Computational and analytical approaches for investigating hydrates: The neat and hydrated solid state forms of 3-(3methylimidazolium-1-yl)propanoate

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Electronic Supplementary Information

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1. Synthesis of 1-(2-carboxyethyl)-3-methylimidazolium chloride ([HOOCEMIM] [Cl]) and 3-(3methylimidazolium-1-yl)propanoate (OOCEMIM)

Reagents and solvents were purchased from commercial sources and used without further purification. 1-(2-carboxyethyl)-3-methylimidazolium chloride (**[HOOCEMIM] [CI]**) and its zwitterion 3-(3-methylimidazolium-1-yl)propanoate (**OOCEMIM**) were prepared according to modified published procedures (Scheme S1).^{1,2} NMR spectra were recorded on a Bruker Avance DPX 300 spectrometer and analysed with the MestReNova software (version 9.0.1). IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument and analysed using the Bruker Opus software (version 7.2).



Scheme S1. Synthesis of [HOOCEMIM] [CI] and OOCEMIM.

1.1. Synthesis of 1-(2-carboxyethyl)-3-methylimidazolium chloride [936251-66-0]

To a solution of 1-methylimidazole (77 g, 0.94 mol) in toluene (300 mL), 3-chloropropionic acid (102 g, 1.0 equiv, 0.94 mmol) was added. The reaction mixture was stirred at 60 °C for two days under an argon atmosphere, whereupon two liquid phases formed gradually. After cooling to room temperature (rt), the supernatant was removed by decantation. The bottom phase was dissolved in methanol (100 mL) at 60 °C. After allowing the solution to cool to rt, diethyl ether (300 mL) was added under vigorous stirring, which again led to a biphasic mixture. Following decantation of the upper ethereal phase, the slightly yellow oil was washed twice with diethyl ether (300 mL each) and subsequently dried under reduced pressure at 50 °C, yielding 165 g (92 %) of crude **[HOOCEMIM] [CI]** as a hygroscopic solid. Single crystals were obtained by slow crystallisation of the crude oil over the duration of a few weeks at room temperature.

¹H NMR (300 MHz, DMSO-*d*₆): δ 2.93 (t, *J* = 6.6 Hz, 2H, CH₂), 3.87 (s, 3H, CH₃), 4.36 (t, *J* = 6.7 Hz, 2H, N-CH₂), 7.82 (t, *J* = 1.8 Hz, 1H, Im), 7.90 (t, *J* = 1.8 Hz, 1H, Im), 9.52 (s, 1H, Im), 12.40 (s, OH) ppm. – ¹³C NMR (75 MHz, DMSO-*d*₆): δ 34.1 (CH₂), 35.8 (CH₃), 44.8 (N-CH₂), 122.4 (Im), 123.5 (Im), 137.1 (Im), 171.5 (COOH) ppm. – FT-IR (ATR): *v* 3384 (br) (*v*OH), 3145, 3095, 3027 (*v*CH), 2795, 2585, 2512 (*v*OH), 1718 (*v*C=O), 1644, 1568 (*v*C=N, *v*C=C), 1447, 1408, 1358, 1335, 1316 (*v*CO, δ_i OH), 1227, 1207, 1192, 1171 (δ_i CH), 974, 919, 878, 861, 822, 763, 751 (δ_a CH) cm⁻¹.

1.2. Synthesis of 3-(3-methylimidazolium-1-yl)propanoate according to Ma et al.²

[HOOCEMIM] [CI] (165 g), as obtained above, was dissolved in methanol (200 mL) and subjected to ion exchange (Amberlite IRA-410, OH form, 1.5 kg) in methanol (1.5 L) by stirring the suspension of resin in the methanolic solution for 3 days at rt. Afterwards, the resin was removed by filtration and washed with methanol (2 x 400 mL). The filtrate and the washings were combined and the solvent was removed by means of a rotary evaporator. The resulting colourless oil was washed with ether (2 x 300 mL) in order to remove methylimidazole impurities (stemming from deprotonated imidazolium species from step 1) and residual methanol. Crystallisation was effected *via* mechanical agitation of the stirring bar during the purification step. The colourless crystalline product was filtered, washed again with diethyl ether (100 mL) and dried *in vacuo*, yielding 144 g (87 %) of **Hy2**. Single crystals of **Hy1** were obtained from a solution of the dihydrate (300 mg) in a mixture of DMSO (2 mL) and water (100 μl).

