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Formation and polymorphic phase transitions of crystalline inclusion compounds between 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl host and acetone guest

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ABSTRACT: The 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl host compound (**1**) was found to form various crystalline inclusion compounds with acetone depending on the crystallization conditions or on the method of preparation (inclusion of acetone vapour, co-crystallization from solution). In order to understand and control the formation of these pseudopolymorphic phases regarding potential uses, single crystals of the existing phases (two 1:2 and one 1:1 compound) were prepared, their structures were solved by single-crystal x-ray diffraction (XRD) analysis and the desolvation and phase transformations were studied using simultaneous thermogravimetry–differential scanning calorimetry (TG–DSC) and variable-temperature powder XRD. The results explain the inclusion and desolvation behaviour and also clarify the observed, apparently accidental formation of a 1:1 or 1:2 inclusion compound at ambient temperature. Copyright © 2001 John Wiley & Sons, Ltd.
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KEYWORDS: pseudopolymorphism; diol host; acetone guest; crystalline inclusion compound; crystal structure; thermogravimetry–differential scanning calorimetry; x-ray diffraction; desolvation

INTRODUCTION

Crystalline inclusion compounds (clathrates) have become of increasing importance in science (molecular recognition, crystal engineering)[1] and technology (separation and storage processes, sensor materials, controlled-release systems).[2] According to topological considerations,[3] they may be classified into channel (tubulate), layer (intercalate) or cage (cryptate) type compounds, showing different formation and stability properties that determine potential applications. In this context, the tendency of crystalline hosts to form inclusion compounds of different stoichiometry and crystal structure involving the same guest (often called pseudopolymorphism) is of particular interest.[4] Inconsistent experimental results in the literature or apparently varying properties of samples are often caused by the existence of pseudopolymorphic phases.[5] However, this behaviour also opens up new possibilities for tailoring or adapting the properties of crystalline inclusions.[6] Although the importance of pseudopolymorphism is widely accepted, this phenomenon has neither been systematically studied nor is sufficiently understood.[4] We regarded this as a stimulus to investigate systematically selected host–guest pairs in this respect.[7]

This paper reports results and shows relations of inclusion compounds formed between 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (**1**) and acetone (Scheme **1**). It was known from the literature[8] and from our own investigations regarding sensor applications of crystalline inclusion hosts[9] that **1** yields an inclusion compound **1a** with acetone of 1:2 host–guest molar composition. However, additional co-crystallization experiments performed at ambient temperature under equilibrium conditions, in order to obtain single crystals, always resulted in a 1:1 stoichiometric compound **1b**. This finding prompted a systematic study of the existing phases, their formation conditions, stability, structure–property relationships and transitions using single-crystal x-ray diffraction (XRD),

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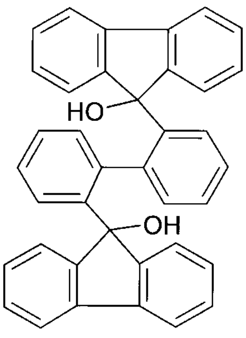


1

1a 1 • acetone (1:2)
1b 1 • acetone (1:1)

Scheme 1

variable-temperature powder XRD and simultaneous thermogravimetry–differential scanning calorimetry (TG–DSC). The results are discussed in terms of a deeper understanding of pseudopolymorphism and a rational control of phase formation.

