Electronic Supplementary Information

Can a small amount of crystal solvent be overlooked or have no structural effect? Isomorphous non-stoichiometric hydrates (*pseudo*-polymorphs): Salicylaldehyde thiosemicarbazone with *no* to 0.20 H_2O

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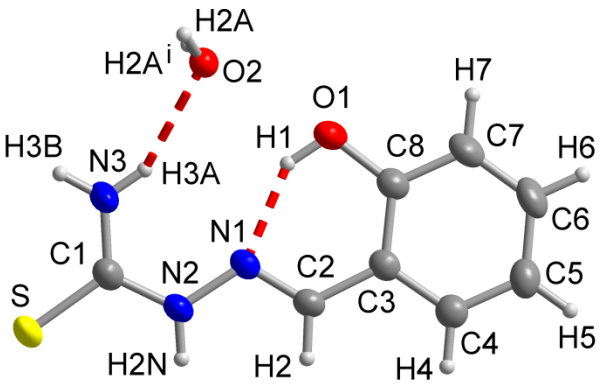

Figure S1 Compound **1**·0.17H_2O (50% thermal ellipsoids) with the identical atom numbering scheme to GEXKID01. This figure is displayed here again for correspondence with Table S1

Table S1 Selected bond distances (Å) and angles (°) in **1**·*x*H_2O

Refcode	GEXKID [a]	GEXKID01	**1**·0.095H_2O	**1**·0.17H_2O	**1**·0.20H_2O
S–C1	1.689(4)	1.690(4)	1.6896(19)	1.6961(15)	1.6931(19)
O1–C8	1.356(3)	1.3584(8)	1.357(2)	1.3580(19)	1.356(3)
N1–C2	1.276(3)	1.2928(6)	1.282(2)	1.2825(19)	1.281(2)
N1–N2	1.380(4)	1.3688(5)	1.382(2)	1.3757(17)	1.378(2)
N2–C1	1.346(4)	1.3489(6)	1.344(2)	1.344(2)	1.340(3)
N3–C1	1.317(4)	1.3326(8)	1.319(3)	1.321(2)	1.317(3)
C2–N1–N2	116.2(2)	115.92(4)	115.87(15)	115.67(12)	115.81(15)
C1–N2–N1	120.9(2)	120.88(6)	121.00(16)	121.26(12)	121.35(16)
N3–C1–N2	118.6(2)	118.57(6)	118.49(17)	118.81(14)	118.65(18)
N3–C1–S	122.2(2)	122.46(6)	122.52(16)	122.29(12)	122.35(16)
N2–C1–S	119.2(2)	118.96(6)	118.98(15)	118.90(11)	118.99(15)
N1–C2–C3	122.6(3)	121.94(6)	122.18(16)	122.23(13)	122.37(16)

[a] The different atomic numbering scheme in the publication of GEXKID has been adjusted accordingly.

Table S2 Results of structure refinement with and without crystal water for **1** $x$$H_2O$.

Highlighted in yellow are the refinement parameters which provide the clearest indication of missed electron density.

Compound	**1**·0.095H_2O	without 0.095 H_2O	**1**·0.17H_2O	without 0.17 H_2O	**1**·0.20H_2O	without 0.20 H_2O
Empirical formula	$C_8H_{9.19}N_3O_{1.10}S$	$C_8H_9N_3OS$	$C_8H_{9.34}N_3O_{1.17}S$	$C_8H_9N_3OS$	$C_8H_{9.40}N_3O_{1.20}S$	$C_8H_9N_3OS$
M/g mol^{-1}	196.95	195.24	198.31	195.24	198.89	195.24
Crystal size/mm	0.31 x 0.11 x 0.04		0.45 x 0.35 x 0.30		0.43 x 0.10 x 0.08	
2 θ range/°	4.32 – 53.2		4.34 – 53.2		4.32 – 53.2	
completeness to 2θ/%	99.8		99.8		99.9	
h; k; l range	±17; –16,17; ±13		±17; ±17; ±13		±17; ±18; ±13	
Temperature/K	203(2)		100(2)		203(2)	
Crystal system	monoclinic		monoclinic		monoclinic	
Space group	C 2/c		C 2/c		C 2/c	
a/Å	13.9737(4)		13.7595(6)		13.8383(16)	
b/Å	14.2331(4)		14.2594(6)		14.3405(17)	
c/Å	10.4655(2)		10.4876(4)		10.5113(12)	
β/°	115.781(2)		115.3670(10)		114.986(4)	
V/Å^3	1874.29(8)		1859.29(13)		1890.7(4)	
Z	8		8		8	
D_{calc}/g cm^{-3}	1.396		1.417		1.397	
F (000)	824		830		832	
μ /mm^{-1}	0.309		0.313		0.308	
Max/min transmiss.	0.9884/0.9089		0.9120/0.8721		0.9755/0.8795	
Refl. collected (R_{int})	10068 (0.0372)	10058	9341 (0.0179)	9335	13981 (0.0393)	13964
Indep. reflections	1968	1965	1952	1951	1991	1989
Obs. refl. [$I > 2\sigma(I)$]	1495	1492	1762	1761	1617	1615
Parameters refined	139	130	139	130	139	130
Max./min. $\Delta\rho$ /e Å^{-3} [a]	0.320/–0.457	1.950/–0.504	0.388/–0.428	4.454/–0.458	0.479/–0.452	4.296/–0.428
R_1/wR_2 [$I > 2\sigma(I)$] [b]	0.0391/0.0932	0.0579/0.1671	0.0341/0.0857	0.0852/0.2407	0.0434/0.1109	0.0989/0.2954
R_1/wR_2 (all reflect.) [b]	0.0568/0.1028	0.0755/0.1826	0.0385/0.0888	0.0903/0.2466	0.0556/0.1198	0.1123/0.3132
Goodness-of-fit on F^2 [c]	1.058	1.087	1.066	1.077	1.039	1.103
Weight. scheme w; a/b [d]	0.0416/1.4139	0.1011/2.0469	0.0389/1.6872	0.1474/7.3901	0.0521/2.0580	0.1985/5.7392

Parameters which are not given are identical to the crystal-water containing refinement. [a] Largest difference peak and hole. – [b] $R_1 = [\Sigma(\|F_o\| - |F_c|)/\Sigma|F_o|]$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. – [c] Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$. – [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0)+2F_c^2)/3$.

Powder X-ray diffraction patterns were measured at ambient temperature using a STOE STADI-P with Debye-Scherrer geometry, Mo-Kα radiation (λ = 0.7093 Å), a Ge(111) monochromator and the samples in glass capillaries on a rotating probe head. Simulated powder patterns were based on single-crystal data and calculated using the STOE WinXPOW software package.[1]

It was difficult to fill the 0.3 mm capillary with the wet sample.

Some drying and mechanical grinding were unavoidable which affected the crystallinity and probably also the microstructure.

(1) STOE WinXPOW Version 1.10; STOE& Cie GmbH, Darmstadt, Germany, 2002.

