Electronic Supplementary Material (ESI) for Chemical Communications

Overcoming the solvation shell during the crystallisation of Diatrizoic acid from DMSO

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Electronic supplementary information

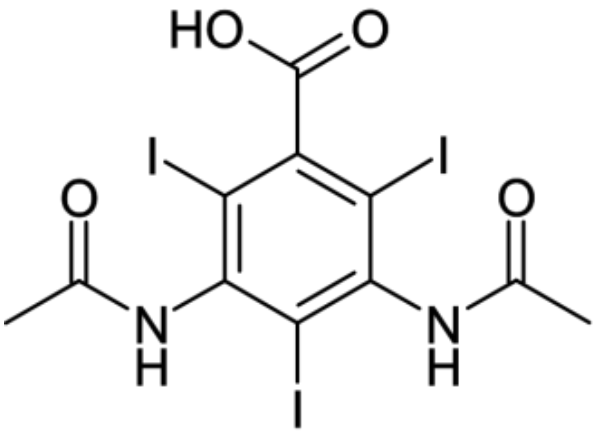

Figure S1 Molecular structure of diatrizoic acid.

Table S2 Distances, angles and energies of the hydrogen and halogen bonds found in the DMSO tetrasolvate crystal structure (energies calculated by PACHA[1]).

Hydrogen bond	Distance (D···A, Å)	Angle (D-H···A, °)	Energy (kJ mol^{-1})
O1-H1···O3S	2.567(5)	148(6)	-47.8
N1-H1A···O1S	2.876(5)	167.3(4)	-23.7
N2-H2···O2S	2.832(5)	170.0(4)	-29.0
I1···O1S (1-x, -y, 1-z)	2.930(3)		-8.3
I3···O4S	2.816(3)		-7.2

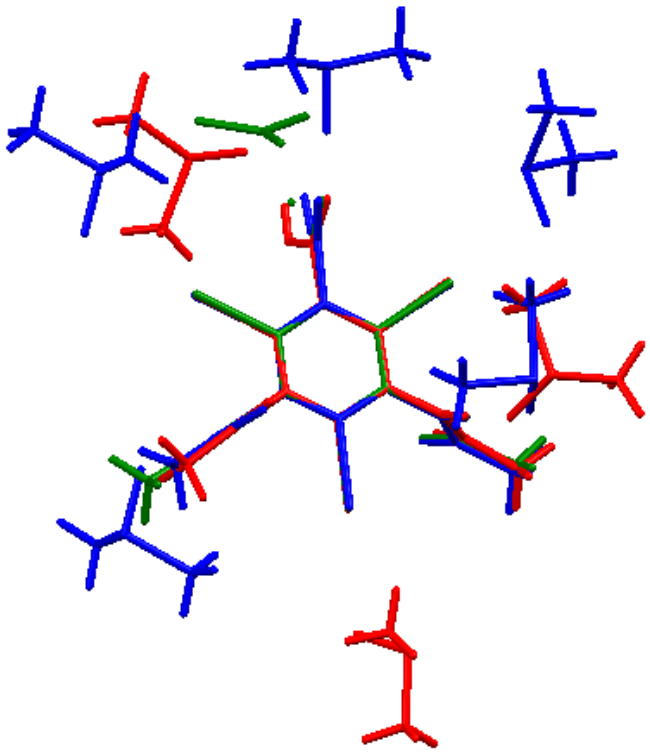

Figure S3 Molecular overlay of the DTA molecules in the three DMSO solvates with their first solvation shell: tetrasolvate – blue, disolvate – red, monosolvate - green

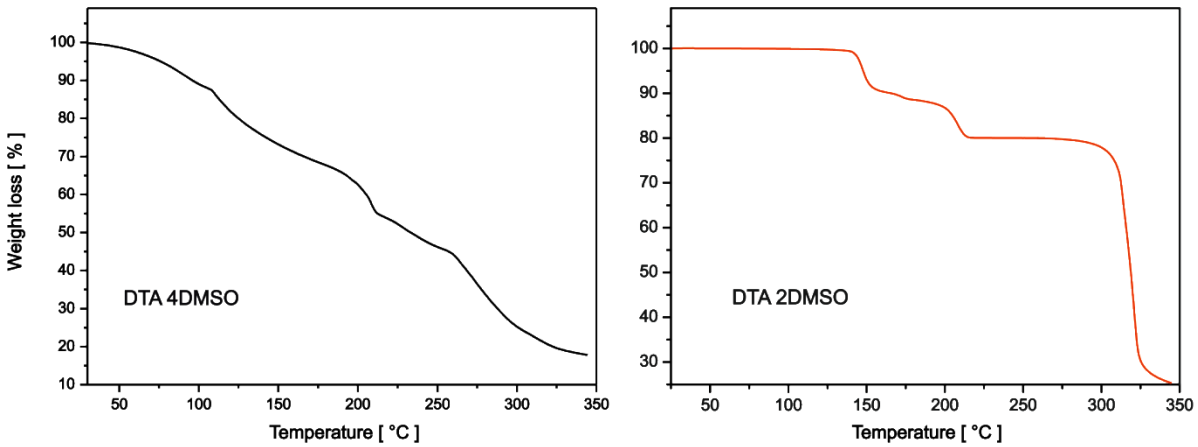

Figure S4 Thermogravimetric trace of the tetrasolvate and the disolvate of DTA. The initial sample of the tetrasolvate was slightly wet in order to start from the fully solvated crystal form. The calculated weight loss is 33.7% but the solvent release is accompanied by decomposition of the material, presumably starting above 200 °C. The trace of the disolvate shows a two-step mass loss adding up to 20.0% (calculated 20.2%), which is equally distributed between the two steps. It is possible that the disolvate desolvates to the monosolvate in the first step, which subsequently releases the remaining solvent.

