Single-Crystal Structures and Vibrational Spectra of Li[SCN] and Li[SCN] · 2 H₂O

Olaf Reckeweg a,c, Armin Schulz b, Björn Blaschkowski c, Thomas Schleid c, and Francis J. DiSalvo d

a Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, U. S. A.
b Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany
c Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Reprint requests to Dr. Olaf Reckeweg. Fax: +1-607-255-4137. E-mail: olaf.reykjavik@gmx.de

Received July 23, 2013

The crystal structure of Li[SCN] · 2 H₂O has been determined by single-crystal X-ray diffraction on commercially available material. Crystals of this compound are colorless, transparent and hygroscopic. Li[SCN] · 2 H₂O adopts the orthorhombic space group Pnma with the cell parameters a = 572.1(3), b = 809.3(4) and c = 966.9(4) pm and Z = 4. Li[SCN] was obtained by dehydration of the afore-mentioned dihydrate and also crystallizes orthorhombically in Pnma with the lattice parameters a = 1215.1(3), b = 373.6(1) and c = 529.9(2) pm (Z = 4). Both compounds contain Li⁺ cations in sixfold coordination. Four water molecules and two nitrogen-attached thiocyanate anions [SCN]⁻ arrange as trans-octahedra [Li(OH)₄(NCS)₂]⁻ in the case of Li[SCN] · 2 H₂O. Anhydrous Li[SCN] displays fac-octahedra [Li(NCS)₃(SCN)]⁻ with six thiocyanate anions grafting via both nitrogen and sulfur atoms, three each. Infrared and Raman spectra of both compounds were recorded and a DSC/TG measurement was performed on Li[SCN] · 2 H₂O.

Key words: Lithium, [SCN]⁻ Anion, Thiocyanates, DSC/TG Measurements, Vibrational Spectra

Introduction

Pseudobinary compounds containing lithium cations next to complex polyatomic anionic moieties have been synthesized and characterized early on, in the case of Li[CN] as early as 1942 [1]. Due to the recently increased interest in materials for lithium batteries, lithium-related research was fueled again and led to reports such as the structure and properties of Li[OCN] [2]. It still came as a surprise to us that physical properties of Li[SCN] and Li[SCN] · 2 H₂O can be found in the literature [3 – 5] and that “Li[SCN] · x H₂O” is commercially available, but no crystal structures have been reported for these two compounds as yet. So here we present the single-crystal structure determinations and the vibrational spectra of Li[SCN] and Li[SCN] · 2 H₂O as well as the DSC/TG measurement for the thermal decomposition of Li[SCN] · 2 H₂O.

