Table S1. Crystal data and routine refinement details for **1** ($C_4H_3NaO_4$, M = 138.05, space group P-1, Z = 2) and **2** ($C_4H_3KO_4$, M = 154.16, space group P-1, Z = 1).

	1					**2**				
T, K	100	150	200	250	300	100	150	200	250	300
a, Å	6.2337(4)	6.2351(4)	6.2374(4)	6.2401(3)	6.2421(4)	5.3298(4)	5.3352(5)	5.3403(5)	5.3472(6)	5.3534(7)
b, Å	6.7932(5)	6.8144(5)	6.8401(4)	6.8687(4)	6.8981(5)	6.4933(4)	6.5195(6)	6.5443(6)	6.5737(7)	6.6038(9)
c, Å	7.4636(5)	7.4635(5)	7.4662(4)	7.4695(4)	7.4726(5)	7.9425(4)	7.9435(7)	7.9451(7)	7.9466(8)	7.9446(11)
α, °	67.8720(10)	67.9990(10)	68.1330(10)	68.2700(10)	68.4070(10)	82.0390(10)	82.093(2)	82.134(2)	82.191(2)	82.252(3)
β, °	72.6380(10)	72.7000(10)	72.7660(10)	72.8360(10)	72.9030(10)	87.9430(10)	87.953(2)	87.969(2)	87.998(2)	88.021(3)
γ, °	63.2960(10)	63.3370(10)	63.3940(10)	63.4500(10)	63.5040(10)	67.2640(10)	67.230(2)	67.198(2)	67.167(2)	67.127(2)
V, Å^3	258.35(3)	259.54(3)	261.08(3)	262.78(2)	264.48(3)	251.03(3)	252.30(4)	253.51(4)	255.01(5)	256.37(6)
D_{calc}, г·см$^{-3}$	1.982	1.973	1.961	1.948	1.936	1.826	1.817	1.809	1.798	1.788
μ, cm^{-1}	9.51	9.46	9.41	9.35	9.29	2.34	2.33	2.32	2.3	2.29
F(000)	156	156	156	156	156	140	140	140	140	140
$2\theta_{max}$, °	60	60	60	59	59	60	60	59	60	59
Reflns measured	3387	3403	3415	3436	3460	3355	3386	3391	3412	3424
Independent reflns	1499	1508	1518	1527	1539	1467	1475	1480	1492	1498
Reflns with I>2σ(I)	1420	1435	1427	1435	1425	1378	1352	1341	1346	1317
Parameters	94	94	94	94	94	95	95	95	95	95
R1	0.0219	0.0231	0.0235	0.0238	0.0242	0.0266	0.0308	0.0310	0.0330	0.0344
wR2	0.0603	0.0628	0.0661	0.0651	0.0679	0.0768	0.0854	0.0868	0.0920	0.0952
GOF	1.065	1.069	1.067	1.043	1.055	1.074	1.051	1.076	1.068	1.066
Residual electron density, e·Å^{-3} (d_{min}/d_{max})	0.478/-0.324	0.411/-0.330	0.399/-0.333	0.402/-0.244	0.373/-0.237	0.590/-0.311	0.531/-0.249	0.509/-0.286	0.459/-0.246	0.451/-0.231

Table S2.   C-C bond lengths [Å] for **1** and **2**.

Bond	salt **1**	salt **2**
C(1)-C(2)	1.4864(3)	1.4908(4)
C(2)-C(3)	1.3355(3)	1.3354(4)
C(3)-C(4)	1.4932(3)	1.4953(4)

Table S3. Weak anion-anion interactions in crystals of **1** and **2** according to the topological analysis of the experimental $\rho(r)$ function.

