Two light-metal dihydrogenisocyanurate hydrates linked by diagonal relationship: syntheses, crystal structures, and vibrational spectra of Li[H2N3C3O3]·1.75 H2O and Mg[H2N3C3O3]2·8 H2O

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ARTICLE

Two Light-Metal Dihydrogenisocyanurate Hydrates Linked by Diagonal Relationship: Syntheses, Crystal Structures, and Vibrational Spectra of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$

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Dedicated to Professor Juri Grin on the Occasion of his 65th Birthday

Abstract. Single-crystalline materials of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ were obtained by dissolving stoichiometric amounts of the respective carbonates with cyanuric acid in boiling water followed by gentle evaporation of excess water after cooling to room temperature. Even though both of these compounds crystallize in the triclinic space group $P\bar{1}$ according to X-ray structure analyses of their colorless and transparent single crystals, they adopt two new different structure types. $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ exhibits the unit-cell parameters a = 884.71(6) pm, b = 905.12(7) pm, c = 964.38(7) pm, α = 67.847(2)°, β = 62.904(2)° and γ = 68.565(2)° (Z = 4), whereas the lattice parameters for $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ are a = 691.95(5) pm, b = 1055.06(8) pm, c = 1183.87(9) pm, α = 85.652(2)°, β = 83.439(2)° and γ = 79.814(2)° (Z = 2). In both cases, the singly deprotonated isocyanuric acid forms monovalent anions consisting of cyclic $[H_2N_3C_3O_3]^-$ units, which are arranged in ribbons typical for most hitherto known monobasic isocyanurate hydrates. The structures are governed by the oxophilic strength of the respective cation which means that they fulfil their oxophilic coordination requirements either solely with water molecules ($[Mg(OH_2)_6]^{2+}$ for Mg^{2+}) or with crystal water and one or two direct coordinative contacts to carbonyl oxygen atoms ($O_{(cy)}$) of $[H_2N_3C_3O_3]^-$ anions ($[(Li(OH_2)_{2-3}(O_{(cy)1-2}]^+$ for Li^+). In both structures occur dominant hydrogen bonds N–H···O within the anionic $[H_2N_3C_3O_3]^-$ ribbons as well as hydrogen bonds O–H···O between these ribbons and the hydrated Li^+ and Mg^{2+} cations.

Introduction

A so-called diagonal relationship seems to exist between certain pairs of elements, which stand diagonally adjacent especially in the second and third periods of the periodic table. Pairs such as boron and silicon or beryllium and aluminium exhibit similar properties, which have become common textbook knowledge.[1] Hence, certain properties of lithium and magnesium compounds confirm such a close relationship for this pair as well. Some prominent examples are the formation of regular ionic oxides (Li_2O and MgO) upon combustion of the metals in air, the facile decomposition of the carbonates ($Li_2[CO_3]$ and $Mg[CO_3]$) into the same oxides and CO_2, the ready formation of colored nitrides (Li_3N and Mg_3N_2) from the elements or the low solubility of the fluorides in ammonia-containing $[NH_4]F$ solutions.[2] Additionally, many of their salts show similar low solubilities in aqueous solution (e.g. Li[OH] and $Mg[OH]_2$, $Li_2[CO_3]$ and $Mg[CO_3]$ or $Li_3[PO_4]$ and $Mg_3[PO_4]_2$), whereas some pairs of similar lithium or magnesium compounds dissolve rather easily in organic solvents (e.g. LiCl and $MgCl_2$ or $Li[ClO_4]$ and $Mg[ClO_4]_2$ in ethanol or aceton). These similarities occur despite the fact that the charge-to-radius quotients of their cations (1 : 0.59 = 1.7 for Li^+ vs. 2 : 0.57 = 3.5 for Mg^{2+}) differ significantly. These figures explain the fact, why Li^+ and Mg^{2+} cations are more strongly hydrated in aqueous solution than heavier congeners (1 : 1.02 = 0.98 for Na^+ and 2 : 0.99 = 2.0 for Ca^{2+}).

To the best of our knowledge, a plethora of alkali- and alkaline-earth metal cyanurates or cyanurate hydrates have been reported and characterized,[3–11] but the monoclinic compound $Li_2[HN_3C_3O_3]\cdot 2\ H_2O$ was the only one containing only Li^+ or Mg^{2+}, respectively. Exploiting a review paper by *Seifer*,[12] we started to reproduce the reported synthesis for lithium and magnesium cyanurates in order to elucidate, if the diagonal relationship prevails under these conditions or if the general trend of "the higher the charge-to-radius quotient is, the more

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hydrated the cation becomes", will be confirmed. We report here the synthesis and crystallographic characterization of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$, two compounds both featuring dihydrogenisocyanurate anions $[H_2N_3C_3O_3]^-$.

Results and Discussion

Crystal Structures

Both title compounds contain two crystallographically different deprotonated $[H_2N_3C_3O_3]^-$ anions (Figure 2 and Figure 7). Due to the deprotonation, these anions exhibit different C–N and C–O bond lengths, if compared to the neutral molecule (d(C–N) = 137 pm and d(C–O) = 121.6 pm[19]). The bond lengths connecting the deprotonated nitrogen to the closest carbon atom is around 135 pm and therefore shorter, while the other pairs of C–N bonds in the ring are somewhat longer ranging from 135 to 139 pm. The C–O bonds close to the deprotonated nitrogen atom are about 1.5 pm longer than expected, whereas the C–O distances within these moieties are in the same range as in the neutral acid molecule $[C_3N_3(OH)_3]$.

In $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ two crystallographically different magnesium dications are coordinated in a well-known and nearly perfect octahedral fashion exclusively by water molecules (Figure 1).