RESULTS AND DISCUSSION

In the first stage of this work, co-crystallization experiments were carried out in order to identify and prepare the existing phases of the inclusion compound. Crystallization of **1** from acetone solution at ambient temperature up to 45 °C by slow evaporation always yields inclusion **1b** with a molar composition **1**–acetone of 1:1 (γ-form). The structure of the 1:1 compound was solved by single-crystal XRD (N. Sardone, Cambridge Crystallographic Data Centre, Code NABNIN, personal communication, 1996) (Fig. 1). It is characterized by a closed, cryptate-type packing. The host conformation is determined by the intramolecular O(1)—H···O(2) hydrogen bond. The acetone molecules are hydrogen bonded via an O(2)—H···O(acetone) bond to the host. This compact crystal structure causes high thermal stability, as indicated in Fig. 2. TG–DSC investigations showed a single step guest release in the temperature range 120–150 °C. This degradation temperature is much higher than the boiling temperature of acetone (56 °C) caused by the closed packing and the specific host–guest interaction. Both TG-DSC and variable-temperature powder XRD, which have been reported to be suitable for detecting new polymorphic or pseudopolymorphic phases,[10] did not reveal any intermediates during decomposition. However, the resulting guest-free host, which is identical with the initial pure host sample (called phase P1), undergoes a polymorphic transition to phase P2 at approximately 220 °C (Fig. 3). This transition could also be found by DSC and is characterized by a small heat of transition of 2.2 kJ mol^{-1} (Fig. 4). Co-crystallization experiments by slow solvent evaporation in acetone solutions near the boiling-point also resulted in two different crystal modifications of the guest-free host (between 45 and 50 °C the modification P1 was crystallized whereas the polymorph P2 was formed above 50 °C), but the quality of the crystals was not sufficient for solving the crystal structures. Nevertheless, the crystallographic parameters could be determined [dimorph P1, $a = 8.808(7)$, $b = 27.500(8)$, $c = 22.556$ Å, $\beta = 98.42(2)$, $V = 5404(5)$ Å^3, $Z = 4$, space group $P2_1/c$; dimorph P2, $a = 11.04(2)$, $b = 16.85(4)$, $c = 14.22(4)$, $\beta = 101.85(2)$, $V = 2589(4)$, space group $P2_1/c$]. Indexation of the diffractograms from the powder XRD measurements of the dimorphs confirmed that the crystals are indeed polymorphs P1 and P2 with the given crystal parameters.

Recently, recommendations for the topological control

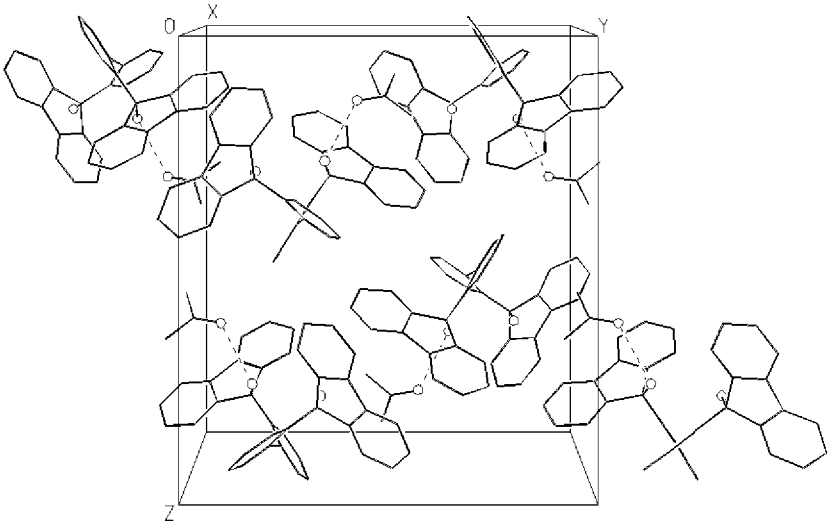


Figure 1. Conformation of the host and guest molecules in the inclusion compound **1b** (γ-phase of molar composition 1:1)

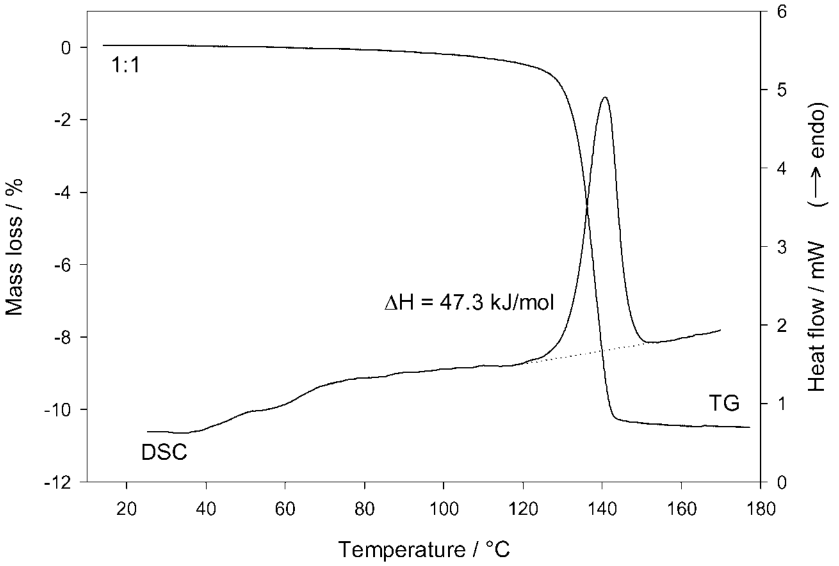


Figure 2. TG–DSC results for the thermal decomposition of the inclusion compound **1b**

