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Supplementary Information

Salts of barbituric and 2-thiobarbituric acids with imidazole: polymorphism, supramolecular structure, thermal stability and water solubility

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Table S1. Crystal data and structure refinement for the compounds.

Identification code	**1**	**2**	**3**
CCDC number	2244541	2244540	2244542
Empirical formula	$C_7H_8N_4O_3$	$C_7H_8N_4O_3$	$C_7H_8N_4O_2S$
Formula weight	196.17	196.17	212.23
Temperature/K	150(2)	150(2)	150(2)
Space group	*P*–1	*C*2/*m*	$P2_1/m$
a/Å	12.0971(3)	21.3255(17)	8.5356(4)
b/Å	12.1081(3)	12.1156(10)	11.9051(6)
c/Å	13.3996(3)	14.6128(12)	10.5692(4)
α/°	80.9330(10)	90	90
β/°	73.8040(10)	119.235(3)	112.3500(10)
γ/°	60.9000(10)	90	90
Volume/Å^3	1646.31(7)	3294.6(5)	993.33(8)
Z	8	16	4
ρ_{calc}/g×cm^{-3}	1.583	1.582	1.419
μ/mm^{-1}	0.127	0.127	0.306
F(000)	816.0	1632.0	440.0
Crystal size/mm^3	0.16 × 0.15 × 0.11	0.26 × 0.11 × 0.08	0.22 × 0.11 × 0.05
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.166 to 55.796	3.194 to 52.768	5.16 to 52.732
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-26 \le h \le 26$, $-13 \le k \le 15$, $-15 \le l \le 18$	$-10 \le h \le 10$, $-11 \le k \le 14$, $-12 \le l \le 13$
Reflections collected	20792	8779	8034
Independent reflections	7799 [R_{int} = 0.0305, R_{sigma} = 0.0389]	3506 [R_{int} = 0.0380, R_{sigma} = 0.0496]	2121 [R_{int} = 0.0276, R_{sigma} = 0.0258]
Data/restraints/parameters	7799/32/601	3506/18/321	2121/0/136
Goodness-of-fit on F^2	1.045	1.042	1.050
Final *R* indexes [$I \ge 2\sigma$ (*I*)]	R_1 = 0.0424, wR_2 = 0.0988	R_1 = 0.0503, wR_2 = 0.1067	R_1 = 0.0342, wR_2 = 0.0828
Final *R* indexes [all data]	R_1 = 0.0539, wR_2 = 0.1068	R_1 = 0.0759, wR_2 = 0.1195	R_1 = 0.0433, wR_2 = 0.0890
Largest diff. peak/hole/*e*Å^{-3}	0.24/–0.27	0.22/–0.30	0.22/–0.23

Table S2. Bond lengths for non-hydrogen atoms in compound **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
O11_1	C12_1	1.2265(17)	O12_3	C14_3	1.2600(17)	N23_5	C22_5	1.321(2)
O12_1	C14_1	1.2687(18)	O13_3	C16_3	1.2666(18)	N23_5	C24_5	1.361(2)
O13_1	C16_1	1.2745(17)	N11_3	C12_3	1.3630(18)	C24_5	C25_5	1.346(2)
N11_1	C12_1	1.3674(18)	N11_3	C16_3	1.3969(18)	N21_6	C22_6	1.3273(19)
N11_1	C16_1	1.3844(18)	N13_3	C12_3	1.3630(19)	N21_6	C25_6	1.369(2)
N13_1	C12_1	1.3623(19)	N13_3	C14_3	1.3910(18)	N23_6	C22_6	1.319(2)
N13_1	C14_1	1.3774(18)	C14_3	C15_3	1.398(2)	N23_6	C24_6	1.3748(19)
C14_1	C15_1	1.395(2)	C15_3	C16_3	1.389(2)	C24_6	C25_6	1.354(2)
C15_1	C16_1	1.391(2)	O11_4	C12_4	1.2262(17)	N21_7	C22_7	1.328(2)
O11_2	C12_2	1.2339(16)	O12_4	C14_4	1.2705(17)	N21_7	C25_7	1.369(2)
O12_2	C14_2	1.2651(17)	O13_4	C16_4	1.2731(16)	N23_7	C22_7	1.324(2)
O13_2	C16_2	1.2632(16)	N11_4	C12_4	1.3663(18)	N23_7	C24_7	1.375(2)
N11_2	C12_2	1.3655(17)	N11_4	C16_4	1.3828(18)	C24_7	C25_7	1.350(2)
N11_2	C16_2	1.3983(17)	N13_4	C12_4	1.3645(18)	N21_8	C22_8	1.3201(19)
N13_2	C12_2	1.3646(18)	N13_4	C14_4	1.3815(17)	N21_8	C25_8	1.3717(19)
N13_2	C14_2	1.3971(17)	C14_4	C15_4	1.392(2)	N23_8	C22_8	1.3201(19)
C14_2	C15_2	1.3915(19)	C15_4	C16_4	1.392(2)	N23_8	C24_8	1.371(2)
C15_2	C16_2	1.391(2)	N21_5	C22_5	1.328(2)	C24_8	C25_8	1.351(2)
O11_3	C12_3	1.2352(17)	N21_5	C25_5	1.371(2)			

Table S3. Bond lengths for non-hydrogen atoms in compound **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
O11_1	C11_1	1.223(3)	C13_2	C12_2[1]	1.397(3)	C12_4	C13_4	1.393(2)
O12_1	C12_1	1.275(2)	O11_3	C11_3	1.235(3)	C13_4	C12_4[1]	1.393(3)
N11_1	C11_1	1.367(2)	O12_3	C12_3	1.266(2)	N21_5	C22_5	1.320(3)
N11_1	C12_1	1.385(3)	N11_3	C11_3	1.363(2)	N21_5	C25_5	1.362(3)
C11_1	N11_1[1]	1.367(2)	N11_3	C12_3	1.394(2)	N23_5	C22_5	1.319(3)
C12_1	C13_1	1.391(3)	C11_3	N11_3[1]	1.363(2)	N23_5	C24_5	1.354(3)
C13_1	C12_1[1]	1.391(3)	C12_3	C13_3	1.396(2)	C24_5	C25_5	1.349(3)
O11_2	C11_2	1.228(3)	C13_3	C12_3[1]	1.396(2)	N21_6	C22_6	1.320(3)
O12_2	C12_2	1.267(2)	O11_4	C11_4	1.240(3)	N21_6	C25_6	1.357(3)
N11_2	C11_2	1.363(2)	O12_4	C12_4	1.264(3)	N23_6	C22_6	1.324(3)
N11_2	C12_2	1.386(3)	N11_4	C11_4	1.358(2)	N23_6	C24_6	1.354(3)
C11_2	N11_2[1]	1.363(2)	N11_4	C12_4	1.396(3)	C24_6	C25_6	1.348(3)
C12_2	C13_2	1.397(3)	C11_4	N11_4[1]	1.358(2)			

[1] $+X, 1-Y, +Z$.

Table S4. Bond lengths for non-hydrogen atoms in compound **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
S11_1	C12_1	1.677(2)	S11_2	C12_2	1.674(2)	N21_3	C22_3	1.321(2)
O12_1	C14_1	1.2671(19)	O12_2	C14_2	1.2684(19)	N21_3	C25_3	1.364(2)
N11_1	C12_1	1.3540(17)	N11_2	C12_2	1.3584(17)	N23_3	C22_3	1.325(2)
N11_1	C14_1	1.393(2)	N11_2	C14_2	1.3916(19)	N23_3	C24_3	1.366(2)
C12_1	N11_1[1]	1.3540(17)	C12_2	N11_2[2]	1.3584(17)	C24_3	C25_3	1.348(2)
C13_1	C14_1[1]	1.3942(19)	C13_2	C14_2[2]	1.3911(19)			
C13_1	C14_1	1.3942(19)	C13_2	C14_2	1.3911(19)			

[1] $+X, 1/2-Y, +Z$; [2] $+X, 3/2-Y, +Z$.

Table S5. Hydrogen bond characteristics for the structural model of compound **1** with the hydrogen atoms refined freely with default standard uncertainty (0.02 Å) for the restraint of 0.88 Å on the N–H bonds (a); for the same model with hydrogens displaced at 0.88 Å along the corresponding N–H bond (b); for the model with geometrically placed hydrogens (lying on the external bisector of the corresponding C–N–C angle; c); for the model with non-spherical atomic scattering factors (d). Superscript at an atom corresponds to the atomic number according to Figs. 1 and 2; the number after underscore corresponds to the residue number according to Fig. 3.

