Mechanochemical Preparation and Solid-State Characterization of 1:1 and 2:1 Ionic Cocrystals of Cyanuric Acid with Alkali Halides

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ABSTRACT: Mechanochemical mixing of cyanuric acid and alkali halides, which show extreme differences in solubility, is a viable, solvent-free method to quantitatively prepare ionic cocrystals (ICCs) of cyanuric acid (CA) with halide salts of alkali metals. In this paper, we report the preparation and structural characterization of a series of new compounds, namely, $CA_2 \cdot MCl$ (M= Rb, Cs), $CA \cdot MBr$ (M= Na, K, Rb, Cs), and $CA \cdot RbI$, and of the two hydrates $CA \cdot NaBr \cdot 2H_2O$ and $CA \cdot KI \cdot H_2O$. Crystal structures were determined directly from X-ray powder diffraction data in all cases with the exception of $CA \cdot KI \cdot H_2O$, for which single crystals were obtained. The effect of cation size on the stoichiometry as well as on the architecture of the ICCs has been discussed.
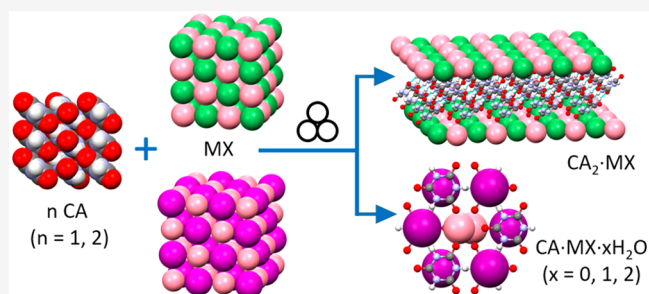
INTRODUCTION

Mechanochemistry refers to reactions that use mechanical energy to facilitate chemical transformations. Mechanochemical approaches are being widely applied across diverse areas of chemical science,[1] since reactions can be promoted quickly and quantitatively either without solvent or with only tiny quantities.[2] In the past, mechanochemistry has been considered a lesser method for chemical synthesis with respect to solution-based approaches. However, the quest for sustainable alternatives to classical synthetic protocols has led to the discovery of new chemical reactions and to the development of a vast series of solvent-free processes.[2]

In the crystal engineering field, mechanochemistry is arguably the most common approach to the synthesis of cocrystals, i.e., of crystalline materials formed by two or more components that are separately solid at ambient conditions.[3−10] Grinding and ball-milling of the solid reactants, whether in "wet" (liquid assisted grinding, also called kneading) or dry conditions, allow one to overcome some of the limitations of other cocrystallization techniques. For instance, the commonly used cocrystallization by slow solvent evaporation often fails because of differences in solubility of the components in a given solvent; analogously, large differences between melting points or the tendency to sublime of one of the components limits the application of cocrystallization by co-melting. On the other hand, the main drawback of mechanochemical preparation of cocrystals is often the difficulty in determining the structural features of the mechanochemical product, because of the obvious lack of crystals suitable for structure determination via X-ray single crystal diffraction. Therefore, to elucidate the crystal structure of the mechanically prepared cocrystals, one can either attempt recrystallization from solution or structure determination directly from powder data. In the former case, however, as mentioned above, the difference in solubility of the components in a given solvent must be taken into account, as dissolution of the cocrystal often implies separation of the components with very different solubility profiles.[11−16] This is especially true in the case of ionic cocrystals (ICCs), composed of an organic moiety and of inorganic salts or complexes, where the difference in solubility in water or organic solvents is usually very large. In all these cases, the best option to determine the nature of the ICC is the structure determination directly from X-ray powder diffraction (XRPD) data.

As a matter of fact, one of the reasons for interest in the ionic cocrystals described herein is precisely the huge difference in solubility and dissolution rate in water of the organic moiety (cyanuric acid, 1,3,5-triazinane-2,4,6-trione, $H_3C_3N_3O_3$, CA hereafter) and of the inorganic salts, demonstrated by the two cases previously communicated (CA·LiCl, CA·NaCl).[17] In this paper, we expand the investigation of the products of the mechanochemical reaction of CA with other MX alkali salts (M = Na, K, Rb, Cs, X = Cl, Br, I).