Experimental Section

Synthesis

All manipulations were performed under normal atmospheric conditions unless otherwise stated. Li[SCN] · x H₂O was bought from Sigma-Aldrich (St. Louis, MO, U. S. A.) as minimally 98% pure material (Mx ~ 65). Li[SCN] could be obtained by transferring some of the hygroscopic Li[SCN] · x H₂O into a glass ampoule and exposing it at 200 °C for two hours to a dynamic vacuum till the pressure was constant and below 200 Pa. Then the temperature was raised within 30 min. up to 300 °C. The sample was kept for 30 more min at this temperature, while still being under dynamic vacuum. The anhydrous material obtained in this way is extremely hygroscopic, colorless with a slight yellowish tint (a more intense yellow substance also showed up above the heated zone of the ampoule). The ampoule with the anhydrous Li[SCN] was flame-sealed and then transferred into an argon-filled glove box, where it was handled further on.
Table 1. Vibrational spectra of Li[SCN] and Li[SCN]·2H₂O compared to literature data. All numbers are given in cm⁻¹, bold print indicates data obtained by IR techniques. All compounds were used as solids, if not indicated otherwise.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(SCN)</th>
<th>ν(SC)</th>
<th>2δ(SCN)</th>
<th>ν(CN)</th>
<th>ν(H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free anion (calcd.) [6, 7]</td>
<td>470</td>
<td>743</td>
<td>–</td>
<td>2066</td>
<td>–</td>
</tr>
<tr>
<td>Li[SCN] [3]</td>
<td>499</td>
<td>764</td>
<td>–</td>
<td>2083</td>
<td>–</td>
</tr>
<tr>
<td>Li[SCN]₆₆ [3]</td>
<td>496</td>
<td>745</td>
<td>–</td>
<td>2072</td>
<td>–</td>
</tr>
<tr>
<td>Li[SCN]</td>
<td>470</td>
<td>771</td>
<td>–</td>
<td>2070</td>
<td>–</td>
</tr>
<tr>
<td>This work</td>
<td>491</td>
<td>731/774</td>
<td>967</td>
<td>2078</td>
<td>1653/3238/3294</td>
</tr>
<tr>
<td>Li[SCN]·2H₂O</td>
<td>457/470</td>
<td>752</td>
<td>927</td>
<td>2050/2089</td>
<td>1660/3393</td>
</tr>
<tr>
<td>This work</td>
<td>480</td>
<td>730/778</td>
<td>958/982</td>
<td>2064</td>
<td>1623/1635/3400</td>
</tr>
<tr>
<td></td>
<td>440/451/473/488</td>
<td>768</td>
<td>933</td>
<td>2100/2116/2124/2185</td>
<td>1628/3252/3360</td>
</tr>
<tr>
<td></td>
<td>469/478</td>
<td>769</td>
<td>951/957</td>
<td>2077/2096/2123</td>
<td>1628/3242/3398</td>
</tr>
</tbody>
</table>

Raman and IR spectroscopy

The crystals of Li[SCN] and Li[SCN]·2H₂O were sealed under a protective argon atmosphere in thin-walled glass capillaries. Raman spectroscopic investigations were performed on a microscope laser Raman spectrometer (Jobin Yvon, 4 mW, equipped with a HeNe laser using an excitation line at λ = 632.817 nm, 50 × magnification, 8 × 240 s accumulation time). The infrared spectra (IR) were obtained with a Bruker AFS 66 FT-IR instrument with the KBr pellet technique (2 mg of product being ground together with 400 mg of dried KBr). The IR spectrum showed some absorptions typical for CO₂ in the region between 1300 and 1600 cm⁻¹ (asymmetric stretching mode), since the measurements were performed in normal atmosphere. The combined IR and Raman spectra for each compound are displayed in Fig. 1b for Li[SCN]·2H₂O and in Fig. 1a for Li[SCN], the exact frequencies and their assigned modes are shown in Table 1.

DSC/TG measurements

19.026 mg of commercial “Li[SCN]·xH₂O” were taken from the batch and placed on a DSC/TG alumina pan. This set-up was introduced into a Netzsch STA 449C instrument under a constant stream of pure argon. Even during this short transfer time the already hydrated material absorbed some
Table 2. Summary of the single-crystal X-ray diffraction structure determination data of Li[SCN] and Li[SCN]·2H₂O.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Li[SCN]</th>
<th>Li[SCN]·2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁</td>
<td>65.02</td>
<td>101.05</td>
</tr>
<tr>
<td>Crystal color</td>
<td>transparent, colorless</td>
<td>transparent, colorless</td>
</tr>
<tr>
<td>Crystal shape</td>
<td>irregular plate</td>
<td>elongated plate</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.05 × 0.03 × 0.01</td>
<td>0.12 × 0.03 × 0.02</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group (no.); Z</td>
<td>Pnma (62); 4</td>
<td>Pnma (62); 4</td>
</tr>
<tr>
<td>Lattice parameters: a, b, c, pm</td>
<td>1215.1(3); 373.6(1); 529.9(2)</td>
<td>572.1(3); 809.3(4); 966.9(4)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>240.6(1)</td>
<td>447.7(2)</td>
</tr>
<tr>
<td>Dₐ₀, g cm⁻³</td>
<td>1.80</td>
<td>1.50</td>
</tr>
<tr>
<td>Dₐ₀, g cm⁻³</td>
<td>128</td>
<td>208</td>
</tr>
<tr>
<td>µ̂(MoKα), mm⁻¹</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Bruker X8 Apex II equipped with a 4 K CCD</td>
<td>Bruker X8 Apex II equipped with a 4 K CCD</td>
</tr>
<tr>
<td>Radiation; λ, pm; monochromator</td>
<td>MoKα; 71.073; graphite</td>
<td>MoKα; 71.073; graphite</td>
</tr>
<tr>
<td>Scan mode; T, K</td>
<td>φ- and θ-scans; 173(2)</td>
<td>φ- and θ-scans; 173(2)</td>
</tr>
<tr>
<td>Ranges 2θ.max, deg; h, k, l</td>
<td>58.65; –16 → 15, –4 → 5, –5 → 7</td>
<td>58.01; –6 → 7, –8 → 11, –13 → 7</td>
</tr>
<tr>
<td>Data correction</td>
<td>LP; SADABS [10]</td>
<td>LP; SADABS [10]</td>
</tr>
<tr>
<td>Transmission: min./max.</td>
<td>0.625/0.746</td>
<td>0.690/0.746</td>
</tr>
<tr>
<td>Reflections: measured/unique</td>
<td>1555/354</td>
<td>2661/649</td>
</tr>
<tr>
<td>Unique reflections with F₀ &gt; 4 σ(F₀)</td>
<td>297</td>
<td>556</td>
</tr>
<tr>
<td>R₁ = ∑</td>
<td>F₁</td>
<td>−</td>
</tr>
<tr>
<td>Factors x/y (weighting scheme)</td>
<td>0.0192/0.15</td>
<td>0.0264/0.02</td>
</tr>
<tr>
<td>Max. shift/εsd, last refinement cycle</td>
<td>&lt; 0.00005</td>
<td>&lt; 0.00005</td>
</tr>
<tr>
<td>Δρₐ₀ (max/min), e⁻Å⁻³</td>
<td>0.29 (75 pm to C)/–0.42 (78 pm to S)</td>
<td>0.21 (143 pm to C)/–0.28 (70 pm to S)</td>
</tr>
<tr>
<td>CSD number</td>
<td>425060</td>
<td>425061</td>
</tr>
</tbody>
</table>

a | b | c |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁ = ∑</td>
<td>F₁</td>
<td>−</td>
</tr>
</tbody>
</table>

Samples of Li[SCN] · 2 H₂O were taken from the container and quickly immersed in dried polybutene oil (Sigma-Aldrich: M₁ ≈ 320, isobutylene > 90%), while Li[SCN] was removed from the glove box already protected by the same dried polybutene oil. In both cases, the evaluation of the crystalline material took place under a polarization microscope. The selected specimens were mounted in a drop of polybutene sustained in a plastic loop, and placed onto the go-miometer. A cold stream of nitrogen (T = 173(2) K) froze the polybutene oil, thus keeping the crystals stationary and protected from oxygen and moisture in the air. Intensity data sets were collected with a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromatized MoKα radiation (λ = 71.073 pm). The intensity data were manipulated with the program package APEX2 [9] that came with the diffractometer. An empirical absorption correction was applied using SADABS [10].

Fig. 2. Graph of the DSC/TG measurement on Li[SCN] · 2 H₂O.
The intensity data were evaluated, and the input files for solving and refining the crystal structure were prepared by XPREP [11]. The program SHELX-97 [12, 13] delivered with the help of Direct Methods the positions of S, C, N and O (if present). The Li and H positions were apparent from the positions of highest electron density on the difference Fourier maps resulting from the first refinement cycles by full-matrix least-squares calculations on F2 in SHELXL-97 [14, 15]. Doing further refinement cycles with all atoms being refined unrestrained, the refinement converged and resulted in stable models for both crystal structures. Additional crystallographic details are described in Table 2. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 3. Table 4 displays selected interatomic distances and angles of the title compounds and their alkali-metal thiocyanate analogs.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-425060 for Li[SCN]·2H2O and CSD-425061 for Li[SCN].

