Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information (ESI)

Anhydrous Ionic co-crystals of cyanuric acid with LiCl and NaCl

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EXPERIMENTAL PART

Materials and instrumentation

All reagents and solvents used in this work were purchased from Sigma-Aldrich and used without further purification.

Solid State Synthesis

ICCs of cyanuric acid were obtained by kneading CA (1 mmol) and the corresponding co-former (1 mmol) for 30-60 minutes in a Retsch MM200 ball miller, operated at a frequency of 25 Hz, in the presence of a few drops of solvent (ethanol and water for CA·NaCl, methanol for CA·LiCl). CA·LiCl was also obtained by manual grinding, but its preparation of CA·LiCl was more difficult due to the high hygroscopicity of LiCl, and 4 to 5 cycles of grinding in a mortar (up to 5 minutes) followed by drying in the oven (15-20 minutes) were necessary to get a pure product.

X-ray powder diffraction measurements

Room temperature X-ray powder diffraction (XRPD) patterns were collected on a PANalytical X'Pert PRO automated diffractometer with transmission geometry equipped with Focusing mirror and Pixcel detector in the 2θ range 5–90° (step size 0.0130°, time/step 118.32 s, VxA 40kV x 40mA). Data analyses were carried out using the Panalytical X'pert Highscore Plus program. The identity between the bulk material obtained via solution and solid-state processes was always verified by comparing calculated and observed powder diffraction patterns.

Synchrotron radiation-XRPD measurements of CA·LiCl and CA·NaCl were performed at the Swiss Light Source (SLS) Material Science (MS) Powder Diffracion (PD)[1] end station with a nominal photon energy of 17KeV. Fine Si640D NIST standard refinement returned a wavelength of 0.709703(2)Å and a residual Zero Error of $2\theta = 0.0048(4)°$. Data were collected with a 1D Mythen II detector[2] in the range 2-120° 2θ, with intrinsic step size of 0.0036 (2θ). Samples were loaded in 0.5 mm glass capillaries and spun at 4Hz during the measurement. Multiframing data were recorded in transmission with an exposure time of 5 seconds to avoid radiation damage; the raw data were then individually inspected before being merged together and flat field corrected.

Structural determination of CA·LiCl.

Laboratory data were preliminarily used to determine the crystal structure. Powder diffraction data were analysed with the software X'Pert HighScore Plus[3] and unit cell parameters were found using DICVOL4 or DICVOL algorithms. Initially CA·LiCl was indexed in the cubic system with a unit cell volume of 161.79 $Å^3$. The cell volume corresponds to the volume of 1x(LiCl $C_3N_3O_3H_3$), hence the structure was solved in the triclinic space group P1 by simulated annealing, performed with EXPO2014,[4] using Li and Cl atoms, and one molecule of cyanuric acid. Ten runs for simulated annealing trial were set, and a cooling rate (defined as the ratio Tn/Tn^{-1}) of 0.95 was used. The Platon[5] ADDSYMM SHELX command was subsequently applied, and data were transformed into the trigonal space group R3m.

The Rietveld refinement was subsequently performed with TOPAS 5.0[6] in the R3m space group on *synchrotron* data measurement in the range $2\theta=6.6\text{-}70.5°$. A shifted Chebyshev function with 10 parameters was used to fit the background and two extra peaks to describe the halos of the amorphous material. The peak shape was modelled for size and strain with the Gaussian and Lorentzian functions present in TOPAS 5.0 and the anisostropic peak broadening was modelled as described by Stephens. [7]

The excess of LiCl used in the reaction was identified as LiCl·H_2O monohydrate, which was refined on the basis of the known crystal structure (see Figure ESI-1).

The refinement converged to R_{wp}=4.89 % and R_p= 4.63%.

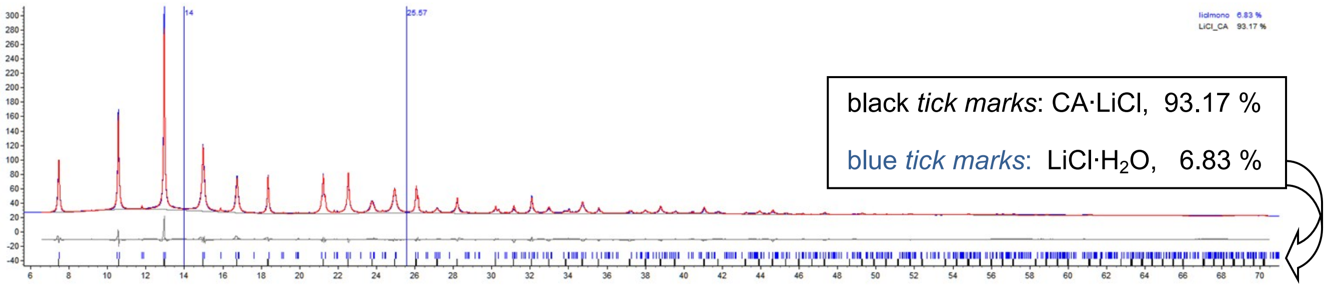


Figure ESI-1.: Rietveld analysis plot of CA·LiCl. Red line is the calculated diffractogram, blue line is the observed diffractogram and grey line is the difference plot. Blue and black tick marks corresponds to CA·LiCl and LiCl·H_2O respectively. Y-axis is reported as $\sqrt{y}$.