Compound 1

	d,[a] Å	$\rho(r)$,[b] e·Å^{-3}	$\nabla^2\rho(r)$,[b] e·Å^{-5}	$h_e(r)$,[c] a.u.	$v(r)$,[c] a.u.	E_{int},[d] kcal/mol
O(4)…O(4)	3.263	0.035597	0.319711	0.000647	-0.00202	0.63504
O(4)…O(3)	3.379	0.040551	0.33458	0.000587	-0.0023	0.720695
H(3)…O(2)	2.564	0.066869	0.77643	0.001372	-0.00531	1.666038
H(2)…O(2)	2.812	0.036407	0.426233	0.000997	-0.00243	0.761483
C(4)…O(1)	3.029	0.058528	0.672077	0.001273	-0.00443	1.388679
O(3)…O(3)	3.166	0.022134	0.517813	0.001583	-0.00221	0.692143
H(3)…O(3)	3.06	0.018598	0.256858	0.000733	-0.0012	0.376192
C(2)…C(1)	3.161	0.069076	0.638192	0.000821	-0.00498	1.561871
C(2)…C(2)	3.219	0.057327	0.505184	0.000731	-0.00378	1.185365

Compound 2

	d,[a] Å	$\rho(r)$,[b] e·Å^{-3}	$\nabla^2\rho(r)$,[b] e·Å^{-5}	$h_e(r)$,[c] a.u.	$v(r)$,[c] a.u.	E_{int},[d] kcal/mol
O(2)…H(3)	2.57	0.073388	0.689766	0.000852	-0.00545	1.709963
O(2)…H(3)	3.011	0.047137	0.313445	0.000351	-0.00255	0.799761
O(2)…C(2)	3.218	0.059014	0.435583	0.00044	-0.00364	1.14144
O(2)…O(2)	3.436	0.041482	0.267631	0.000333	-0.00211	0.662023
O(3)…C(2)	3.703	0.0353	0.470167	0.001173	-0.00253	0.794113
O(3)…H(2)	2.728	0.026683	0.496942	0.001434	-0.00229	0.717243
O(1)…C(4)	3.002	0.05568	0.66557	0.001334	-0.00424	1.329065
C(4)…C(4)	3.266	0.032014	0.399747	0.000998	-0.00215	0.674886

a – distances (the H(2) and H(3) hydrogen atoms are fixed at the calculated C-H bond lengths derived by the DFT optimization of anionic dimer with the fixed O…O distance: 1.083 Å), b – values at (3,-1) corresponding bond critical points (*bcp*) of $\rho(r)$, c – estimations of energy densities at *bcp* ($h_e(r)$ – total electron energy density, $v(r)$ – potential energy density) according to Kirzhnitz model and local virial theorem, d – interaction energy E_{int} estimated as $-0.5 \cdot v(r)$.

The H…O interactions (C-H…O contacts) can be the only additional "force" that influence charge distribution within carboxylate groups and, hence, **DWP** peculiarities. However, one can see that 1) energies of such interactions are not more 1.7 kcal/mol that smaller than the weakest metal-oxygen bond (2.0 kcal/mol in **2**) and 2) these interactions are formed only by the O(2) and O(3) atoms which are not involved in the H-bond. Moreover, the energy difference caused by C-H…O interaction is very similar in both **1** and **2** (2 and 1.8 kcal/mol respectively) and what is more important it is antibate to the difference calculated from metal-oxygen interactions. Namely, the COOH group form more stronger C-H…O bonding than the COO group, although the negative charge of the oxygen atom forming C-H…O interactions has to become larger like that value of the oxygen atom forming interactions with a cation. One can suppose that these interactions are conformed to cation-anion interactions.

Table S4. Temperature evolution of the metal-oxygen distances and corresponding energies of cation-anion interactions in **1** and **2**.

	Temperature, K	Na(1)-O(2)	Na(1)-O(1)	Na(1)-O(4)	Na(1)-O(4)	Na(1)-O(3)	Na(1)-O(3)
distance, Å	100[x]	2.3693(8)	2.3703(8)	2.3894(8)	2.566(8)	2.4056(8)	2.4089(8)
	150	2.3713(9)	2.3735(9)	2.3932(9)	2.5817(9)	2.4083(9)	2.4145(9)
	200	2.3731(9)	2.3766(9)	2.3985(9)	2.5947(10)	2.4098(9)	2.4205(10)
	250	2.3749(9)	2.3815(10)	2.4032(9)	2.6112(10)	2.4126(9)	2.4276(10)
	300	2.3765(10)	2.3855(10)	2.4086(10)	2.6269(11)	2.4132(10)	2.4365(11)
energy, kcal/mol[a]	100[x]	4.506227	4.487903	4.153241	2.08623	3.890909	3.839744
	150	4.469662	4.429818	4.089999	1.966899	3.848991	3.75461
	200	4.437033	4.374337	4.00356	1.873781	3.825919	3.665699
	250	4.404667	4.2882	3.928592	1.762528	3.783259	3.563477
	300	4.376115	4.219271	3.844364	1.663403	3.774186	3.439757
	Difference[b]	0.130112	0.268632	0.308876	0.422826	0.116723	0.399987
	type[c]	strong	strong	strong	weak	strong	strong