Cyanuric acid was first synthesized by Friedrich Wöhler in 1829 by thermal decomposition of urea and uric acid,[18] and its

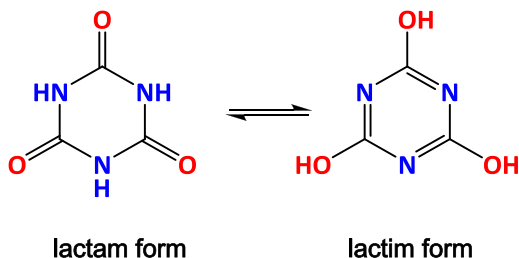crystal structure was determined by Wiebenga in 1952.[19] CA is a highly symmetrical molecule and is often mentioned as a perfect example of lactam−lactim tautomerism (see Scheme 1).

Scheme 1. Lactam−Lactim Tautomerism of Cyanuric Acid

The lactim form structure is prevalent in solution,[20] whereas the lactam form, also referred to as isocyanuric acid, is the thermodynamically stable form in the solid state.[21] Both forms, however, are commonly called "cyanuric acid".[22] In view of its highly symmetrical structure, with three hydrogen bonding C=O acceptor sites and three hydrogen bonding N−H donor sites, CA has been employed in a number of structural and crystal engineering studies, often in conjunction with melamine, as the two molecules possess total complementarity of donor and acceptor groups for the formation of NH⋯N and NH⋯O hydrogen bonds.[23−25]

In view of the analogy with the structure of barbituric acid,[26] which we have previously shown to form stable ionic cocrystals with inorganic salts, we explored and reported on the preparation and properties of ICCs of CA with LiCl and NaCl.[17] Interestingly, CA·LiCl has been recently investigated as a promising solar-blind nonlinear optical material in NLO technology.[27] The study represents an important development, within ionic cocrystal engineering strategies, with respect to the use of cyanurate salts,[28−38] because it allows exploitation of the electronic properties of neutral cyanuric acid in the presence of alkali cations. These findings provided further motivation to expand the family of ICCs of cyanuric acid by cocrystallization with alkali halides of a general formula MX, where M = Na, K, Rb, Cs and X = Cl, Br, I, beyond the initial results obtained with LiCl and NaCl.

It is worth recalling that CA·LiCl and CA·NaCl possess highly symmetrical arrangements of the organic moiety around the alkali cations.[17] The architectures are sustained by direct O⋯M$^+$ interactions of the CA molecules with the alkali cations, and of N—H⋯Cl$^-$ hydrogen bonds with the chloride anions. These are the types of interactions operating in solution of protic solvents, e.g., water, so that these ICCs can also be regarded as special types of solid-state solvates; cocrystallization of CA with NaCl significantly improves the solubility of CA in water and increases the intrinsic dissolution rate of CA, simultaneously decreasing the solubility of NaCl of an order of magnitude.[17]

Besides testing thoroughly the mechanochemical reaction CA + MX (M= Na, K, Rb, Cs, and X= Cl, Br, I), we also hoped to gain insight into the factors controlling the crystal structure stability and whether the formation of 1:1 or 2:1 cocrystals could be attributed to the relationship between cation and anion sizes and the formation of ICCs. The results are grouped in Table 1. In all cases discussed herein, the ICCs were prepared by mechanical mixing[2,3] of CA with the inorganic

Table 1. Ionic Cocrystals of Cyanuric Acid and Alkali Halides Discussed Herein

CA	Cl	Br	I
Li	CA·LiCl[17]	^{a}	^{a}
Na	CA·NaCl[17]	CA·NaBr, CA·NaBr·2H$_2$O	^{a}
K	^{b}	CA·KBr	CA·KI·H$_2$O
Rb	CA$_2$·RbCl	CA·RbBr	CA·RbI
Cs	CA$_2$·CsCl	CA·CsBr	^{b}

^{a}Deliquescent product. ^{b}Physical mixture of the reagents.

salts via kneading with a few drops of solvent (water, ethanol, or methanol), which is the only viable route to their synthesis (see Scheme 2).

Scheme 2. General Scheme for the Mechanochemical Reaction of Cyanuric Acid with Alkali Metal Halides [M = Na, K, Rb, Cs; X = Cl, Br, I]
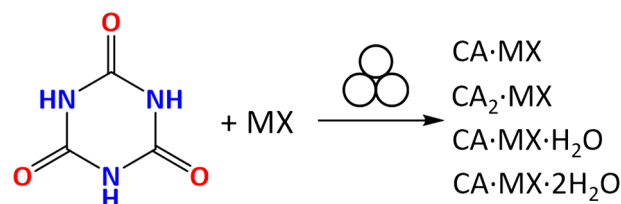
As a matter of fact, in all the cocrystallization approaches mediated by slurry (in both H$_2$O and MeOH) unreacted CA was recovered. Similarly, crystallization/recrystallization from H$_2$O or MeOH invariably led to a separate crystallization of the components. The only exception was the recrystallization of CA with KI, which produced a small number of single crystals suitable for X-ray diffraction, while the majority of the solid recovered was a mixture of the starting materials. Structural determination directly from powder data was thus essential, in view of the polycrystalline nature of the product and of the difficulty in growing single crystals from solution.