¹H NMR (300 MHz, DMSO- d_6): δ 2.32 (t, J = 6.4 Hz, 2H, CH₂), 3.83 (s, 3H, CH₃), 4.22 (t, J = 6.4 Hz, 2H, N-CH₂), 7.63 (t, J = 1.8 Hz, 1H, Im), 7.75 (t, J = 1.8 Hz, 1H, Im), 9.30 (s, 1H, Im) ppm. – ¹³C NMR (75 MHz, DMSO- d_6): δ 35.5 (CH₂), 38.6 (CH₃), 47.5 (N-CH₂), 122.5 (Im), 122.9 (Im), 137.0 (Im), 170.7 (COO⁻) ppm. – FT-IR (ATR): v 3489, 3401, 3247, 3155, 3113, 3056 (water, vCH), 1570, 1560 (vC=C, vC=N, v_{as} COO⁻), 1393 (v_s COO⁻), 1298, 1277, 1256, 1179, 1166 (δ_i CH), 932, 890, 807, 766, 687, 644 (δ_a CH) cm⁻¹.

1.3. NMR and IR spectra of 1-(2-carboxyethyl)-3-methylimidazolium chloride and its zwitterion



Figure S1. ¹H NMR spectrum of [HOOCEMIM] [CI].



Figure S2. ¹³C NMR spectrum of [HOOCEMIM] [CI].



Figure S3. IR spectrum of [HOOCEMIM] [CI].



Figure S4. ¹H NMR spectrum of OOCEMIM.



Figure S5. ¹³C NMR spectrum of OOCEMIM.



Figure S6. IR spectrum of OOCEMIM.

2. Single Crystal Structures

2.1. Crystallographic Data for OOCEMIM and [HOOCEMIM] [CI]

		114	112	
	АП	НУІ	нуг	
Crystal data				
Chemical formula	C ₇ H ₁₀ N ₂ O ₂	$C_7H_{10}N_2O_2\cdot H_2O$	$C_7H_{10}N_2O_2\cdot 2(H_2O)$	C ₇ H ₁₁ CIN ₂ O ₂
Mr	154.17	172.19	190.2	190.63
Crystal system,	Orthorhombic,	Monoclinic,	Triclinic,	Monoclinic,
space group	P212121	P21/C	<i>P</i> -1	C2/c
Temperature (K)	193	173	183	183
a, b, c (Å)	6.6643 (4),	7.7258 (7),	7.3825 (4),	20.1911 (9),
	8.7065 (5),	12.6758 (12),	8.4170 (4),	7 9146 (3)
	12.8000 (8)	8.8421 (9)	8.8371 (4)	22 5627 (11)
0 (0)			440.055 (4)	22.3027 (11)
α, β, γ (°)	90,	90,	113.255 (1),	90,
	90,	105.55 (1),	105.180 (1),	92.268 (2),
	90	90	95.990 (2)	90
V (Å ³)	742.69 (8)	834.22 (14)	473.36 (4)	3602.8 (3)
Ζ	4	4	2	16
Radiation type	Μο Κα	Μο Κα	Μο Κα	Μο Κα
μ (mm⁻¹)	0.10	0.11	0.11	0.39
Crystal size (mm)	0.22 × 0.21 × 0.18	0.39 × 0.38 × 0.06	0.18 × 0.16 × 0.12	0.18 × 0.16 × 0.12
Data collection				
Diffractometer	Bruker D8 QUEST	Xcalibur, Ruby,	Bruker D8 QUEST	Bruker D8 QUEST
	PHOTON 100	Gemini ultra	PHOTON 100	PHOTON 100
Absorption	Multi-scan	Multi-scan	-	Multi-scan
correction				
T _{min} , T _{max}	0.889, 0.942	0.880, 1.000		0.885, 0.928
No. of measured,	20701,	4951,	13851,	52787,
independent and	1534,	1521,	1801,	3347,
observed [/ >	1492	1286	1662	3106
$2\sigma(I)$] reflections				
Rint	0.029	0.028	0.031	0.030
(sin θ/λ) _{max} (Å ⁻¹)	0.628	0.602	0.611	0.606
Refinement				
$R[F^2 > 2\sigma(F^2)],$	0.027,	0.034,	0.034,	0.027,
wR(F ²),	0.071,	0.086,	0.094,	0.073,
S	1.09	1.05	1.07	1.03
No. of reflections	1534	1521	1801	3347
No. of parameters	102	119	136	228
No. of restraints	0	2	4	0
H-atom treatment	constrained	independent and	independent and	independent and
		constrained	constrained	constrained
$\Delta angle_{max}$, $\Delta angle_{min}$ (e Å ⁻³)	0.19, -0.16	0.18, -0.17	0.26, -0.2	0.24, -0.25
Absolute structure	0.1 (2)			
parameter				

Table S1. Experimental Details

Computer programs: Bruker Apex II, Bruker SAINT-V 8.34A, SHELXL2013 (Sheldrick, 2013³), ORTEP for Windows (Farrugia, 2012⁴), WinGX publication routines (Farrugia, 2012⁴), SHELXTL-XT-2014/4 and SHELXL2014/7 (Sheldrick, 2014³).

2.2. [HOOCMMIM] [CI]

Single crystals of **[HOOCEMIM] [CI]** were obtained according to section 1.1. Data collection was carried out, using *Mo* radiation, on a Bruker APEX-II CCD diffractometer controlled by the APEX2 software. Data integration and reduction were performed using the SAINT software.⁵ The Crystal structure was solved and refined with SHELXT and SHELXL,³ respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon atoms were generated by a riding model in idealised geometries and their positions refined with $U_{iso}(H) = 1.5 U_{eq}(C)$ for $-CH_3$ groups and $U_{iso}(H) = 1.2 U_{eq}(C)$ for other H atoms.

The salt crystallises in the monoclinic space group C2/c with Z'=2. The two crystallographically independent cations adopt a bent conformation differing in the orientation of the COOH function (Figure S7). The COOH function of each independent **HOOCEMIM** cation forms a strong hydrogen boning interaction with the chloride anion, $O-H\cdots$ Cl⁻ (Figure S8).



Figure S7. Overlay of the two [HOOCEMIM] cations present in the salt structure.



Figure S8. Hydrogen bonding interactions (O–H…Cl⁻) observed in [HOOCEMIM][Cl].



Figure S9. Packing diagram of [HOOCEMIM][CI] viewed along the *b* crystallographic axis.



2.3. Displacement ellipsoid plots

Figure S10. A view of the structure of **AH**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



Figure S11. A view of the structure of **Hy1**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



Figure S12. A view of the structure of **Hy2**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



Figure S13. A view of the structure of **[HOOCEMIM][CI]**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

3. CrystalExplorer Calculations

Interaction ^b	Symmetry	Distance	EF	Ep	ED	ER	<i>E</i> tot ^c
	operation	(Å)	(kJ mol⁻¹)	(kJ mol ^{−1})	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(kJ mol ⁻¹)
		AH: E	$_{tot}(cluster) = -$	-351.8 kJ mol ⁻¹	(1011101)	((
1 (2x)	-x v+1/2 -7+1/2	5.09	-116.7	-46 5	-30.4	46 7	-155 4
2(2x)	-x+1/2 - y + 1/2	7 28	-70 5	-25.8	-10	43.8	-75.4
3 (2x)	-x+1/2 -y $z+1/2$	7.20	-37.8	_19.9		20.1	-53.6
4 (2x)	x+1/2, y, z+1/2 = x+1/2	7.31	-8.6	-15.3	14_4	8	-28
$\frac{1}{5}(2x)$	X V 7	6 59	_9.9	_17.4	13.4	24.1	-20 1
6 (2x)	-x + 1/2 - 7 + 1/2	8 35	_13.7	_1.4	_1 3	0	-16.7
7 (2x)	-x, y+1/2, z+1/2	8 31	-6.1	-5.6	-2.8	0.8	-12.6
8 (2x)	x, y + 1/2, 2 + 1/2	6.01	10.1	-4.7	-22.0	13.9	_3 5
9 (2x)	× v z	87	14.5	-1.2		15.5	13.5
5 (2)	<i>λ, y, L</i>	Hv1·F	 (cluster) = -	-467.05 kl mol ⁻¹	_	0	15.5
1 (1x)	-X -V -7	5 57	_157 9	-50 1	-29.3	55.6	_195.2
$\frac{1}{2}(2x)$, y, z	6.76	_74.5	_15.8	_8.9	10.0	_92
$\frac{2(2x)}{3(1x)}$	-X -V -7	5.22	_35.3	_19.0	_32.3	10.0	-68
$\frac{3(1X)}{4(2x)}$	-x, -y, -z	0.00	-52.8	-12.4	-32.3	19.2	-63.2
5 (2x)	λ, y, 2	3.35	-52.8	-12.5	_4.0	62.9	-03.2
5 (2X) 6 (2x)	-	4.45 6.72	-64.5	-24.5	-0.7	20.5	-54.0
0 (2X)	-	0.72	-57.9	-17.5	-5.7	12.0	-52.0
7 (2X)	x, y, z	0.0	-31.5	-14.9	-0.4	13.8	-41.3
8 (2X)		4.61	-23.4	-7.3	-7.5	23.7	-22.0
9 (1X)	-x, -y, -z	6.04	11.1	-13.4	-33.3	15.2	-17.7
10 (2x)	<i>x</i> , - <i>y</i> +1/2, <i>z</i> +1/2	8.77	-9.2	-5.0	-1.7	0	-14.8
11 (2X)	-	6.2	-9.9	-4.2	-7.3	11.8	-12.7
12 (2x)	-	7.44	-2.6	-1.3	-2.6	0.9	-5.4
13 (2x)	-	4.27	1.2	-3.4	-4.1	5.0	-1./
14 (2x)	-	6.15	2.1	-0.4	-0.6	0	1.4
15 (2x)	x, -y+1/2, z+1/2	4.49	4.3	-0.2	-0.6	0.1	3.9
16 (2x)	-	5.17	7.3	-1.4	-4.0	1.8	4.3
17 (2x)	<i>x</i> , - <i>y</i> +1/2, <i>z</i> +1/2	6.05	33.2	-28.1	-15.5	16.0	10.7
18 (1x)	-x, -y, -z	12.32	30.3	-3.4	-3.4	1.0	27.2
		Hy2; E	_{tot} (cluster) = -	-529.45 kJ mol ⁻¹			
1 (1x)	-x, -y, -z	5.49	-191.1	-59.4	-21.0	62.9	-225.5
2 (1x)	-x, -y, -z	6.70	-99.1	-33.4	-15.5	16.6	-132.7
3 (1x)	-x, -y, -z	4.67	-40.5	-16.7	-33.3	16.0	-74.3
4 (2x)	x, y, z	9.86	-53.9	-14.7	-8.1	11.3	-68.0
5 (2x)	-	5.41	-76.9	-22.9	-5.3	67.0	-61.5
6 (1x)	-Χ, -Υ, -Ζ	7.24	-48.7	-3.1	-1.4	0	-55.1
7 (2x)	-	5.31	-57.4	-15.9	-3.9	37.0	-52.9
8 (2x)	-	6.52	-59.4	-19.0	-4.9	48.2	-51.4
9 (1x)	-x, -γ, -z	5.68	-8.5	-17.0	-32.3	16.2	-39.6
10 (2x)	-	2.76	-47.2	-9.6	-3.9	50.2	-29.4
11 (2x)	-	5.06	-21.6	-4.5	-5.5	7.9	-25.9
12 (2x)	x, y, z	7.4	-8.4	-10.9	-7.7	2.3	-22.2
13 (2x)	-	6.05	-21.6	-5.1	-7.8	18.2	-22.1
14 (1x)	-x, -y, -z	8.41	-18.7	-1.5	-1.0	0	-21.7
15 (2x)	-	5.62	-17.9	-3.5	-4.7	8.7	-20.2
16 (2x)	-	4.69	-11.1	-1.9	-2.4	0.6	-14.8
17 (2x)	-	8.8	-9.6	-1	-0.3	0	-11.2
18 (2x)	x, y, z	10.03	-6.4	-2.1	-0.8	0	-9
19 (2x)	x, y, z	10.49	-6.8	-1.7	-0.6	0	-8.9
20 (2x)	-	8.21	-6.8	-0.7	-0.9	0.1	-8.4
21 (2x)	-	5.17	0.5	-2.1	-4.3	2.8	-3
22 (2x)	-	5.51	0.9	-1.5	-2.6	1	-1.9
23 (2x)	-	5.17	0.3	-0.1	-0.2	0	0.1

Table S2. Overview of selected pairwise energetic contributions^a for **OOCEMIM** solid-state forms. Interactions involving water are highlighted in grey.

	-		1	1				
Interaction [®]	Symmetry	Distance	Ε _E	E _P	E _D	E _R	E tot ^c	
	operation	(Å)	(kJ mol ^{−1})	(kJ mol⁻¹)	(kJ mol⁻¹)	(kJ mol⁻¹)	(kJ mol⁻¹)	
Hy2 (continued)								
24 (2x)	-	4.01	5.3	-3.7	-7.4	7.1	0.8	
25 (2x)	-	5.92	1.2	0	-0.1	0	1.2	
26 (2x)	-	7.91	4.2	-0.3	-0.4	0	3.9	
27 (2x)	-	3.41	10.4	-4.1	-8.3	6.6	4.9	
28 (2x)	-	6.24	6.2	-0.6	-0.6	0	5.6	
29 (2x)	-	6.95	6	-0.3	-0.3	0	5.9	
30 (1x)	-x, -y, -z	9.19	11	-3.8	-2.3	0	6.9	
31 (1x)	-x, -y, -z	3.87	8.4	-0.9	-1.7	0.5	7.1	
32 (1x)	-х, -у, -z	3.84	8.4	-0.4	-0.5	0.1	8.2	
33 (2x)	-	7.15	11	-1.6	-2.5	1.1	9	
34 (2x)	-	7.51	11.6	-0.8	-0.3	0	11.4	
35 (2x)	x, y, z	9.41	20.6	-1	-0.6	0	20.5	
36 (1x)	-x, -y, -z	11.02	22.5	-2.3	-1.4	0	20.8	
37 (1x)	-x, -y, -z	11.81	28	-3	-2.9	0.6	25.2	
38 (2x)	x, y, z	8.94	30.6	-1.3	-0.7	0	30.8	
39 (1x)	-XVZ	11.34	55.9	-4.3	-0.9	0.1	55.2	

^aElectrostatic (E_E), polarisation (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. ^bListed interactions present either once (1x) or twice (2x). ^c $E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.⁶

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