	Temperature, K	K(1)-O(2)	K(1)-O(2)	K(1)-O(1)	K(1)-O(4)	K(1)-O(4)	K(1)-O(3)	K(1)-O(3)
distance, Å	100[x]	2.8878(9)	2.6806(8)	2.8086(8)	2.8649(8)	2.9163(9)	2.6773(8)	2.7357(9)
	150	2.898(10)	2.6805(9)	2.8135(9)	2.8705(9)	2.9250(9)	2.678(8)	2.7397(9)
	200	2.9111(10)	2.6823(9)	2.8182(9)	2.8757(9)	2.9376(10)	2.6796(9)	2.7462(10)
	250	2.9263(11)	2.6833(9)	2.8246(9)	2.8832(9)	2.9498(10)	2.6813(9)	2.7528(10)
	300	2.9396(11)	2.6844(9)	2.8294(10)	2.8889(10)	2.9623(10)	2.6836(9)	2.7601(10)
energy, kcal/mol[a]	100[x]	2.159258	4.267154	2.548301	2.125153	1.807772	4.315517	3.542367
	150	2.090715	4.268611	2.507984	2.087522	1.757516	4.305207	3.49533
	200	2.006201	4.242475	2.469976	2.05324	1.68974	4.281745	3.420365
	250	1.912854	4.228031	2.419244	2.00489	1.626869	4.256973	3.346067
	300	1.835118	4.212207	2.381953	1.968988	1.565131	4.223709	3.265967
	Difference[b]	0.32414	0.054947	0.166348	0.156165	0.242641	0.091808	0.2764
	type[c]	weak	strong	weak	weak	weak	strong	Strong

a – Energy of cation-anion interactions calculated at 100K as $E_{int} = -0.5 \cdot v(r)$ ($v(r)$ – potential energy density at *bcp* estimated by Kirzhnitz model from high-resolution **XRD** data) and at other temperatures according to power fits approximating energy/distance relation (see manuscript); b – the difference between cation-anion interaction energy values at 100 and 300K; c - qualitative strength of a diatomic interaction (see also manuscript); x – distance at 100K are given from the refinement with 2θ<60° (MoKα radiation).

Table S5. Temperature evolution of **ADP** measured by **XRD** for **1** and **2**: anisotropic parameters for non-hydrogen atoms (λ_i – eigenvalues of mean-square harmonic displacement matrix, $U_{eq} = 1/3\ \Sigma\ \lambda_i$) and isotropic parameter U_{iso} for the H(1).

	Salt 1					**Salt 2**				

C(1)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.00812	0.01038	0.013	0.01563	0.01852	0.00943	0.01167	0.01404	0.01704	0.01973
λ_1, Å^2	0.0108	0.0133	0.017	0.0203	0.0244	0.0117	0.0141	0.0174	0.0212	0.0251
λ_2, Å^2	0.0073	0.0102	0.0124	0.016	0.0187	0.0095	0.0124	0.0157	0.0189	0.0219
λ_3, Å^2	0.0062	0.0077	0.0097	0.0106	0.0124	0.0071	0.0085	0.009	0.011	0.0122

C(2)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.00867	0.01132	0.0139	0.01692	0.01972	0.01008	0.01276	0.01554	0.01862	0.02197
λ_1, Å^2	0.0102	0.0136	0.0171	0.0209	0.025	0.0125	0.0172	0.0215	0.0268	0.0324
λ_2, Å^2	0.0098	0.0126	0.0157	0.0195	0.0222	0.0114	0.0134	0.0163	0.0189	0.0225
λ_3, Å^2	0.006	0.0077	0.0089	0.0103	0.012	0.0063	0.0077	0.0088	0.0102	0.0111

C(3)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.00878	0.01094	0.01389	0.01641	0.0197	0.00992	0.01211	0.01487	0.01781	0.02102
λ_1, Å^2	0.0115	0.0148	0.0188	0.0229	0.0281	0.012	0.0155	0.0196	0.0239	0.0296
λ_2, Å^2	0.0088	0.0109	0.0141	0.0164	0.0193	0.0118	0.0139	0.0166	0.0196	0.0221
λ_3, Å^2	0.0061	0.007	0.0088	0.01	0.0118	0.006	0.007	0.0084	0.01	0.0114

