b]	4*f*	0.315(7)	0.424(3)	0.211(6)	900[c]

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensors; [b] Site occupancy was restrained to $^2/_3$; [c] The isotropic displacement factor of the hydrogen atom was constrained to the equivalent displacement factor of oxygen as the last unconstrained atom as suggested in ref. [13].

crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-430375 for $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and CSD-430376 for $NaCs_5[TCM]_2 \cdot 4\ H_2O$.

2.3 Raman spectroscopy

The single-crystals of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$ were sealed in thin-walled glass capillaries. Raman spectroscopic investigations were performed on a microscope laser Raman spectrometer (Jobin Yvon, 4 mW, equipped with a HeNe laser with an excitation line at $\lambda = 632.817$ nm, 50× magnification, 8 × 240 s accumulation time). The results are displayed in Fig. 1, the exact frequencies and their assigned modes are shown in Table 5.

3 Results and discussion

3.1 Raman spectra

The frequencies obtained from the Raman spectra of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$ compare well to the vibrational frequencies reported in the literature for $Na_3[TCM] \cdot 3\ H_2O$ [2] or $Rb_3\ [TCM] \cdot H_2O$ [5] (Table 5) and confirm therefore the presence of the tricyanomelaminate anion.

Table 4: Selected bond lengths (pm) and angles (deg) of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$.

$NaRb_5[TCM]_2 \cdot 4\ H_2O$			$NaCs_5[TCM]_2 \cdot 4\ H_2O$		
Rb1–	N1 2×	304.7(3)	Cs1–	N1 2×	318.1(2)
	N11 2×	309.1(3)		N11 2×	327.7(12)
	O2	309.3(5)		O2	326.3(4)
	N31 2×	318.9(3)		N31 2×	327.7(2)
Rb2–	O1	302.7(4)	Cs2–	O1	318.3(3)
	N33 2×	309.5(4)		N33 2×	323.5(3)
	N21 2×	316.5(3)		N21 2×	328.3(2)
	N13 2×	318.0(3)		N13 2×	332.0(3)
	O2	339.8(5)		O2	344.4(4)
Rb3–	O3 2×	299.1(3)	Cs3–	O3 2×	314.9(3)
	N1 2×	304.9(3)		N1 2×	320.7(2)
	N31 2×	305.9(3)		N31 2×	320.4(3)
	N11 2×	322.0(3)		N11 2×	334.4(2)
Rb4–	O3	297.1(3)	Cs4–	O3	312.3(3)
	N33	304.1(3)		N33	322.6(3)
	N33	308.1(3)		N33	322.9(3)
	N13	310.8(3)		N13	329.6(2)
	N23	314.1(4)		N23	330.7(3)
	N21	314.9(3)		N21	329.5(2)
	N13	318.4(4)		N13	330.3(3)
	N3	341.7(3)		N3	364.8(2)
Na–	O2	240.4(5)	Na–	O2	245.1(4)
	O1	242.2(5)		O1	243.5(4)
	N23 2×	246.9(4)		N23 2×	251.7(3)
	N13 2×	251.1(4)		N13 2×	252.9(3)
N1–	C1	134.9(5)	N1–	C1	134.7(3)
	C2	134.9(4)		C2	134.6(3)
N2–	C2	135.1(4)	N2–	C2	134.2(4)
	C3	135.2(5)		C3	135.5(3)
N3–	C1	134.9(4)	N3–	C1	135.3(3)
	C3	135.3(5)		C3	135.5(3)
C12–	N11	130.4(5)	C12–	N11	131.6(3)
	N13	117.7(5)		N13	116.0(3)
C22–	N21	131.1(5)	C22–	N21	132.0(4)
	N23	116.9(5)		N23	115.9(4)
C32–	N31	132.0(5)	C32–	N31	131.0(4)
	N33	116.0(5)		N33	116.7(4)
C1–N1–C2		115.4(3)	C1–N1–C2		115.6(2)
C2–N2–C3		115.1(3)	C2–N2–C3		115.1(2)
C1–N3–C3		115.1(3)	C1–N3–C3		115.1(2)
N11–C12–N13		174.1(4)	N11–C12–N13		173.3(3)
N21–C22–N23		174.2(4)	N21–C22–N23		173.2(3)
N31–C32–N33		173.9(4)	N31–C32–N33		171.8(3)