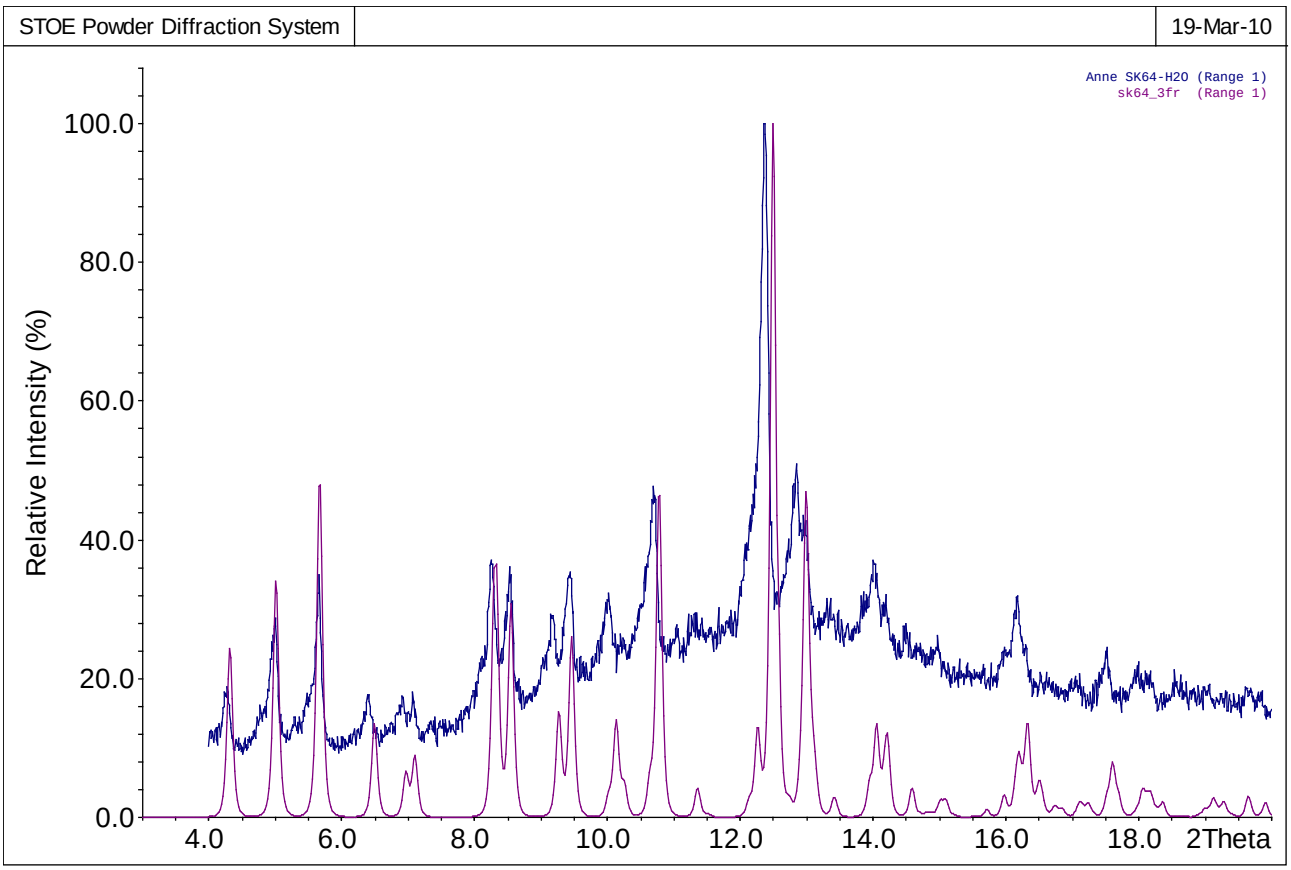

Fig. S2 X-ray powder diffractogram. The lower purple curve is simulated from single-crystal X-ray data of **1**·0.20H_2O. The upper blue curve is measured on a crystal sample of **1**·0.20H_2O.

Analytical information and data

IR spectra were recorded in KBr disks with a Matson 1000 FT-IR spectrophotometer in the range of 4000-450 cm^{-1}. ^1H NMR spectra were obtained on a Bruker spectrometer at 250 MHz in [D_6]DMSO.

Crystals of samples **1**·0.095H_2O and **1**·0.17H_2O were filtered off, washed with methanol and air dried (yield 0.165 g, 51% based on 2-hydroxybenzaldehyde).

Crystals of sample **1**·0.20H_2O were filtered off, washed with water and air dried (yield 0.21 g, 65% based on 2-hydroxybenzaldehyde).

All samples gave identical analytical data when dried: M.p. 227 °C. IR (KBr): 3446 (s, OH), 3315 (s, NH), 3177 (s, NH), 3031 (m), 2992 (m), 1615 (vs, C=N), 1538 (vs, C=S) 1492 (m), 1469 (m), 1369 (m), 1285 (vs), 1208 (m), 1154 (w), 1115 (w), 838 (m), 761 (m), 708 (w), 631 (m), 477 (w) cm^{-1}. – UV/Vis (in EtOH, $c = 0.50 \times 10^{-3}$ mol/l, light yellow solution, λ_{max} [nm] with ε [$l \cdot mol^{-1} \cdot cm^{-1}$]): 226 (900), 305 (1532), 332 (1832). – ^1H NMR ([D_6]DMSO): δ = 11.35 (N*H*), 9.86 (O*H*), 8.34 (C*H*=N), 8.07 (NH_2), 7.89-6.75 (4 H; aryl hydrogens). The peaks at 11.35, 9.87 and 8.07 ppm disappeared upon adition of D_2O. – $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 178.08, 156.82, 140.07, 131.52, 127.19, 120.76, 119.70, 116.45. – $C_8H_9N_3OS$ (dried sample) (195.24) calc. C 49.21, H 4.65, N 21.52, S 16.42; found C 48.74, H 4.59, N 21.17, S 16.36%.