Can a small amount of crystal solvent be overlooked or have no structural effect? Isomorphous non-stoichiometric hydrates (pseudo-polymorphs): the case of salicylaldehyde thiosemicarbazone†

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Compound (*E*)-2-(2-hydroxybenzylidene)hydrazinecarbothioamide (salicylaldehyde thiosemicarbazone) (1) is discussed as an isomorphous non-stoichiometric hydrate, that is, while the relative amount of the water guest molecules varies all the crystal structures are "nearly the same" and all the molecular structures of 1 are "the same". Compound 1 can crystallize isomorphous with no and different non-stoichiometric small amounts of crystal water (0.095, 0.17 and 0.20H_2O per formula unit were found). Unit cell dimensions and the crystal packing of the molecules with their hydrogen bonding are virtually unaffected by the presence or absence of the crystal water.

Introduction

Polymorphism is a phenomenon wherein the same substance exhibits different crystal packing arrangements,[1–3] and is of practical importance in, *e.g.*, pharmaceutical processes where different physical properties of polymorphic forms can substantially alter the viability and quality of a product.[4] When different crystal types are the result of hydration or solvation, that is, there exist different solvates of a given compound, the phenomenon may be called pseudo-polymorphism (although this term is a matter of dispute[5]).[6,7]

As a subsection of pseudo-polymorphism, non-stoichiometric hydrates are vital issues ranging from natural gas hydrates,[8] solid-state metal oxides[9] to biological[10] and pharmaceutical compounds,[11] such as vitamin B1,[12] anaesthetics,[13] caffeine,[14] β-cyclodextrin,[15] indapamide[16] and emodepside[17] where they also relate to the stability to humidity. Yet, isomorphous hydrates appear to be rare.[10,12,17]

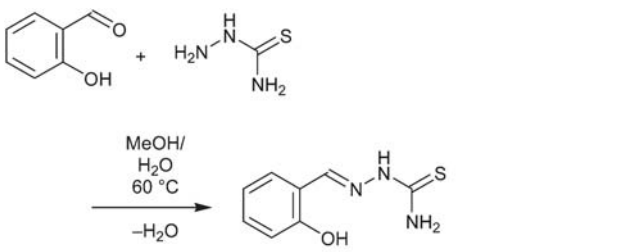
Compound salicylaldehyde thiosemicarbazone ((*E*)-2-(2-hydroxybenzylidene)hydrazinecarbothioamide) **1** (eqn (1) and Fig. 1) is discussed here as a case of a non-stoichiometric hydrate with apparently no effect of the crystal water guest molecule on the crystal packing.

Results and discussion

The structures of **1**·0.095H_2O, **1**·0.17H_2O and **1**·0.20H_2O are the pseudo-polymorphs of the salicylaldehyde thiosemicarbazone crystal structure of **1** (with no crystal water), reported earlier as a normal (Refcode GEXKID)[19] and a high-resolution (Refcode GEXKID01) X-ray structure.[18] Compound **1** crystallizes with 0.095H_2O, 0.17H_2O, 0.20H_2O and with no crystal water in the same space group with very similar lattice constants (Table 2 and Fig. 2). When taking into account the different temperatures for the datasets (100 K or 203 K), one can note a very slight increase in the length of the *c*- and *b*-axes and a decrease in the *a*-axis length with increasing water content (Fig. 2). This cell constant variation with water content is, however, in the same range as the variation with temperature.

The molecular structure of the salicylaldehyde thiosemicarbazone part **1** is identical in its configuration, bond distances and angles to the previous descriptions within experimental error (which should be taken as at least 3-times the standard deviation) (Table S1 in ESI†). While the identical molecular structure of **1** could have been expected, the packing of **1** and its hydrogen-bonding scheme (Table 1, Fig. 3 and 4) virtually does not show an effect on the presence or absence of crystal water. Usually, a molecular compound and its solvate have different crystal structures.