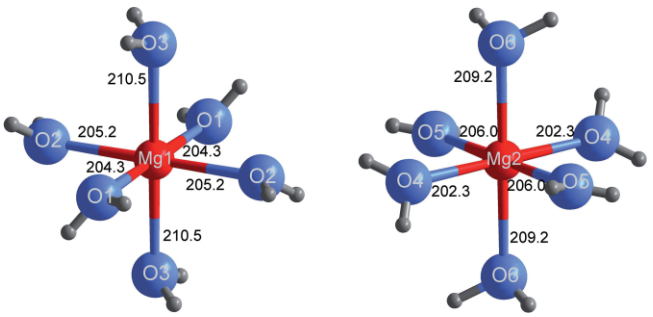

Figure 1. The two crystallographically different $[Mg(OH_2)_6]^{2+}$ cations in $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ (Mg–O distances in pm).

These $[Mg(OH_2)_6]^{2+}$ complexes (d(Mg–O) = 202–211 pm) form closest packed layers in coplanar orientation to the crystallographic *ac* plane with the *b* lattice parameter as distance between the cationic layers (Figure 2 and Figure 3). Together with two additional non-coordinating water molecules ($H_2O_{(w)}$) within these layers, a two-dimensional network of hydrogen bonds is nicely formed in a way that every single of the above-mentioned $[Mg(OH_2)_6]^{2+}$ octahedra becomes hydrogen-bonded to six water molecules (two O···H–$O_{(w)}$ and four O–H···O bonds), whereas each one of the $H_2O_{(w)}$ molecules is involved in three hydrogen bonds (one $O_{(w)}$–H···O and two $O_{(w)}$···H–O). In this regard these cationic layers can be considered as $^2_\infty\{[[Mg(OH)_2)_6]\cdot(H_2O)_{6/3}]^{2+}\}$ sheets. In between those layers dihydrogenisocyanurate anions $[H_2N_3C_3O_3]^-$ form typical almost planar ribbons (Figure 4) running nearly parallel to the crystallographic *c* axis, which are stacked offset parallel along the *a* axis at a distance of half of its translation period (Figure 2, Figure 3, and Figure 4).

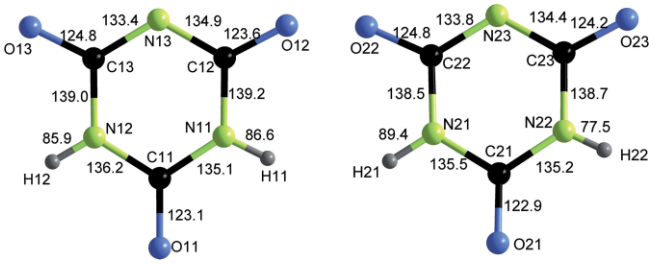

Figure 2. The two crystallographically different $[H_2N_3C_3O_3]^-$ anions in $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ (interatomic distances in pm).

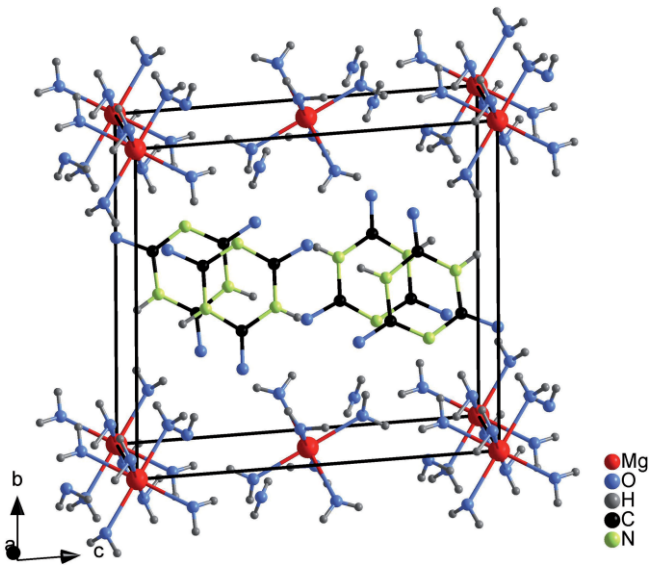

Figure 3. View at the crystal structure of $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ along [100].

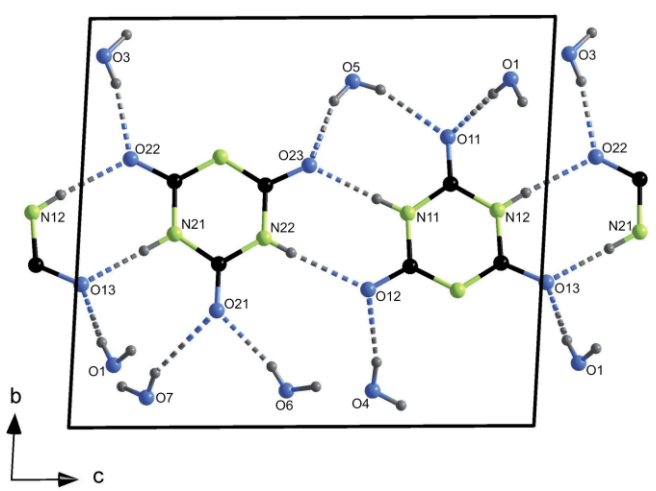

Figure 4. Ribbons of hydrogen-bonded $[H_2N_3C_3O_3]^-$ anions running along [001] in the crystal structure of $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ with attached interstitial water molecules; non-hydrogen atoms involved in hydrogen bonding are labeled.