of crystalline inclusion compounds have been made according to the rule, 'if a host–guest complex obtained at room temperature is of cryptate type, its tubulate (or another more open) form can be prepared by decreasing the crystallization temperature.'[11] Considering that the prepared inclusion compound of composition 1:1 (**1b**) has a cryptate-type structure, low-temperature crystallization may yield a more open crystalline structure with a higher guest content such as the recently reported compound of 1:2 molar composition (**1a**).[8,9] Actually, co-crystallization experiments conducted below −5 °C by slow solvent evaporation at the solubility limit yielded a crystalline inclusion of molar host–guest composition 1:2, called the α-form. Comparing its powder diffractogram with that of another sample of the same composition prepared by vapour sorption at 25 °C from acetone vapour saturated at 23 °C (called the β-form),[9] complete disagreement was observed (Fig. 5). This suggests the existence of a second polymorphic form of the 1:2 compound (**1a**). Therefore, we extended the crystallization experiments by applying non-equilibrium conditions of high supersaturation (fast evaporation of acetone from an open beaker or fast cooling of a saturated solution at room temperature with an ice-bath). As a result, crystals of the 1:2 β-form could be obtained which has been proved by comparison of the appropriate powder diffractograms (Fig. 5). Crystals of the β-phase have to be quickly separated from the mother liquor and stored dry because they rapidly convert to the 1:1 γ-phase

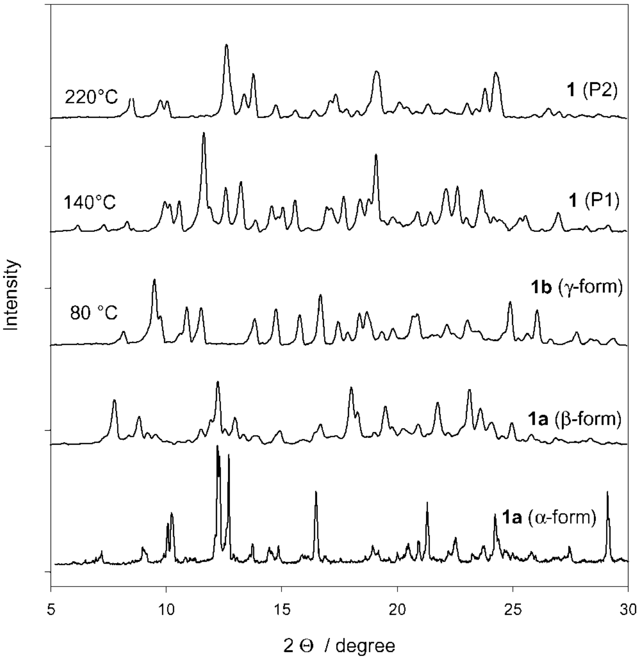


Figure 3. Diffractograms of the inclusion compounds between **1** and acetone and the polymorphs of the free host (**1**)

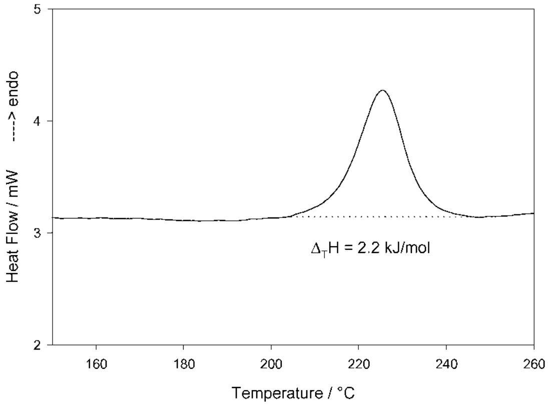


Figure 4. DSC curve for the polymorphic phase transition P1→P2 of the pure host **1**

