Salts and cocrystals of chloranilic acid with organic bases; is it possible to predict a salt formation?

Supplement data

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Contents

S1 Crystal structure of [2-MePyNa]CA·H_2O

The sodium cation revelas penta-coordination in which chloranilate dianions serve as bridging groups (Fig. S1/1) forming an infinite polymeric ribbon whereas the apical position occupies a water molecule (Fig. S1/2).

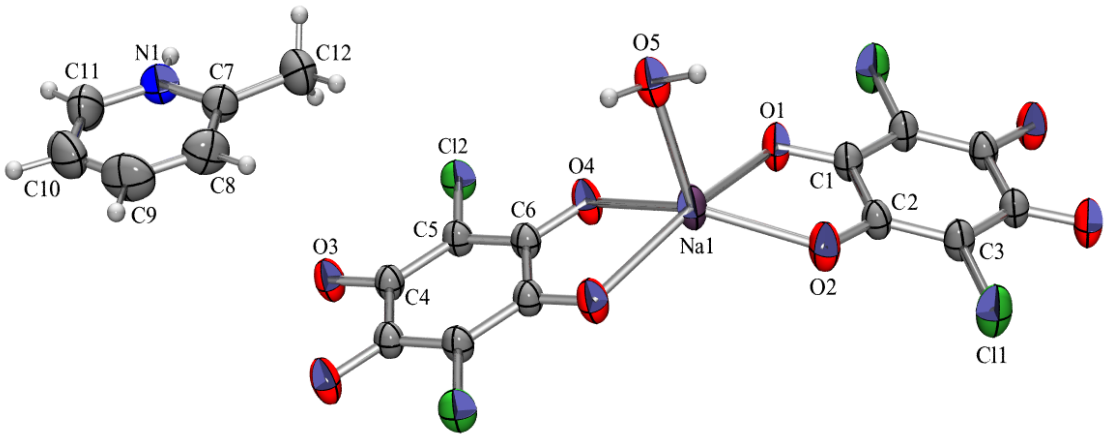

Fig. S1/1 The asymmetric unit of [2-MePyNa]CA·H_2O. Sodium cation is surrounded by four oxgen atoms from two dianions and a water molecule completing a penta-coordination. Atomic displacement ellipsoids are drawn at the 50 % probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

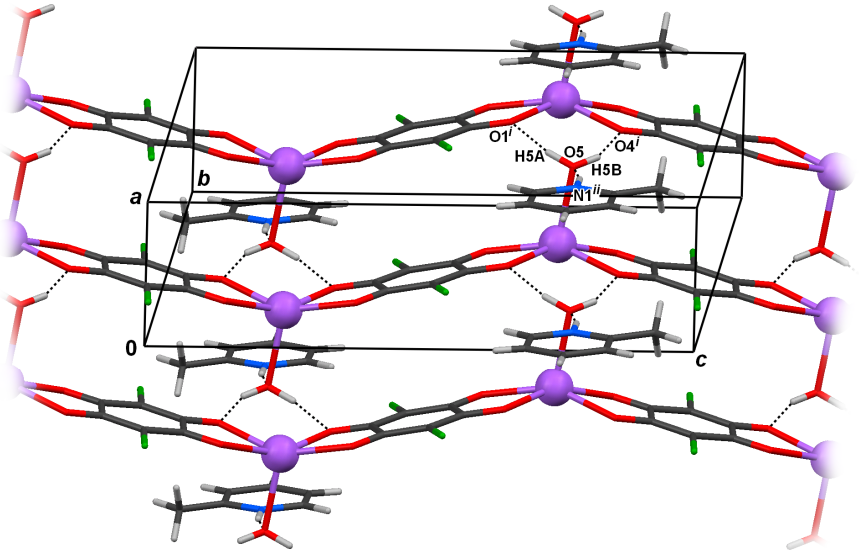

Fig. S1/2 Chains of alternating sodium cations and chloranilate dianions are hydrogen bonded using O–H···O interactions between water molecule and chloranilate dianions; 2-methylpyridinium cations are hydrogen bonded to water molecule by N^{+}–H···O. Packing is completed by C–H···O and C–H···Cl hydrogen bonds. Symmetry codes: *i*) $1 - x$, $1 - y$, $1 - z$; *ii*) x, $1 + y$, z.

