Electronic Supporting Information for:

Self-Assembly of Water-Mediated Supramolecular Cationic Archimedean Solids

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General

FTIR spectra (Figure S6) were recorded with Bruker Alpha FTIR spectrometer equipped with Platinum ATR module. Thermal properties of the compounds (Figure S7, Table S2) were measured with Perkin Elmer STA 6000 TG/DTA using Pt crucible in flowing (45 l/min) air atmosphere using sample sizes between 3-5 mg. Temperature was ramped at a heat rate of 5 °C/min from 27 to 650 °C.

Additional analyses and figures

Table S1 shows the full hydrogen bond distances and angles list for structure **2b**. Additional illustrations of the reported structures are presented in figures S1-S5.

 Table S1. Hydrogen bonding parameters for structure 2b.

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D	Н	Α	<i>d</i> (D-H)/Å	<i>d</i> (H-A)/Å	<i>d</i> (D-A)/Å	D-H-A/°
01	H1C	$O7A^1$	0.878(7)	2.124(12)	2.997(14)	171.9(4)
01	H1C	07B ¹	0.878(7)	1.827(11)	2.561(12)	139.7(6)
01	H1D	O2A	0.878(6)	1.835(7)	2.689(9)	163.5(4)
01	H1D	O2B	0.878(6)	1.974(16)	2.825(17)	163.0(7)
O2A	H2AA	03	0.878(6)	1.903(5)	2.775(8)	172.3(5)
O2A	H2AB	F12 ²	0.872(6)	2.115(3)	2.892(7)	147.9(4)
O2B	H2BA	03	0.878(14)	1.706(5)	2.540(14)	157.5(13)
03	H3C	N3 ³	0.870(4)	1.958(4)	2.827(6)	176.5(4)
03	H3D	04	0.871(5)	1.820(5)	2.690(7)	176.4(4)
04	H4C	N7 ¹	0.871(5)	1.984(4)	2.851(6)	172.7(4)
04	H4D	05A	0.875(6)	2.184(13)	2.984(14)	151.9(4)
04	H4D	O5B	0.875(6)	1.660(10)	2.529(12)	171.9(5)
05A	H5AA	$F32A^3$	0.886(10)	2.367(12)	3.077(15)	137.3(7)
05A	H5AA	$F32B^3$	0.886(10)	2.204(12)	3.011(15)	151.2(8)
05A	H5AB	F25	0.877(10)	2.083(3)	2.951(10)	170.0(8)
O5B	H5BA	$F31^3$	0.872(10)	1.848(5)	2.703(12)	166.1(9)
06	H6C	014	0.864(15)	1.950(5)	2.768(16)	157.4(11)
06	H6D	05A	0.915(16)	2.119(15)	3.01(2)	166.1(10)
07A	H7AA	F28B	0.890(13)	1.72(4)	2.60(4)	169.8(10)
07A	H7AB	06	0.877(12)	1.967(15)	2.84(2)	172.8(9)
08	H8C	09	0.873(12)	1.753(13)	2.625(17)	177.5(7)
08	H8D	F16	0.890(13)	2.314(4)	2.929(10)	126.2(7)
09	H9C	014A ⁵	0.884(12)	1.923(14)	2.804(18)	174.8(11)
09	H9D	O10 ⁶	0.894(14)	2.073(11)	2.966(18)	176.8(8)
010	H10C	F24	0.881(8)	2.045(4)	2.843(9)	149.9(7)
010	H10D	$F5^{6}$	0.878(7)	2.105(4)	2.966(8)	166.7(6)
010	H10D	$F6^6$	0.878(7)	2.433(5)	3.057(11)	128.4(7)
011	H11C	N1 ⁷	0.867(5)	2.006(5)	2.836(7)	159.8(4)
011	H11D	010	0.884(7)	1.932(9)	2.798(11)	165.8(4)
012A	H12C	N11 ⁶	0.874(13)	1.994(5)	2.863(14)	173.3(8)
012A	H12D	011	0.888(13)	1.745(5)	2.630(14)	173.0(7)
012B	H12E	$N11^{6}$	0.88(2)	1.986(4)	2.84(2)	162.7(15)
012B	H12F	011	0.87(2)	2.000(6)	2.81(2)	156.4(14)

013A	H13C	012A	0.865(9)	2.046(12)	2.866(15)	157.7(7)
013A	H13D	F21A ⁸	0.881(10)	1.82(4)	2.69(4)	172.0(18)
013A	H13D	F21B ⁸	0.881(10)	2.08(2)	2.94(3)	164.6(11)
013B	H13F	O12B	0.784(14)	1.69(2)	2.47(3)	170(2)
014A	H14C	08	0.88(2)	1.852(10)	2.67(2)	152.3(9)
014A	H14D	013A ⁹	0.895(13)	2.023(12)	2.916(18)	175.8(12)
014B	H14E	013B ⁹	0.93(2)	1.50(2)	2.43(3)	175.1(13)
014B	H14F	08	0.85(2)	2.066(9)	2.91(2)	173.0(13)