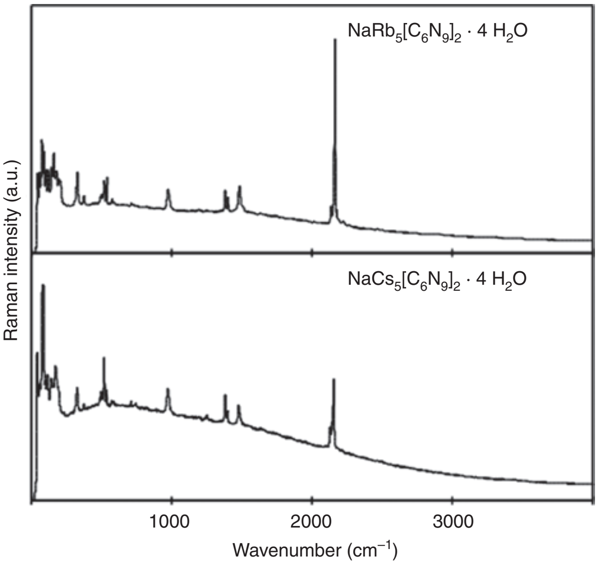

Fig. 1: Raman spectra of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$. On the vertical axis, Raman intensities are displayed in arbitrary units.

3.2 The crystal structures of $NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$

$NaRb_5[TCM]_2 \cdot 4\ H_2O$ and $NaCs_5[TCM]_2 \cdot 4\ H_2O$ are found to be isotypic. Generally speaking, the crystal structure is somewhat typical for [TCM] containing compounds. It is built up from layers of sodium and rubidium or cesium cations, respectively, and of the [TCM] anion. The tricyanomelaminate anion consists of a six-membered triazine ring with three N–C–N substituents each bound to a carbon atom of the triazine ring (Fig. 2). One of the nearly linear substituents is turned by 180°, thereby reducing the molecular symmetry of the anion from C_{3h} to C_s – if one neglects the slight deviations from planarity. All C–N bond lengths and angles (Table 5) are in

Table 5: Raman and IR data[a] of different $[C_6N_9]^{3-}$ compounds compared to $Na_3[TCM] \cdot 3\ H_2O$ and $Na_3[TCM]$ (ref. [2]). Raman results are given as bold face numbers; all numbers are given in cm^{-1}.

	$NaRb_5[TCM]_2 \cdot 4\ H_2O$	$NaCs_5[TCM]_2 \cdot 4\ H_2O$	$Na_3[TCM] \cdot 3\ H_2O$ (ref. [2])	$Rb_3[TCM] \cdot H_2O$ (ref. [5])
	329 m	**326**	–	–
δ_{as}(ring-sub.)	**376 w**	**374 w**	383.3	**376 w**
δ_s(lattice)	**500 w**	**499 w**		**498 w**
δ_s(N–C≡N)	**521 m**	**519 s**	513.5	**519 w**
ν_s(N–C≡N)	**538 m**	**535 m**	570.8/589.4	**538 w**
δ_s(ring)	**976 m**	**973 m**	998.8	**980 w**
ν_{as}(ring-N)	**1382 m**	**1383 m**	1397.0	**1386 w**
ν_{as}(ring-N)	**1402 m**	**1399 m**	1397.0	1395 vs
ν_s(ring-N)	**1486 m**	**1477 m**	1517.5	**1486 w, br**
δ(H–O–H) + ν_{as}(O–H)	**1635 vw**	**1629 vw**	1616.7	1626 m
ν_s(C≡N)	**2135 m**	**2129 m**	–	**2127 w**
ν_s(C≡N)	**2164 vs**	**2155 vs**	2193.1	**2158 vs**

[a] s, Strong; vs, very strong; m, medium; w, weak; vw, very weak weak; br, broad.

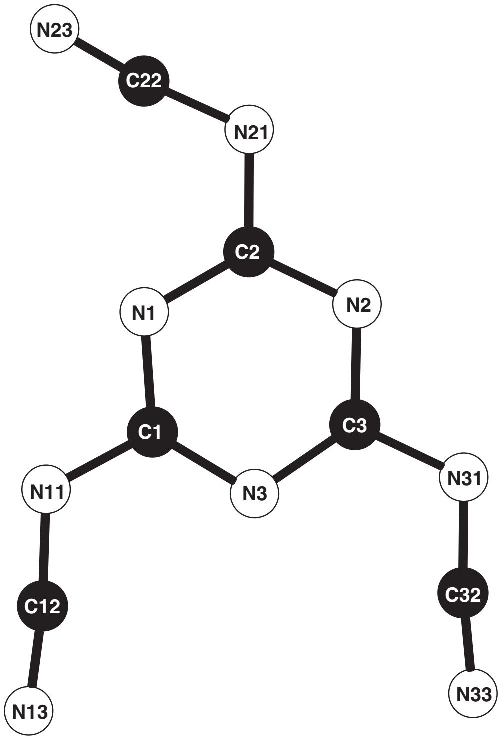

Fig. 2: The [TCM] anion as found in NaA_5[TCM]$_2$ · 4 H_2O (A = Rb or Cs).