S2 Crystal strucutre of (2,6-Me-4-NH_2-Py)$_2$CA·5H_2O

In the structure of 2,6-dimethyl-4-aminopyrimidinium pentahydrate (Fig. S2/1), five water molecules generate intensive hydrogen bonding layers (Table S2) parallel to $(\bar{1}01)$ described by graph-set notation: four-membered ring $R_4^4(8)$, a six-membered ring of a chair-shape, $R_6^4(12)$, and a seven-membered ring of a chair-shape, $R_7^6(14)$. Graph-set descriptors of hydrogen bonded water molecule clusters organized into layers according to the nomenclature introduced by Infantes *et al.*[1] is L4(6)6(8)7(7) (Fig. 18 in the article), where L denotes the two-dimensional hydrogen bonding network of water cluster. This network is realized by four symmetry-independent water molecules whereas the fifth one (O6) is attached as a pendant (acceptor) to O3. To the best of our knowledge, no L4(6)6(8)7(7) water layers have been reported or found in the CSD[1,2].

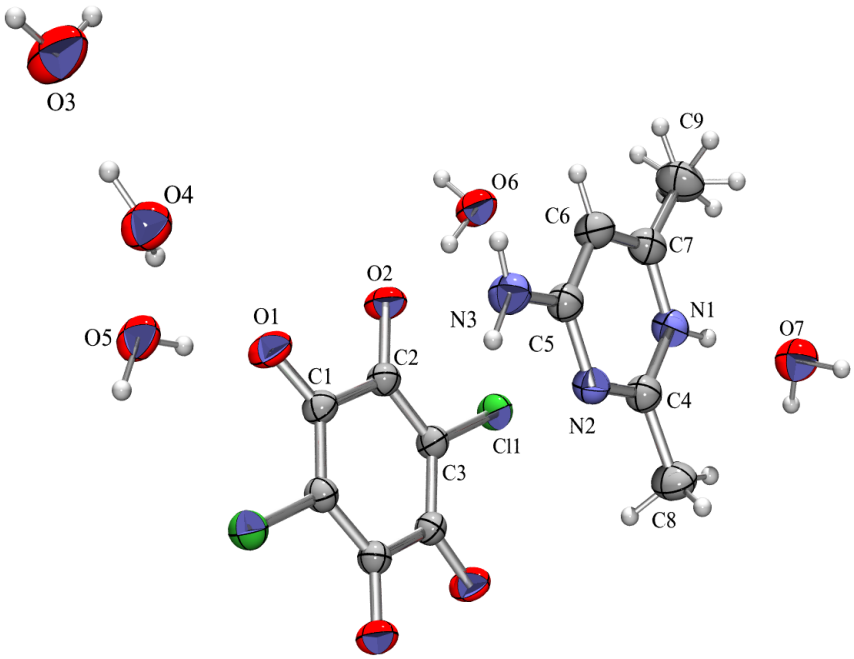

Fig. S2/1 The asymmetric unit of (2,6-Me-4-NH_2-Py)$_2$CA·5H_2O. Atomic displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

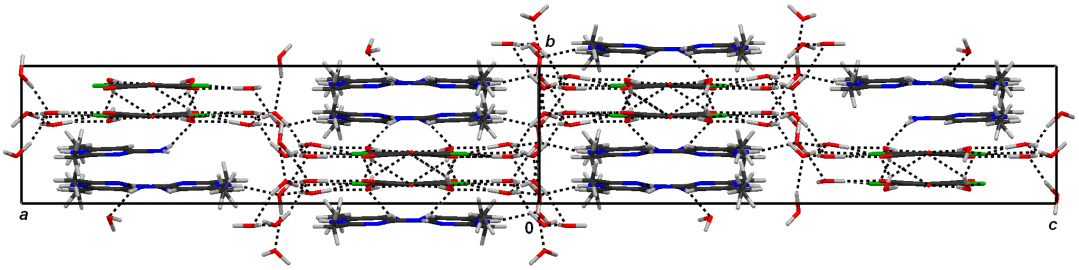

Fig. S2/2 Crystal packing of **(**2,6-Me-4-NH_2-Py)$_2$CA·5H_2O viewed in the direction [101]. Although the structure is layered, the planar ions are shifted and there are no π···π interactions.

