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Supporting Information

Interplay between hydrogen bonding and metal coordination in alkali metal tartrates and hydrogen tartrates

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Contents

1. Analysis of structure similarity relationships

1.1. General

Crystal packing comparisons were carried out using version 2.0 of the program *XPac*[1] and quantitative dissimilarity parameters were generated in the previously described manner.[2] All comparisons were based on geometrical parameters generated from all C and O atoms of the anion, whereas metal centres and water molecules were not included in these calculations.

1.2. Supramolecular constructs

1.2.1. Connectivity motif **I**: chain type A-*syn*

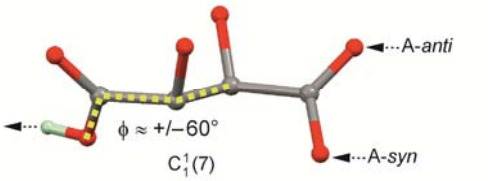


Figure S1. Definition of the geometries A-*syn* and A-*anti* chains of (carbonyl)O–H···O=C(carboxylate) bonded $HTart^-$ ions.

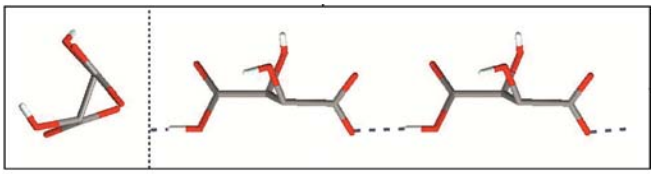


Figure S2. Chain type A-*syn*.

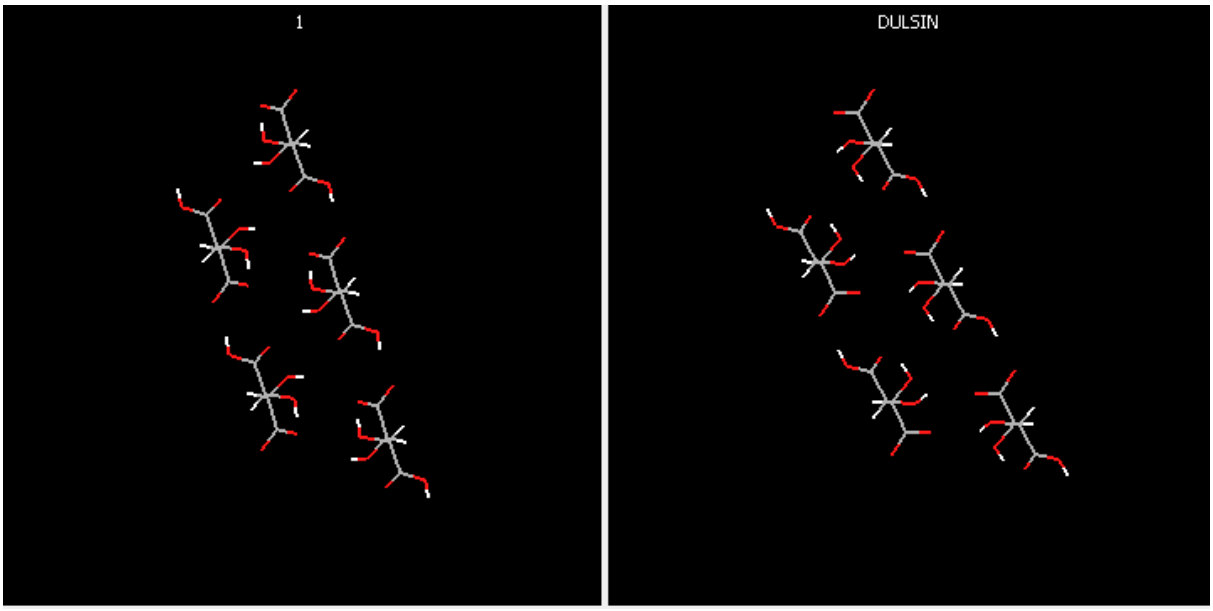
Table S1. Lattice vectors (*t*) associated with the chain type A-*syn*.