■ EXPERIMENTAL SECTION

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

Solid-State Synthesis. All the ICCs were obtained by kneading with ethanol, methanol, or water. CA (1 mmol) and the corresponding coformer (1 or 0.5 mmol for both RbCl and CsCl) were kneaded for 60 min with a Retsch MM200 ball miller operated at the frequency of 25 Hz, using stainless steel jars (5 mL) and two 3 mm balls, with the addition of a drop of solvent. CA·KI·H$_2$O crystals suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation of a methanol saturated solution of the kneading product.

Thermogravimetric Analysis (TGA). TGA measurements (Figures SI-11 to SI-18) for all compounds were performed with a PerkinElmer TGA7 in the temperature range 30−400 °C, under an N$_2$ gas flow, at the heating rate of 5 °C min^{-1}.

X-ray Powder Diffraction Measurements. Room-temperature X-ray powder diffraction (XRPD) patterns were collected on a PANalytical X'Pert PRO automated diffractometer, equipped with an X'celerator detector, in the 2θ range 3−50° (step size 0.0334, time/step 30.480 s, V×A 40 × 40). Data analyses were carried out using the PANalytical X'pert Highscore Plus program.

Structural Characterization from Powder Data. Powder diffraction data were analyzed with the software X'Pert HighScore Plus. 10−20 peaks were chosen in the 2θ range 3−50°, and unit cell parameters were found using the DICVOL4 algorithm. The structures

were initially solved by simulated annealing performed with EXPO2014,[39] using one metal ion, halogen atoms, and one or two molecules of cyanuric acid. Ten runs for simulated annealing trial were set, and a cooling rate (defined as the ratio T_n/T_{n-1}) of 0.95 was used. Platon[40] ADDSYMM SHELX command was consequently applied to find the space group with the highest reasonable symmetry. Afterward, the best solutions were used for Rietveld refinements, performed with the software TOPAS5.0.[41] Structural data for all compounds investigated in this work are listed in Table SI-1.

Single Crystal X-ray Diffraction. Single crystal data for CA·KI·H₂O were collected at RT on an Oxford X'Calibur S CCD diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.71073 Å). Data collection and refinement details are listed in Table SI-1. The structure was solved by the intrinsic phasing methods and refined by least-squares methods against F^2 using SHELXT-2018[42] and SHELXL-2018[42] with Olex2 interface.[43] Non-hydrogen atoms were refined anisotropically. H_{OH} and H_{NH} atoms were either located from a Fourier map or added in calculated positions and refined riding on their respective nitrogen or oxygen atoms. The software Mercury 4.0[44] was used for graphical representations and for powder pattern simulation on the basis of single crystal data.

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 email: deposit@ccdc.cam.ac.uk). CCDC numbers 1997990−1997998.

■ RESULTS AND DISCUSSION

As shown in Table 1, mechanical mixing of CA with MX salts (M = Na, K, Rb, Cs, and X = Cl, Br, I) yielded a series of ICCs, analogous to the ICCs CA·LiCl and CA·NaCl, discussed previously.[17] Reactions were carried out by kneading (also called liquid assisted grinding, LAG[2]) with the addition of a small quantity of solvent to a physical mixture of the reactants in adequate stoichiometric ratios. In all cases, recrystallization from water, methanol, and ethanol was attempted with the aim of obtaining single crystals suitable for X-ray diffraction. In view of the large differences in solubilities mentioned above, all attempts proved unsuccessful, and only starting materials were recovered. At variance with this behavior, the ICC between CA and KI yielded a small number of single crystals, which turned out to be the monohydrate CA·KI·H₂O. For all the other ICCs, therefore, structures had to be determined from X-ray powder diffraction data, which revealed, inter alia, that most ICCs discussed here are anhydrous. The formation of anhydrous compounds of alkali salts is per se rather unusual, since the majority of ICCs of alkali halides prepared this far[11,14,15] tends to form hydrates, while anhydrous forms can be only obtained, in some cases, by subsequent dehydration processes, and are, in general, highly hygroscopic. We attribute this difference to the peculiar structure of CA, i.e., to its small size and highly symmetrical shape, a combination that affords optimal packings with spherical ions, as will be apparent in the following.