Compound	N	H	O	N–H, Å	H···O, Å	N···O, Å	N–H···O, deg.
	N^1_1	H^1_1	O^4_3	0.879(13)	2.100(14)	2.9561(17)	164.2(15)
	N^1_2	H^1_2	O^4_4	0.860(13)	2.046(14)	2.8988(16)	171.2(15)
	N^1_3	H^1_3	O^4_1	0.877(14)	1.999(14)	2.8751(16)	176.1(16)
	N^1_4	H^1_4	O^4_2	0.862(14)	2.040(14)	2.8904(16)	168.8(16)
	N^3_1	H^3_1	O^6_3	0.895(13)	1.973(14)	2.8669(16)	176.5(16)
	N^3_2	H^3_2	O^6_4	0.861(13)	2.195(14)	3.0056(16)	156.6(15)
	N^3_3	H^3_3	O^6_1	0.877(13)	2.061(14)	2.9198(16)	165.9(15)
1 (a)	N^3_4	H^3_4	O^6_2	0.883(14)	2.005(14)	2.8869(15)	177.0(16)
	N^1_5	H^1_5	O^4_3	0.933(14)	1.816(14)	2.7444(17)	172.8(17)
	N^1_6	H^1_6	O^6_2	0.898(13)	1.764(14)	2.6585(16)	173.4(16)
	N^1_7	H^1_7	O^6_3	0.907(14)	1.765(14)	2.6664(16)	171.8(17)
	N^1_8	H^1_8	O^4_2	0.905(14)	1.761(14)	2.6607(15)	172.4(16)
	N^3_5	H^3_5	O^6_1	0.902(14)	1.714(14)	2.6014(16)	167.2(17)
	N^3_6	H^3_6	O^4_4	0.897(14)	1.741(14)	2.6337(15)	173.3(16)
	N^3_7	H^3_7	O^4_1	0.889(14)	1.777(14)	2.6593(16)	171.6(17)
	N^3_8	H^3_8	O^6_4	0.896(14)	1.736(14)	2.6216(16)	169.3(16)
	N^1_1	H^1_1	O^4_3	0.88	2.10	2.9561(17)	164.3
	N^1_2	H^1_2	O^4_4	0.88	2.03	2.8988(16)	172.0
	N^1_3	H^1_3	O^4_1	0.88	2.00	2.8751(16)	175.9
	N^1_4	H^1_4	O^4_2	0.88	2.02	2.8904(16)	167.9
	N^3_1	H^3_1	O^6_3	0.88	1.99	2.8669(16)	175.9
	N^3_2	H^3_2	O^6_4	0.88	2.19	3.0056(16)	155.0
	N^3_3	H^3_3	O^6_1	0.88	2.06	2.9198(16)	164.8
1 (b)	N^3_4	H^3_4	O^6_2	0.88	2.01	2.8869(15)	177.5
	N^1_5	H^1_5	O^4_3	0.88	1.87	2.7444(17)	174.0
	N^1_6	H^1_6	O^6_2	0.88	1.78	2.6585(16)	175.3
	N^1_7	H^1_7	O^6_3	0.88	1.79	2.6664(16)	174.1
	N^1_8	H^1_8	O^4_2	0.88	1.78	2.6607(15)	173.5
	N^3_5	H^3_5	O^6_1	0.88	1.73	2.6014(16)	169.0
	N^3_6	H^3_6	O^4_4	0.88	1.76	2.6337(15)	174.1
	N^3_7	H^3_7	O^4_1	0.88	1.79	2.6593(16)	171.5
	N^3_8	H^3_8	O^6_4	0.88	1.75	2.6216(16)	171.3
	N^1_1	H^1_1	O^4_3	0.88	2.09	2.9560(17)	166.3
	N^1_2	H^1_2	O^4_4	0.88	2.03	2.8982(16)	168.3
	N^1_3	H^1_3	O^4_1	0.88	2.00	2.8752(16)	177.4
	N^1_4	H^1_4	O^4_2	0.88	2.02	2.8898(16)	167.6
	N^3_1	H^3_1	O^6_3	0.88	1.99	2.8668(16)	175.2
	N^3_2	H^3_2	O^6_4	0.88	2.19	3.0049(15)	153.1
	N^3_3	H^3_3	O^6_1	0.88	2.08	2.9190(16)	158.2
1 (c)	N^3_4	H^3_4	O^6_2	0.88	2.01	2.8865(15)	172.8
	N^1_5	H^1_5	O^4_3	0.88	1.88	2.7460(17)	169.9
	N^1_6	H^1_6	O^6_2	0.88	1.78	2.6589(16)	172.0

	N^1_7	H^1_7	O^6_3	0.88	1.80	2.6666(16)	170.0
	N^1_8	H^1_8	O^4_2	0.88	1.79	2.6618(16)	171.5
	N^3_5	H^3_5	O^6_1	0.88	1.73	2.6021(16)	169.8
	N^3_6	H^3_6	O^4_4	0.88	1.76	2.6344(16)	169.8
	N^3_7	H^3_7	O^4_1	0.88	1.78	2.6600(16)	174.1
	N^3_8	H^3_8	O^6_4	0.88	1.76	2.6227(16)	166.8
1 (d)	N^1_1	H^1_1	O^4_3	1.006(13)	1.970(14)	2.9562(13)	165.7(11)
	N^1_2	H^1_2	O^4_4	0.974(12)	1.934(13)	2.9013(13)	172.1(11)
	N^1_3	H^1_3	O^4_1	1.017(14)	1.861(14)	2.8764(13)	176.0(11)
	N^1_4	H^1_4	O^4_2	0.959(13)	1.944(13)	2.8917(13)	169.1(11)
	N^3_1	H^3_1	O^6_3	1.002(13)	1.866(13)	2.8657(13)	175.8(11)
	N^3_2	H^3_2	O^6_4	0.986(12)	2.081(13)	3.0067(12)	155.5(1)
	N^3_3	H^3_3	O^6_1	0.982(12)	1.960(13)	2.9172(13)	164.4(11)
	N^3_4	H^3_4	O^6_2	0.998(13)	1.891(14)	2.8881(12)	176.6(11)
	N^1_5	H^1_5	O^4_3	1.051(16)	1.699(17)	2.7451(13)	172.8(13)
	N^1_6	H^1_6	O^6_2	1.040(15)	1.620(15)	2.6551(13)	172.4(12)
	N^1_7	H^1_7	O^6_3	1.013(14)	1.658(14)	2.6640(13)	171.5(13)
	N^1_8	H^1_8	O^4_2	1.014(13)	1.648(14)	2.6566(12)	172.2(12)
	N^3_5	H^3_5	O^6_1	1.030(14)	1.581(14)	2.5975(13)	167.8(13)
	N^3_6	H^3_6	O^4_4	1.028(13)	1.606(14)	2.6303(12)	173.9(12)
	N^3_7	H^3_7	O^4_1	0.995(14)	1.666(14)	2.6565(13)	173.0(12)
	N^3_8	H^3_8	O^6_4	1.042(13)	1.584(14)	2.6172(12)	170.5(12)

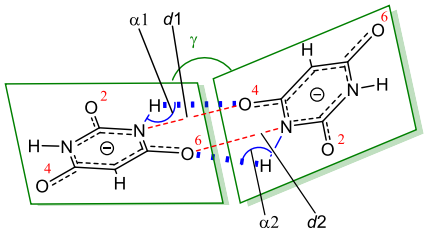
Table S6. Hydrogen bond characteristics for the structural model of compound **2** with the hydrogen atoms refined freely with standard uncertainty (0.02 Å) for the restraint of 0.88 Å on the N–H bonds (a); for the same model with hydrogens displaced at 0.88 Å along the corresponding N–H bond (b); for the model with geometrically placed hydrogens (lying on the external bisector of the corresponding C–N–C angle; c); for the model with non-spherical atomic scattering factors (d). Superscript at an atom corresponds to the atomic number according to Figs. 1 and 2; the number after underscore corresponds to the residue number according to Fig. 3.