Structure	CSD	Ref.	*t*	Length (Å)
1a	.	.	010	7.065
1b	DULSIN	3	$0\bar{1}0$	7.146
15	ZZZSSS01	4	100	7.242

Table S2. *XPac* dissimilarity parameters *x* for pairwise structure comparisons involving a cluster of three anions which represents the A-*syn* chain.

Structure 1	Structure 2	*x*	Notes
1a	**1b**	2.2	*a*
1a	**15**	5.2	.
1b	**15**	5.8	*b*

a = The structures **1a** and **2b** have a double-stranded chain of H-bonded $HTart^-$ ions in common, whose two strands are A-*syn* chains (see Figure S3and Figure 2c).
b = The structures **1b** and **15** have a layer in common which is composed of A-*syn* chains related by 2_1 symmetry (see Figure S4).



Na(D,L-HTart) · H_2O, triclinic form **(1a)** Na(D,L-HTart) · H_2O, monclinic form **(1b)**

Figure S3. Common 1D SC (supramolecular construct)[1] of structures **1a** and **1b**: double-stranded chain of H-bonded $HTart^-$ ions, whose two strands are A-*syn* chains (x = 2.2 for the cluster of five $HTart^-$ ions representing this SC).

Na(D,L-HTart) · H_2O, monoclinic form **(1b)** Na(L-HTart) · H_2O **(15)**

Figure S4. Common 2D SC of structures **1b** and **15**: layer of H-bonded $HTart^-$ ions composed of A-*syn* chains (x = 8.1 for the cluster of seven $HTart^-$ ions representing this SC). Corresponding lattice parameters: **1b**: 010 / 7.146 Å, 101 / 10.887 Å, 90°; **2b**: $\bar{1}00$ / 7.242 Å, 001 / 10.592, 90°.

1.2.2. Connectivity motif **I**: chain type A-*anti*

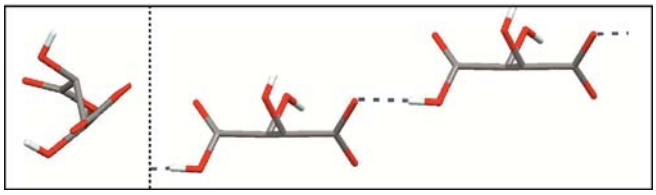


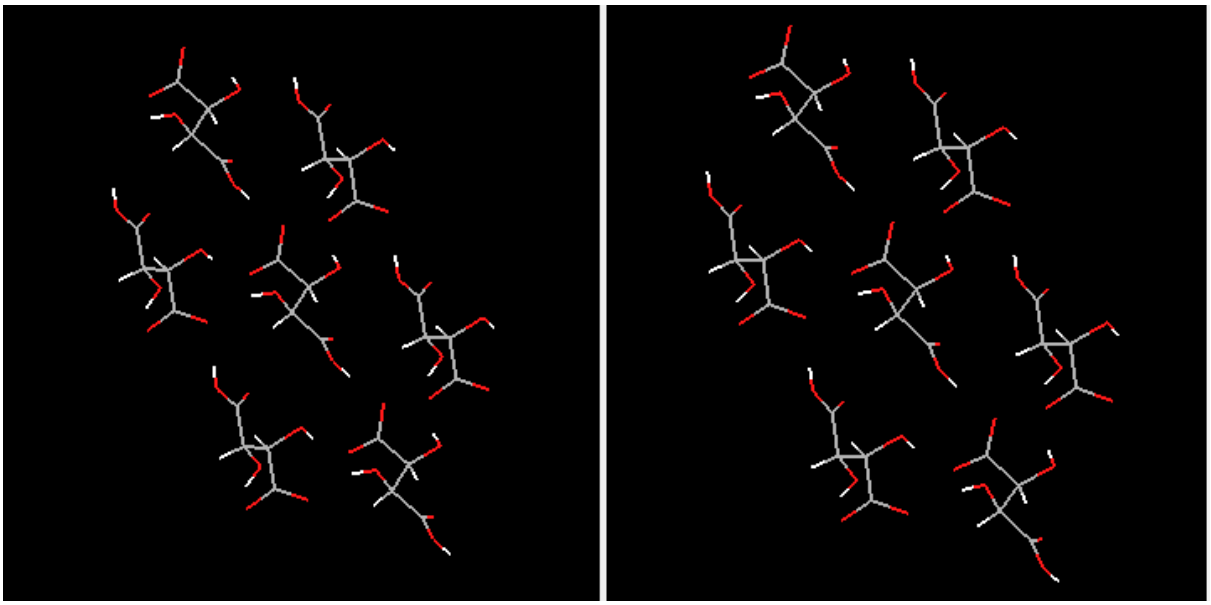
Figure S5. Chain type A-*anti*.

Table S3. Lattice vectors (*t*) associated with the chain type A-*anti*.

Structure	CSD	Ref.	*t*	Length (Å)
2b	XAHZIQ	5	100	7.683
5	XAHZAI	5	100	7.579
6	XAHZEM	5	100	7.626
13	YEKYIW	6	$\bar{1}00$	7.615
14	YELNIM	7	$00\bar{1}$	7.594
16	ZZZRZW01	8	001	7.604
17	KAMBIJ	9	001	7.653
18	CSHTAR10	10	001	7.692

Table S4. *XPac* dissimilarity parameters *x* for pairwise structure comparisons involving a cluster of three anions which represents the A-*syn* chain. The dissimilarity parameters *x'* refer to larger structure fragments, either the complete substructure of $HTart^-$ ions (a) or to a layer of H-bonded $HTart^-$ ions (b) represented by six anions (see Figure S6).

Structure 1	Structure 2	*x*	*x'*
13	**14**	9.8	.
13	**16**	3.3	.
13	**17**	3.5	.
13	**18**	4.2	.
13	**5**	3.4	.
13	**6**	3.6	.
13	**2b**	4.3	.
14	**16**	9.4	.
14	**17**	9.8	.
14	**18**	10.9	.
14	**5**	9.9	.
14	**6**	10.5	.
14	**2b**	11.0	.
16	**17**	1.2	1.6 [(a)]
16	**18**	2.7	3.7 [(a)]
16	**5**	2.4	2.1 [(b)]
16	**6**	1.8	2.1 [(b)]
16	**2b**	2.5	3.6 [(b)]
17	**18**	1.6	2.2 [(a)]
17	**5**	3.0	1.7 [(b)]
17	**6**	1.8	1.7 [(b)]
17	**2b**	1.7	2.5 [(b)]
18	**5**	4.1	4.1 [(b)]
18	**6**	2.5	2.6 [(b)]
18	**2b**	1.4	1.4 [(b)]
5	**6**	1.7	1.8 [(a)]
5	**2b**	3.5	3.9 [(a)]
6	**2b**	1.8	2.3 [(a)]



K(L-HTart) (**16**) K(D,L-HTart) (**5**)

Figure S6. Common 2D SC present in the structures **2b**, **5**, **6** and **16** – **18**: layer of H-bonded $HTart^-$ ions containg A-*syn* chains.