S3 Crystal strucutre of 2-MePyClH$_2$CA·H$_2$O

In the cocrystal of 2-MePyCl·H$_2$CA·H$_2$O (Fig. S3/1) water molecule modifies hydrogen bonding sequence using its double donor functionality and connects acid molecule and the unit $Cl^-\cdots H–N^+$ into the hydrogen bonding sequence $O–H\cdots O(–H\cdots Cl^-\cdots H–N^+)_2$ (Fig. S3/2, Table S1) in the form of 1D-infinite ribbons in the direction [100].

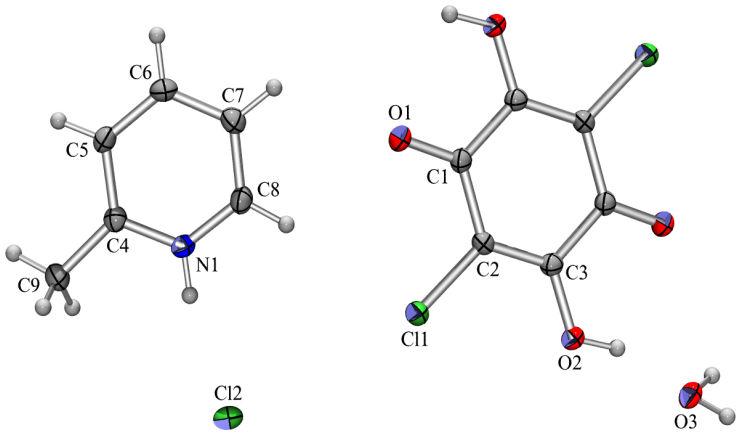

Fig. S3/1 The asymmetric unit in the cocrystal of 2-methylpyridinium chloride monohydrate with chloranilic acid. Atomic displacement ellipsoids are drawn at the 50 % probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

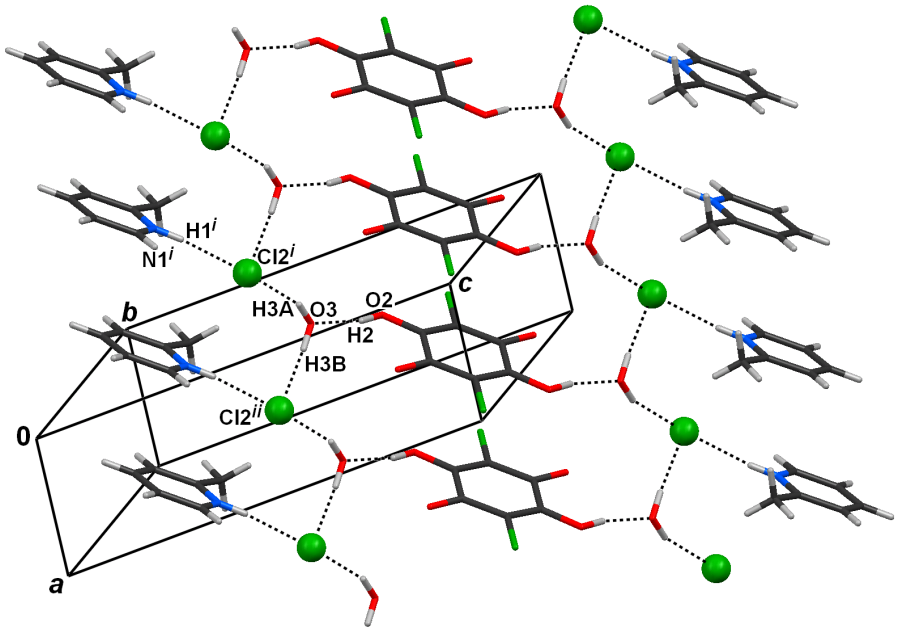

Fig. S3/2 Infinite ribbons of $[(2\text{-MePy})_2Cl_2(H_2O)_2H_2CA]$ units in in the monohydrate of cocrystal of 2-methylpyridinium chloride with chloranilic acid.