¹2-X,1-Y,2-Z; ²1-X,1-Y,2-Z; ³1+X,1+Y,+Z; ⁴1+X,+Y,+Z; ⁵1-X,-Y,1-Z; ⁶1-X,1-Y,1-Z; ⁷+X,1+Y,+Z; ⁸-X,1-Y,1-Z; ⁹1+X,-1+Y,+Z

Crystal Growth & Design

Structural analysis of 1a

Unlike the other three compounds, the colorless crystals of **1a** contain no water molecules in their lattice. Instead, cation **1** stabilizes an unusual trianion, namely $K[PF_6]_4^{3-}$. The formation of such species¹ can be explained by the size, shape and charge matching of the cation and anion. The K⁺...PF₆⁻ interactions are expected to be mostly ionic making the $K[PF_6]_4^{3-}$ anion very flexible and able to distort in order to accommodate the packing. In **1a**, $K[PF_6]_4^{3-}$ anion adopts a flattened tetrahedral geometry which seems as a good structural match with cation **1** (Figure S1) as no voids are left in the crystal lattice for solvent molecules to occupy. The crystal packing of **1a** is dominated by Coulombic interactions between the cations and anions. It is noteworthy that the trigonal pocket of the cation, formed by the three quaternary ammonium centers of the DABCO groups, is occupied with one of the PF₆⁻ groups of the K[PF₆]_4³⁻ anion. In addition, anions themselves share a short contact using one of the PF₆⁻ groups with adjacent K⁺, thereby forming an infinite anion continuum parallel to *c*-axis with K⁺...K⁺ distance of 8.494 Å (Figure S1).



Figure S1. The cation-anion and $K^* \cdots PF_6^-$ interactions in **1a** are shown in left, displaying one of the PF_6^- anions in the cationic pocket of cation **1.** Right: overall packing scheme of anions and cations in the structure of **1a** viewed along the crystallographic *c*-axis.



Figure S2. Left: The asymmetric unit of structure **2a** with grown molecular moieties. Right: The structural ordering of ionic counterparts and water in structure **2a**. Thermal ellipsoids are presented at the 30% probability level (applies to all figures). Disordered atoms are omitted from the picture.



Figure S3. Left: The asymmetric unit of structure **1b**', with grown molecular moieties, showing the disordered cation in grey. Right: The structural ordering of ionic counterparts and water in structure **1b**. Disordered atoms are omitted from the picture.



Figure S4. Illustration of the hydrogen bonding pattern in structure 2b. Disordered atoms are excluded from the picture.

Structural analysis of 1b'

The severe disorder in the cavity inside the cage $(1)_4(W_6)_4$ prevents precise structural analysis of its contents. However, the residual electron density clearly indicates that a single cation lies in the cavity along with the already visible PF₆⁻ anion. This cation is disordered, by symmetry, to four positions and thus each one of the DABCO groups is overlapped by the DABCO group of adjacent cation. Furthermore, a second distinguishable water molecule in the asymmetric unit, in addition to O1, lies inside the cage and is hydrogen bonded to both O1 and the tertiary amine of the DABCO groups of the disordered cation. Consequently, a pseudo-dodecameric (partially occupied) water cluster is formed by symmetry (Figure S5) in the junction point of two $(1)_4(W_6)_4$ cages. To confirm the structural analysis regarding the disordered cation, we also refined the structure in an orthorhombic crystal system. The cation lying inside the cavity was well resolved also in lower symmetry. Similar cationic arrangement was also found inside the cation-cage of **2a**, but since it was even more disordered, the refined model including the disordered cation is not presented here.



Figure S5. Left: Illustration of the four-fold disorder of cation 1 inside the cage $(1)_4(W_6)_4$. The four cations are colored as orange, yellow, violet and green whereas the blue moiety in the middle is a single PF₆⁻ anion lying at the pocket of the disordered cation. Right: The pseudo-dodecameric water cluster observed in **1b** where occupations of water molecules indicated with orange color are only ½. All non-OH hydrogens are omitted from the picture.