1.2.3. Connectivity motif **II**

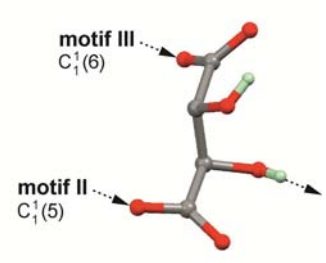


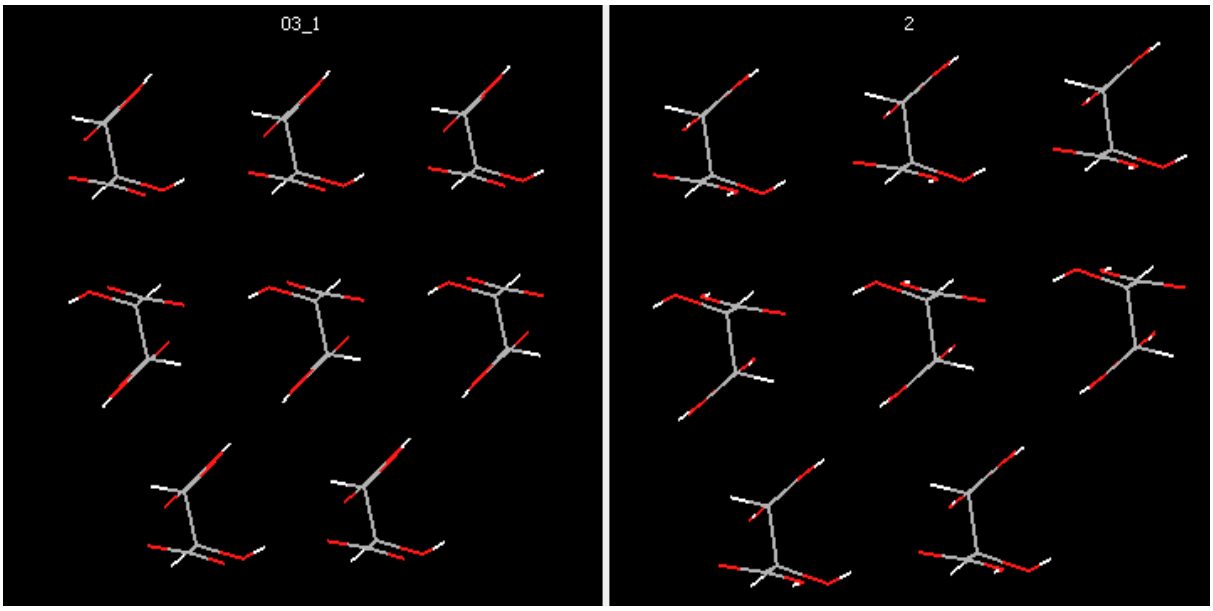
Figure S7. Defintion of the connectivity motifs **II** and **III**.

Table S5. Lattice vectors (*t*) associated with the translation of the chain motif **II** and the geometry subsets **IIa** and **IIb**.

Structure	CSD	Ref.	*t*	Length (Å)	Geometry
2a	.	.	100	5.065	**IIa**
3	.	.	100	5.073	**IIa**
12	UNIROZ	11	100	5.064	**IIb**
14	YELNIM	7	100	5.251	**IIb**
19a	UNIRUF	11	100	5.044	**IIb**
19c	.	12	010	5.014	.
20a	UNISIU	11	010	5.019	**IIb**
20b	.	12	$0\bar{1}0$	4.970	**IIb**
23	NADTRT	13	001	4.959	**IIa**
28	ZZZLZE01	14	$0\bar{1}0$	5.014	.