### Results and Discussion

#### Optical spectra

The frequencies obtained from the infrared (IR) and Raman spectra of the title compounds compare well to the calculated frequencies for the free [SCN]− anion [6, 7] and to the vibrational frequencies reported in the literature [3, 8] (Table 4). The bands known for H2O (about 1640 and 3400 cm⁻¹) appeared in the IR spectra of both compounds as well as the frequencies known for CO2 (668 and 2360 cm⁻¹), since the measurements could not be performed under strictly inert conditions and the materials being very hygroscopic, but the Raman spectroscopic measurements done on single crystals in capillaries showed clearly the absence or the presence of water in Li[SCN] and Li[SCN]·2H2O, respectively.

#### DSC/TG measurements

The DSC/TG measurement on Li[SCN]·2H2O showed an endothermic effect below 40°C connected

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff site</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Ueq (pm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>4c</td>
<td>0.3985(3)</td>
<td>1/4</td>
<td>0.0590(8)</td>
<td>247(9)</td>
</tr>
<tr>
<td>S</td>
<td>4c</td>
<td>0.18762(5)</td>
<td>1/4</td>
<td>0.85799(11)</td>
<td>142(2)</td>
</tr>
<tr>
<td>C</td>
<td>4c</td>
<td>0.10922(17)</td>
<td>1/4</td>
<td>0.1105(4)</td>
<td>125(5)</td>
</tr>
<tr>
<td>N</td>
<td>4c</td>
<td>0.05491(16)</td>
<td>1/4</td>
<td>0.2911(4)</td>
<td>188(5)</td>
</tr>
<tr>
<td>Li</td>
<td>4c</td>
<td>0.1073(5)</td>
<td>1/4</td>
<td>0.2833(3)</td>
<td>246(6)</td>
</tr>
<tr>
<td>S</td>
<td>4c</td>
<td>0.70072(7)</td>
<td>1/4</td>
<td>0.62914(5)</td>
<td>213(2)</td>
</tr>
<tr>
<td>C</td>
<td>4c</td>
<td>0.4603(3)</td>
<td>1/4</td>
<td>0.53326(18)</td>
<td>191(3)</td>
</tr>
<tr>
<td>N</td>
<td>4c</td>
<td>0.2983(2)</td>
<td>1/4</td>
<td>0.46250(18)</td>
<td>302(4)</td>
</tr>
<tr>
<td>O</td>
<td>8d</td>
<td>0.66201(14)</td>
<td>0.58204(11)</td>
<td>0.91819(10)</td>
<td>211(2)</td>
</tr>
<tr>
<td>H1</td>
<td>8d</td>
<td>0.681(3)</td>
<td>0.567(2)</td>
<td>0.9030(18)</td>
<td>497(54)</td>
</tr>
<tr>
<td>H2</td>
<td>8d</td>
<td>0.656(3)</td>
<td>0.493(2)</td>
<td>0.7777(19)</td>
<td>584(57)</td>
</tr>
</tbody>
</table>

* Ueq is defined as a third of the orthogonalized Uij tensors, here: Ueq = \frac{1}{3}(U_{11} + U_{22} + U_{33}).

<table>
<thead>
<tr>
<th>Atom</th>
<th>U11</th>
<th>U22</th>
<th>U13</th>
<th>U23</th>
<th>U13</th>
<th>U12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>181(21)</td>
<td>319(27)</td>
<td>239(23)</td>
<td>0</td>
<td>-56(18)</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>123(3)</td>
<td>201(3)</td>
<td>103(3)</td>
<td>0</td>
<td>15(2)</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>96(10)</td>
<td>139(11)</td>
<td>140(12)</td>
<td>0</td>
<td>-49(9)</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>129(9)</td>
<td>299(12)</td>
<td>138(10)</td>
<td>0</td>
<td>0(8)</td>
<td>0</td>
</tr>
<tr>
<td>Li</td>
<td>165(12)</td>
<td>305(16)</td>
<td>267(17)</td>
<td>0</td>
<td>4(13)</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>195(2)</td>
<td>242(2)</td>
<td>202(3)</td>
<td>0</td>
<td>-25(2)</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>218(7)</td>
<td>197(7)</td>
<td>157(8)</td>
<td>0</td>
<td>40(7)</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>236(7)</td>
<td>436(9)</td>
<td>232(9)</td>
<td>0</td>
<td>-24(7)</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>203(4)</td>
<td>229(5)</td>
<td>200(5)</td>
<td>-16(4)</td>
<td>-16(4)</td>
<td>-6(3)</td>
</tr>
</tbody>
</table>

* The anisotropic displacement factor takes the form: Uij = \exp(-2\pi²(b^2a^2U_{11} + b^2c^2U_{22} + c^2a^2U_{33} + 2bka^2c^2U_{13} + 2bka^2c^2U_{13} + 2bka^2b^2U_{12})).
with virtually no decrease of mass. This may be attributed to either a phase transition or melting as found for Ca[SCN]$_2$ · 2 H$_2$O [8]. The subsequently following loss of mass can be roughly separated into three steps. The first step ranges from room temperature to about 150 °C with a mass loss of 23.3%, the second step ranges from 150 to 280 °C with about 13.2% mass decrease, and the last one is finished at 538 °C. The first two steps (added up: 36.5% mass loss) can be attributed to the loss of water, which would cause a decrease in mass by 17%. Because these two dehydration steps did not show the equivalent weight loss of 2 × 17%, this behavior leaves no evidence for the formation of the monohydrate Li[SCN] · H$_2$O, which was postulated already, but never could be observed or isolated [5]. If one assumes a two-step dehydration to be correct, the composition of the intermediate would be close to Li[SCN] · 0.75 H$_2$O. Our measurements show furthermore that the dehydration is complete just before the melting point of Li[SCN] at 276 °C, which is indicated by an endothermic peak. Increasing the temperature further results in a slow decrease of mass resulting from the beginning decomposition shown by DSC at 415 °C. The yellow substance forming at this stage is found to be sulfur. But sulfur would account only for 33.0% of the mass loss, the observed decrease in mass is more like 39.0%, however. Elemental lithium and compounds such as Li$_2$C$_2$, Li$_3$N or Li$_2$[CN$_2$] are not subliming, evaporating or decomposing [17] under ambient pressure and temperatures below 600 °C as used for the DTA/DSC/TG studies. Due to the set-up of the instrument we had no opportunity to check the composition of the residue or the vapor. Therefore, we compared our results to experiments with a similar compound under comparable conditions, e. g. the thermal analysis of Li[N(CN)$_2$] [18].

In this case, the residual material was chemically analyzed to have the composition “Li$_{0.2}$CN$_{0.7}$”. For our experiment, this would hypothetically mean a residual mass of 23.2%, which is very close to our experimental value of 24.5%.