Compound	N	H	O	N–H, Å	H···O, Å	N···O, Å	N–H···O, deg.
2 (a)	N^1_1	H^1_1	O^4_3	0.891(16)	2.016(16)	2.906(2)	177(2)
	N^1_2	H^1_2	O^4_4	0.867(16)	2.030(16)	2.892(2)	173(2)
	N^1_3	H^1_3	O^4_1	0.877(16)	2.023(16)	2.900(2)	178(2)
	N^1_4	H^1_4	O^4_2	0.886(16)	2.028(16)	2.911(2)	175(2)
	N^1_5	H^1_5	O^4_3	0.890(16)	1.811(16)	2.697(2)	173(2)
	N^1_6	H^1_6	O^4_2	0.897(16)	1.773(17)	2.659(2)	169(2)
	N^3_5	H^3_5	O^4_1	0.870(16)	1.782(17)	2.642(2)	170(2)
	N^3_6	H^3_6	O^4_4	0.894(16)	1.790(16)	2.672(2)	168(2)
2 (b)	N^1_1	H^1_1	O^4_3	0.88	2.03	2.906(2)	177.5
	N^1_2	H^1_2	O^4_4	0.88	2.02	2.892(2)	172.4
	N^1_3	H^1_3	O^4_1	0.88	2.02	2.900(2)	178.5
	N^1_4	H^1_4	O^4_2	0.88	2.03	2.911(2)	175.2
	N^1_5	H^1_5	O^4_3	0.88	1.82	2.697(2)	173.8
	N^1_6	H^1_6	O^4_2	0.88	1.79	2.659(2)	169.9
	N^3_5	H^3_5	O^4_1	0.88	1.77	2.642(2)	168.9
	N^3_6	H^3_6	O^4_4	0.88	1.80	2.672(2)	169.8
2 (c)	N^1_1	H^1_1	O^4_3	0.88	2.03	2.905(2)	176.5
	N^1_2	H^1_2	O^4_4	0.88	2.01	2.891(2)	177.8
	N^1_3	H^1_3	O^4_1	0.88	2.02	2.899(2)	174.9
	N^1_4	H^1_4	O^4_2	0.88	2.05	2.911(2)	165.5
	N^1_5	H^1_5	O^4_3	0.88	1.83	2.697(2)	170.5
	N^1_6	H^1_6	O^4_2	0.88	1.79	2.659(2)	167.5
	N^3_5	H^3_5	O^4_1	0.88	1.78	2.642(2)	167.9
	N^3_6	H^3_6	O^4_4	0.88	1.80	2.673(2)	169.1
2 (d)	N^1_1	H^1_1	O^4_3	1.04(2)	1.87(2)	2.9053(19)	177.2(16)
	N^1_2	H^1_2	O^4_4	0.97(2)	1.93(2)	2.895(2)	171.8(18)
	N^1_3	H^1_3	O^4_1	1.00(2)	1.90(2)	2.8984(19)	177.0(18)
	N^1_4	H^1_4	O^4_2	0.99(2)	1.92(2)	2.9121(19)	172.8(17)
	N^1_5	H^1_5	O^4_3	1.05(3)	1.64(3)	2.6944(19)	174(2)
	N^1_6	H^1_6	O^4_2	1.05(3)	1.61(3)	2.6552(19)	171(2)
	N^3_5	H^3_5	O^4_1	1.01(3)	1.64(3)	2.6403(19)	170(3)
	N^3_6	H^3_6	O^4_4	1.04(2)	1.64(2)	2.6687(19)	169(2)

Table S7. Hydrogen bond characteristics for the structural model of compound **3** with the hydrogen atoms refined freely with default standard uncertainty (0.02 Å) for the restraint of 0.88 Å on the N–H bonds (a); for the same model with hydrogens displaced at 0.88 Å along the corresponding N–H bond (b); for the model with geometrically placed hydrogens (lying on the external bisector of the corresponding C–N–C angle; c); for the model with non-spherical atomic scattering factors (d). Superscript at an atom corresponds to the atomic number according to Figs. 1 and 2; the number after underscore corresponds to the residue number according to Fig. 3.

Compound	N	H	O	N–H, Å	H···O, Å	N···O, Å	N–H···O, deg.
3 (a)	N^1_1	H^1_1	O^4_2	0.870(14)	1.956(14)	2.8244(17)	175.8(17)
	N^1_2	H^1_2	O^4_1	0.863(14)	1.942(14)	2.8030(17)	175.6(16)
	N^1_3	H^1_3	O^4_2	0.864(14)	1.855(14)	2.7106(17)	169.9(18)
	N^3_3	H^3_3	O^4_1	0.857(14)	1.853(15)	2.6942(17)	166.7(18)
3 (b)	N^1_1	H^1_1	O^4_2	0.88	1.95	2.8244(17)	175.2
	N^1_2	H^1_2	O^4_1	0.88	1.93	2.8030(17)	175.1
	N^1_3	H^1_3	O^4_2	0.88	1.84	2.7106(17)	168.7
	N^3_3	H^3_3	O^4_1	0.88	1.83	2.6942(17)	166.2
3 (c)	N^1_1	H^1_1	O^4_2	0.88	1.95	2.8240(17)	175.9
	N^1_2	H^1_2	O^4_1	0.88	1.92	2.8028(17)	178.6
	N^1_3	H^1_3	O^4_2	0.88	1.85	2.7108(17)	165.8
	N^3_3	H^3_3	O^4_1	0.88	1.83	2.6939(17)	167.6
3 (d)	N^1_1	H^1_1	O^4_2	1.047(14)	1.776(14)	2.8225(11)	177.5(10)
	N^1_2	H^1_2	O^4_1	1.037(15)	1.768(15)	2.8029(12)	176.0(11)
	N^1_3	H^1_3	O^4_2	1.007(14)	1.709(15)	2.7067(11)	170.2(14)
	N^3_3	H^3_3	O^4_1	1.007(15)	1.698(16)	2.6907(11)	167.8(13)

Table S8. Geometry characteristics of a pair of HBA^- anions that hydrogen-bonded with each other in a side-to-side fashion in structures found in Cambridge Structural Database (CSD; version 5.43, updates up to November 2022) and in **1**–**3**. γ (deg.) – Dihedral angle between the mean planes; *d*1,2 (Å) – N···O distance; α1,2 (deg.) – N–H···O angle, R_1 (%) – factor, *Z* – cell formula units; *Z′* – number of HBA^- in crystallographically independent part; T (K) – experiment temperature.