The powder pattern of CA·NaCl was indexed in the hexagonal system, space group P6$_3$mc, with a volume cell of 325.231 Å^3 and a plausible solution was found with EXPO 2014 with the simulated annealing algorithm. The structure was analysed with Platon, ADDSYMM SHELX command was applied and a unit cell of a higher symmetry was found. Afterwards, the structure described with P6$_3$/mmc symmetry was used for Rietveld refinements in the range 2θ=5-90°, which were performed with the software TOPAS 5.0. The background was described by modelling the empty capillary and by the Chebyshev function with 2 parameters. The peak shape was modelled for size and strain with the Gaussian and Lorentzian functions present in TOPAS 5.0.

A small quantity of NaCl present was identified in the product pattern, and its profile was refined on the basis of the known crystal structure (see Figure ESI-2).

The refinement converged to R_{wp}=4.55 % and R_p= 4.03%.

Structural data for are listed in Table ESI-1.

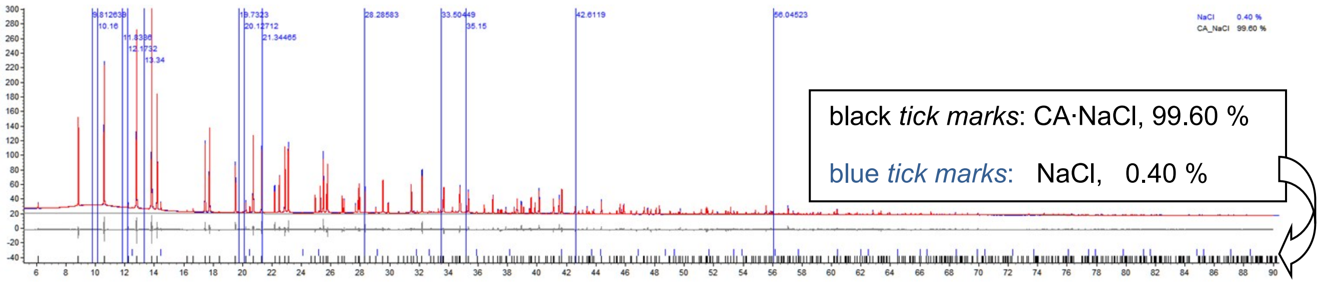


Figure ESI-2. : Rietveld analysis plot of CA·NaCl. Red line is the calculated diffractogram, blue line is the observed diffractogram and grey line is the difference plot. Black and blue tick marks corresponds to CA·NaCl and NaCl respectively. Y-axis is reported as $\sqrt{y}$.

Table ESI-1. Structural data for CA·LiCl and CA·NaCl.

	CA·LiCl	**CA·NaCl**
Formula	$C_3H_3N_3O_3LiCl$	$C_3H_3N_3O_3NaCl$
Fw (g mol^{-1})	171.47	187.52
Crystal system	Trigonal	Hexagonal
Space group	R3m	$P6_3/mmc$
Z	3	2
a (Å)	7.7079(1)	7.6807(1)
b (Å)	7.7079(1)	7.6807(1)
c (Å)	9.4483(3)	6.3662(1)
α (°)	90.0	90.0
β (°)	90.0	90.0
γ (°)	120.0	120.0
V (Å^3)	486.1(1)	325.23(1)
R_wp	4.9	4.5

The programs Vesta[8], Schakal[9] and Mercury[10] were used for graphical representations of the structures. Crystal data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk). CCDC numbers 1524847 and 1524848 for CA·LiCl and CA·NaCl, respectively.

Thermogravimetric Analysis (TGA)

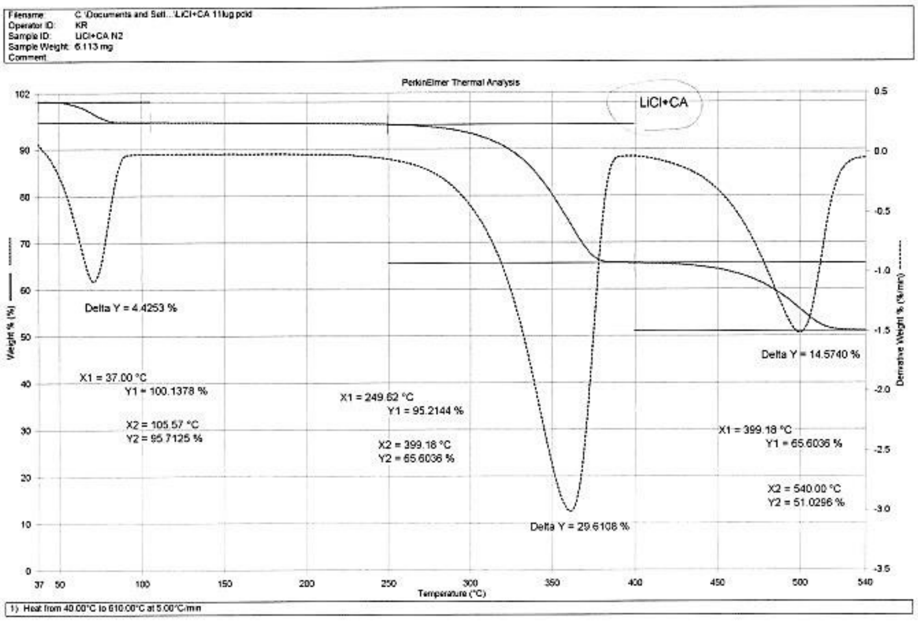
TGA measurements were performed using a Perkin-Elmer TGA7 in the temperature range 30-400 °C under an N_2 gas flow, at a heating rate of 5 °C min^{-1}.