Ionic Cocrystals of CA with MCl (M = Li, Na, K, Rb, Cs). The structural features of the LiCl and NaCl cocrystals with CA have been described previously and need not be discussed here in detail.[17] The interaction of CA with alkali chloride salts formed by the smallest cations of the group resulted into formation of materials in 1:1 stoichiometry.

On increasing the size of the cations, passing from Li⁺ and Na⁺ to Rb⁺ and Cs⁺, a change in stoichiometry is observed, resulting in the formation of the isomorphous pair CA₂·RbCl and CA₂·CsCl (see below). When the reaction of CA with KCl

was attempted, however, no ICC could be obtained, irrespective of stoichiometry or method employed (kneading with ethanol, H₂O, and methanol, etc.). This might indicate that the K⁺ cation is either too large to form a stable 1:1 ICC with CA, and too small to form a stable 2:1 ICC. In order to circumvent this problem, attempts were made to prepare ICCs as solid solutions via mechanochemistry. The stoichiometric ratios 1:0.5:0.5 and 1:0.8:0.2 were chosen for CA:NaCl:KCl mixtures, while 2:0.5:0.5 and 2:0.8:0.2 were chosen for CA:RbCl:KCl mixtures. The idea was that of exploring the possibility of accommodating a smaller quantity of K⁺ cations within the lattices of CA·NaCl or CA₂·RbCl. The experiment, however, proved unsuccessful, and in all cases a physical mixture of the reagents was obtained.

The ICCs CA₂·RbCl and CA₂·CsCl are isomorphous. Figure 1 shows the main packing features for the rubidium ICC. This
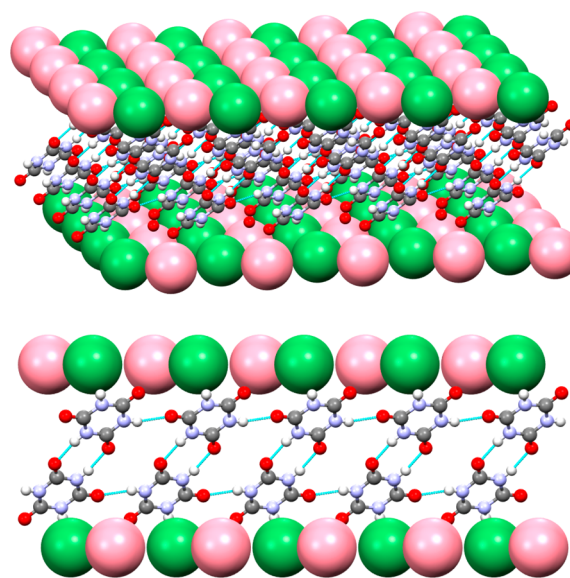

Figure 1. (Top) Layered structure of CA₂·RbCl (CA₂·CsCl is isomorphous); (bottom) CA molecules are "sandwiched" in between "RbCl" 2D-layers, and interact to each other via hydrogen bonds of the NH···O type (light blue). Pink: Rb⁺ cations; green: Cl⁻ anions.

is a typical example of nonstandard coordination found with large alkali metal cations: the number of contacts involving the Rb⁺ ion and the surrounding CA oxygens and chloride anions is large, and no regular polyhedron can be drawn around the cation. The crystal is better described as a layered structure with alternating "RbCl" or "CsCl" and double CA sheets (Figure 1, top), with CA molecules interacting to each other via N—H···O hydrogen bonds, and directing one-third of the N—H and C=O groups toward the anions and the cations, respectively (Figure 1, bottom).

The two ICCs, CA₂·RbCl and CA₂·CsCl, although isomorphous, show a markedly different behavior toward moisture. The former ICC is stable if exposed to air at room temperature, whereas the latter is highly hygroscopic, readily adsorbing water from the atmosphere and becoming a sticky solid. A change in the XRPD pattern is observed for CA₂·CsCl upon hydration, but the initial anhydrous pattern is restored upon heating.