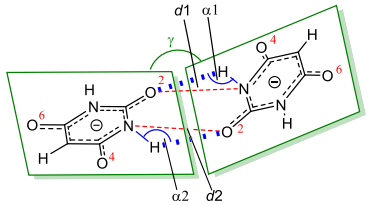


CSD Refcode	γ	*d*1	*d*2	α1	α2	R_1	*Z*	*Z′*	T	Compound name
EVELAV	49.9	2.83	2.83	173.5	173.5	6.5	8	1	150	8-(dimethylamino)-N,N-dimethylnaphthalen-1-aminium barbiturate unknown solvate
VUKFIR	42.6	2.80	2.83	163.7	169.4	5.1	6	0.5	298	catena-[(μ_2-4,4'-bipyridine-N,N')-tetra-aqua-nickel(II) bis(barbiturate) hexahydrate]
VUKFOX	42.5	2.80	2.83	163.5	169.8	5.3	6	0.5	298	catena-[(μ_2-4,4'-bipyridine-N,N')-tetra-aqua-copper(II) bis(barbiturate) hexahydrate]
VUKFEN	38.2	2.81	2.81	169.3	169.3	3.3	3	0.25	298	catena-[(μ_2-4,4'-bipyridine-N,N')-tetra-aqua-cobalt(II) bis(barbiturate) hexahydrate]
BUYYIE	38.0	2.82	2.82	167.6	167.6	4.2	3	0.25	293	catena-[(μ_2-4,4'-bipyridine)-tetra-aqua-zinc(II) bis(barbiturate) hexahydrate]
BUYYEA	37.2	2.83	2.83	170.3	170.3	3.3	3	0.25	293	catena-[(μ_2-4,4'-bipyridine)-tetra-aqua-iron(II) bis(barbiturate) hexahydrate]
BENWUO	30.8	2.81	2.83	177.2	174.4	3.7	4	2	100	2-[(2,6-dimethylphenyl)amino]-N,N-diethyl-2-oxoethanaminium barbiturate
BENWUO	18.1	2.75	2.75	170.9	174.6	3.7	4	2	100	2-[(2,6-dimethylphenyl)amino]-N,N-diethyl-2-oxoethanaminium barbiturate
KEDZAV	16.0	2.80	2.92	174.4	176.5	5.8	16	4	120	8-dimethylaminonaphthalene-1-dimethylammonium barbiturate methanol solvate
KEDZAV	14.3	2.78	2.97	174.7	170.1	5.8	16	4	120	8-dimethylaminonaphthalene-1-dimethylammonium barbiturate methanol solvate
INEYOQ	12.8	2.79	2.79	176.9	176.9	5.7	4	0.5	293	catena-[(μ_2-1,2-bis(4-pyridyl)ethane)-tetra-aqua-cobalt(II) bis(barbiturate) tetrahydrate]
KEDZAV	10.9	2.86	2.89	174.3	179.3	5.8	16	4	120	8-dimethylaminonaphthalene-1-dimethylammonium barbiturate methanol solvate
INEYUW	10.8	2.79	2.79	175.3	175.3	3.6	4	0.5	293	catena-[(μ_2-1,2-bis(4-pyridyl)ethane)-tetra-aqua-iron(II) bis(barbiturate) tetrahydrate]
INEZEH	10.7	2.81	2.81	176.0	176.0	5.0	4	0.5	293	catena-[(μ_2-1,2-bis(4-pyridyl)ethane)-tetra-aqua-manganese(II) bis(barbiturate) tetrahydrate]
ZABVAD	10.6	2.77	2.87	158.4	171.4	4.7	4	2	301	2-amino-6-methylpyridinium barbiturate dihydrate
WOPLIY	10.6	2.79	2.79	177.5	176.2	3.7	8	1	120	tributyl-N-(4-methoxyphenyl)phosphoraniminium barbiturate
GATLIY	9.3	2.80	2.80	173.0	173.0	3.3	4	0.5	293	catena-[(μ_2-(trans)-4,4'-ethene-1,2-diyldipyridine)-tetra-aqua-iron(II) bis(barbiturate) tetrahydrate]
KEDZAV	7.6	2.77	2.90	172.9	176.5	5.8	16	4	120	8-dimethylaminonaphthalene-1-dimethylammonium barbiturate methanol solvate
ERELUL01	6.6	2.79	2.98	177.9	175.5	4.5	4	1	150	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL01	6.6	2.80	2.97	174.7	178.0	4.5	4	1	150	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL	6.2	2.80	2.99	165.5	175.6	5.6	4	1	120	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL	6.2	2.79	2.97	171.9	176.1	5.6	4	1	120	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
NEBFUY	5.8	2.84	2.98	174.1	178.5	5.5	4	2	296	4-(3-carboxy-1-ethyl-6-fluoro-4-oxo-1,4-dihydroquinolin-7-yl)-1-methylpiperazin-1-ium barbiturate hydrate
JURLUG	4.7	2.79	2.80	172.4	170.3	2.7	4	1	293	aqua-bis(1,10-phenanthroline)-copper bis(barbiturate) trihydrate
QEPFIB	4.6	2.79	2.81	169.1	176.2	9.2	4	2	293	methylammonium barbiturate
QEPFIB	4.6	2.81	2.84	173.0	168.3	9.2	4	2	293	methylammonium barbiturate

DEFWUJ	3.3	2.82	3.12	177.2	170.6	2.5	4	0.5	295	tetraaqua-bis(barbiturate)-cobalt(II)
ESIDES	2.6	2.78	2.94	176.9	169.8	3.9	4	1	150	hexa-aqua-magnesium bis(barbiturate) trihydrate
DEFWUJ01	2.1	2.82	3.09	164.2	170.1	9.4	4	0.5	150	tetra-aqua-bis[6-oxypyrimidine-2,4(1H,3H)-dione]-cobalt
GUYRUN03	1.2	2.72	3.14	167.4	164.9	4.9	8	0.5	296	triaqua-bis(6-oxidopyrimidine-2,4(1H,3H)-dione)-copper(II)
GUYRUN02	1.1	2.71	3.11	174.4	168.3	1.2	8	0.5	93	triaqua-bis(barbiturato-O)-copper(II)
GUYRUN04	1.1	2.72	3.13	163.5	164.8	2.7	8	0.5	150	triaqua-bis[6-oxypyrimidine-2,4(1H,3H)-dione]-copper
ERELUL01	0.8	2.83	2.84	174.7	172.1	4.5	4	1	150	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL01	0.8	2.86	2.86	167.8	173.5	4.5	4	1	150	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
QEPFOH	0.6	2.90	2.91	178.4	177.1	6.2	8	1	293	dimethylammonium barbiturate
CUHBAL	0.0	2.91	2.91	164.5	164.5	5.1	4	1	296	catena-[(μ-pyridine-4-carbohydrazide)-triaqua-cobalt(II) bis(barbiturate) trihydrate]
CUHBEP	0.0	2.91	2.91	170.1	170.1	3.5	4	1	296	catena-[(μ-pyridine-4-carbohydrazide)-triaqua-zinc(II) bis(barbiturate) trihydrate]
ERELUL	0.0	2.82	2.82	178.0	178.0	5.6	4	1	120	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL	0.0	2.85	2.85	178.8	178.8	5.6	4	1	120	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL	0.0	2.85	2.85	173.1	173.1	5.6	4	1	120	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ERELUL	0.0	2.86	2.86	172.3	172.3	5.6	4	1	120	catena-[tetrakis(μ-barbiturate)-hexadeca-aqua-tetra-calcium tetrakis(barbiturate)]
ESOZOD	0.0	2.86	2.86	172.8	172.8	4.9	4	1	173	2,4-diaminopyridinium barbiturate
EVELAV	0.0	2.82	2.82	174.9	174.9	6.5	8	1	150	8-(dimethylamino)-N,N-dimethylnaphthalen-1-aminium barbiturate unknown solvate
GATLEU	0.0	2.79	2.79	173.4	173.4	3.6	1	0.5	293	(trans)-4,4'-ethene-1,2-diyldipyridinium bis(barbiturate) dihydrate
GIGQOD	0.0	2.89	2.89	178.3	178.3	5.1	2	1	293	2-amino-4,6-dimethylpyrimidinium barbiturate trihydrate
GIGQOD	0.0	2.85	2.85	175.3	175.3	5.1	2	1	293	2-amino-4,6-dimethylpyrimidinium barbiturate trihydrate
KEWSOX	0.0	2.83	2.83	173.4	173.4	5.9	4	1	296	4-(3-carboxy-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinolin-7-yl)piperazin-1-ium barbiturate monohydrate
KINFEV	0.0	2.80	2.80	174.1	174.1	2.9	8	1	100	aqua-(2,2'-bipyridyl)-(barbiturate)-chloro-copper(II) dihydrate
MYTUW	0.0	2.86	2.86	175.2	175.2	7.7	4	1	293	1-aminoisoquinolinium barbiturate hemihydrate
MYVEI	0.0	2.81	2.81	177.6	177.6	5.9	2	1	300	1,10-phenanthrolinium barbiturate monohydrate
MYVIM	0.0	2.86	2.86	174.8	174.8	5.4	2	1	300	4-methoxypyridinium barbiturate dihydrate
OQOXOJ	0.0	2.87	2.87	177.6	177.6	3.9	4	0.5	293	diaqua-bis(4,4'-dimethyl-2,2'-bipyridine)-nickel(II) bis(barbiturate) tetrahydrate
OQOXUP	0.0	2.87	2.87	173.4	173.4	5.8	4	0.5	293	diaqua-bis(4,4'-dimethyl-2,2'-bipyridine)-manganese(II) bis(barbiturate) tetrahydrate
QAFSOF	0.0	2.95	2.95	173.8	173.8	4.6	8	1	295	pyrimidine-2,4,6-trione barbiturate sesquihydrate
RAYJOT	0.0	2.85	2.85	176.6	176.6	1.4	2	1	295	catena-[(μ-aqua)-bis(μ-barbiturate)-aqua-barium]
REZFIM	0.0	2.90	2.90	161.1	161.1	9.0	2	1	293	(barbiturate)(hydridotris(5-methyl-3-phenyl-1-pyrazolyl)borato)zinc(II) methanol solvate
SUYNIM	0.0	2.91	2.91	174.3	174.3	9.0	2	1	293	1,3-dihydroxy-4,5-dimethyl-1H-imidazol-3-ium barbiturate
SUYNIM	0.0	2.86	2.86	174.0	174.0	9.0	2	1	293	1,3-dihydroxy-4,5-dimethyl-1H-imidazol-3-ium barbiturate
UFUWAW	0.0	2.86	2.86	178.0	178.0	6.1	4	0.5	100	diaqua-bis(1,10-phenanthroline)-cobalt(II) bis(barbiturate) dihydrate

ZIMTIA	0.0	2.79	2.79	174.9	174.9	5.5	8	1	293	potassium barbiturate hemikis(pyrimidine-2,4,6(1H,3H,5H)-trione) sesquihydrate
1	13.0	2.87	2.96	176.5	164.2	4.2	8	4	150	imidazolium barbiturate
	13.0	2.90	3.01	171.2	156.6					
	16.6	2.88	2.92	176.1	165.9					
	16.6	2.89	2.89	177.0	168.8					
2	7.0	2.91	2.91	177.2	177.2	5.0	16	2	150	imidazolium barbiturate
	11.0	2.89	2.89	173.2	173.2					
	7.0	2.90	2.90	178.2	178.2					
	11.0	2.91	2.91	175.2	175.2					
3	0.7	2.82	2.80	175.8	178.6	3.4	4	1	150	imidazolium 2-thiobarbiturate

Table S9. Geometry characteristics of a pair of HBA^- anions that hydrogen-bonded with each other in a head-to-head fashion in structures found in Cambridge Structural Database (CSD; version 5.43, updates up to November 2022) and in **1**–**3**. γ (deg.) – Dihedral angle between the mean planes; *d*1,2 (Å) – N···O distance; α1,2 (deg.) – N–H···O angle, R_1 (%) – factor, *Z* – cell formula units; *Z′* – number of HBA^- in crystallographically independent part; T (K) – experiment temperature.