In the absence of crystal water, H-bonded layers are formed by **1** in GEXKID, including molecular pairs related by a center of symmetry



1
salicylaldehyde thiosemicarbazone,
(*E*)-1-(2-hydroxybenzylidene)thiosemicarbazide,
(*E*)-2-(2-hydroxybenzylidene)hydrazinecarbothioamide (1)

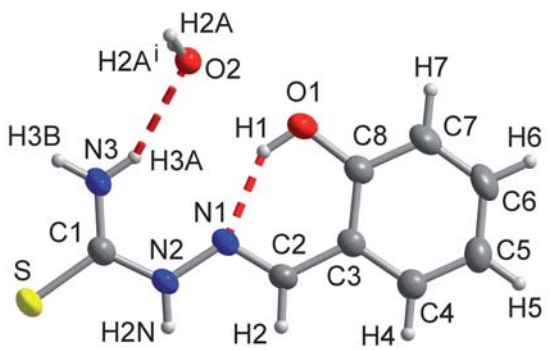


Fig. 1 Compound **1**·0.17H_2O (50% thermal ellipsoids) with the identical atom numbering scheme to GEXKID01.[18] Selected hydrogen bonds are shown as dashed lines; symmetry transformation $i = -x, y$ and $0.5 - z$.

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† Electronic supplementary information (ESI) available: Bond lengths and angles; comparison of structure refinement with and without crystal water for **1**·*x*H_2O; analytical data of **1**. CCDC reference numbers 692824, 771708 and 771709. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00041h

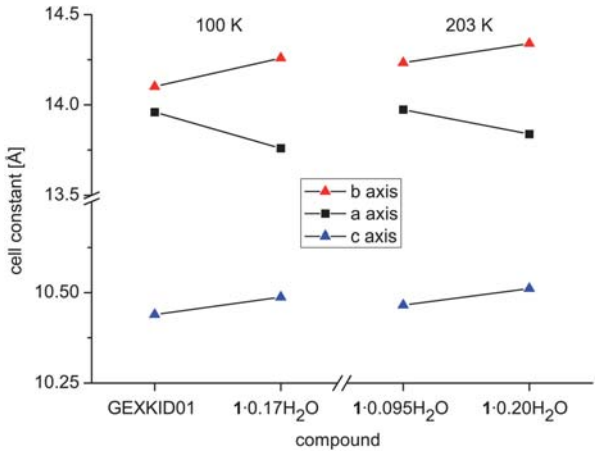

Fig. 2 Variation in cell constants with water content at the different temperatures (100 K and 203 K) of the crystallographic datasets of $\mathbf{1}\cdot x\mathrm{H_2O}$. Note the expanded ordinate scale.

with (amide)N2–H2N···S hydrogen bonds in $R_2^2(8)$ rings (Fig. 3, left) like the common head-to-tail carboxylic acid–acid graph-set motif.[20] The partly occupied crystal water molecules then join these 2D layers into a 3D hydrogen-bonded network (Fig. 3, right). The vector of the new (amine)N3–H3B···O2 hydrogen bond lies primarily along the *a*-axis (Fig. 3, right) which can explain the slight decrease in the length of the *a* cell constant (Fig. 2). Besides the noted hydrogen bonds (Table 2) there are no other supramolecular interactions, like π–π or C–H···π interactions. There are no reasonable π-stacking interactions of the phenyl rings in **1**. The centroid–centroid distances (>4.7 Å) together with large slip angle (β, $\gamma > 46°$) and slippages (>3.4 Å) exclude any meaningful phenyl π-stacking.[21–23]

The partly occupied water molecule in **1** forms hydrogen bonds to the sulfur atom as deduced from its found and refined H atom positions. This may be surprising at first in view of possible contacts from the water-O2 to the hydroxy-O1 (2.815(3) Å) and to the amine-N3 atoms (2.982(2) Å) which fall well into known O(–H)···O/N contacts. From the maximum negative electrostatic potential at the S atom of 1 (−59.617 au) it is, however, clear that the O1 atom (−22.403 au) and N3 (−18.456 au) are much weaker hydrogen-bond acceptors.[18] Besides, the vicinity of O2···N3 stems from the N3–H···O2 hydrogen bond.

The identical packing in the crystal structures of GEXKID and $\mathbf{1}\cdot 0.17\mathrm{H_2O}$ can even better be seen in their packing diagrams (Fig. 4). Noteworthy, the region of the crystal water in $\mathbf{1}\cdot 0.095\mathrm{H_2O}$, $\mathbf{1}\cdot 0.17\mathrm{H_2O}$ or $\mathbf{1}\cdot 0.20\mathrm{H_2O}$ is not calculated by PLATON as a solvent accessible void, neither in the two GEXKID structures nor in the solvent-depleted structures of **1** (Table 1).