Table S1 Geometric parameters of hydrogen bonding in crystal strucutres of 2-[MePyNa]CA·H_2O, (2,6-Me-4-NH_2-Py)$_2$CA·5H_2O and 2-MePyCl·H_2CA·H_2O.

	d(*D*-H)/Å	d(H···*A*)/Å	d(*D*···*A*)/Å	(*D*-H···*A*)/º	Symm. op. on *A*
[2-MePyNa]CA·H_2O					
$N1^+$-H1···O5	0.90 (3)	1.88 (3)	2.764 (2)	167 (2)	$1-x, 1-y, 2-z$
O5-H5A···O1	0.90 (2)	1.87 (2)	2.725 (2)	158 (2)	$1+x, y, z$
O5-H5B···O4	0.91 (2)	1.92 (2)	2.753 (2)	151 (2)	$1+x, y, z$
C8-H8···O3	0,90 (3)	2.57 (3)	3.334 (2)	143 (2)	$1+x, y, z$
C9-H9···O3	0.96 (3)	2.26 (3)	3.178 (3)	160 (2)	$2-x, -y, 2-z$
C11-H11···Cl1	0.96 (3)	2.82 (3)	2.754 (2)	165 (2)	$-1+x, 1+y, 1+z$
(2,6-Me_2-4-H_2Py)$_2$CA·5H_2O					
$N1^+$-H1···O7	0.90 (4)	1.94 (4)	2.830 (3)	171 (2)	x, y, z
N3-H3A···N2	0.86 (5)	2.18 (5)	3.043 (4)	177 (3)	$-x, y, ½-z$
N3-H3B···O6	0.85 (2)	2.15 (2)	2.964 (2)	162 (2)	$½-x, ½-y, 1-z$
O3-H3A···O6	0.93 (4)	1.93 (4)	2.849 (3)	170 (2)	$x, 1-y, ½+z$
O3-H3B···O7	0.92 (8)	1.86 (7)	2.781 (4)	172 (4)	$½-x, ½-y, 1-z$
O4-H4A···O3	0.92 (2)	1.83 (2)	2.738 (2)	167 (6)	x, y, z
O4-H4B···O5	0.91 (5)	1.93 (3)	2.807 (2)	161 (6)	x, y, z
O5-H5A···O1	0.90 (5)	1.84 (5)	2.733 (3)	175 (3)	x, y, z
O5-H5B···O4	0.94 (5)	1.88 (5)	2.814 (3)	175 (3)	$-x, 1-y, 1-z$
O6-H6A···O2	0.92 (5)	1.96 (5)	2.872 (4)	168 (3)	x, y, z
O6-H6B···O1	0.90 (2)	2.12 (4)	2.911 (2)	147 (4)	$½-x, 3/2-y, 1-z$
O6-H6B···O2	0.90 (2)	2.33 (3)	3.062 (2)	138 (4)	$½-x, 3/2-y, 1-z$
O7-H7A···O4	0.94 (2)	1.89 (3)	2.795 (2)	162 (4)	$x, -y, -½+z$
O7-H7B···O5	0.93 (3)	1.80 (3)	2.737 (3)	172 (4)	$x, 1-y, -½+z$
C6-H6B···O2	0.93	2.57	3.417 (2)	152	$½-x, ½-y, 1-z$
C9-H9B···O1	0.96	2.52	3.306 (2)	139	$½-x, ½-y, 1-z$
C9-H9D···O1	0.96	2.50	3.306 (2)	142	$½-x, ½-y, 1-z$
2-MePyCl·H_2CA·H_2O					
$N1^+$-H1···$Cl2^-$	0.85 (2)	2.22 (2)	3.056 (1)	169 (2)	x, y, z
O2-H2···O3	0.88 (3)	1.69 (3)	2.531 (1)	162 (3)	x, y, z
O3-H3A···$Cl2^-$	0.85 (2)	2.32 (3)	3.127 (1)	160 (2)	$-½-x, -½+y, 3/2-z$
O3-H3B···$Cl2^-$	0.87 (2)	2.22 (2)	3.094 (1)	176 (2)	$½-x, -½+y, 3/2-z$
C5-H5···O3	0.92 (2)	2.55 (2)	3.465 (2)	169 (5)	$3/2-x, ½-y, 3/2-z$
C7-H7···O1	0.94 (2)	2.58 (2)	3.145 (2)	122 (2)	x, y, z
C6-H6···Cl1	0.95 (2)	2.90 (2)	3.580 (2)	130 (2)	$3/2+x, ½-y, ½+z$