Ionic Cocrystals of CA with MBr (M = Li, Na, K, Rb, Cs). The ICCs obtained with NaBr, KBr, and RbBr are all characterized by a 1:1 stoichiometry. So far, preparation of

CA·LiBr has proven unsuccessful, yielding unreacted material often together with some unidentified solids. The mechanochemical reaction of CA with alkali bromides proceeds to completion in a shorter time with respect to the analogous chloride salts; as an example, the reaction of a mixture NaCl and NaBr with CA yielded quantitatively CA·NaBr within 15 min, while after that time CA and NaCl were still unreacted.

Mechanochemical reaction of NaBr with CA in 1:1 stoichiometric ratio resulted in different products, depending on the solvent used in the kneading process: when a few drops of methanol or ethanol were added to the reagents mixture, the anhydrous ICC of formula CA·NaBr was obtained, which is isomorphous with CA·NaCl.[17] When the same experiment was performed using drops of water, however, the hydrated ICC of formula CA·NaBr·2H$_2$O was obtained (see Figure 2).
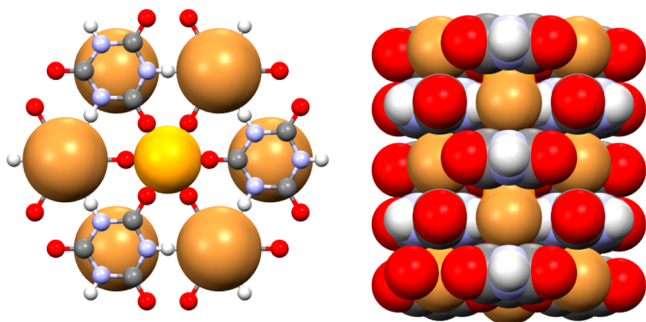

Figure 2. Octahedral coordination around Na$^+$ in CA·NaBr (left). The compound is isostructural with CA·NaCl.[20] A lateral view (right) showing the intercalation of bromide anions with CA molecules along the c-axis. Yellow: Na$^+$ cations; brown: Br$^-$ anions.

In the hydrated ICC CA·NaBr·2H$_2$O, three water molecules enter the coordination sphere of the cations, taking the place of three CA molecules: as the stoichiometric ratio CA·NaBr is still 1:1, two water molecules act as bridges between pairs of Na$^+$ cations (see Figure 3).

On passing to the larger cations K$^+$, Rb$^+$, and Cs$^+$, we see again the formation of anhydrous ICCs. In the case of the potassium, the resulting ICC is quasi-isostructural with the
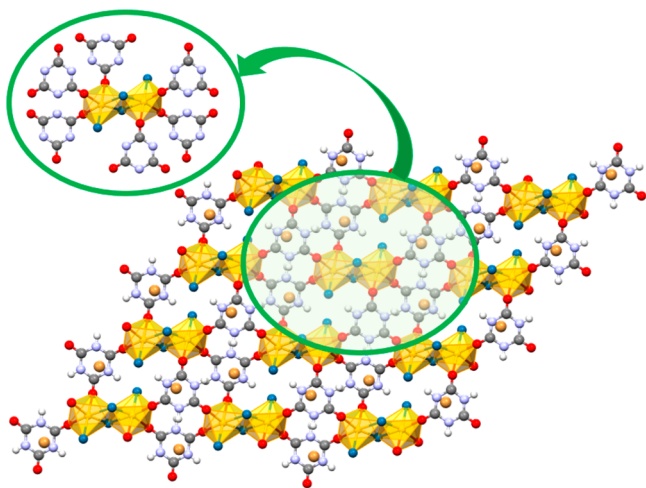

Figure 3. Pairs of sodium cations in CA·NaBr·2H$_2$O (view in the 110 plane) are bridged by water molecules (in blue), which are part of the octahedral coordination spheres.

sodium chloride ICC, with each potassium surrounded by six CA molecules, which are intercalated between anions along the a-axis in channel-like fashion, as shown in Figure 4b (compare with Figure 2).
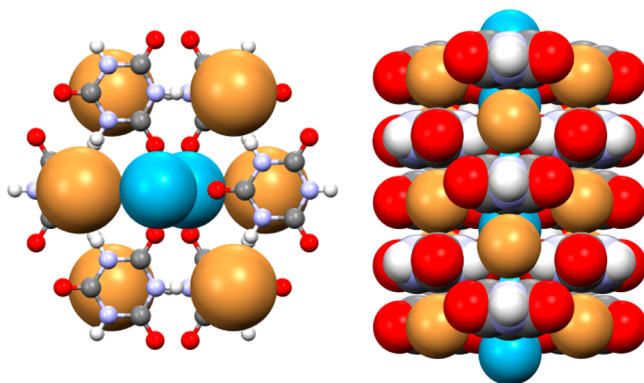

Figure 4. Structure of CA·KBr viewed down the a-axis (left) and a side-view showing the alternation of bromide anions and CA molecules (right). Light blue: K$^+$ cations; brown: Br$^-$ anions.