FTIR analysis

Cations 1 and 2 do not contain any functional groups in their backbone that would significantly interfere with water vibration bands in the IR spectrum. Therefore the IR absorption bands of both OH-stretch and HOH-bend modes are clearly interpretable from the FTIR spectra of 1b, 2a and 2b (Figure S6). All three compounds show weak but fairly sharp peaks around 1630-1650 cm⁻¹ and 3630-3650 cm⁻¹. In addition, two broad absorption bands are observed at 3225 and 3361 cm⁻¹ for **1b** and **2b** and a single broad band at 3407 cm⁻¹ for **2a**. First of all, the peaks at 1630-1650 cm⁻¹ correspond to the HOH-bending modes of water molecules observed in liquid water (1645 cm⁻¹) and ice (1650 cm⁻¹).² Secondly, peaks observed at around 3650 cm⁻¹ of the IR spectra of 1b, 2a and 2b most likely arise from water molecules acting as twocoordinate species,³ although this region is also fairly close to the symmetric stretch mode of a noncoordinated water molecule observed in water vapor (3657 cm⁻¹).2 Therefore, although it is plausible that this region is induced by water molecules escaping the crystals during IR measurements, it is more probable that these peaks arise from weak hydrogen bonding interactions between water and PF₆⁻ anions. The maxima of the broad bands at 3227 cm⁻¹ (1b) and 3225 cm⁻¹ (2b) are virtually identical to the OH-stretch observed for ice I_h (3220 cm⁻¹) which basic-structure consists of hexameric units. The other maxima, evident at 3361 cm⁻¹ in IR spectra of both **1b** and **2b**, are more close to the frequency of a water hexamer in a helium droplet (3325 cm⁻¹). On the other hand, for a neutral DABCO monohydrate, a much simpler hydrate species where water acts as two-way HB-donor, two peaks (3226 and 3388 cm⁻¹) are reported that are almost an exact match to both **1b** and **2b**.⁴ The broad band in this region of spectrum of **2a** shows only a single broad maximum (3407 cm⁻¹) with likely underlying broad peaks in the 3200 cm⁻¹ region.



Figure S6. FTIR spectra of compounds 1a (black), 1b (blue), 2a (red) and 2b (green). Dashed lines correspond to the IR spectra of dehydrated compounds.

Thermal Analysis

Under the constant air stream of TG apparatus, the dehydration of all hydrate compounds **1b**, **2b** and **2a** start readily above room temperature (see Figure S7 and Table S3). In this first step the "loosely" hydrogen bonded water, filling the voids, is removed from the structures, whereas in the second main step (generally above 250 °C, see Table S2) the ionic host itself is thermally decomposed. In a dynamic heating process all water is lost from the crystal lattices of **1b** and **2b** already below 100°C (weight losses of 8.5% and 13.2%, respectively) whereas the dehydration process of **2a** is a slightly slower (weight loss of 6.4% in the range of 25-170°C). The prolonged water vaporization from the crystal lattice of **2a** is most likely a consequence of strong external ionic stabilization of the (**2**)₄(W)₆ cage by K[PF₆]₄⁻³ anions, that conceals all the water in the structure. By holding a new set of samples of **1b**, **2b** and **2a** at 80°C for 12h, the absorption peaks which arise from O-H and H-O-H vibrations disappear from the IR spectra, leaving the emptied ionic host intact and the spectra otherwise unchanged (Figure S6). It can also be noted that **1a** shows significantly higher thermal stability in contrast to the other three compounds. This behavior may arise from Coulombic stabilization of the salt due to its 1:1 cation-anion ratio of +3 cation and -3 anion.

Table S2. TG-data of compounds **1a**, **2a**, **1b** and **2b**. T_{dh} corresponds to the temperature range where water molecules are vaporized from the crystals whereas at T_{dec} the decomposition of the ionic host starts.

	T _{dh} (°C)	T _{dec} (°C)	∆wt-% _{dh} (obs)	∆wt-% _{dh} (calc)
1a	-	328.5	-	-
2a	27-165	255.3	6.4	6.7
1b	27-93	278.1	8.5	9.2
2b	27-67	252.6	13.2	11.9



Figure S7. TG-graphs of 1a, 2a, 1b, and 2b.

References

¹ For earlier reports of this anion, see for example: a) A. Rodriguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, A. Scuiller, C. Decroix, V. Marvaud, J. Vaissermann, M. Verdaguer, I. Rosenman, M. Julve, *Inorg. Chem.* **2001**, *40*, 5868-5877 b) A. V. George, L. D. Field, E. Y. Malouf, A. E. D. McQueen, S. R. Pike, G. R. Purches, T. W. Hambley, I. E. Buys, A. H. White, D. C. R. Hockless, B. W. Skelton, *J. Organomet. Chem.* **1997**, *538*, 101-110.

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⁴ G. Laus , V. Kahlenberg, K. Wurst , T. Lörting, H. Schottenberger, *CrystEngComm* **2008**, *10*, 1638-1644.