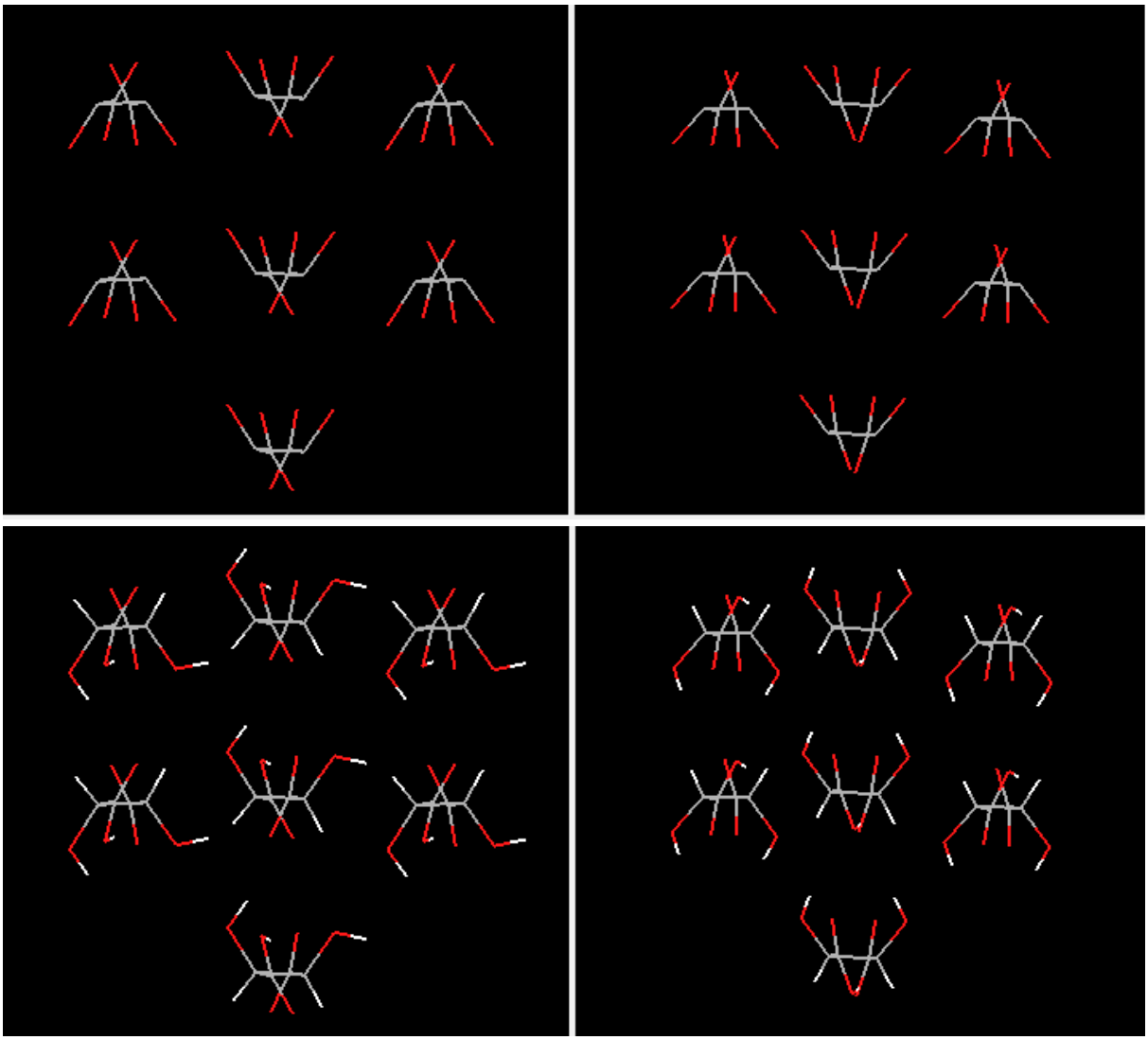
Table S6. *XPac* dissimilarity parameters *x* for pairwise structure comparisons involving a cluster of three anions. This cluster represents the geometry of the H-bonded chain which is based on motif **II**. The dissimilarity parameters *x'* refer to the larger 2D structure fragments shown in Figure S8 and Figure 5 (a) or in Figure S9 (b).

Structure 1	Structure 2	*x*	*x'*
Geometry subset **IIa**			
2a	**3**	4.4	3.4 [(a)]
2a	**23**	3.1	.
3	**23**	5.6	.
Geometry subset **IIb**			
12	**14**	7.0	8.3 [(b)]
12	**19a**	8.8 10.7	.
12	**20a**	10.8	.
12	**20b**	11.5	.
14	**19a**	4.7 6.2	.
14	**20a**	6.1	.
14	**20b**	9.3	.
19a	**20a**	1.9 5.1	.
19a	**20b**	5.8 10.9	.
20a	**20b**	10.5	.



LiCs(D,L-Tart) · $2H_2O$ (**3**) Cs(D,L-HTart), triclinic form (**2a**)

Figure S8. Common 2D SC of structures **3** and **2a**: layer of H-bonded $HTart^-$ ions composed of chains of the **IIa** geometry type. Corresponding lattice parameters: **3**: 100 / 5.073 Å, $00\bar{1}$ / 10.509 Å, 81.2°; **2a**: 100 / 5.064 Å, 001 / 9.957 Å, 85.5°.



Li(L-HTart) (**12**) Na(L-HTart) (**14**)

Figure S9. Common 2D SC of structures **12** and **14**: layer of H-bonded $HTart^-$ ions composed of chains of the **IIb** geometry type. Corresponding lattice parameters: **12**: 100 / 5.064 Å, 010 / 8.330 Å, 90°; **14**: 100 / 5.064 Å, $0\bar{1}0$ / 7.782 Å, 90°. The top and bottom diagrams show the same layer of anions without and with H atoms. Note the differences in the H positions between the two structures.

2. Crystal packing arrangement in the series *M*(D,L-HTart)

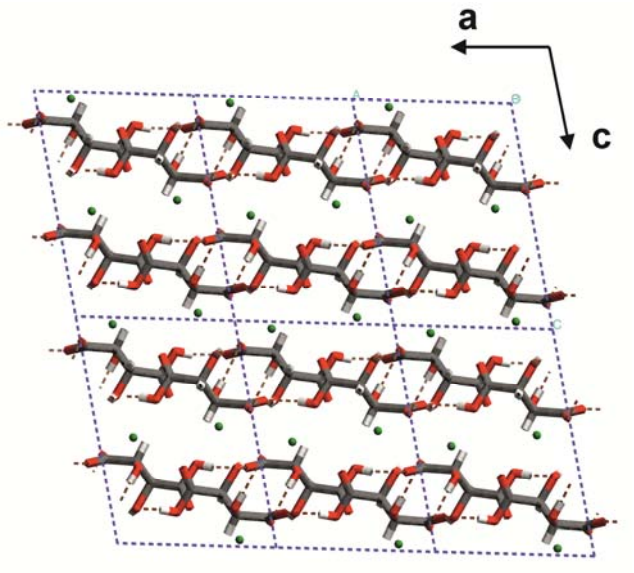


Figure S10. The packing of $HTart^-$ (rods) and M^+ (balls) ions in the crystal structure of the series *M*(D,L-HTart) with *M* = Cs (**2b**), K (**5**) and Rb (**6**) (view along [010]).[5] The M^+ ions (green balls) are arranged between two layers which are composed exclusively of H-bonded D-$HTart^-$ or L-$HTart^-$ ions and which lie parallel to (110).

3. Crystallisation experiments

Table S7. Overview of crystalline phases obtained from mixtures of 0.2 molar aqueous solutions of alkali metal or ammonium hydroxides (*M*OH) and D,L-tartaric acid (D,L-H_2Tart) in the wells of a 96 well plate (crystallisation at room temperature). No. = number of crystallization experiment (multiple phases were identified for nos. 8, 9, 15, 16, 23, 27); Rat. = ratio *M*OH : D,L-H_2Tart or ratio *M*OH : *M*'OH : D,L-H_2Tart; *d* = number of days from the preparation of the mixture to the harvest of the crystal; SXRD / UC: phase identification on the basis of SXRD unit cell data; SXRD / FS = phase identification on the basis of a full structure determination; # = label of the phase in Table 5.