How to interpret the structure of $\mathbf{1}\cdot 0.095\mathrm{H_2O}$, $\mathbf{1}\cdot 0.17\mathrm{H_2O}$ or $\mathbf{1}\cdot 0.20\mathrm{H_2O}$ in comparison to GEXKID? Could the small amount of crystal water have been overlooked in the structures of GEXKID. Probably not in this light-atom structure: intentional refinements of the datasets of $\mathbf{1}\cdot x\mathrm{H_2O}$ without the crystal water molecule led to a significant increase in the maximum electron density, in the R_1 and wR_2 values and in the weighting parameters (see Table S2 in ESI†). Especially the highest electron density peak of already 1.95 e Å^{-3} in the

Table 1 Hydrogen bonding distances (Å) and angles (°) in $\mathbf{1}\cdot x\mathrm{H_2O}$

>Hydrogen bond/Refcode[24]	GEXKID[19a,b]	GEXKID01[18b]	$\mathbf{1}\cdot 0.095\mathrm{H_2O}$	$\mathbf{1}\cdot 0.17\mathrm{H_2O}$	$\mathbf{1}\cdot 0.20\mathrm{H_2O}$
O1–H1	0.78(3)	0.93(10)	0.88(3)	0.89(2)	0.91(3)
H1···N1	1.97(3)	1.836(9)	1.87(3)	1.88(2)	1.86(3)
O1···N1	2.664(3)	2.6553(9)	2.6567(19)	2.6617(15)	2.665(2)
O1–H1···N1	149(3)	145.7(8)	148(2)	146.3(19)	147(3)
N2–H2N	0.89(3)	0.986(11)	0.90(2)	0.87(2)	0.86(3)
H2N···S^{ii}	2.56(3)	2.438(11)	2.53(2)	2.54(2)	2.56(3)
N2···S^{ii}	3.439(3)	3.413(3)	3.4199(18)	3.4061(14)	3.4102(18)
N2–H2N···S^{ii}	169(3)	170.0(8)	170.1(19)	169.9(17)	171(2)
N3–H3A	0.80(3)	1.004(10)	0.86(3)	0.85(2)	0.87(3)
H3A···O2	Not applicable	Not applicable	2.30(3)	2.25(2)	2.23(3)
N3···O2	No H_2O	No H_2O	3.033(3)	2.9815(17)	2.997(2)
N3–H3A···O2	—	—	144(2)	145(2)	148(3)
N3–H3B	0.93(3)	1.012(10)	0.86(3)	0.87(2)	0.85(3)
H3B···O1^{iii}	2.03(3)	1.914(10)	2.09(3)	2.09(3)	2.13(3)
N3···O1^{iii}	2.953(3)	2.9251(10)	2.954(2)	2.9549(18)	2.981(2)
N3–H3B···O1^{iii}	176(2)	177.2(10)	177(3)	176(2)	176(3)
O2–H2A	Not applicable	Not applicable	0.92(5)	0.86(7)	0.96(7)
H2A···S^{iv}	No H_2O	No H_2O	2.05(6)	2.11(7)	2.10(7)
O2···S^{iv}	—	—	2.931(5)	2.956(2)	3.014(3)
O2–H2A···S^{iv}	—	—	159(11)	168(5)	159(6)
Solvent accessible void (calc. by PLATON)[19]	No	No	No (Also no solvent accessible void in H_2O depleted structures)	No	No
Packing index (calc. by PLATON, "calc. void")[25,26]	70.7%	70.7%	67.4% (Because of solvent disorder only to be calculated on the solvent depleted structures of **1**)	68.0%	66.8%

[a] The different atomic numbering scheme in the publication of GEXKID has been adjusted accordingly. Symmetry transformations: *ii* = $-x+0.5, -y+0.5, -z$; *iii* = $x, 1-y, z-0.5$; *iv* = $-x, 1-y, -z$. [b] Hydrogen bonding interactions in GEXKID and GEXKID01 calculated by PLATON.[20]

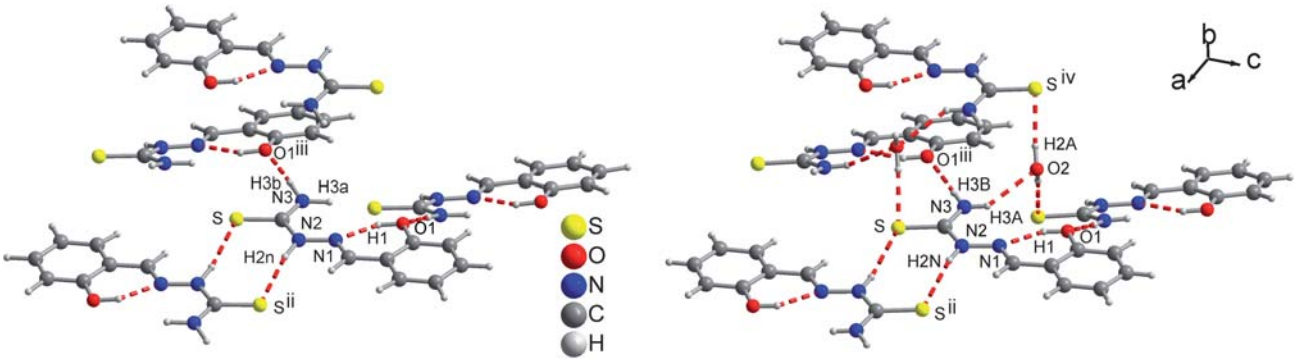

Fig. 3 Hydrogen-bonding scheme (red dashed lines) in GEXKID01 (left) and in **1**·0.17H_2O (right); see Table 1 for details.