The ribbons themselves consist of both crystallographically independent dihydrogenisocyanurate anions, which occur alternatingly, so that the well-known one-dimensional se-

quence of isocyanurate anions with four linking hydrogen atoms per unit results.[9,10] These ribbons contain formally isolated moieties, but due to their strong N–H···O hydrogen bonds, they form nearly planar (angle between neighboring isocyanurate planes: 1.1°) one-dimensional infinite ribbons $^{1}_{\infty}\{[H_2N_3C_3O_3]^-\}$, whose planes are arranged perpendicularly to the cationic layers $^{2}_{\infty}\{[[Mg(OH)_2)_6]\cdot(H_2O)_{6/3}]^{2+}\}$ (Figure 3).

A further stabilization of the anionic ribbons as well as the cationic layers results from additional hydrogen bonds between the lone-pair electrons of oxygen and deprotonated nitrogen atoms of the dihydrogenisocyanurate anions with hydrogen atoms of the coordinative bound water molecules of the complex $[Mg(OH_2)_6]^{2+}$ cations. In total, a three-dimensional hydrogen-bond network with distances and angles typical for this kind of compounds[20] results, which is able to stabilize hydrated Mg^{2+} cations in layers as well as dihydrogenisocyanurate anions in ribbons within the crystal structure of $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$.

The crystal structure of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ also shows hydrated lithium cations (Figure 5, Figure 6, and Figure 8) and analogous infinite ribbons of hydrogen-bonded dihydrogenisocyanurate anions (Figure 6, Figure 7, and Figure 9), but unlike the magnesium compound the isocyanurate units here are directly involved into the coordination spheres of the Li^+ cations. The more complicated cationic substructure of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ shows three crystallographically different Li^+-cation positions with different coordination patterns (Figure 5, Figure 6, Figure 7, Figure 8, and Figure 9).

Li1 is coordinated by a trigonal bipyramid of five oxygen atoms, of which two, which also form the equatorial plane of the bipyramidal complex unit, belong to carbonyl oxygen atoms of $[H_2N_3C_3O_3]^-$ anions, while the other three are part of water molecules (Figure 5, left). Li2 and Li3 are with about 100 pm distance very close to each other and exhibit next to identical tetrahedral coordination patterns by three water molecules and one cyanurate anion represented by an oxygen atom (Figure 5, mid and right), but both Li^+-cation positions are only half occupied. The lithium cations all reside within the

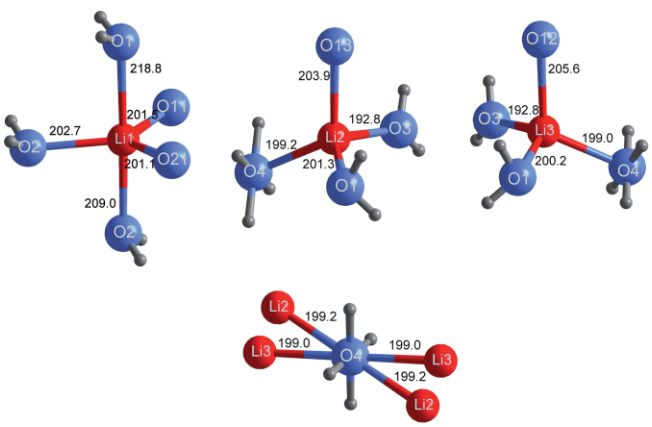

Figure 5. The three crystallographically different Li^+ cations in $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ with their oxygen coordination spheres (top) and the disordered water molecule at the origin (0,0,0) represented by O4 (bottom; Li–O distances in pm).

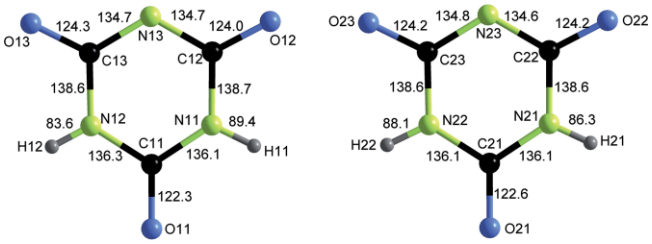

Figure 7. The two crystallographically different $[H_2N_3C_3O_3]^-$ anions in $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ (interatomic distances in pm).

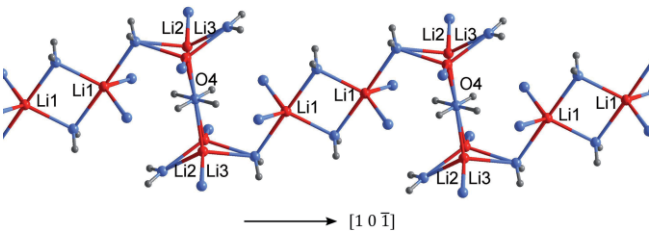

Figure 8. The lithium-oxygen substructure of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ as zigzag chain running along [10$\bar{1}$].

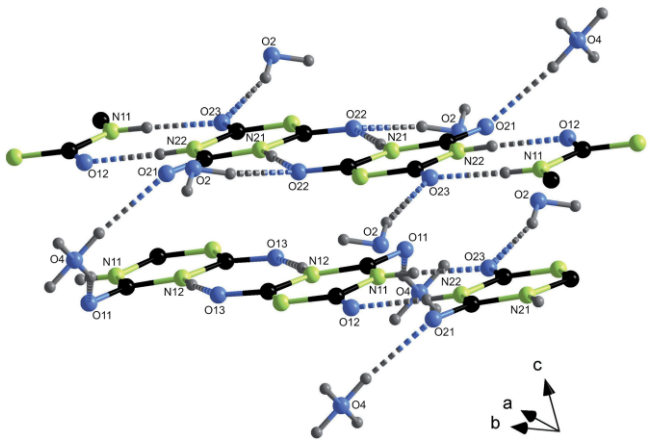

Figure 9. Hydrogen-bond and stacking arrangement of the $[H_2N_3C_3O_3]^-$ anions in the crystal structure of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$; non-hydrogen atoms involved in hydrogen bonding are labeled.