C(4)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.00797	0.01031	0.01258	0.01516	0.01792	0.009	0.01125	0.01354	0.01618	0.01888
λ_1, Å^2	0.01	0.0134	0.0155	0.0183	0.0221	0.0115	0.0147	0.0176	0.0207	0.024
λ_2, Å^2	0.0078	0.0103	0.0129	0.0166	0.0202	0.0086	0.0113	0.014	0.0171	0.0206
λ_3, Å^2	0.0061	0.0073	0.0093	0.0106	0.0115	0.0069	0.0078	0.009	0.0108	0.012

Na(1) / **K(1)**

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.01006	0.01338	0.01698	0.02093	0.02526	0.01067	0.01399	0.01773	0.02184	0.02608
λ_1, Å^2	0.0135	0.0184	0.0237	0.0298	0.0368	0.0145	0.0194	0.0251	0.031	0.0377
λ_2, Å^2	0.0094	0.012	0.0154	0.0184	0.0222	0.0099	0.0132	0.0167	0.0209	0.0249
λ_3, Å^2	0.0073	0.0098	0.0119	0.0146	0.0168	0.0076	0.0094	0.0114	0.0136	0.0157

O(1)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.01079	0.01424	0.01821	0.0222	0.02646	0.0112	0.01435	0.01787	0.02184	0.02586
λ_1, Å^2	0.0179	0.0238	0.0308	0.0385	0.0466	0.0177	0.0237	0.0304	0.0371	0.0445
λ_2, Å^2	0.0093	0.0121	0.0152	0.0189	0.0216	0.0095	0.0117	0.0143	0.018	0.021
λ_3, Å^2	0.0052	0.0069	0.0086	0.0092	0.0112	0.0064	0.0077	0.0089	0.0104	0.012

O(2)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.01105	0.01455	0.01826	0.02214	0.02648	0.01327	0.01738	0.02169	0.02661	0.03192
λ_1, Å^2	0.0161	0.0221	0.0289	0.0353	0.0431	0.0205	0.0279	0.0366	0.0456	0.0556
λ_2, Å^2	0.0093	0.0119	0.0149	0.0182	0.0211	0.011	0.0142	0.0172	0.0209	0.0248
λ_3, Å^2	0.0078	0.0097	0.011	0.0129	0.0152	0.0083	0.0101	0.0112	0.0133	0.0153

O(3)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.0111	0.01443	0.01845	0.02269	0.0269	0.01178	0.01505	0.01905	0.02298	0.02727
λ_1, Å^2	0.0165	0.0223	0.029	0.0364	0.0436	0.0162	0.0218	0.0288	0.0351	0.0421
λ_2, Å^2	0.0099	0.012	0.0156	0.0187	0.0225	0.0112	0.0141	0.0171	0.021	0.0248
λ_3, Å^2	0.007	0.009	0.0108	0.013	0.0146	0.0079	0.0092	0.0113	0.0128	0.0149

O(4)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{eq}, Å^2	0.00974	0.01276	0.01604	0.01962	0.02373	0.01076	0.01377	0.01715	0.02089	0.02446
λ_1, Å^2	0.0142	0.0187	0.0245	0.0305	0.0382	0.0164	0.0209	0.0272	0.0328	0.0396
λ_2, Å^2	0.0093	0.0125	0.0152	0.0186	0.0216	0.01	0.0127	0.0154	0.0192	0.0216
λ_3, Å^2	0.0057	0.0071	0.0084	0.0097	0.0114	0.0059	0.0077	0.0089	0.0107	0.0122

H(1)

Temperature, K	100	150	200	250	300	100	150	200	250	300
U_{iso}, Å^2	0.03753	0.04863	0.05102	0.05367	0.06441	0.08347	0.08865	0.08926	0.10121	0.10508
st.un.[a]	0.00473	0.0059	0.00574	0.00591	0.00668	0.00936	0.00965	0.00908	0.00898	0.00942

a – standard uncertainty of the H(1) atom U_{iso} value derived by least-squares technique. Note that the uncertainty on U_{eq} values of non-hydrogen atoms were less than 0.001 Å^2.

