Table S2. Intramolecular geometry of orotic acid and the hydrooroatate anion in gas phase and crystalline surroundings.

		Orotic acid, H_3L			Hydroorotate anion, H_2L^-								DFT (hydroorotate) - DFT (orotic acid)
		DFT [a]	Crystal [b]	Δ [c]	DFT [a]	Ag^+ [d]	Δ	K^+ [d]	Δ	Rb^+ [d]	Δ	NH_4^+ [e]	Δ	
N1-C2	(Å)	1.391	1.363	0.028	1.375	1.367	0.008	1.390	-0.015	1.405	-0.030	1.370	0.005	-0.016
N1-C6		1.376	1.365	0.011	1.373	1.369	0.004	1.360	0.013	1.357	0.016	1.372	0.001	-0.003
N3-C2		1.396	1.373	0.023	1.391	1.367	0.024	1.386	0.005	1.379	0.012	1.396	-0.005	-0.005
N3-C4		1.413	1.369	0.044	1.419	1.366	0.053	*	*	*	*	1.368	0.051	0.006
C4-C5		1.464	1.433	0.031	1.446	1.427	0.019	*	*	*	*	1.443	0.003	-0.018
C5-C6		1.354	1.346	0.008	1.360	1.346	0.014	*	*	*	*	1.347	0.013	0.006
C6-C7		1.494	1.498	-0.004	1.561	1.510	0.051	1.535	0.026	1.520	0.041	1.524	0.037	0.067
C2-O3		1.215	1.227	-0.012	1.227	1.223	0.004	1.225	0.002	1.221	0.006	1.221	0.006	0.012
C4-O4		1.219	1.237	-0.018	1.231	1.257	-0.026	*	*	*	*	1.233	-0.002	0.012
C7-O1		1.343	1.306	0.037	1.261	1.241	0.020	*	*	*	*	1.247	0.014	-0.082
C7-O2		1.214	1.197	0.017	1.244	1.256	-0.012	1.225	0.019	1.234	0.010	1.250	-0.006	0.030
O1-C7-O2	(°)	124.3	125.5	-1.2	131.9	127.4	4.5	130.2	1.7	126.9	5.0	126.8	5.1	7.6
C5-C6-C7		124.9	124.2	0.7	124.5	123.0	1.5	*	*	*	*	122.2	2.3	-0.4
N1-C6-C7		113.1	114.1	-1.0	112.7	116.1	-3.4	119.6	-6.9	119.7	-7.0	116.6	-3.9	-0.4
C6-C7-O1		113.1	114.1	-1.0	112.6	115.5	-2.9	*	*	*	*	116.7	-4.1	-0.5
C6-C7-O2		122.6	120.4	2.2	115.6	117.1	-1.5	*	*	*	*	126.8	-11.2	-7.0
dev. from plane [d]		0	0.0133		0.0	0.0608		0 [f]		0 [f]		0.0415		
N3-C6-C7 [g]	(°)	172.3	173.2		171.9	175.3		0 [f]		0 [f]		176.1		

* symmetry equivalents

a) B3LYP/6-311++G(2d,2p)
b) Orotic acid monohydrate. F. Takusagawa and A. Shimada. *Bull. Chem. Soc. Jpn* . 1973, 46, 2011.
c) d (DFT) - d (crystal)
d) Bis-hydroorotato-disilver(I) monohydrate, potassium hydroorotate and rubidium hydroorotate. This work.
e) Ammonium hydroorotate monohydrate. J. Solbakk, *Acta Chem. Scand.* 1971, 25, 3006.
d) Average atomic deviation from the least-squares plane defined by all atoms (Å).
f) Symmetry imposed.
g) Tilt angle of the carboxylic group defined as the angle between the line connecting N3-C6 and C6-C7.

Atomic numbering scheme: