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Crystal Structure and Dimorphism of Silicon Tetraisocyanate $Si(NCO)_4$

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Abstract. Silicon tetraisocyanate $Si(NCO)_4$ was obtained by reacting $SiCl_4$ and AgNCO in boiling toluene. The colourless liquid was analyzed by Raman and NMR spectroscopy. Structural studies on solid $Si(NCO)_4$ (melting point: +26 °C) have revealed it to exist in two polymorphic modifications. According to the results of single-crystal X-ray diffraction, at T = –173 °C, α-$Si(NCO)_4$ exhibits triclinic symmetry ($P\bar{1}$; a = 10.05(5), b = 10.50(2), c = 14.32(1) Å, α = 91.62(1)°, β = 92,32(1)°, γ = 99.68(1)°; V = 1488.56(3) Å^3; Z = 8). Above T = –33 °C, a monoclinic phase evolves, β-$Si(NCO)_4$ ($P2_1/c$; a = 10.78(3), b = 7.11(1), c = 10.27(5) Å, β = 99,06(9)°; V = 777.39(1) Å^3; Z = 4). The charge distribution was studied for both polymorphs. In the solid state, $Si(NCO)_4$ is a tetrahedral molecule with the Si–N=C=O linkages bent at the nitrogen atoms.

Introduction

Recently, we started evaluating molecular inorganic isocyanates as molecular precursors for the synthesis of new (amorphous) ceramics.[1–4] For a proper understanding of the underlying mechanisms of transforming the molecular through oligomeric precursor states towards the final solid-state materials, knowing structural data of the initial molecular precursors is an indispensable prerequisite. Although silicon tetraisocyanate, $Si(NCO)_4$, has been known already for decades[5] and has been applied for the preparation of SiO_2 thin films by CVD processes,[6] there is still some dispute concerning details of the (molecular) structure of $Si(NCO)_4$. Structural studies on crystalline material were impeded by the fact, that this molecular isocyanate is liquid at ambient conditions and highly sensitive to moisture. Based on spectroscopic results, a double bond was assigned to the silicon–nitrogen linkage.[7,8] This would make the nitrogen atom formally isoelectronic with carbon. In this view, the lone-pair of electrons on the nitrogen atom would interact with empty orbitals on silicon resulting in a linear Si–N=C=O connectivity. These interpretations have not yet been confirmed, and more recent Raman studies even challenged the so-far accepted tetrahedral constitution of $Si(NCO)_4$.[9,10] In order to settle these discrepancies, we performed a structural study on solid $Si(NCO)_4$.

Experimental Section

Synthesis

$Si(NCO)_4$ was prepared according to the procedure previously published.[11] In brief, dried AgNCO (from KOCN and $AgNO_3$) was suspended in absolute toluene (distilled and stored over sodium wire) and freshly distilled $SiCl_4$ was dropped to this suspension whilst stirring. An excess of 10 % AgNCO was used. The suspension was stirred under argon for 24 h under reflux. The color of the suspension changed from colorless to violet-grey due to precipitation of AgCl. Heating to reflux was found to be essential, most likely, because the high-temperature polymorph of AgNCO, present under these conditions, is the reactive species.[12] After filtering, the solvent of the resulting clear solution was evaporated in vacuo and the slightly yellow liquid residue was distilled at T = 186 °C at ambient pressure. The yield was quantitative. $Si(NCO)_4$, a moisture-sensitive colorless liquid was stored under argon. For growing single-crystals, $Si(NCO)_4$ was mixed with a small amount of toluene and stored at T = –4 °C, for several days.

Single-Crystal X-ray Diffraction

The collection of the X-ray diffraction intensities was performed on a SMART-APEX CCD diffractometer (Bruker AXS Inc.) with graphite-monochromated Mo-K_α radiation. Low temperature measurements at 173 °C were carried out using a 700 series cryostream cooler (Oxford Cryosystems). The reflection intensities were integrated with the SAINT subprogram[13] contained in the SMART software package.[14] An empirical absorption correction (SADABS)[15] was applied. The crystal structures were solved by direct methods and refined by full-matrix least-squares with the SHELXTL software package.[16] Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata(at)fiz-karlsruhe.de; on quoting the appropriate CSD number (423745 for α-$Si(NCO)_4$ and 423746 for β-$Si(NCO)_4$).