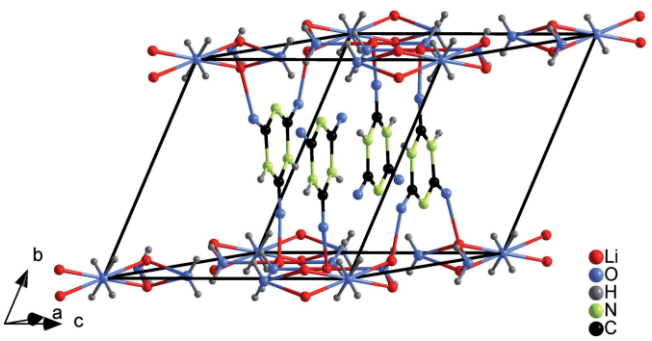

Figure 6. Linkage of the dihydrogenisocyanurate anions to the Li^+ cations (Li1–Li3) via their oxygen atoms in the crystal structure of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$.

crystallographic *ac* plane forming chains with the sequence ···Li2/Li3···Li1···Li1···Li3/Li2··· (Figure 8). These chains are connected within the *ac* plane to each other by water molecules H_2(O4) with O4 in the origin (0,0,0; site symmetry: $\bar{1}$) and two kinds of half-occupied hydrogen atoms (Figure 5, bottom), now forming zigzag lines, which propagate parallel to [10$\bar{1}$].

The ribbons of dihydrogenisocyanurate anions $[H_2N_3C_3O_3]^-$ are sandwiched by the cationic layers (Figure 6) and held in place by the interaction of the lithium cations with the carbonyl oxygen atoms of the $[H_2N_3C_3O_3]^-$ anions. These are stacked offset parallel relative to each other and perpendicular to the *ac* plane. The carbon atoms of one layer emerge directly above the nitrogen atoms of the neighboring one, they show C···N distances of approximately 330 pm.

The layers are held together not only by these weak C···N interactions, but also by water molecules coordinating the carbonyl oxygen atoms adjacent to the deprotonated nitrogen atoms of each $[H_2N_3C_3O_3]^-$ anion (Figure 9).

Vibrational Spectra

The vibration frequencies obtained from the IR and Raman spectra (Figure 10) of the title compounds coincide well to those reported for the rich variety of other alkali- and alkaline-earth metal isocyanurate hydrates, e.g. in references[9,10], and therefore confirm the presence of isocyanurate moieties in both investigated compounds.

The assignment of the obtained bands for $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ is based on the comprehensive publication by *Seifer*[12] and listed together with their frequencies in Table 4. Since the spectra were obtained under atmospheric conditions, modes typical for absorbed water and carbon dioxide were also observed.

X-ray Powder Diffraction and Thermogravimetric Analysis

Our X-ray powder diffraction experiments confirm that $Li[H_2N_3C_3O_3]\cdot 1.75H_2O$ was obtained nearly phase-pure, whereas $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ contained some unknown by-products. Figure 11 and Figure 12 show the powder diffraction

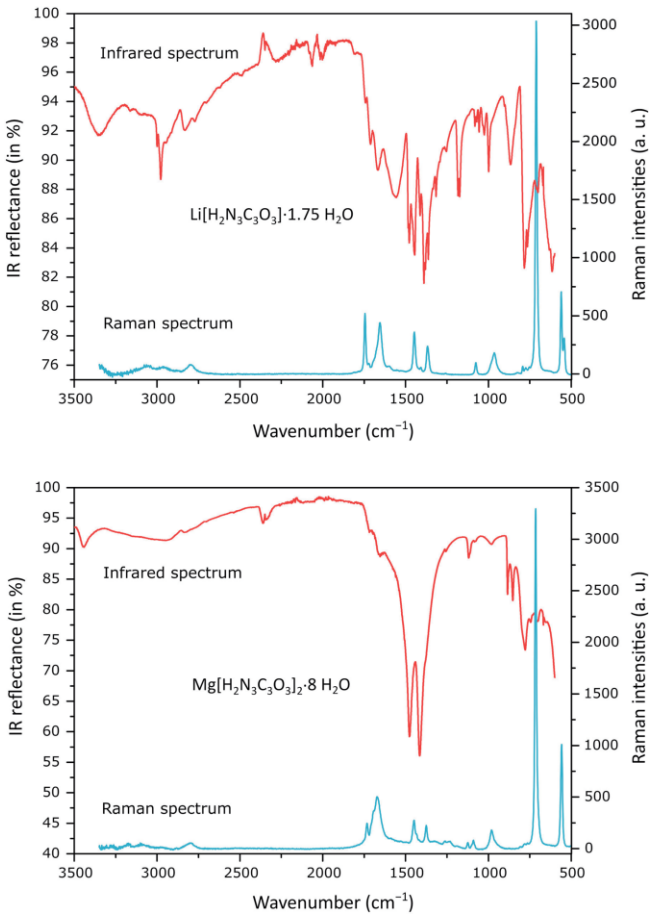

Figure 10. Infrared and Raman spectra of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ (top) and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ (bottom) showing the characteristic frequencies for dihydrogenisocyanurate anions.