In these cocrystals, as well as in those of the CA·MI type (M = Na, K, Rb) (see below), there is a clear tendency for the anions to interact directly with the π-system of the cyanuric acid molecules. This type of anion−π interactions involving cyanuric acid has been the subject of a computational study by Frontera et al.[45]

The ionic cocrystals CA·RbBr and CA·CsBr constitute an isomorphous pair (see Table SI-1). Again, as in the case of the isomorphous pair CA$_2$·RbCl and CA$_2$·CsCl, the packing can be described as alternating sheets of cations/anions and, this time due to a 1:1 stoichiometry, of monolayers of CA molecules (see Figure 5).
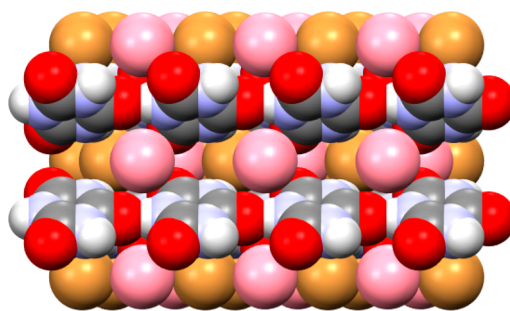

Figure 5. Layered structure of CA·RbBr (CA·CsBr is isomorphous), with CA molecules sandwiched between layers of rubidium cations and bromide anions; layers are extending parallel to the ab-plane. Note the similarity with the layered structure of the 2:1 ICCs CA$_2$·RbCl and CA$_2$·CsCl, although this time the CA molecules are arranged in monolayers (1:1 stoichiometry). Pink: Rb$^+$ cations; brown: Br$^-$ anions.

Ionic Cocrystals with MI (M = Na, K, Rb). In this subset of ICCs, we report the successful characterization of two compounds, namely, the anhydrous CA·RbI, which is isomorphous with CA·KBr (see Figure 6), and the monohydrate CA·KI·H$_2$O. All efforts to characterize the products of the mechanochemical reactions of CA with LiI, NaI, and CsI were frustrated. In particular, the reaction with LiI resulted in the formation of a new phase, which was highly
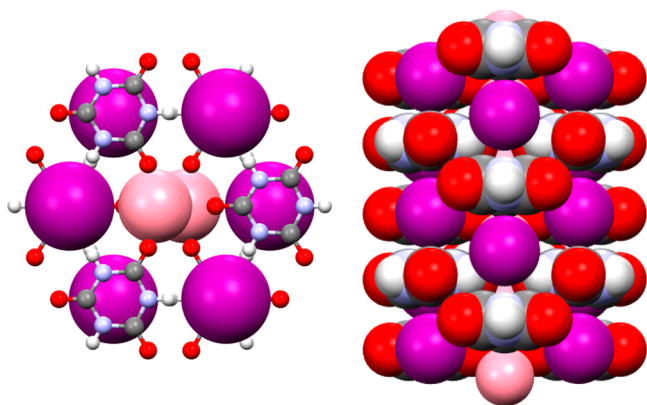
Figure 6. Arrangement of cations, anions, and CA molecules, viewed down the crystallographic *a*-axis in crystalline CA·RbI (left), which is isomorphous with CA·KBr (see Figure 5), and a side-view showing the alternation of bromide anions and CA molecules (right). Pink: Rb$^+$ cations; purple: I$^-$ anions.

hygroscopic and unstable upon standing in the air at ambient conditions, turning into a deliquescent substance in a matter of minutes. Analogous behavior was observed for the products with NaI and CsI (see Table 1). In this respect, CA·LiCl appears to afford the only stable combination of size and stoichiometric ratio for an ICC of CA with the Li$^+$ cation.