CSD Refcode	γ	d1	d2	α1	α2	R_1	*Z*	*Z′*	T	Compound Name
AMBARB	0.0	2.81	2.81	162.3	162.3	15.0	4	1	295	ammonium barbiturate
AMBARB01	0.0	2.83	2.83	172.3	172.3	3.9	4	1	293	ammonium barbiturate
CUHBOZ	0.0	2.86	2.86	167.4	167.4	2.9	1	0.5	296	tetra-aqua-bis(pyridine-3-carboxamide)-cobalt(II) bis(barbiturate) dihydrate
CUHBUF	0.0	2.87	2.87	167.5	167.5	3.0	1	0.5	296	tetra-aqua-bis(pyridine-3-carboxamide)-zinc(II) bis(barbiturate) dihydrate
CURKEH	0.0	2.89	2.89	171.7	171.7	8.2	2	1	296	4-(3-carboxy-1-ethyl-6,8-difluoro-4-oxo-1,4-dihydroquinolin-7-yl)-2-methylpiperazin-1-ium barbiturate pyrimidine-2,4,6(1H,3H,5H)-trione hydrate
CURKIL	0.0	2.82	2.82	175.5	175.5	8.8	2	1	296	4-(3-carboxy-1-ethyl-6,8-difluoro-4-oxo-1,4-dihydroquinolin-7-yl)-2-methylpiperazin-1-ium barbiturate isophthalic acid methanol solvate monohydrate
DEFXAQ	0.0	2.85	2.85	178.7	178.7	4.0	4	0.25	295	catena-[bis(μ-barbiturate)-diaqua-cobalt(II)]
ESIDES	15.1	3.04	2.90	169.5	175.8	3.9	4	1	150	hexa-aqua-magnesium bis(barbiturate) trihydrate
GATLEU	0.0	2.88	2.88	176.0	176.0	3.6	1	0.5	293	(trans)-4,4'-ethene-1,2-diyldipyridinium bis(barbiturate) dihydrate
GATLIY	9.3	2.85	2.85	176.0	176.0	3.3	4	0.5	293	catena-[(μ-(trans)-4,4'-ethene-1,2-diyldipyridine)-tetra-aqua-iron(II) bis(barbiturate) tetrahydrate]
HOLFET	0.0	2.86	2.86	171.9	171.9	11.9	2	1	295	(1-(4,6-diamino-5h-1,3,5-triazine-2-yl)-1,3,6,10,13-penta-azacyclotetradecane)-bis(perchlorato)-copper(II) barbiturate trihydrate
INEYOQ	12.8	2.83	2.83	170.9	170.9	5.7	4	0.5	293	catena-[(μ-1,2-bis(4-pyridyl)ethane)-tetra-aqua-cobalt(II) bis(barbiturate) tetrahydrate]
INEYUW	10.8	2.84	2.84	174.4	174.4	3.6	4	0.5	293	catena-[(μ-1,2-bis(4-pyridyl)ethane)-tetra-aqua-iron(II) bis(barbiturate) tetrahydrate]
INEZEH	10.7	2.86	2.86	172.2	172.2	5.0	4	0.5	293	catena-[(μ-1,2-bis(4-pyridyl)ethane)-tetra-aqua-manganese(II) bis(barbiturate) tetrahydrate]
JURLUG	4.7	2.87	2.91	174.8	168.4	2.7	4	1	293	aqua-bis(1,10-phenanthroline)-copper bis(barbiturate) trihydrate
KEWSOX	0.0	2.92	2.92	163.1	163.1	5.9	4	1	296	4-(3-carboxy-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinolin-7-yl)piperazin-1-ium barbiturate monohydrate
KINFEV	0.0	2.76	2.76	168.1	168.1	2.9	8	1	100	aqua-(2,2'-bipyridyl)-(barbiturate)-chloro-copper(II) dihydrate
MUYVIM	0.0	2.96	2.96	173.7	173.7	5.4	2	1	300	4-methoxypyridinium barbiturate dihydrate
NEBFUY	5.8	2.98	2.85	162.8	169.0	5.5	4	2	296	4-(3-carboxy-1-ethyl-6-fluoro-4-oxo-1,4-dihydroquinolin-7-yl)-1-methylpiperazin-1-ium barbiturate hydrate
OQEPAD	0.0	2.85	2.85	167.3	167.3	5.1	4	0.5	293	tetra-aqua-(5,5'-dimethyl-2,2'-bipyridine)-cobalt(II) bis(barbiturate) dihydrate
RAGLAO	0.0	2.87	2.87	179.1	179.1	1.9	4	0.25	295	catena-(bis(μ-barbiturate)-diaqua-di-manganese(II))
RAGLAO01	0.0	2.85	2.85	176.2	176.2	2.7	4	0.25	120	catena-(bis(μ-barbiturate)-diaqua-manganese)
REZFIM	0.0	2.91	2.91	162.4	162.4	9.0	2	1	293	(barbiturate)(hydridotris(5-methyl-3-phenyl-1-pyrazolyl)borato-)zinc(II) methanol solvate
UFUWAW	0.0	2.88	2.88	175.1	175.1	6.1	4	0.5	100	diaqua-bis(1,10-phenanthroline)-cobalt(II) bis(barbiturate) dihydrate
ZABVAD	10.6	2.97	2.84	165.4	171.5	4.7	4	2	301	2-amino-6-methylpyridinium barbiturate dihydrate

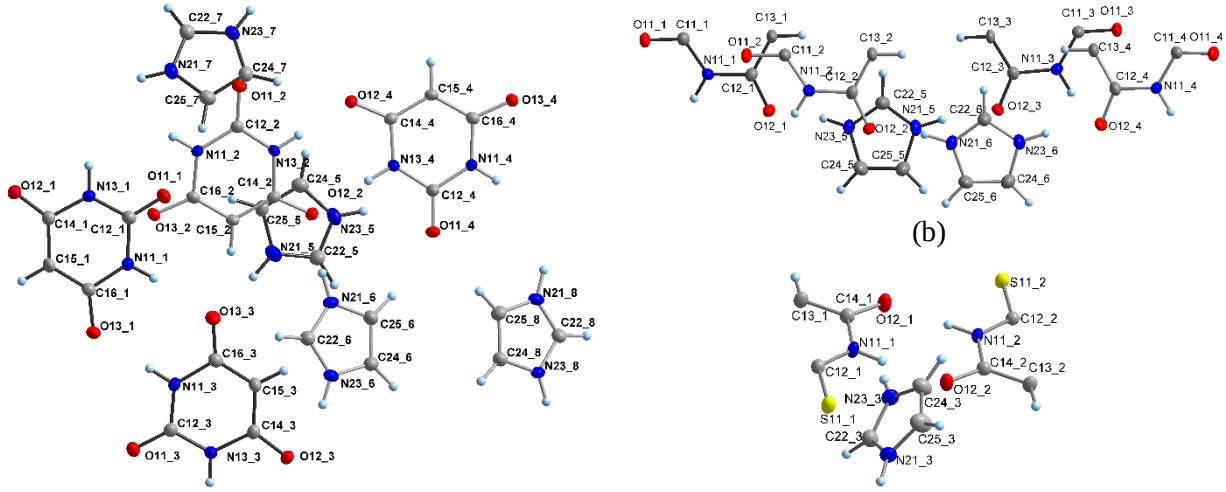


Fig. S1. Crystallographically independent part of structures **1**–**3** with numbering of non-hydrogen atoms. Atomic displacement ellipsoids are shown at the 50% probability level.

Fig. S2. Photographs of **1** (left) and **2** (right) in the crystal and powder forms.

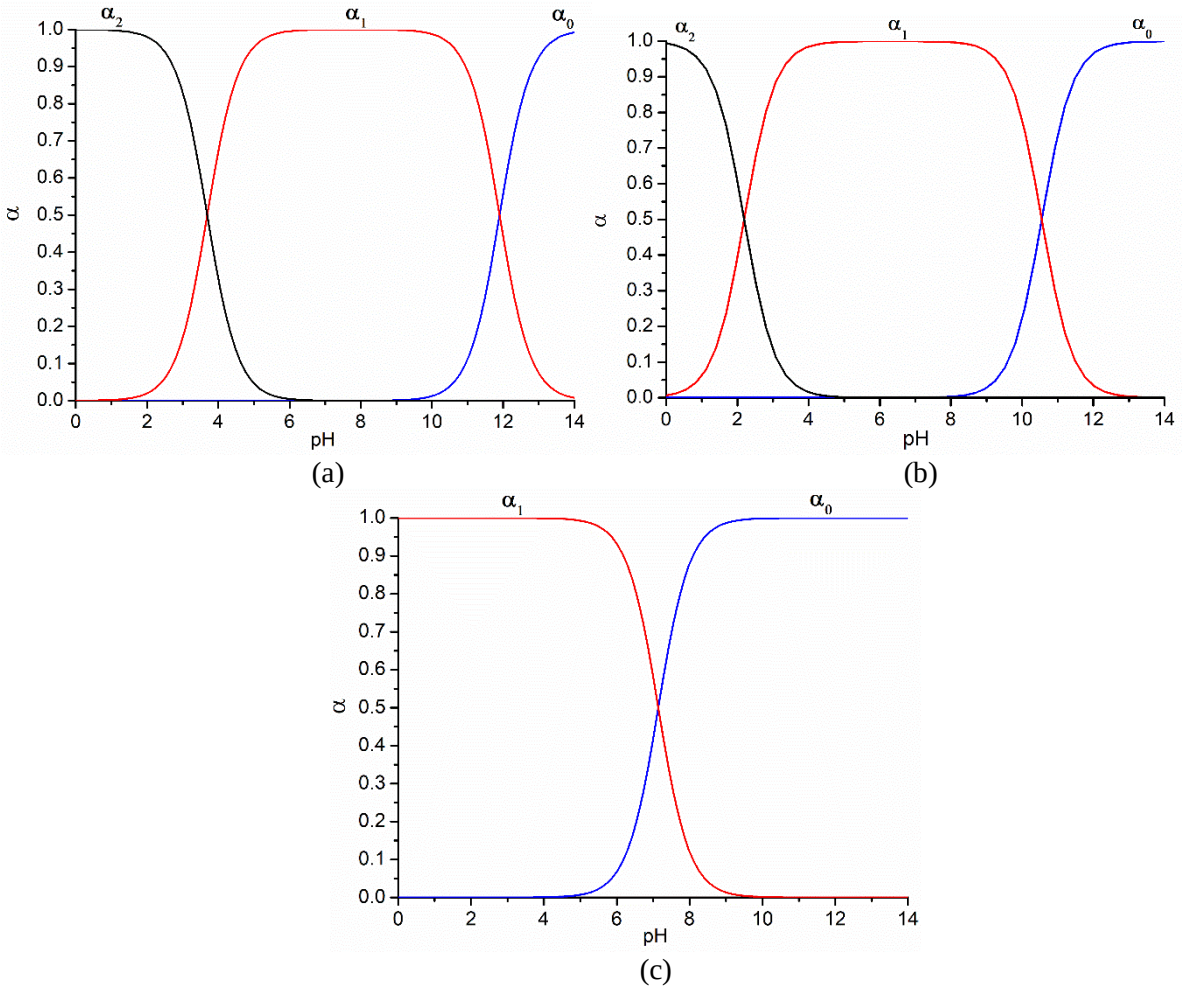
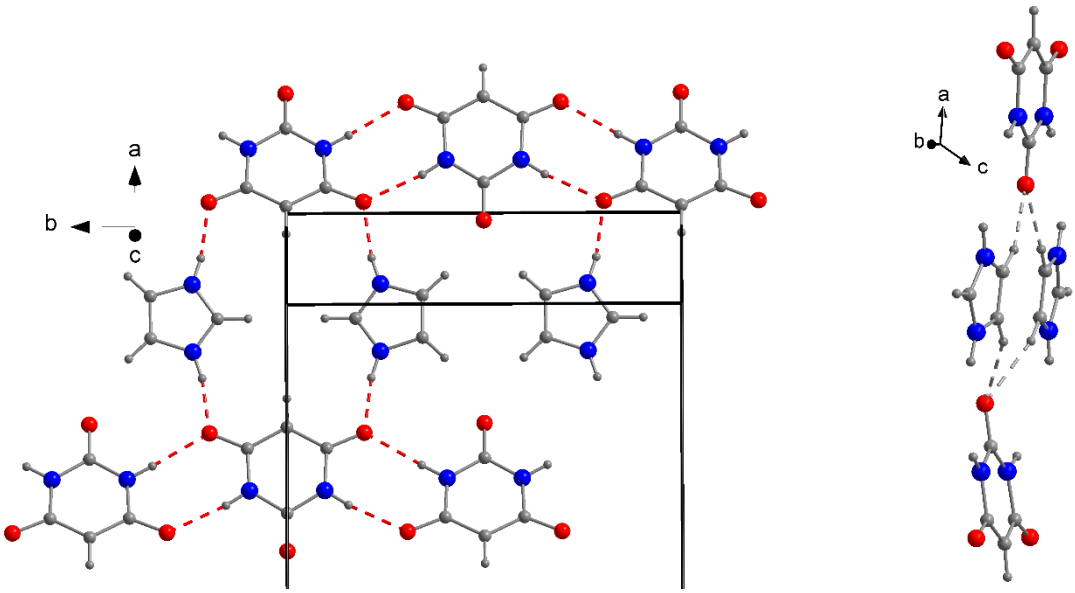
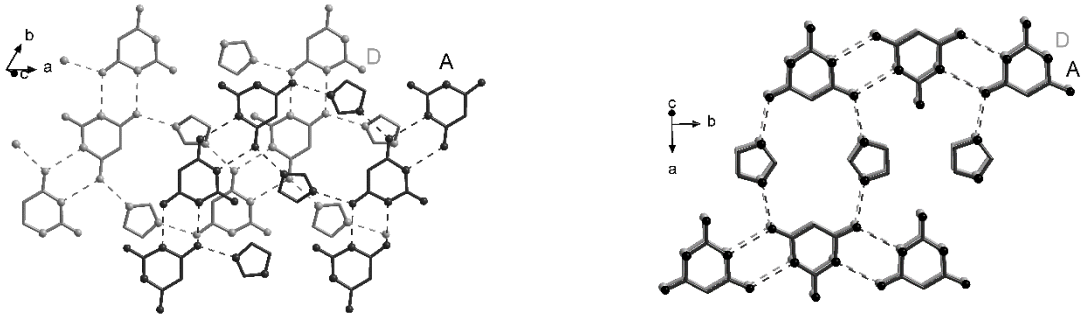


Fig. S3. Species distribution diagrams of H_2BA (a), H_2TBA (b) and Im (c) as a function of pH: α_2 [H_2(T)BA], α_1 [H(T)BA^-] (a, b) or [HIm^+] (c), α_0 [(T)BA^{2-}] (a, b) or [Im] (c) (C = 0.01 mol/L).



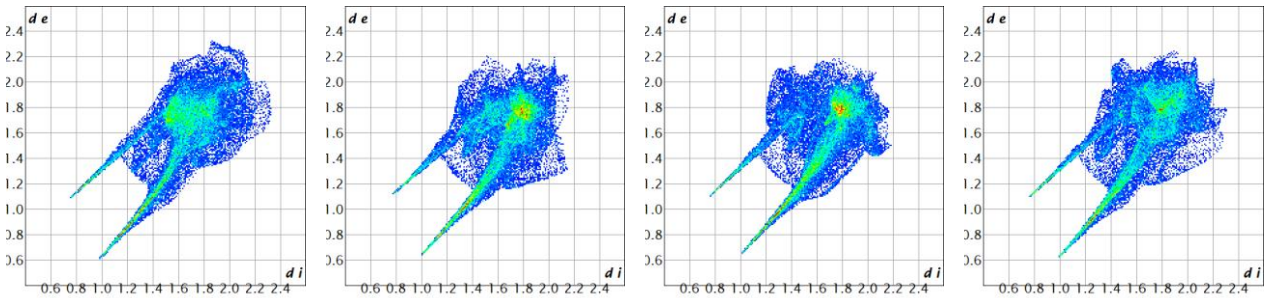
(a) (b)

Fig. S4. The structure of a layer in **2** composed from hydrogen-bonded HBA^- and HIm^+ ions (a). The hydrogen bonds N–H···O are highlighted with red dashed lines. A fragment of the layer showing weak C–H···O contacts (b) highlighted with grey dashed lines.