the expected range when compared to the lengths and angles of similar compounds. The sodium atom is coordinated in an octahedral fashion by four nitrogen and two *trans*-positioned water molecules. The four crystallographically independent Rb or Cs atoms, respectively, are eight-fold coordinated in an irregular fashion by nitrogen and/or oxygen atoms. The crystal water molecules are found both in the plane of the alkali metal cations, but also displaced from the cation layers (both up and down) completing the coordination sphere of the cations (Fig. 3).

4 Conclusion

The compounds NaRb$_5$[TCM]$_2$ · 4 H_2O and NaCs$_5$[TCM]$_2$ · 4 H_2O were synthesized, their crystal structures have been determined and the Raman spectra of both title compounds recorded. The Raman data as well as the crystal structure are similar to that of previously reported alkali metal tricyanomelaminate compounds such as A_3[TCM] (A = Na [3], K and Rb [4]), A_3[TCM] · H_2O (A = K and Rb) [5]

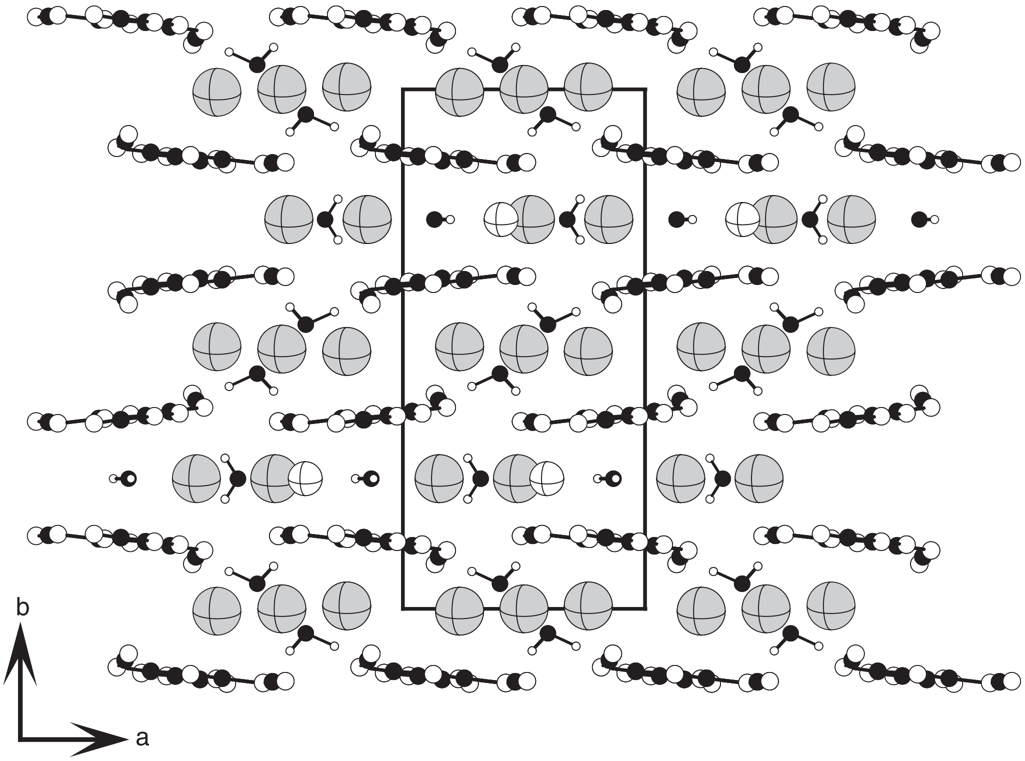

Fig. 3: Non-perspective view on the unit cell of NaA_5[TCM]$_2$ · 4 H_2O parallel to the crystallographic *c* axis (C, black circles; N, white circles; O, black circles; H, white circles; Na, white ellipsoids; Rb or Cs, gray ellipsoids).

or Rb[$H_2C_6N_9$] · ½ H_2O [6]. Due to the employed synthesis, no pure product could be acquired so far, which prevented the acquirement of DSC/TG data as yet.

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