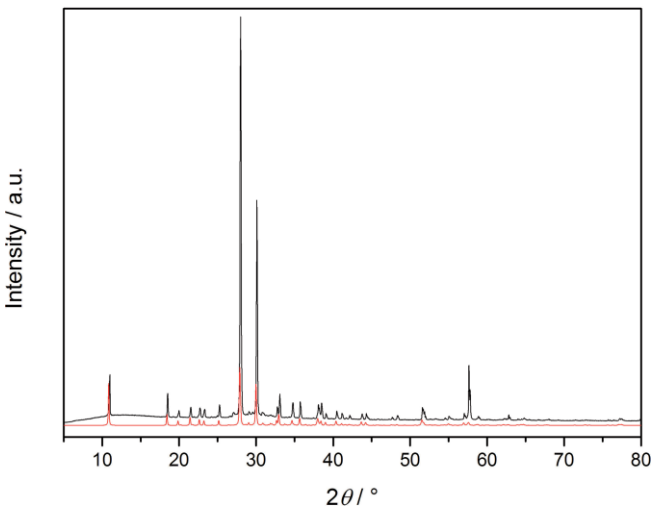

Figure 11. Powder X-ray diffraction pattern (Cu-K_α radiation) of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ (black) compared with a calculated pattern (red) based on the X-ray single-crystal structure determination.

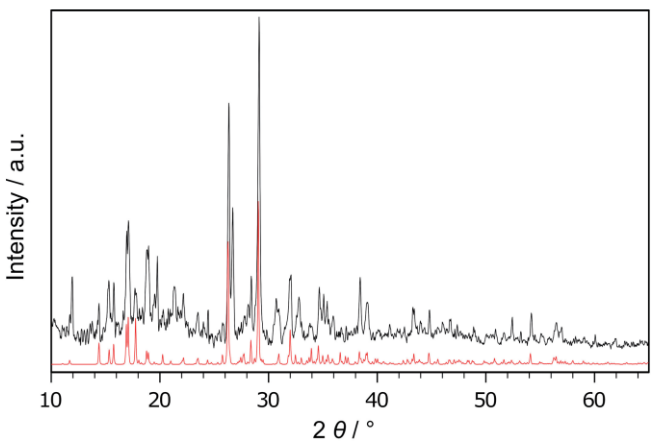

Figure 12. Powder X-ray diffraction pattern (Cu-K_α radiation) of $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ (black) compared with a calculated pattern (red) based on the X-ray single-crystal structure determination.

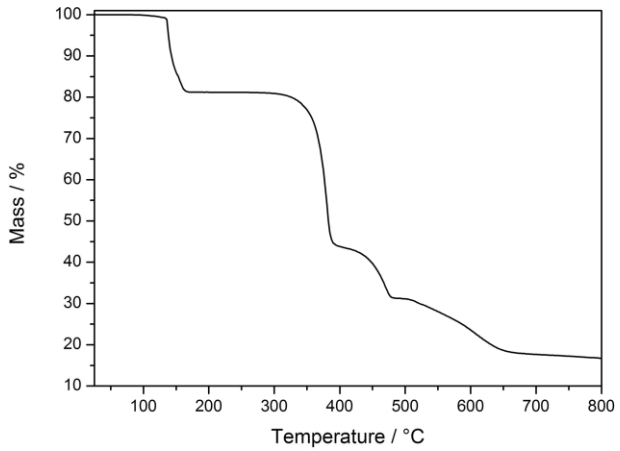

Figure 13. Thermogravimetry plot of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$.

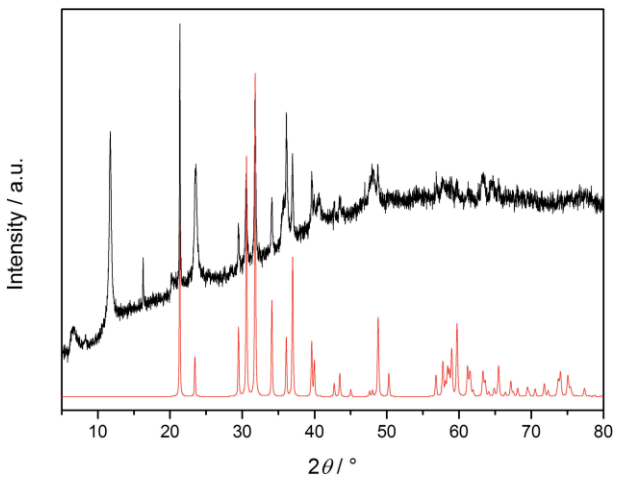

Figure 14. Powder X-ray diffraction pattern (Cu-K_α radiation) of the decomposition product obtained at 700 °C (black) compared with a calculated pattern of $Li_2[CO_3]$[21] (red).

patterns in comparison with the patterns calculated based on the respective X-ray single-crystal structure determination.

In order to examine its thermal degradation, a thermogravimetric investigation for $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ was carried out. Figure 13 displays a plot of the mass loss during heating of a sample of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$. The loss of 18.8 % above 160 °C corresponds very well with the calculated loss of 1.75 H_2O molecules per formula unit (18.9 %), whereas the following decomposition comprises several overlapping steps towards the main final product lithium carbonate (proven by powder X-ray diffraction shown in Figure 14). A further as-

Table 1. Single-crystal X-ray diffraction data of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$.