Intrinsic dissolution test for CA·NaCl.

Dissolution rate in ultrapure water solution at room temperature was performed for cyanuric acid and CA·NaCl. Measurements were carried out using a Varian Cary 50 spectrophotometer equipped with a fiber optic dip probe. Absorbance of the solutions was continuously measured during 2 minutes.

Solubility test for CA·NaCl.

A small amount of CA·NaCl was weighed, and portions of it were added to a test tube containing 1mL of water at room temperature, and shaken until the solid was completely dissolved. The procedure was repeated until no more CA·NaCl could be dissolved. The remaining co-crystal was weighed and the difference with the initial quantity calculated as the amount of the co-crystal dissolved. The experiment was repeated 3 times and the average value was used.



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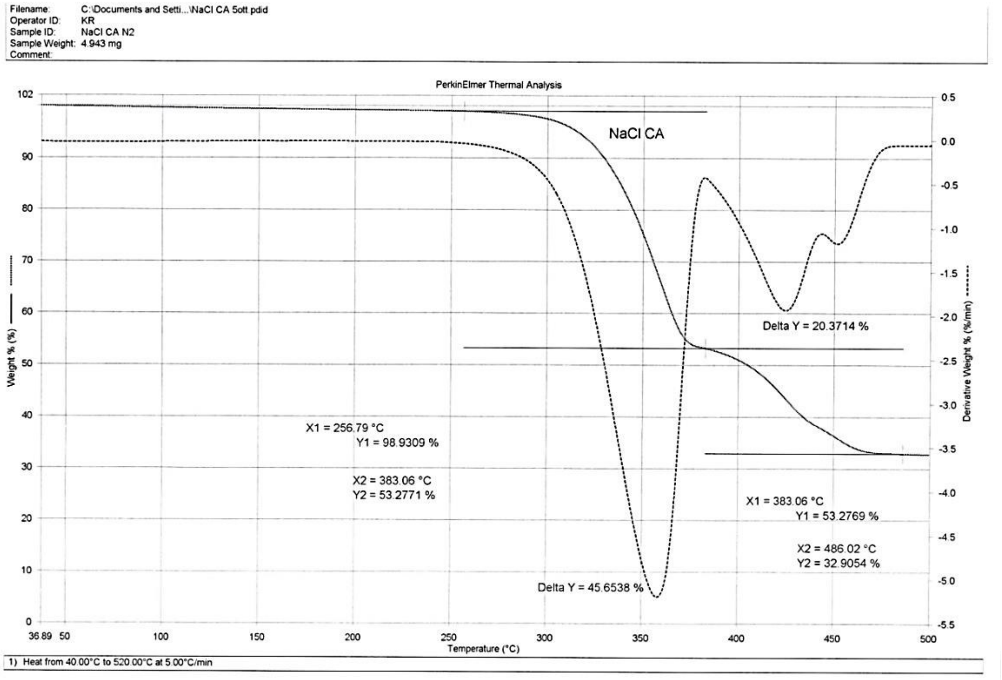
Operator ID: KR
Sample ID: LiCl+CA N2
Sample Weight: 6.113 mg
Comment:

1) Heat from 40.00°C to 610.00°C at 5.00°C/min

Fig. ESI-3. TGA trace for CA·LiCl as obtained from the solid-state reaction. The first weight loss corresponds to excess water adsorbed on the crystals surface, due to the excess of LiCl used in the reaction, which, upon desiccation in the oven, forms monohydrated LiCl (see Fig. ESI-1). The upper solid line, parallel to the x-axis and used to mark the first loss of water, incorrectly suggests that a plateau is present between 37 and 50°C. For this reason the derivative curve has been traced (dotted curve), which shows how water release is active already at 37°C, i.e. at the beginning of the measurement (thus indicating loss of surface water, that is followed by release of crystallization water from $LiCl \cdot H_2O$).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Sample ID: NaCl CA N2
Sample Weight: 4.943 mg
Comment:

1) Heat from 40.00°C to 520.00°C at 5.00°C/min

Fig. ESI-4. TGA trace for CA·NaCl as obtained from the solid-state reaction.

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