S4 Crystallographic data of [2-MePyNa]CA·H_2O (2,6-Me-4-NH_2-y)$_2$CA·5H_2O and 2-MePyCl·H_2CA·H2O.

Table S2 Crystallographic, data collection and structure refinement details for structures of [2-MePyNa]CA·H_2O, (2,6-Me-4-NH_2-Py)$_2$CA·5H_2O and 2-MePyCl·H_2CA·H_2O.

Compound	**[2-MePyNa]CA·H_2O**	**(2,6-Me-4-NH_2-Py)$_2$CA·5H_2O**	**2-MePyCl·H_2CA·H_2O**
Empirical formula	$C_{12}H_{10}Cl_2NO_5Na$	$C_9H_{20}ClN_3O_7$	$C_9H_{11}Cl_2NO_3$
Formula wt. / g mol^{-1}	342.11	317.72	252.09
Crystal dimensions / mm	0.22 x 0.11 x 0.06	0.28 x 0.8 x 0.05	0.18 x 0.05 x 0.03
Space group	$P\bar{1}$	$C\,2/c$	$P\,2_1/n$
a / Å	4.9601 (2)	30.417 (4)	4.2140 (1)
b / Å	8.4990 (4)	6.7259 (2)	19.9252 (4)
c / Å	16.4150 (7)	25.341 (4)	13.3364 (3)
α / °	88.135 (4)	90	90
β / °	84.817 (3)	145.35 (3)	98.591 (2)
γ / °	88.068 (4)	90	90
Z	2	8	4
V / Å^3	688.47 (5)	2947 (2)	1107.22 (4)
D_{calc} / g cm^{-3}	1.650	1.432	1.512
μ / mm^{-1}	4.764	2.636	5.195
Θ range / °	2.70 – 75.84	3.49 – 76.29	4.02 – 76.12
T / K	293 (2)	293 (2)	150 (2)
Diffractometer type	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova
Range of h, k, l	$-6 < h < 5$; $-10 < k < 10$; $-20 < l < 19$	$-37 < h < 38$; $-7 < k < 8$; $-31 < l < 31$	$-5 < h < 4$; $-25 < k < 24$; $-16 < l < 16$
Reflections collected	7053	13348	10559
Independent reflections	2759	3054	2283
Observed reflections ($I \geq 2\sigma$)	2535	2789	2185
Absorption correction	Multi-scan	Multi-scan	Multi-scan
R_{int}	0.0171	0.0213	0.0255
R (F)	0.0318	0.0360	0.0279
R_w (F^2)	0.0907	0.109	0.0736
Goodness of fit	1.099	1.086	1.055
H atom treatment	Free	Mixed	Free
No. of parameters	230	233	180
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.259; -0.223	0.375; -0.184	0.343; -0.225

S5 References

1. L. Infantes, J. Chisholm, S. Motherwell, *CrystEngComm*, 2003, **5**, 480-486.
2. M. Mascal, L. Infantes, J. Chisholm, *Angew. Chem., Int. Ed.*, 2006, **45**, 32-36.