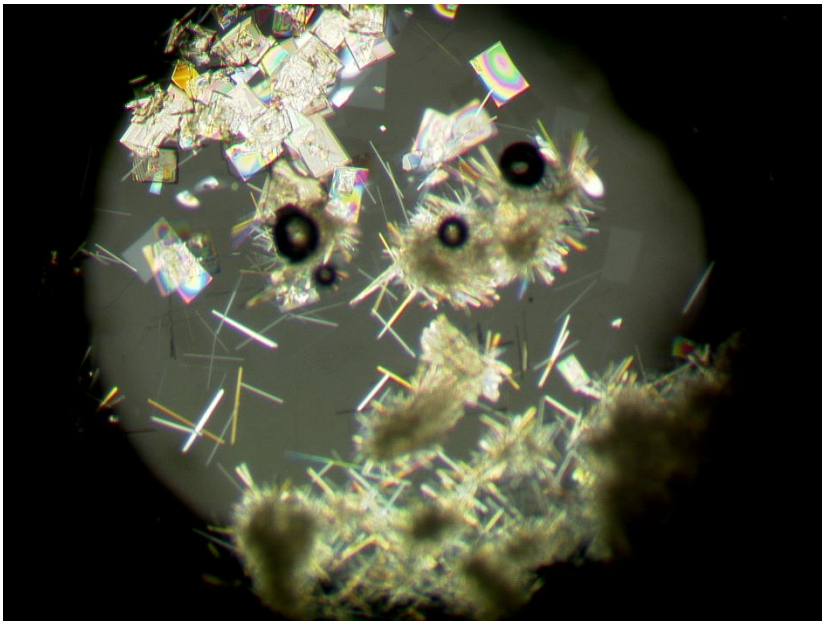

Figure S5 Photo micrograph of the DMSO tetrasolvate melt. Both the disolvate and the monosolvate nucleate in the melt; the disolvate as prismatic/needle shaped crystals to the bottom of the preparation, the monosolvate as plates at the upper end of the micrograph.

Table S6 Distances, angles and energies of the hydrogen and halogen bonds found in the DMSO disolvate crystal structure.

Hydrogen bond	Distance (D···A, Å)	Angle (D-H···A, °)	Energy (kJ mol^{-1})
O1-H1···O2S	2.514(15)	146(9)	-49.1
N1-H1A···O1S	2.846(17)	177.6(13)	-19.5
N2-H2···O4 (½-x, -½+y, z)	2.738(17)	155.1(13)	-38.3
I2···O1S (1-x, -½+y, ½-z)	2.901(11)		-3.4
I1···O2 (1-x, 1-y, 1-z)	3.177(10)		-2.4

Table S7 Distances, angles and energies of the hydrogen and halogen bonds found in the DMSO monosolvate crystal structure.

Hydrogen bond	Distance (D···A, Å)	Angle (D-H···A, °)	Energy (kJ mol^{-1})
O1-H1···O1S	2.531(8)	179(11)*	-47.2
N1-H1N···O3 (3/2-x, 1-y, -½+z)	2.790(5)	173.3(5)	-37.3
I2···O2 (½+x, ½-y, ½-z)	3.098(6)		-3.0

* The O1-H1···O1S hydrogen bond angle has a large s.u. value because of the high mobility of the solvent molecule in the crystal structure.

Experimental

Single crystal diffraction

Single crystals of suitable size were prepared in perfluoropolyether oil on MiTeGen sample holders. Crystallographic measurements were carried out at 120 K using a Bruker SMART CCD 6000 single crystal diffractometer equipped with an open flow N_2 Cryostream (Oxford cryosystems) device using a graphite monochromated MoKα radiation (λ = 0.71073 Å). For data reduction, the SAINT suite was used, the structures were solved with SHELXS[2] and refined with olex refine using the Olex2 interface.[3] All non-hydrogen atoms were treated anisotropically, the hydrogen atoms added in calculated positions and refined isotropically as riding models.

Thermomicroscopy

Hot-stage microscopic investigations were performed on an Olympus BX51 microscope (Olympus, Southend-on-Sea, UK) equipped with a Linkam THMS600 hot-stage operated with a TMS94 controller (Linkam Scientific Instruments Ltd., Tadworth, UK). Photomicrographs were taken with a JVC KY-F75U digital camera with 4.3 Megapixel resolution operated with the KY-LINK 2.0 software (JVC, London, UK).

Thermogravimetry

Thermogravimetric analysis was run on a Perkin Elmer Pyris 1 TGA purged with CP grade helium at a rate of 50 ml min^{-1}. The temperature was programmed to rise from room temperature (30 °C) to 350 °C at a heating rate of 10 °C min^{-1}.

1. M. Henry, *ChemPhysChem*, 2002, **3**, 561-569.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112-122.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.