Table S6. Distance and estimated energy of cation-anion interactions for two examples from Cambridge Structural Database.

CARVAS

	Na-O(2)	Na-O(1)	Na-O(4)	Na-O(3)	$E_{O(4)}/E_{O(1)}$[b]	E_{COO}/E_{COOH}[b]
distance, Å	2.508	2.326	2.369 2.736	2.474 2.462		
energy, kcal/mole[a]	2.601583	5.384693	4.51174 1.122926	2.968089 3.110763	0.249974	3.727242

KHDFRM05

	K-O(2)	K-O(1)	K-O(4)	K-O(3)	$E_{O(4)}/E_{O(1)}$	E_{COO}/E_{COOH}
distance, Å	2.884 2.805 2.752		2.785	3.019 2.794 2.849 2.926		
energy, kcal/mole[a]	2.185427 2.817703 3.354977		3.008342	1.438021 2.920839 2.443722 1.914649	3.008342	3.367467

a – energy of cation-anion interactions estimated according to power fits approximating energy/distance relation (see manuscript); b – energy difference between total cation-anion energy calculated for the O(1) and O(4) atoms ($E_{O(4)}/E_{O(1)}$) and between two carboxylate groups (E_{COO}/E_{COOH}), atoms are labeled according to **1** and **2**: the O(1) atom participates in the SSHB and formally is proton donor, the O(4) atom is proton acceptor, the O(2) atom is the H-bond-free atom of the proton donating carboxylate group, the O(3) atom is the H-bond-free atom of the proton accepting carboxylate group.
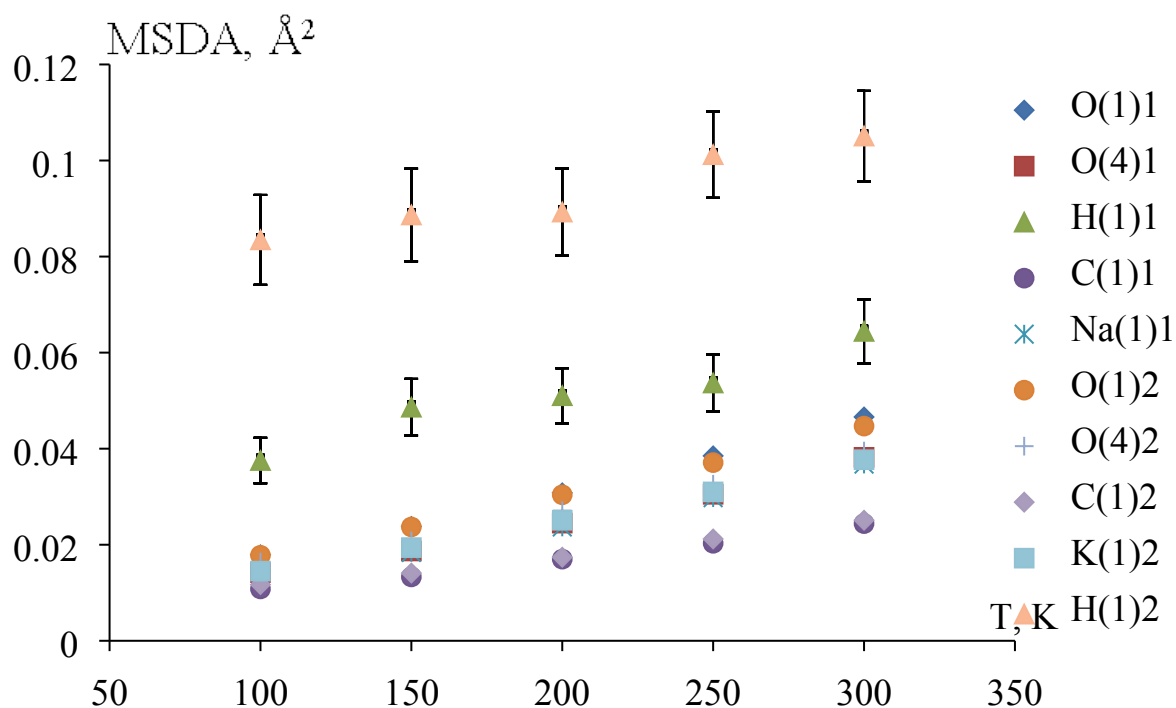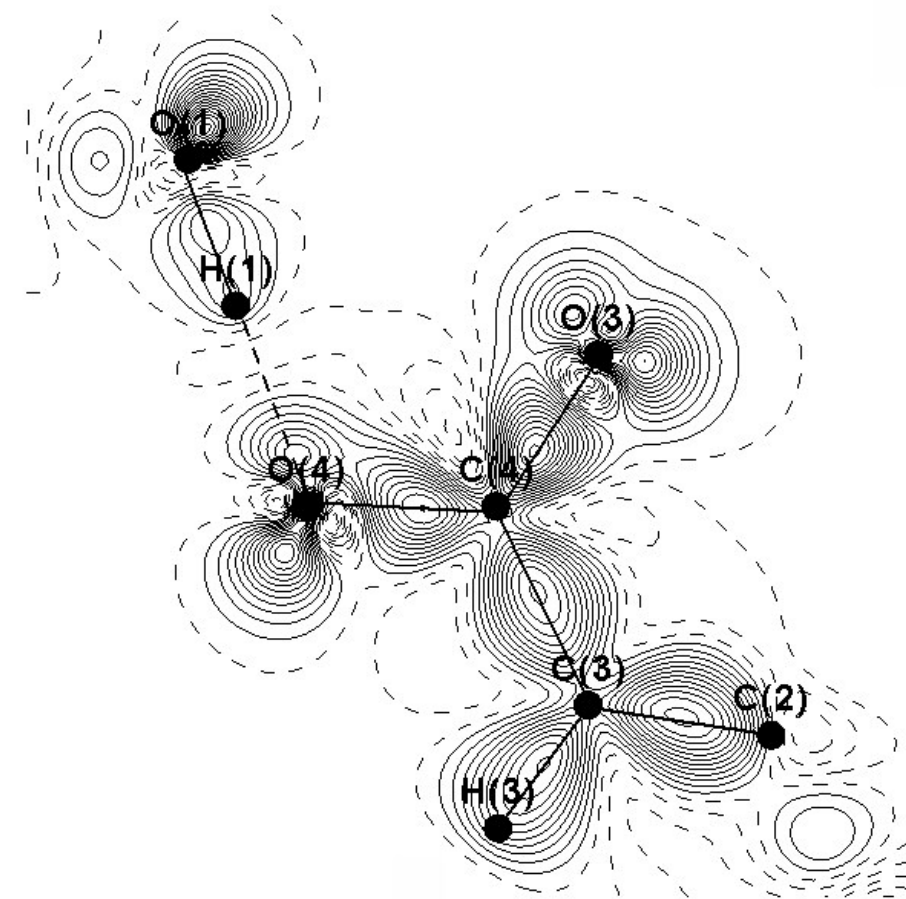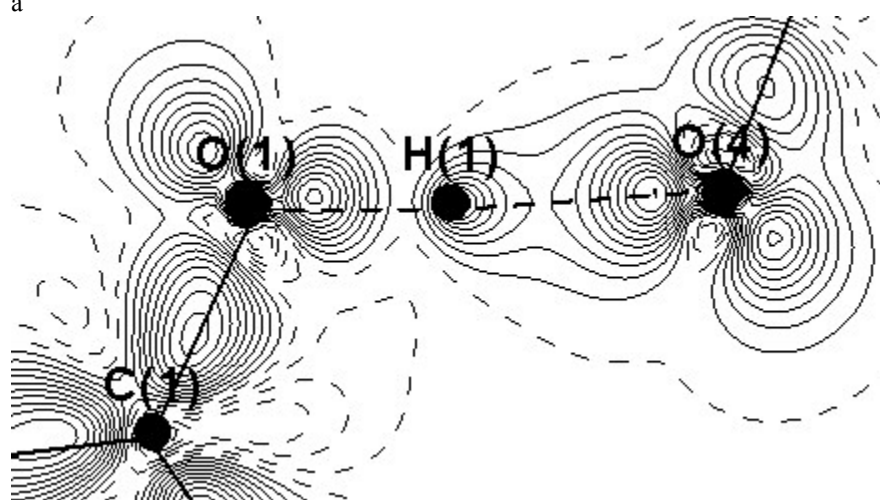
a
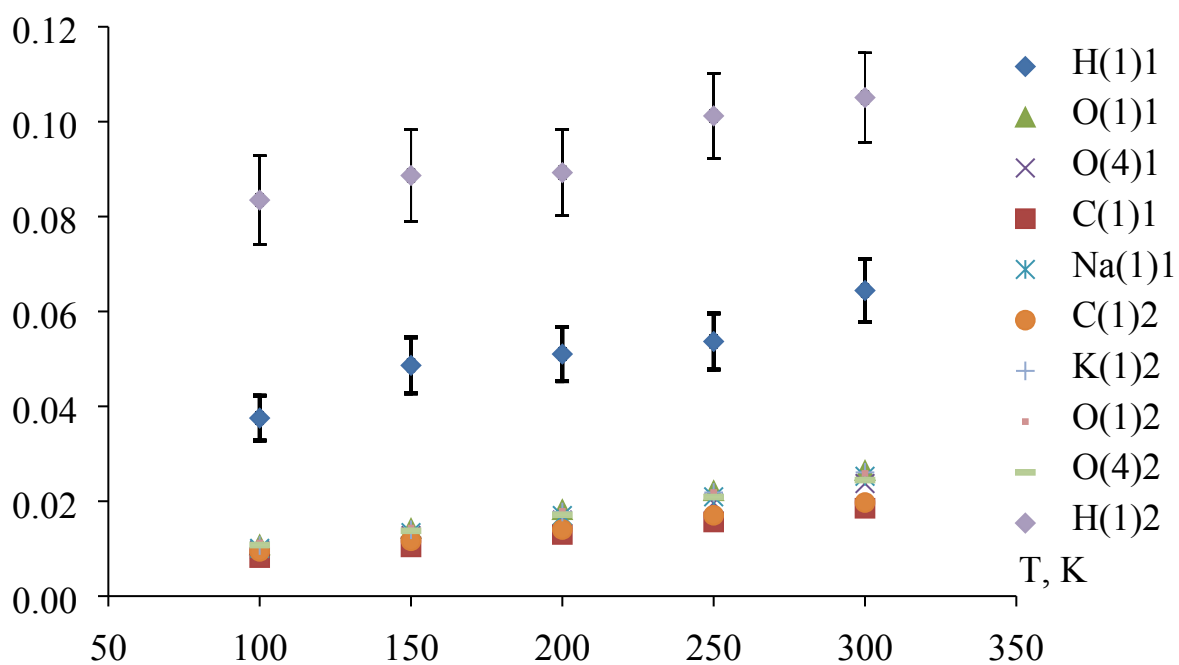
b