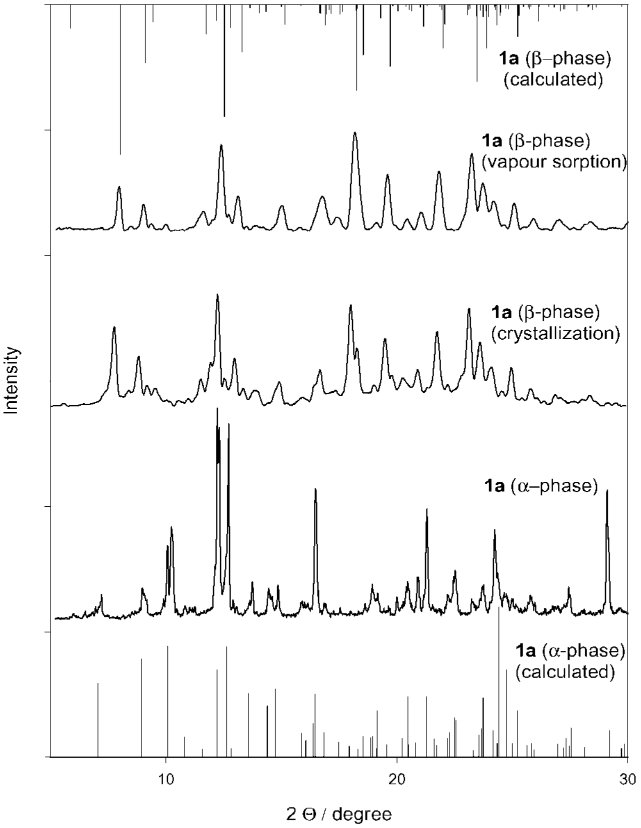
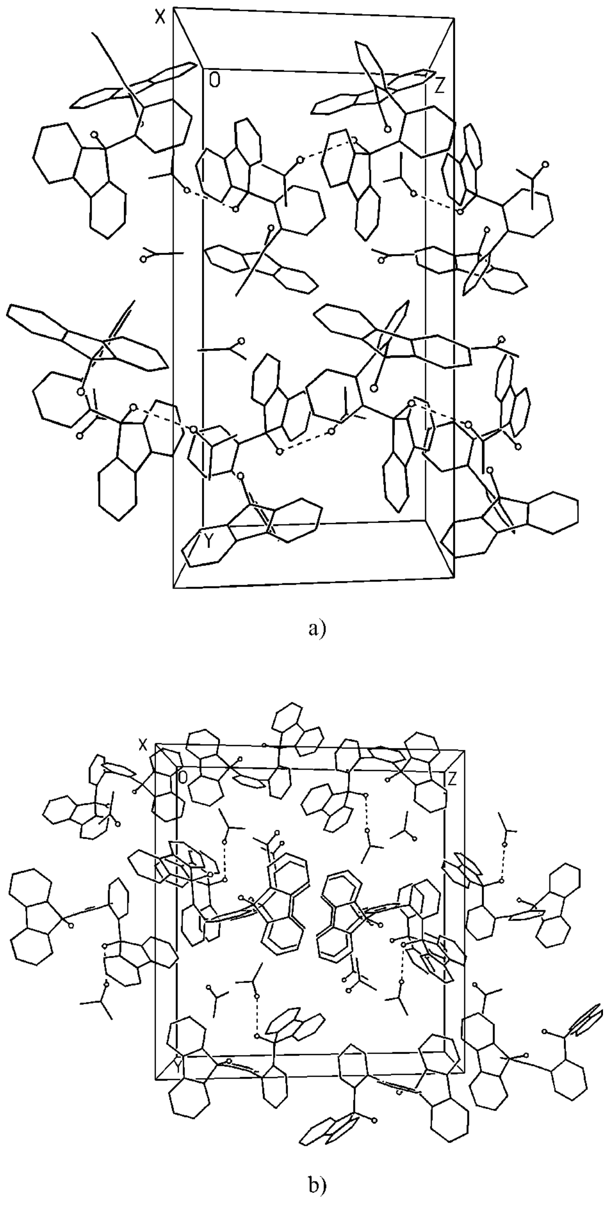


Figure 5. Diffractograms for the polymorphic phases of the inclusion compound **1a**

in contact with the solution. This indicates that the *β*-phase is a thermodynamically unstable phase only stabilized owing to kinetic reasons.

The crystal structures of both the α- and *β*-phases of **1a** were solved using single-crystal XRD at −90 °C. Additional variable-temperature powder XRD measurements down to −120 °C proved that no unknown phase transitions occur during cooling. Calculated powder diffractograms from the single-crystal data are also in good agreement with the measured patterns (Fig. 5). The molecular packing characteristic and the crystallographic data of the two polymorphic phases are shown in Fig. 6 and Table 1, respectively. The molecular conformations of the host molecule in all three phases of the inclusion compounds are very similar because they are dominated by the same intramolecular hydrogen bond O(1)—H···O(2). In contrast to the *γ*-form (**1b**), the crystal packing of **1a** is of the tubulate type. One of the two acetone molecules is hydrogen-bonded to the host molecules by the O(2)—H···O(acetone) bond. The non-hydrogen-bonded acetone molecules show fairly high thermal motions despite the fact that experimental data were collected at −90 °C. In the α-phase of **1a** only non-hydrogen-bonded acetone molecules are located in constricted channels parallel to the crystallographic *a*-axis, whereas in the case of the *β*-phase both hydrogen-bonded and non-hydrogen-bonded acetone molecules are located in less constricted channels also running in the direction of the *a*-axis. Both acetone molecules in the *β*-phase of **1a** are disordered with site occupation factors of 0.562/0.438 (hydrogen-bonded) and 0.604/0.396 (non-hydrogen-bonded).