	$Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$	$Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$
M_r	166.54	424.59
Crystal color	colorless, transparent	colorless, transparent
Crystal shape	pseudo-cubic block	rectangular platelet
Crystal size /mm^3	0.12 × 0.12 × 0.11	0.12 × 0.09 × 0.04
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Z	4	2
Lattice parameters:		
a /pm	884.71(6)	691.95(5)
b /pm	905.12(7)	1055.06(8)
c /pm	964.38(7)	1183.87(9)
α /°	67.847(2)	85.652(2)
β /°	62.904(2)	83.439(2)
γ /°	68.565(2)	79.814(2)
V /Å^3	618.92(8)	843.72(11)
$D_{calcd.}$ /g·cm^{-3}	1.79	1.67
$F(000)$ /e^-	342	444
μ /mm^{-1}	0.16	0.19
Diffractometer	Nonius Kappa-CCD (Bruker AXS)	Nonius Kappa-CCD (Bruker AXS)
Radiation, λ /pm; monochromator	Mo-K_α, 71.07; graphite	Mo-K_α, 71.07; graphite
T /K	293(2)	293(2)
Ranges: $2\theta_{max}$ /deg; h, k, l	55.01; ±11, ±11, ±12	54.87; ±8, ±13, ±15
Data correction	Background, LP	Background, LP
Refl. measured / unique	19962 / 2847	25274 / 3846
Observed refl. with $F_o > 4\ \sigma(F_o)$	2144	3002
R_{int} / R_σ	0.064 / 0.030	0.075 / 0.036
Refined parameters	272	320
R_1 [a] / wR_2 [b] / GooF [c] (all refl.)	0.051 / 0.096 / 1.009	0.051 / 0.095 / 1.021
Factors x / y (weighting scheme) [b]	0.0597 / 0	0.0555 / 0.04
Max. shift / esd, last refinement cycle	< 0.0001	< 0.00005
$\Delta\rho_{fin}$ (max, min) /e$^-$Å^{-3}	0.21 (50 pm to N13), –0.25 (66 pm to H4A)	0.27 (84 pm to O7), –0.25 (70 pm to C22)

a) $R_1 = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$. b) $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, 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.

signment of specific reaction steps would be highly speculative.

Conclusions

Dihydrogenisocyanurate hydrates of lithium and magnesium were synthesized and structurally characterized as $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ with X-ray single-crystal diffraction. The vibrational spectra of both compounds were acquired indicating clearly the presence of doubly protonated isocyanurate anions and water molecules. Owing to the strong tendency of Mg^{2+} to become maximally hydrated (as indicated by its high charge-to-radius quotient), $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ contains octahedral $[Mg(OH_2)_6]^{2+}$ cations as well as more than four-and-a-half times the amount of water as found for $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and twice the amount than in other isocyanurate compounds containing only one type of alkali- or alkaline-earth metal. Thus, the diagonal relationship between lithium and magnesium is overruled by the hydrophilic character of Mg^{2+}, but the coagulation of the $[H_2N_3C_3O_3]^-$ anions to ribbons via two times two N–H···O hydrogen bonds for each one remains the same as observed in most other monobasic isocyanurate hydrates, further extending earlier findings[10] that this topology is ubiquitous for all alkali- and alkaline-earth metal isocyanurates up to even lighter cations.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters[a] of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$. The Wyckoff sites for all atoms are 2*i* except for O4 at 1*a*.

Atom	x	y	z	U_{eq} /pm^2 [a]
Li1	0.3790(2)	0.9996(2)	0.67333(3)	308(4)
Li2[b]	0.1572(5)	0.0631(7)	0.0528(6)	390(10)
Li3[b]	0.1890(5)	0.9392(7)	0.0833(6)	400(10)
O1	0.39827(11)	0.99968(11)	0.89158(11)	296(2)
H1A	0.475(2)	0.919(2)	0.921(2)	477(42)
H1B	0.433(2)	0.079(2)	0.882(2)	538(48)
O2	0.36616(11)	0.99978(11)	0.46211(11)	286(2)
H2A	0.338(2)	0.914(2)	0.466(2)	471(42)
H2B	0.298(2)	0.083(2)	0.424(2)	492(44)
O3	0.09580(13)	0.00036(12)	0.28292(12)	510(3)
H3A	0.039(3)	0.082(2)	0.325(2)	668(55)
H3B	0.082(3)	0.918(2)	0.366(2)	682(57)
O4	0	0	0	505(4)
H4A[c]	0.034(4)	0.072(4)	–0.086(4)	453(120)
H4B[c]	0.094(5)	–0.098(5)	–0.069(5)	657(156)
O11	0.30324(10)	0.78701(9)	0.79874(10)	286(2)
O12	0.29168(10)	0.69391(10)	0.16426(11)	309(2)
O13	0.13822(9)	0.30614(9)	0.01210(11)	298(2)
N11	0.49166(12)	0.45416(11)	0.18877(11)	239(2)
H11	0.403(2)	0.405(2)	0.224(2)	309(33)
N12	0.21915(12)	0.54605(11)	0.91187(11)	233(2)
H12	0.114(2)	0.594(2)	0.929(2)	332(35)
N13	0.42688(11)	0.29222(11)	0.92707(12)	249(2)
C11	0.34131(13)	0.63691(13)	0.83770(1)	210(2)
C12	0.44726(13)	0.62420(13)	0.14218(13)	219(2)
C13	0.25959(13)	0.37598(13)	0.95319(13)	215(2)
O21	0.19673(10)	0.21123(9)	0.69320(10)	279(2)
O22	0.36317(9)	0.69157(10)	0.48009(11)	304(2)
O23	0.20914(10)	0.30823(9)	0.32562(11)	301(2)
N21	0.28161(12)	0.45270(11)	0.58233(11)	239(2)
H21	0.391(2)	0.407(2)	0.562(2)	330(35)
N22	0.00746(11)	0.54731(11)	0.31299(12)	238(2)
H22	0.097(2)	0.594(2)	0.264(2)	401(38)
N23	0.07322(11)	0.70753(10)	0.57285(11)	236(2)
C21	0.15996(13)	0.36136(13)	0.65672(13)	209(2)
C22	0.24054(13)	0.62269(13)	0.54303(13)	215(2)
C23	0.05198(13)	0.37721(13)	0.35551(13)	213(2)

a) U_{eq} is defined as a third of the orthogonalized U_{ij} tensors. b) Fixed site occupation factor (s.o.f.) of $^1/_2$. c) Coupled site occupation factors according to s.o.f.(H4A) = 0.53(4) + s.o.f.(H4B) = 0.47(4) = 1.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters[a] of $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$. The Wyckoff sites for all atoms are 2*i* except for Mg1 at 1*a* and Mg2 at 1*f*.