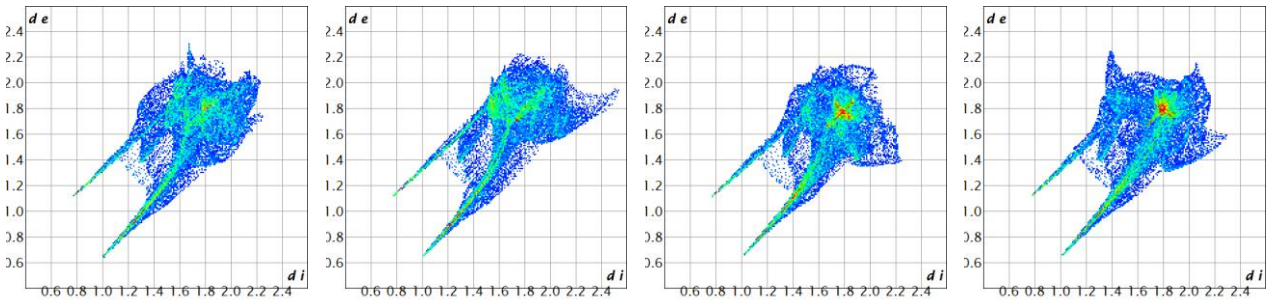
(a) (b)

Fig. S5. Arrangement of inversion-related A and D layers in compounds **1** (a) and **2** (b). The corresponding B and C layers are not shown for clarity.



1 ***2*** ***3*** ***4***

Fig. S6. Fingerprint plots for four crystallographically independent HBA^- anions in compound **1** calculated in CrystalExplorer. *di* And *de* are the distances (Å) from the Hirshfeld surface to the nearest nucleus inside and outside the surface, correspondingly.

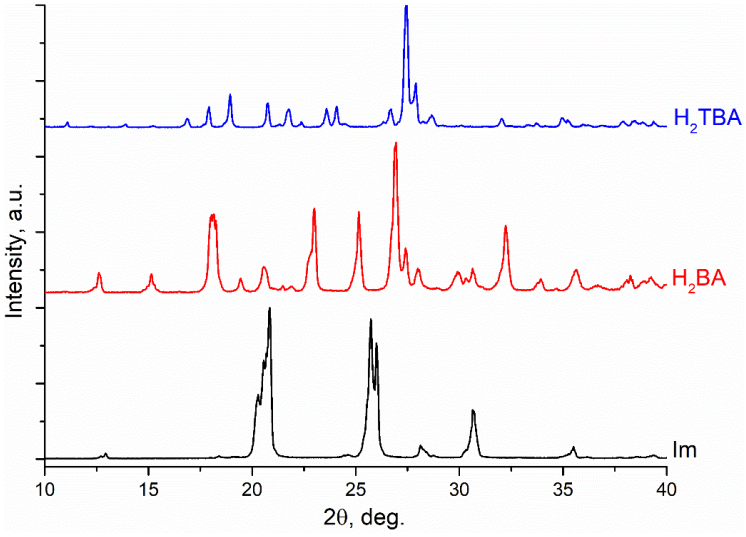


1 ***2*** ***3*** ***4***

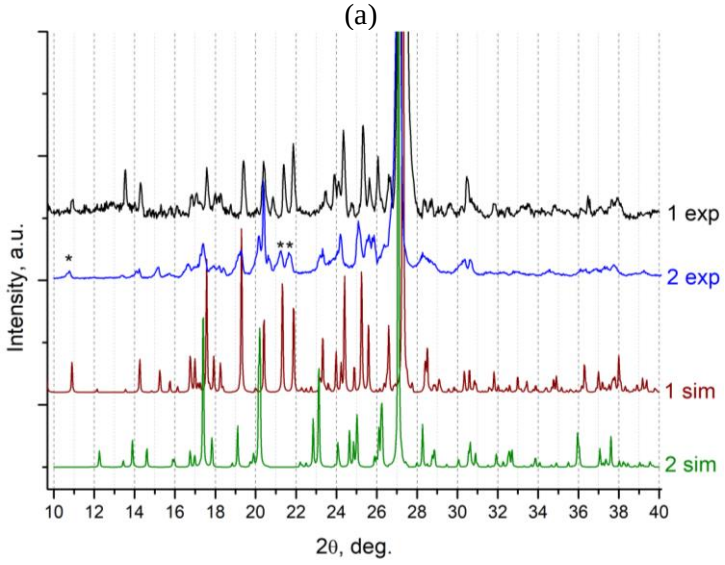
Fig. S7. Fingerprint plots for four crystallographically independent HBA^- anions in compound **2** calculated in CrystalExplorer. *di* And *de* are the distances (Å) from the Hirshfeld surface to the nearest nucleus inside and outside the surface, correspondingly.

1 ***2***

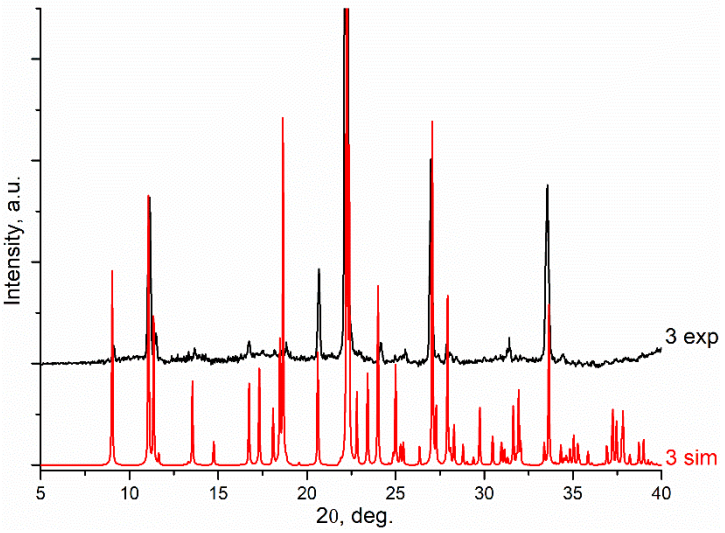
Fig. S8. Fingerprint plots for two crystallographically independent $HTBA^-$ anions in compound **3** calculated in CrystalExplorer. *di* And *de* are the distances (Å) from the Hirshfeld surface to the nearest nucleus inside and outside the surface, correspondingly.



(a)

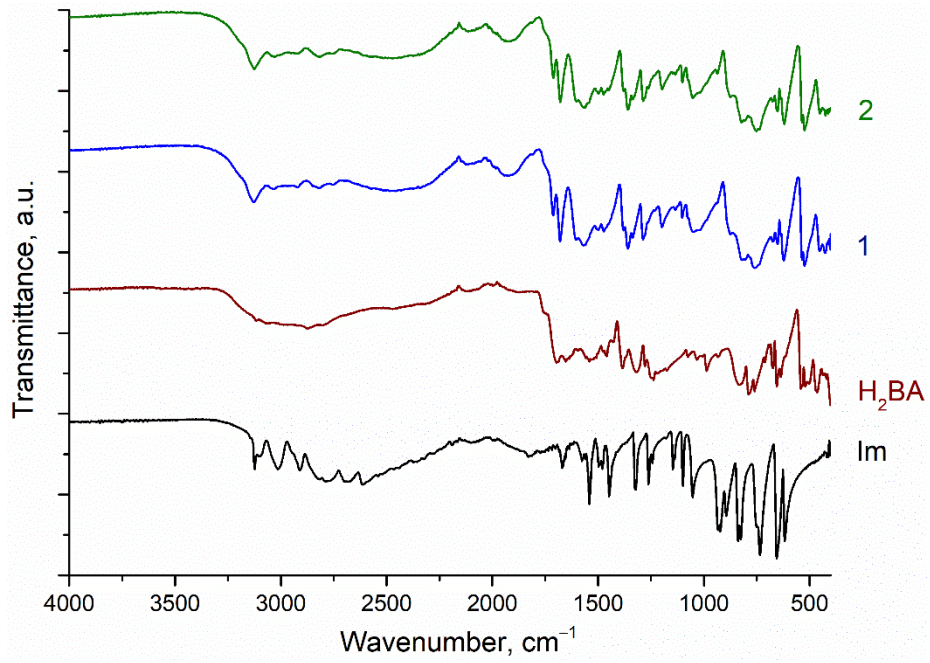


(b)