As stated above, the two ICCs CA·KBr and CA·RbI are isomorphous (see Table S1): the Rb$^+$ radius is larger than the one for K$^+$, but the size of the anion also increases on passing from Br$^-$ to I$^-$; therefore, a larger anion requires a larger cation. If the cation remains the same but we use a larger anion, as is the case with KI, a water molecule is required per formula unit to "fill in" the extra volume left in the crystal. In this way, the monohydrate CA·KI·H$_2$O is formed, for which structural determination from single crystal data was possible. CA·KI·H$_2$O was found to be quasi-isostructural with the ICCs CA·NaCl, CA·NaBr, CA·KBr, and CA·RbI (see Figure 7): distortion of the packing arrangement is observed, accompanied by loss of symmetry from orthorhombic *Pnma* to monoclinic *P*2$_1$/*c*.

It is remarkable how these cocrystal structures can be rationalized according to a simple model based on the ratio between cation and anion sizes (see Table 3).[46] The ion relative dimensions appear to play a fundamental role in
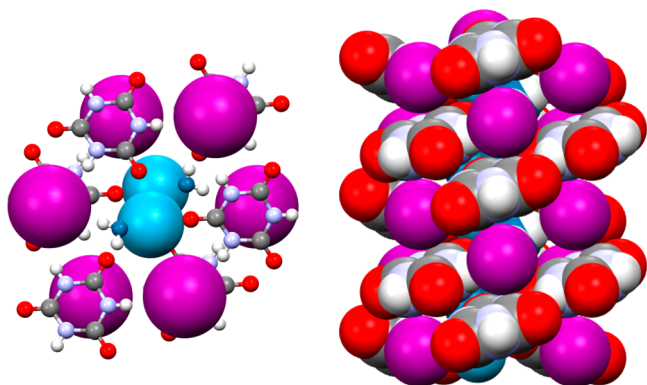
Table 3. Shannon & Prewitt Ionic Radii, Used Here for Ion Size Comparison[46]

| cation	radius^a (pm)	anion	radius^a (pm)
Li$^+$	73		
Na$^+$	116	Cl$^-$	167
K$^+$	152	Br$^-$	182
Rb$^+$	166	I$^-$	206
Cs$^+$	181		

^{a}Coordination number is 6 for all ions except lithium, for which the C.N. Four is considered.

determining not only whether a given ICC of CA can or cannot be obtained but also the stable stoichiometry for the compounds.

Three situations can be distinguished:

(i) When the size of the cation is markedly smaller than the size of the anion, as in the case of LiCl (Scheme 3), the lithium
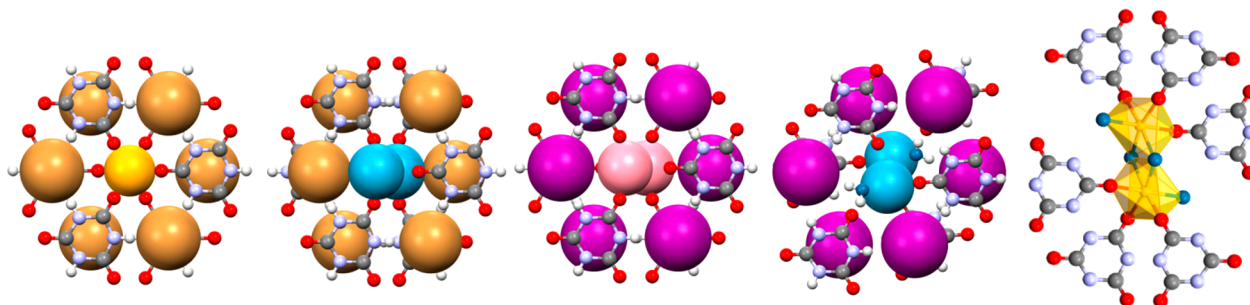
**Scheme 3. Cation Size Is Markedly Smaller than the Size of the Anion: CA·LiCl.[17]**
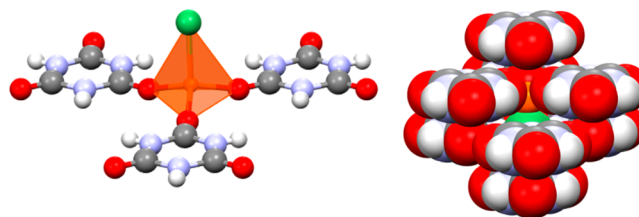
cation is tetrahedrally coordinated by CA molecules and a chloride anion, but the ICC is better described as formed by Li$^+$Cl$^-$ "ionic pairs" surrounded by eight CA molecules in a cubic fashion;[17] the CA:MX stoichiometric ratio is 1:1. Increasing the anion size further does not seem to allow stable packings, and crystalline CA·LiBr, CA·LiI are not obtained.