Atom	x	y	z	U_{eq} /pm^2 [a]
Mg1	0	0	0	254(2)
O1	0.02941(17)	0.15267(10)	0.08913(10)	343(3)
H1A	0.068(3)	0.812(2)	0.875(2)	536(59)
H1B	0.096(3)	0.208(2)	0.061(2)	538(56)
O2	0.11849(16)	0.08448(11)	0.85253(9)	330(2)
H2A	0.156(3)	0.155(2)	0.848(2)	501(55)
H2B	0.070(3)	0.076(2)	0.793(2)	517(56)
O3	0.28499(14)	0.90841(11)	0.03395(9)	342(3)
H3A	0.289(3)	0.841(2)	0.062(2)	491(58)
H3B	0.340(4)	0.960(3)	0.080(3)	786(83)
Mg2	$^1/_2$	0	$^1/_2$	254(2)
O4	0.46277(18)	0.08728(12)	0.64920(10)	378(3)
H4A	0.393(2)	0.157(2)	0.654(2)	561(61)
H4B	0.466(3)	0.051(2)	0.712(2)	500(56)
O5	0.38009(18)	0.84358(11)	0.57164(11)	392(3)
H5A	0.346(3)	0.796(1)	0.534(2)	529(60)
H5B	0.359(3)	0.823(2)	0.632(2)	703(78)
O6	0.21684(15)	0.08846(11)	0.46400(10)	325(2)
H6A	0.202(3)	0.147(2)	0.430(2)	394(54)
H6B	0.118(4)	0.098(3)	0.527(3)	941(90)
O11	0.28890(16)	0.70644(9)	0.78244(9)	353(3)
O12	0.24117(16)	0.33472(10)	0.62825(8)	365(3)
O13	0.22009(17)	0.35031(10)	0.01068(8)	396(3)
N11	0.26307(17)	0.52046(11)	0.70474(10)	292(3)
H11	0.264(2)	0.556(2)	0.636(2)	319(40)
N12	0.26041(18)	0.52669(11)	0.89718(10)	303(3)
H12	0.263(2)	0.569(2)	0.956(2)	339(42)
N13	0.22882(17)	0.33168(11)	0.82076(10)	298(3)
C11	0.27188(19)	0.59186(13)	0.79349(11)	264(3)
C12	0.24427(19)	0.39080(13)	0.71584(12)	268(3)
C13	0.23610(19)	0.39822(13)	0.91112(11)	284(3)
O21	0.21183(17)	0.28489(10)	0.30511(9)	381(3)
O22	0.27572(15)	0.65632(10)	0.10266(8)	339(2)
O23	0.26133(19)	0.63868(11)	0.48752(9)	471(3)
N21	0.24243(18)	0.47250(11)	0.20561(10)	304(3)
H21	0.244(2)	0.432(2)	0.1418(15)	306(40)
N22	0.23965(19)	0.46139(12)	0.39834(11)	321(3)
H22	0.236(2)	0.426(2)	0.458(2)	319(43)
N23	0.26641(17)	0.65986(11)	0.29548(10)	303(3)
C21	0.23011(19)	0.39877(13)	0.30412(11)	272(3)
C22	0.26207(19)	0.60131(13)	0.19968(1)	261(3)
C23	0.25621(19)	0.59074(13)	0.39548(12)	309(3)
O7	0.44470(17)	0.07326(13)	0.16387(10)	414(3)
H7A	0.377(4)	0.133(3)	0.179(2)	933(89)
H7B	0.460(4)	0.900(3)	0.890(3)	952(94)
O8	0.05840(18)	0.90978(13)	0.34576(10)	367(3)
H8A	0.111(4)	0.950(3)	0.368(2)	819(78)
H8B	0.131(3)	0.849(2)	0.331(2)	499(62)

a) U_{eq} is defined as a third of the orthogonalized U_{ij} tensors.

Experimental Section

Syntheses: 260 mg (2.02 mmol) cyanuric acid [$C_3N_3(OH)_3$] (98 %, crystalline, Acros Organics, Shanghai, People's Republic of China) were added to 70 mg (0.95 mmol) $Li_2[CO_3]$ (p.a., powder; Merck, Darmstadt, Germany) or 80 mg (0.95 mmol) $Mg[CO_3]$ (99.99 %, powder; Merck, Darmstadt, Germany), respectively. These starting material mixtures were given separately to 5 mL of deionized water in a small beaker. This slurry was boiled for ten minutes resulting in a clear solution in the case of the lithium containing sample, while the solution with the magnesium compound remained opaque. Some CO_2 evolved in both cases. After 3 d of slow evaporation under ambient conditions, pseudo-cubic, colorless and transparent single crystals of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and platy, colorless and transparent single crystals of $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$ had formed. Both compounds are air- and water-resistant under atmospheric conditions up to weeks.