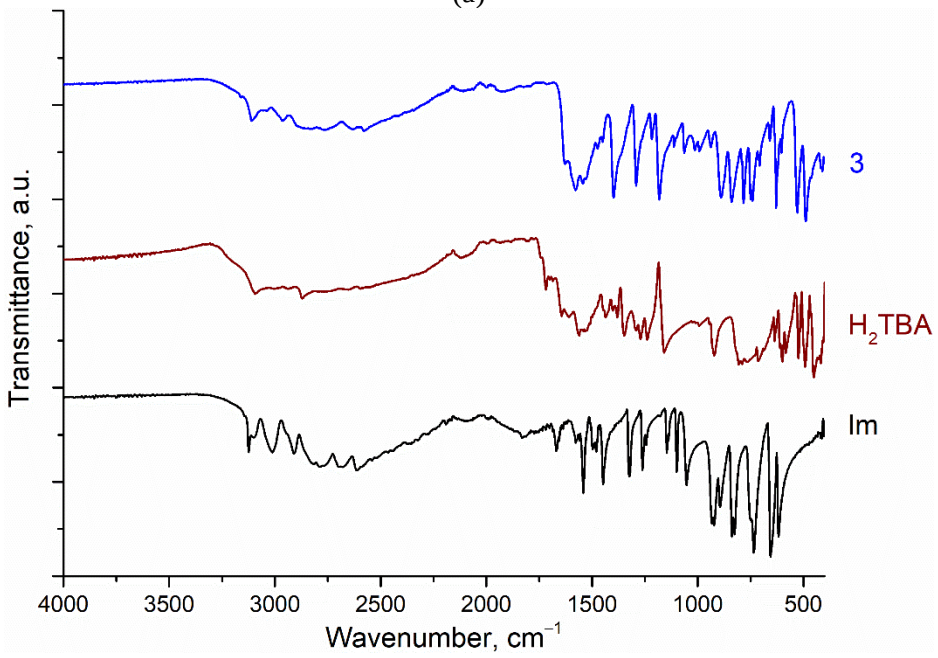


(c)

Fig. S9. Powder X-ray diffraction (XRD) patterns of the starting materials (a), salts **1**, **2** (b) and **3** (c) from the experimental study (exp) and simulated from the single-crystal XRD data (sim). Some characteristic peaks of **1** observed in the experimental XRD pattern of **2** (b) are highlighted as *.



(a)



(b)

Fig. S10. Infrared spectra of the starting materials and salts **1**–**3**.

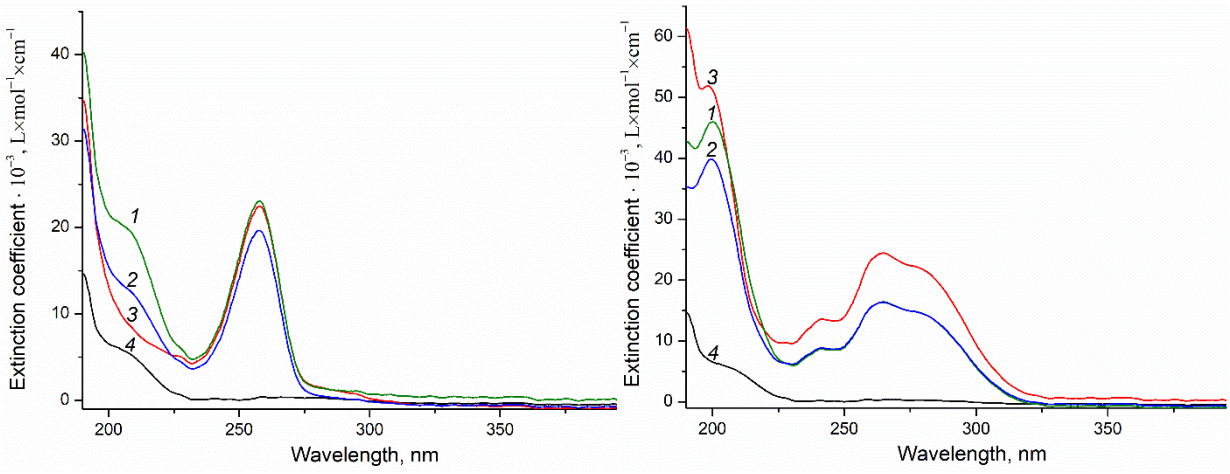
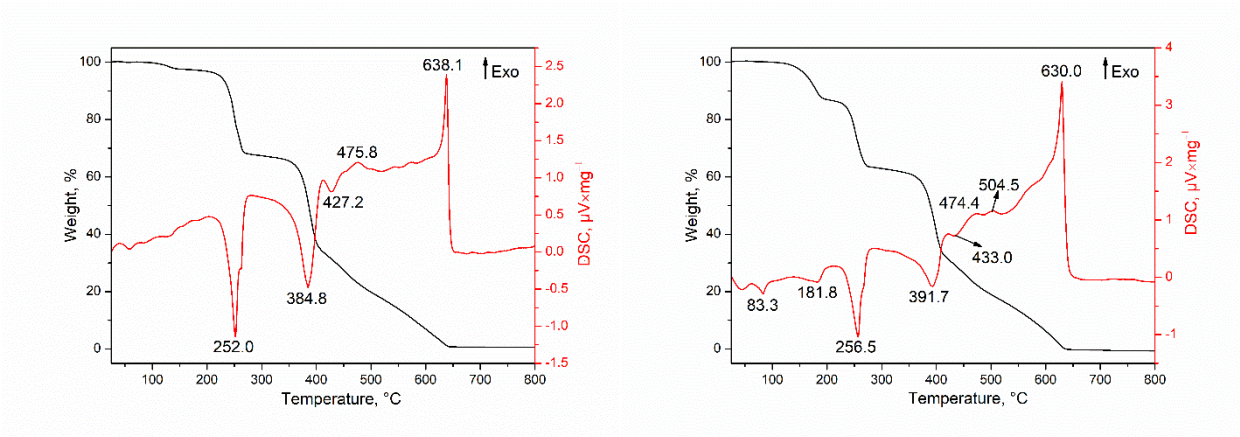
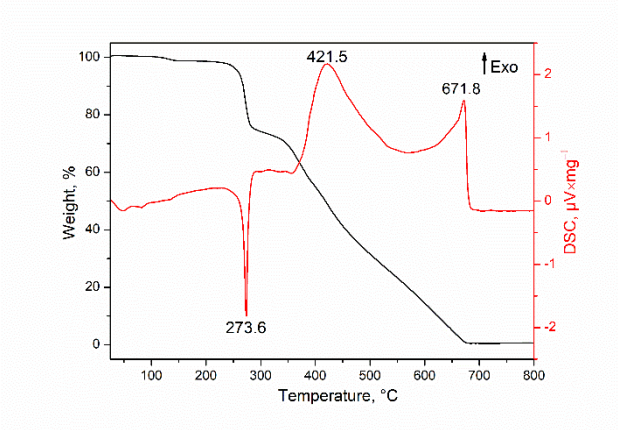


Fig. S11. Ultraviolet spectra of aqueous solutions (t = 25 °C) of H_2BA : Im mixture (C_{acid} = 3·10^{-5} mol/L, C_{Im} = 6·10^{-5} mol/L, pH 6.30; *1*a), salt **2** (C_{acid} = C_{Im} = 4·10^{-5} mol/L, pH 6.57; *2*a), H_2BA (C = 3·10^{-5} mol/L, pH 6.84; *3*a), Im (C = 6·10^{-5} mol/L, pH 7.26; *4*a) and H_2TBA : Im mixture (C_{acid} = 3·10^{-5} mol/L, C_{Im} = 6·10^{-5} mol/L, pH 6.13; *1*b), salt **3** (C_{acid} = C_{Im} = 4·10^{-5} mol/L, pH 6.04; *2*b), H_2TBA (C = 3·10^{-5} mol/L, pH 6.83; *3*b), Im (C = 6·10^{-5} mol/L, pH 7.26; *4*b).



(a) (b)



(c)

Fig. S12. TG-DSC curves of salts **1**–**3** (a)–(c) in air.