No.	*M*	*M'*	Rat.	*d*	SXRD / UC	SXRD / FS	Phase	#	CSD refcode	Ref.
1	Li	-	1:1	15	+	+[c]	Li(D,L-HTart) · H_2O	**13**	YEKYIW01	5
2	Na	-	1:1	7	+	+[d]	Na(D,L-HTart) · H_2O [e]	**1a**	.	*this work*
3	K	-	1:1	7	+	+[b]	K(D,L-HTart)	**5**	XAHZAI	5
4	Rb	-	1:1	7	+	+[b]	Rb(D,L-HTart)	**6**	XAHZEM	5
5	Cs	-	1:1	7	+	+[d]	Cs(D,L-HTart) [e]	**2a**	.	*this work*
6	NH_4	-	1:1	7	+	+[b]	NH_4(D,L-HTart)	.	PUXKAU01	5
7	Li	-	2:1	20	+	+[c]	Li_2(D,L-Tart) · $3H_2O$	**7**	CEGPEK	15
8a	Na	-	2:1	30	+		Na_2(D or L-Tart) · $2H_2O$	**23**	NADTRT	13
8b	Na	-	2:1	365	+	+	Na_2(D,L-Tart)	**24**	COZGED	16
9a	K	-	2:1	20	+		K(D,L-HTart)	**5**	XAHZAI	5
9b	K	-	2:1	365	+	+	D,L-Tart · H_2O	.	TARTDL01	17
10	Rb	-	2:1	30	+		Rb_2(D or L-Tart)	**29**	ZZZVZO02	18
11	Cs	-	2:1	15	+	+	Cs_2(D or L-Tart)	**30**	SOFJOM	18
12	NH_4	-	2:1	20	+	+	NH_4(D,L-Tart)	.	ZZZJII01	19
13	Li	Na	1:1:1	365	+	+[c]	LiNa(D,L-Tart) · $2H_2O$	**8**	CEGPIO	15
14	Li	K	1:1:1	20	+	+[c]	LiK(D,L-T art) · H_2O	**9**	JEFVIA	15
15a	Li	Rb	1:1:1	20	+	+[c]	LiRb(D,L-Tart) · H_2O	**10**	JEFVOG	15
15b	Li	Rb	1:1:1	300	+	+	Rb(D or L-HTart)	**17**	KAMBIJ	9
16a	Li	Cs	1:1:1	20	+	+[c]	LiCs(D,L-Tart) · H_2O	**11**	CEGPOU	15
16b	Li	Cs	1:1:1	20	+	+[d]	LiCs(D,L-Tart) · $2H_2O$	**3**	.	*this work*
17	Li	NH_4	1:1:1	20	+	+[c]	LiNH$_4$(D,L-Tart) · H_2O	.	ZZZKDE01	15
18a	Na	K	1:1:1	20	+		K(D,L-HTart)	**5**	XAHZAI	5
18b	Na	K	1:1:1	20	+		Na(D,L-HTart) · H_2O	**1a**	.	*this work*
19	Na	Rb	1:1:1	[a]			.	.	.	.
20	Na	Cs	1:1:1	15	+	+	Na_2CO_3 · H_2O	.	.	20
21	Na	NH_4	1:1:1	300	+	+	Na_2CO_3 · $NaHCO_3$ · $2H_2O$	.	.	21
22	K	Rb	1:1:1	7	+	+[b]	$K_{0.5}Rb_{0.5}$(D,L-HTart)	.	XAHZAI01	5
23b	K	Cs	1:1:1	20	+		K(D,L-HTart)	**5**	XAHZAI	5
23a	K	Cs	1:1:1	20	+	+	$CsHCO_3$	.	.	22
24	K	NH_4	1:1:1	7	+	+[b]	$K_{0.56}(NH_4)_{0.44}$(D,L-HTart)	.	XAHZAI02	5
25	Rb	Cs	1:1:1	20	+	+[b]	$(Cs_{0.5}Rb_{0.5})_2$(D or L-Tart)	**4**	.	*this work*
26	Rb	NH_4	1:1:1	20	+	+[b]	$Rb_{0.61}(NH_4)_{0.39}$(D,L-HTart)	.	XAHZEM01	5
27a	Cs	NH_4	1:1:1	20	+	+[b]	Cs(D,L-HTart) [f]	**2b**	XAHZIQ	5
27b	Cs	NH_4	1:1:1	20	+		NH_4(D,L-HTart)	.	PUXKAU01	5

[a] No crystalline product was obtained.
[b] Crystal structure published in the first report.[5]
[c] Crystal structure published in the second report.[15]
[d] Crystal structure contained in this report.
[e] Triclinic polymorph.
[f] Monoclinic polymorph.

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