Crystallographic Studies: Crystals of the title compounds were selected from the material remaining after the evaporation of the water and sealed into thin-walled glass capillaries and mounted on a Nonius Kappa-CCD diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 71.07 pm). Intensity data were collected for suitable specimen of sufficient quality of each compound at room temperature. The processing of the diffraction data was performed with the software package that came with the diffractometer.[13] The intensity data were corrected for Lorentz and polarization effects as well as for absorption with the program HABITUS.[14] Systematic absences were analyzed and led to the triclinic space group $P1$ (no. 1) or $P\bar{1}$ (no. 2). The only structure solution that could be refined was in $P\bar{1}$ for both the lithium and the magnesium compound. In the case of $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$, the positions of the carbon, nitrogen and oxygen atoms, were obtained by using Direct Methods with the program SHELXS-97,[15,16] whereas the positions of lithium and hydrogen became apparent from the highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares calculations on F^2 (SHELXL-97[17,18]). For $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$, the cationic positions became apparent from the structure solution and the rest of the positions of the lighter atoms was taken from highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares calculations on F^2. Doing further refinement cycles, the refinement converged well and resulted in a stable model for the crystal structures after introducing and refining fractional occupation for some lithium and hydrogen positions for $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and for some hydrogen positions for $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$. Experimental details and further data of the single crystal structure determination are summarized in Table 1, the atomic coordinates, anisotropic and equivalent isotropic displacement coefficients are listed in Table 2 and Table 3.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html), on quoting the depository numbers CSD-1951681 for $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and CSD-1951160 for $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$.

X-Ray Powder Diffraction: The X-ray powder diffraction pattern of $Li[H_2N_3C_3O_3]\cdot 1.75H_2O$ was recorded with a Seifert 3003 TT diffractometer at room temperature in Bragg-Brentano geometry using

Table 4. Vibrational data for $Li[H_2N_3C_3O_3]\cdot 1.75\ H_2O$ and $Mg[H_2N_3C_3O_3]_2\cdot 8\ H_2O$. The assignment and their ranges are based on reference[12]. Vibrations with wavenumbers smaller than 400 cm^{-1} are lattice vibrations and were not assigned.

Assignment	Range	$[H_3C_3N_3O_3]$	lithium compound		magnesium compound	
			IR	Raman	IR	Raman
δ(NCO)	420–480	445				438
δ(C=O)	550–570			544		
δ(C=O)	550–570	527		561		558
δ(CNC), δ(NCO)			618		640	
δ(CNC), δ(NCO)		690, 735	700		667	
π(CO)	710–790	757	774	711	702	714
π(CO), ω(H_2O)	710–790	779	783		745, 778	
δ(C_3N_3)	835–875	840	866		853	
δ(C_3N_3), γ(H_2O)	835–875				884	
δ(C_3N_3), ρ(H_2O)	960–990		998	965	988	980
ν(C–O)	1030–1090	1049	1025			
ν(C–O)	1030–1090		1056, 1080, 1178	1077	1119	1090, 1124
δ(NH)	1221–1260		1254			1231
ν(C–N)	1351–1390		1315			1310
ν(C–N)	1351–1390	1396	1378, 1389	1368		1375
		1413	1412		1415	
ν(C_3N_3)	1420–1498	1455	1444, 1478	1448	1476	1449
ν(C_3N_3)	1500–1590		1560			
ν(C–N), δ(NH), δ(H_2O)	1600–1680		1666	1657	1635	1637
ν(C=O)	1710–1780	1689	1710			1693
ν(C=O)	1710–1780	1753	1740	1745		
ν(C=O)	1710–1780	1778				
Hydrogen bonds	2700–2840	2779	2620, 2703			
Hydrogen bonds	2700–2840	2821	2771, 2830	2800	2813	2798
ν(NH)	3050–3070	2883	2978		2900	3062
ν(NH)	3050–3070	3043	3000			
ν(NH)	3143–3170	3168	3162			3139
ν(NH)	3143–3170	3199				2798
ν(NH), ν(H_2O)	3420–3490		3350		3441	
ν(NH), ν(H_2O)	3420–3490				3488	

Cu-K_α radiation, a germanium METEOR 1D line detector, and a nickel filter to suppress K_β radiation (X-ray tube operated at 40 kV and 40 mA, scan range: 5–80°, increment: 0.02°, 40 scans per data point, integration time: 100 s per degree). The pattern of $Mg[H_2N_3C_3O_3]_2 \cdot 8\,H_2O$ was recorded with a Stoe & Cie STADI P diffractometer equipped with a germanium-monochromatized Cu-K_α radiation (λ = 154.06 pm) and an image plate detector.

Raman and IR Spectroscopy: Powders of both title compounds were brought into the beam line of a Thermo Scientific DXR Smart Raman device (10 mW, with an excitation line at λ = 780 nm, 400 lines/mm, 200–3350 cm^{-1}) for Raman spectroscopic investigations and their infrared spectra (600–4000 cm^{-1}) were collected with a Bruker Nicolet iS5 FT-IR spectrometer with attenuated total reflection (ATR) sampling technique. The IR spectra show some absorptions typical for CO_2 (2300–2400 cm^{-1}), since the synthesis and measurements were performed under atmospheric conditions. The combined IR and Raman spectra of $Li[H_2N_3C_3O_3] \cdot 1.75\,H_2O$ and $Mg[H_2N_3C_3O_3]_2 \cdot 8\,H_2O$ are displayed in Figure 10, the exact frequencies and their assigned modes are listed in Table 4.

Thermogravimetric Study: The TG analysis was performed for a sample of $Li[H_2N_3C_3O_3] \cdot 1.75\,H_2O$ with a NETZSCH STA/TG 409 PC Luxx thermobalance in a nitrogen atmosphere (flow rate: 70 ml·min^{-1}) in corundum crucibles (heating rate: 5 K·min^{-1}).

Keywords: Magnesium; Lithium; Dihydrogencyanurate hydrates; Crystal structures; Vibrational spectra

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