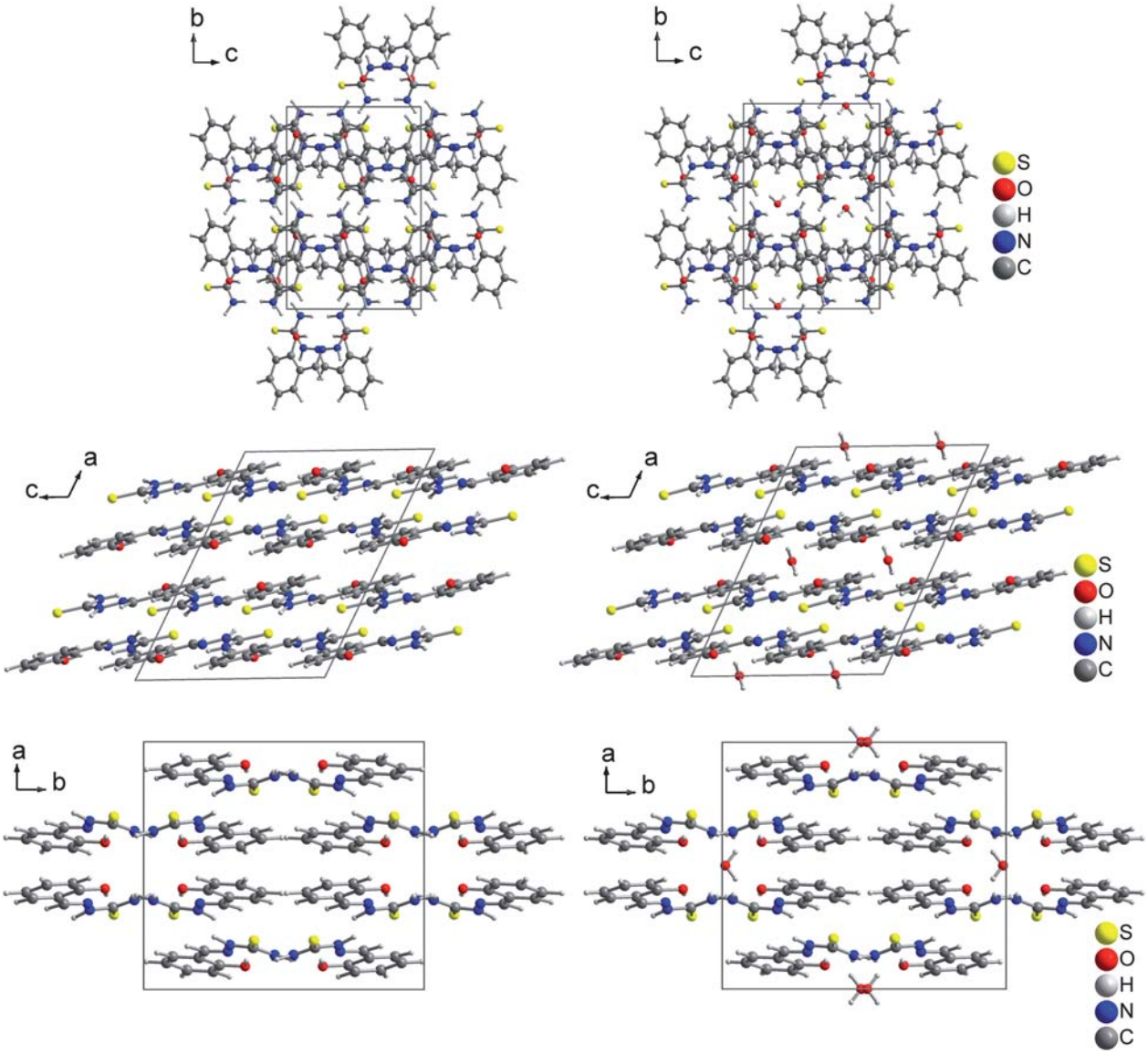

Fig. 4 Crystal packing of the molecules in GEXKID (left) and **1**·0.17H_2O (right) projected along the different crystal axes.

Table 2 Crystal data and structure refinement for $\mathbf{1}\cdot x\mathrm{H_2O}$

Compound	GEXKID[19]	GEXKID01[18e]	$\mathbf{1}\cdot 0.095\mathrm{H_2O}$	$\mathbf{1}\cdot 0.17\mathrm{H_2O}$	$\mathbf{1}\cdot 0.20\mathrm{H_2O}$
Empirical formula	$C_8H_9N_3OS$	$C_8H_9N_3OS$	$C_8H_{9.19}N_3O_{1.10}S$	$C_8H_{9.34}N_3O_{1.17}S$	$C_8H_{9.40}N_3O_{1.20}S$
M/g mol^{-1}	195.24	195.24	196.95	198.31	198.89
Crystal size/mm	0.30 × 0.28 × 0.22	0.36 × 0.33 × 0.30	0.31 × 0.11 × 0.04	0.45 × 0.35 × 0.30	0.43 × 0.10 × 0.08
2θ range/°	−55	4.36–102.68	4.32–53.2	4.34–53.2	4.32–53.2
Completeness to 2θ (%)	—	100	99.8	99.8	99.9
h; k; l range	−17, +15; 0, 18; 0, 13	−30, +23; 0, 30; 0, 22	±17; −16, 17; ±13	±17; ±17; ±13	±17; ±18; ±13
Temperature/K	298	100(2)	203(2)	100(2)	203(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a/Å	14.206(3)	13.9599(6)	13.9737(4)	13.7595(6)	13.8383(16)
b/Å	14.244(4)	14.1007(5)	14.2331(4)	14.2594(6)	14.3405(17)
c/Å	10.457(4)	10.4394(3)	10.4655(2)	10.4876(4)	10.5113(12)
β/°	116.18(2)	116.581(3)	115.781(2)	115.3670(10)	114.986(4)
V/Å^3	1898.9(8)	1837.73(12)	1874.29(8)	1859.29(13)	1890.7(4)
Z	8	8	8	8	8
D_{calc}/g cm^{-3}	1.366	1.411	1.396	1.417	1.397
F (000)	816	816	824	830	832
μ/mm^{-1}	0.290	0.314	0.309	0.313	0.308
Max/min transmiss.	0.941/0.899	Not given	0.9884/0.9089	0.9120/0.8721	0.9755/0.8795
Refl. collected (R_{int})	—	10 219 (0.0000)	10 068 (0.0372)	9341 (0.0179)	13981 (0.0393)
Indep. refl.	1924	10 219	1968	1952	1991
Obs. refl.	1322 [$I > 2.5\sigma(I)$]	5539 [$I > 3\sigma(I)$]	1495 [$I > 2\sigma(I)$]	1762 [$I > 2\sigma(I)$]	1617 [$I > 2\sigma(I)$]
Parameters refined	154	154	139	139	139
Max/min $\Delta\rho$/e Å^{-3}[a]	0.49/−0.23	Not given	0.320/−0.457	0.388/−0.428	0.479/−0.452
R_1/wR_2 [$I > 2\sigma(I)$][b]	0.0429/0.0453	0.0401/0.1157	0.0391/0.0932	0.0341/0.0857	0.0434/0.1109
R_1/wR_2 (all refl.)[b]	—	[$I > 3\sigma(I)$]	0.0568/0.1028	0.0385/0.0888	0.0556/0.1198
Goodness-of-fit on F^2[c]	—	1.062	1.058	1.066	1.039
Weight scheme w; a/b[d]	0.0003/0.0000	0.0686/0.3212	0.0416/1.4139	0.0389/1.6872	0.0521/2.0580