### Crystal structures

Both compounds crystallize in the orthorhombic space group Pnma (no. 62) with all atoms (Li, S and N) being located on special positions 4c (y/b = 1/4 and 3/4). In anhydrous Li[SCN], the Li$^+$ cations are surrounded octahedrally by three nitrogen atoms (d(Li–N) = 206 pm and 2 × 241 pm) and three sulfur atoms (d(Li–S) = 2 × 266 pm and 278 pm) from six different thiocyanate anions [SCN]$^−$ in a way that fac-[LiN$_3$S$_3$] octahedra ([Li(NCS)$_3$](SCN)$_3$)$^{3−}$. In turn, each [SCN]$^−$ anion is surrounded by a trigonal antiprism of Li$^+$ cations (Fig. 3b). Along [010], the [LiN$_3$S$_3$] octahedra are first condensed by sharing trans-oriented edges via one sulfur and one nitrogen atom to form chains $\{[\text{LiN}_3\text{S}_2\text{S}_2\text{N}]\}$ and further through common cis-oriented edges via two nitrogen atoms to generate double chains $\{[\text{LiN}_3\text{S}_2\text{S}_2\text{S}_1\text{N}]/[\text{LiN}_3\text{S}_2\text{S}_2\text{S}_1\text{N}]\}$. A three-dimensional structure from the hexagonal rod-packing motif of these double chains (Fig. 4) is erected in such a way that on one hand corners of the double chains share their terminal sulfur atoms $\{[\text{LiN}_3\text{S}_2\text{S}_2\text{S}_1\text{N}]/[\text{LiN}_3\text{S}_2\text{S}_2\text{S}_1\text{N}]\}$ and on the other hand additional bonding contacts between them are formed via the covalent bonds of the thiocyanate units (−S–C≡N: d(N≡C) = 116 pm, d(S–C) = 164 pm; −S(N–C–S) = 179°). Thereby each [SCN]$^−$ anion is connecting three of the above-mentioned double chains of fused fac-[LiN$_3$S$_3$] octahedra (Fig. 4).

In the dihydrate Li[SCN] · 2 H$_2$O, the lithium atom is surrounded in an almost octahedral fashion...
Fig. 3a. Coordination of Li$^+$ in Li[SCN].

Fig. 3b. Coordination of [SCN]$^-$ in Li[SCN].

Fig. 4. View at the unit cell of Li[SCN] along [010].

Fig. 5. Coordination of Li$^+$ in Li[SCN] · 2H$_2$O.

by four water molecules ($d$(Li–O) = 2 × 208 pm and 2 × 213 pm) and two nitrogen atoms of two different [SCN]$^-$ anions as trans-octahedra [Li(OH)$_2$(NCS)$_2$]$^-$. One nitrogen atom with a Li–N distance of 205 pm happens to be very close to the sum of the ionic radii (205 pm) with its Li$^+$ partner according to Shannon [16], while the other Li–N contact of 296 pm might be best called a weak coordinative bond (Fig. 5). This Li–N contact with the rather large interatomic distance does not only complete the distorted octahedral environment of lithium, but also connects the trans-octahedra to each other forming $\left\{[\text{Li}([\text{OH}_2]_2\text{NCS}_2)]_{2/2}\right\}$ chains (Fig. 6). These chains are packed next to each other to form a kind of
The crystal structures of the lithium thiocyanates Li[SCN] and Li[SCN] · 2 H2O have been successfully determined from single-crystal X-ray diffraction data. The vibrational spectra of both compounds show the results expected for ionic thiocyanates similar to that for the calcium thiocyanate analogs. DSC/TG measurements show a two-step dehydration of Li[SCN] · 2 H2O with inequivalent weight losses indicating that a monohydrate reported as “Li[SCN] · H2O” does not exist. The dehydration is finished completely just before the melting point of Li[SCN] at 276 °C. At higher temperatures Li[SCN] decomposes into elemental sulfur and a conglomerate of different compounds with the approximate general composition “Li0.2 CN0.7” such as observed before for the thermal decomposition of Li[N(CN)2].

Acknowledgement

We thank Mr. Benjamin Bruha (Max-Planck-Institut für Festkörperforschung, Stuttgart) for collecting the IR spectra and Mr. Christof Schneck (Institut für Anorganische Chemie, Universität Stuttgart) for the DTA/DSC/TG measurements. Thanks are also due to an anonymous referee for helpful comments leading to considerable improvements.