The particular structural properties of the two polymorphic inclusion compounds of **1a** also control the thermal degradation behaviour studied by TG–DSC (Fig. 7). Both polymorphs decompose in two distinct steps. The mass loss in each step corresponds to the release of one acetone molecule, suggesting the loss of the non-hydrogen-bonded acetone first followed by a transition into **1b** (1:1 inclusion compound). This assumption was confirmed by variable-temperature powder XRD, showing always the *γ*-form (**1b**) as an intermediate after the



a)

b)

Figure 6. Packing structures of the inclusion compound **1a** with composition 1:2: (a) α-phase; (b) *β*-phase

Table 1. Crystal data and some selected experimental details for the crystal structures of α- and β-phases of the inclusion compound **1a**

	α-Phase	β-Phase
Empirical formula	$C_{44}H_{38}O_4$	$C_{44}H_{38}O_4$
Formula weight	630.74	630.74
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
T (°C)	−90	−90
a (Å)	10.855(2)	7.6970(10)
b (Å)	25.032(5)	21.849(8)
c (Å)	12.404(2)	20.603(4)
α (°)	90	90
β (°)	97.20(3)	95.720(10)
γ (°)	90	90
V (Å^3)	3343.9(11)	3447.6(15)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.253	1.215
Radiation	Mo Kα	Cu Kα
F(000)	1336	1336
Absorption coefficient (mm^{-1})	0.079	0.603
Crystal size (mm)	0.40 × 0.30 × 0.10	0.50 × 0.20 × 0.20
θ-Range (°)	1.63–25.00	2.96–64.93
Index range	h (0–12), k (0–29), l (−14 to +14)	h (0–8), k (0–25), l (−24 to +24)
Reflections collected	6187	6096
Independent reflections	5860	5619
Data/restraints/parameters	2789/0/442	2527/19/431
Goodness-of-fit on F^2	0.943	0.990
R	0.076, 0.197	0.0934, 0.2049
R_w	0.1653, 0.1929	0.2565, 0.2965
Largest diff. peak and hole (e Å^3)	0.455/−0.435	0.536/−0.325

first degradation step (Fig. 3). Furthermore, the DSC results show identical heat effects for the second degradation steps of the polymorphs of **1a** and for the degradation of **1b** (47–48 kJ mol^{-1}) to the guest-free host, respectively. The lower onset temperature of this phase transition for the β-form of **1a** [Fig. 7(b)] might be due to poorer crystallinity of the intermediate γ-phase of **1b**, also represented by larger peak widths of the appropriate powder diffractogram.

The heat effects accompanying the transition of **1a** to **1b** (first stage) are much smaller and close to the heat of vaporization of acetone (31.27 kJ mol^{-1}),[12] indicating also the liberation of a non-bonded acetone molecule at this stage.

The main difference between the two polymorphs of **1a** is the temperature range for phase transition to **1b**. The α-phase of **1a** is converted into the γ-phase (**1b**) in the temperature range from room temperature to 40 °C, whereas the β-phase of **1a** is decomposed and converted at higher temperatures, in the range 50–80 °C. This apparently higher thermal stability of the thermodynamically unstable phase may be explained by a diffusion-retarding influence of the hydrogen-bonded acetone molecules in the channels and a higher activation energy for the lattice conversion of the β-phase due to the relatively large packing dissimilarities. The different crystal packings of the two polymorphs of **1a** could also be the reason why no $\alpha \rightarrow \beta$ transition was observed.

EXPERIMENTAL

Synthesis. The synthesis of the free host compound **1** has been described elsewhere.[13] The inclusion compounds were obtained by crystallization from acetone under different conditions (see above).