(ii) When the size of the cation is smaller than the size of the anion (Scheme 4), ICCs with 1:1 stoichiometry are observed forming isomorphous (NaBr), isostructural (KBr, RbI), or quasi-isostructural (KI, with the presence of water) structures with respect to CA·NaCl; in the case of NaBr, water can be accommodated in the crystal, and a derivative structure with pairs of cations bridged by water molecules is also observed. (iii) When cation and anion have similar radii, layered structures are obtained (Scheme 5). The stoichiometry is 2:1 in the case of the chlorides RbCl and CsCl, and 1:1 for the bromides RbBr and CsBr.

These trends are reminiscent of those relating structural types of crystalline alkali halides with the notable difference that, in these ICCs, it is the very stoichiometry of the product (1:1 or 2:1) that is dictated by the need to obtain close-packed crystal structures. In this respect, we take as a negative counterproof that we have been unable to obtain ICCs with LiBr and LiI. Packings of the large anions with the very tiny Li$^+$ cation appears to lead to unstable arrangements. In fact, the products of the mechanochemical reactions are extremely hygroscopic and deliquescent materials that proved impossible to handle. Similarly, the passage from NaCl to RbCl and CsCl marks the "switch" in stoichiometry from 1:1 to 2:1 with the chlorides. In this respect, it is noteworthy that no ICC could be obtained with KCl, suggesting that the K$^+$/Cl$^-$ radius ratio is not optimal in either 1:1 or 2:1 cocrystals structures.

Figure 7. Main packing motif in the crystals structure of CA·KI·H$_2$O (view down the *b*-axis). Note the similarity with the packing arrangement for CA·NaBr, CA·KBr, and CA·RbI. Light blue: K$^+$ cations; violet: I$^-$ anions; blue: water oxygens.

Scheme 4. Cation Size Is Smaller than the Size of the Anion[a]

[a]From left to right: CA·NaBr, CA·KBr, CA·RbI, CA·KI·H$_2$O, CA·NaBr·2H$_2$O.

Scheme 5. Cation size Is Similar to the One of the anion[a]
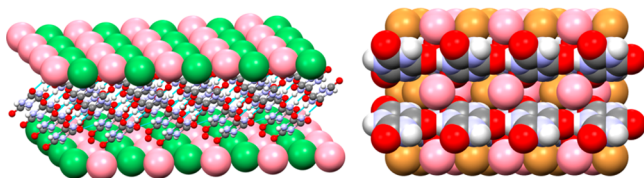
[a]Left: CA$_2$·RbCl (and isomorphous) CA$_2$·CsCl); right: CA·RbBr (and isomorphous CA·CsBr).

CONCLUSIONS

Mechanochemical mixing of solid reactants is not only a viable, solvent-free, alternative to solution methods for the preparation of new compounds and materials, but often it is the only way to overcome the problems caused by large differences in solubilities of the reactants.[2,3] This is especially true in crystal engineering exercises aimed at the preparation of hybrid materials between organic fragments and inorganic salts or coordination compounds, e.g., ionic cocrystals.[6] As a matter of fact, mechanochemical methods have been successfully applied in a number of cocrystal syntheses. For example, mechanical mixing of urea with Mg and Ca salts has been used to prepare ionic cocrystals with the aim to provide additional primary and secondary nutrients, such as P, Ca, Mg, and S, in sustainable soil fertilization.[47−50]

In this paper, we have systematically applied grinding and ball-milling in both dry and wet conditions to prepare an entirely new series of ICCs of CA with alkali halides. Beside the interest in associating cyanuric acid with soluble alkali salts for its potential industrial applications,[22,51] there is the attractive possibility of using stable crystalline solids containing neutral CA in solar-blind nonlinear optical material in NLO technology.[27]

The main problem to overcome in mechanochemical preparations is the polycrystalline nature of the products that does not permit single crystal structure analysis. Furthermore, the extreme difference in solubility between cyanuric acid and the alkali salts prevents the recrystallization of the products as single crystals, because when the polycrystalline product is dissolved in water, immediate separation of the insoluble organic moiety from the soluble inorganic component is observed. It has been necessary to recast to systematic crystal structures the determination directly from the powder diffraction data allowing, inter alia, rationalization of the reasons for the absence of some ICCs and also identification of structural types and reasons for the switch from 1:1 to 2:1 stoichiometry on increasing cation and/or anion sizes.

ASSOCIATED CONTENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

CA, cyanuric acid; XRPD, X-ray powder diffraction

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