Fig. S1. Temperature dependence of mean-square displacement parameters λ_1 (non-hydrogen atoms) and U_{iso} (the H(1) atom) for both **1** and **2** (a); temperature dependence of mean-square displacement parameters U_{eq} (non-hydrogen atoms) and U_{iso} (the H(1) atom) for both **1** and **2** (b). The digit on the right of closing bracket in the series caption denotes corresponding salt.

a

b

Fig. S2. Deformation density distribution in the area of the SSHB in **1** (a) and **2** (b). Negative an zero values are dashed, solid lines correspond to positive values (0.05 step from -1 up to 1).

Appendix A1.

Power functions fitting E/d relation and presented in the manuscript are not so reasonable from the statistic point of view. The Box-Cox transformation gives for K:

$$E_K^{-0.5} = -2 + 0.94d, R^2 = 0.998$$

and for Na:

$$E_{Na}^{-0.5} = -2.23 + 1.14d, R^2 = 0.998.$$

In other words,

$$E_K = \frac{1.13}{(d - 2.13)^2}; \quad E_{Na} = \frac{0.77}{(d - 1.96)^2}. \quad (*)$$

Corresponding calculation however gives energy values being nearly the same with the power fits. Furthermore, the equations (*) do not satisfy physical meaning at boundary conditions while the power fits do: at d = 0 E → + ∞, while at d →+ ∞ E → 0.

Although the power functions given in the manuscript (E_{int} = 18670$d^{-9.656}$ and E_{int} = 35321$d^{-9.149}$) fit the E/d relation quite well, they should be used with caution since the standard error for a and x (E~$a*d^x$) are more than 2000 and 0.13 respectively (for corresponding R^2 values 0.9911 and 0.9954).