TG–DSC investigations. The thermal decomposition was studied by means of a model 111 simultaneous TG–DSC system (Setaram, France) using open aluminium crucibles, sample weights of ~4 mg, a linear heating rate of 5 K min^{-1} and argon at 1 1 h^{-1} as purge gas for all measurements. Crystals were taken from the mother liquor, blotted dry on filter-paper and transferred into the crucibles for weighing and measuring.

Variable-temperature x-ray powder diffraction. Variable-temperature x-ray diffraction patterns were collected on a D 5000 powder diffractometer (Siemens, Germany) equipped with a variable-temperature capillary technique and a PSD-50M position-sensitive detector (Braun, Germany), using Cu Kα radiation. The temperatures were set at the furnace controller, and after a ~20 min holding time at the appropriate temperature the x-ray pattern were recorded. Measurements below room temperature were performed using a Cryojet cooling system (Oxford Instruments, UK). Some problems occurred on registration of the diffractogram of the α-

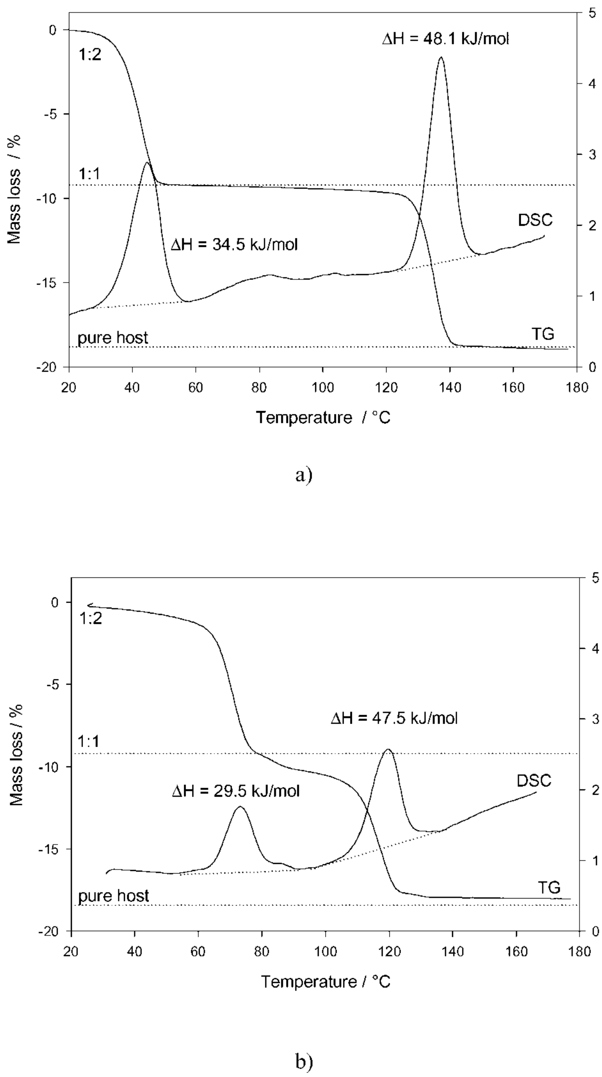


Figure 7. TG–DSC results for the thermal decomposition of the inclusion compound **1a** with composition 1:2: (a) α-phase; (b) β-phase

phase of **1a** because of its instability at room temperature and transformation to the γ-phase. In order to avoid the phase transition during sample preparation, liquid nitrogen was poured over the samples of the α-phase during grinding to fine powders, which were transferred quickly to the diffractometer.

The calculations of powder patterns were carried out using the Cerius^2 software package (Molecular Simulations, USA) and structural data from single crystals.

X-ray structure determination. Crystal parameters were determined and intensities of reflections collected at $-90\,^\circ$C on an Enraf-Nonius CAD-4 diffractometer using Mo Kα ($\lambda = 0.71073$ Å) for the α-phase and Cu Kα ($\lambda = 1.54178$ Å) for the β-phase. Crystal data and selected experimental details are given in Table 1.

The structures were solved by direct methods using the program SHELXS-86.[14] The refinement of the structures was carried out with the program SHELXL-93[15] with anisotropic displacement parameters for non-hydrogen atoms. The H-atoms of all structures were placed at the calculated positions.

SUPPLEMENTARY DATA

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited as supplementary data at the Cambridge Crystallographic Data Centre. Lists of the observed and calculated structure factors and the anisotropic displacement parameters for the non-hydrogen atoms may be obtained from the authors (B.T.I. and J.S.) on request. Crystallographic data and computer graphics of the structures can also be viewed at the epoc website at http:/www.wiley.com/epoc.

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