[a] Largest difference peak and hole. [b] $R_1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$; w$R_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [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 $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$. [e] High-resolution dataset for experimental charge density analysis.

water-depleted refinement of $\mathbf{1}\cdot 0.095\mathrm{H_2O}$ provides clear evidence of missed electron density. The problem of overlooking solvent electron density can, however, occur in structures containing heavier-atoms.

Conclusions

We suggest to have in **1** a host–guest complex in which the amount of the water guest is variable and non-stoichiometric (between <1 and 0), with almost no effect on the crystal packing. We should be able to isolate several crystals of **1** in which the relative amount of the water guest varies continuously with all the crystal structures being "nearly the same" and all the molecular structures of **1** being "the same". An envisioned stoichiometric hydrate of **1**, *i.e.* $\mathbf{1}\cdot 1.0\mathrm{H_2O}$, appears to be unstable in the mother liquor. The three structures of $\mathbf{1}\cdot x\mathrm{H_2O}$ may originate by H_2O loss from a unit amount ($1.0H_2O$) of crystal water[6,27] and we have a case of a crystal-to-crystal transformation.[28] It is obvious that there is a dependency of the non-stoichiometric water content in **1** on the crystallization solvent (see Experimental section). In future investigations we will also address the dependency of temperature of crystallization and time between crystal formation and data collection. The latter is hoped to show the (in)stability of a potential stoichiometric hydrate in water.

Experimental section

Thiosemicarbazide, 2-hydroxybenzaldehyde and solvents with high purity were purchased from Merck and Fluka and used as received.

Salicylaldehyde thiosemicarbazone (1), samples $\mathbf{1\cdot 0.095H_2O}$ and $\mathbf{1\cdot 0.17H_2O}$

Thiosemicarbazide (0.20 g, 2.19 mmol) and 2-hydroxybenzaldehyde (0.20 g, 1.64 mmol) were placed in the main arm of a branched tube. A solution of methanol and water (1 : 1, v/v) was added to fill the arms. The tube was sealed and the arm containing the reagents immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 5 days, colorless crystals were deposited in the cooler arm.

Sample $\mathbf{1}\cdot 0.20\mathrm{H_2O}$: thiosemicarbazide (0.20 g, 2.19 mmol) and 2-hydroxybenzaldehyde (0.20 g, 1.64 mmol) were placed in the main arm of a branched tube. Water was added to fill the arms. The tube was sealed and the arm containing the reagents immersed in an oil bath at 60 °C while the other arm was kept at ambient temperature. After 3 days, colorless crystals were deposited in the cooler arm.

All samples gave identical analytical data when dried (see ESI†). Samples for X-ray diffraction were kept under mother liquor. Upon drying the crystals loose their single-crystallinity. Time between crystallization and data collection was about two weeks.

GEXKID[19] was crystallized from ethanol (without any further information provided) and for GEXKID01[18] no crystallization conditions were given in the publication or ESI†.

X-Ray crystallography

Single crystals of **1** were carefully selected under a polarizing microscope. *Data collection*: Bruker Apex2 AXS CCD diffractometer, Mo-Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, double-pass

method, ω-scan, temperature 100(2) or 203(2) K. Cell refinement and data reduction with SAINT,[29] experimental absorption correction with SADABS.[30] *Structure analysis and refinement*: the structures were solved by direct methods (SHELXS-97); refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite.[31] All non-hydrogen positions were refined with anisotropic displacement parameters. Hydrogen atoms on carbon were positioned geometrically and refined using riding models with $U_{iso}(H) = 1.2U_{eq}(CH)$. H Atoms on hydroxy and partly occupied crystal water oxygen atom, on the amine and on the hydrazone nitrogen atom were found and refined with $U_{iso}(H) = 1.5U_{eq}(O,N)$.

Crystal data and details on the structure refinement are given in Table 2. Graphics were drawn with DIAMOND.[32]

Acknowledgements

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