X-ray Powder Diffraction

For the XRD analysis, the liquid was filled in a 0.3 mm lithium borate glass capillary (Hilgenberg, glass no. 14), sealed and measured in transmission geometry. Ambient and low-temperature powder X-ray diffraction studies were performed on a STOE STADI P instrument with a linear PSD detector and with Cu-$K_{\alpha1}$ radiation (λ = 1.5406 Å) obtained from a curved Johansson-type monochromator using Ge

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(111). The special cooling setup used in this study consisted of a cold air blower with a AD51 Dry Air Unit (Oxford Cryosystems) allowing to maintain constant temperatures at $T < 0$ °C. The peak profiles and lattice parameters were determined by a LeBail-fit using the program GSAS.[17]

Thermal Analysis

For DSC (DSC 404, Netzsch), the sample was heated in a corundum crucible with a heating rate of 10 K·min^{-1} under argon, the cooling rate was 2 K·min^{-1}.

Spectroscopy

For the Raman experiments the sample was filled in a 0.3 mm lithium borate glass capillary (Hilgenberg, glass no. 14). The spectra were recorded with an excitation line of 632.817 nm (Labram 010, single grating) at acquisition times between 5 to 300 sec with a laser power between 0.4 and 0.004 mW. Liquid NMR spectra of the samples dissolved in [D$_8$]toluene were recorded using a Bruker Avance DPX-300 SB operating at 7.05 T. In the ^{13}C spectra, one signal was recorded at $\delta = 122.2$ ppm.

Theory

Atomic charges calculations were performed using the program CRYSTAL06.[18] Calculations have been performed using DFT with the hybrid functional B3LYP. The basis sets used were [5s4d1d] for silicon,[19] [3s2p1d] for carbon[20] and [3s2p1d] for nitrogen.[21] Concerning the oxygen atom, the inner [2s1p] exponents were taken as described in.[22] For the sp-exponent, a range from 0.5 to 0.191 was used and for the d-exponent a value of 0.8 was provided. Overall, the basis set for oxygen was [4s3p1d]. The geometrical parameters used were those obtained from the single-crystal studies.

Results and Discussion

Liquid Si(NCO)$_4$ was analyzed at room temperature by Raman spectroscopy. Bands were found at 1471 cm^{-1}, 618 cm^{-1}, 494 cm^{-1}, 294 cm^{-1} and 251 cm^{-1}, in full accordance with previously published data.[7] More recently, the Raman data was analyzed assuming a molecular structure with silicon coordinated tetrahedrally by four NCO ligands forming an isocyanate.[9]

The melting point of Si(NCO)$_4$ was determined as T = +26 °C by DSC (data not shown). X-ray powder diffraction studies have been performed starting with a frozen sample of Si(NCO)$_4$ in a capillary at T = –33 °C. All of the recorded reflections were indexed based on a monoclinic unit cell (a = 10.75 Å, b = 7.24 Å, c = 10.42 Å, β = 99.72°). The observed powder pattern and the resulting Le-Bail fit is shown in Figure 1.

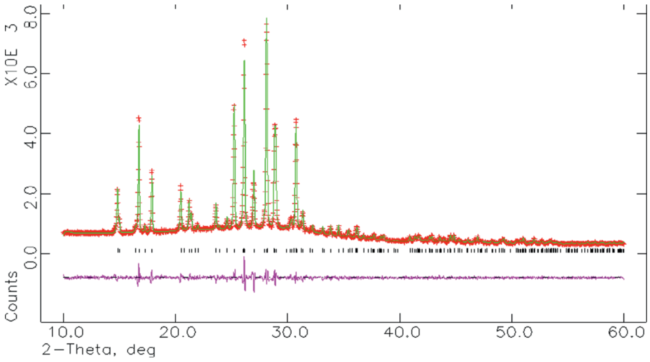

Figure 1. Le-Bail fit of the measured powder pattern of β-Si(NCO)$_4$ at T = –30 °C: monoclinic, a = 10.75 Å, b = 7.24 Å, c = 10.42 Å, β = 99.72°.

Single crystals were transferred directly from the cold solution (toluene solution cooled with acetone/dry ice) into a precooled inert oil. A crystal selected and picked in the oil matrix, was cooled down to T = –173 °C and measured at this temperature. The crystal structure was solved in the triclinic space group $P\bar{1}$. This structural data did not comply with the X-ray powder diffraction data obtained at T = –33 °C. In order to check whether this discrepancy could be the result of a phase transition, the single-crystal was warmed from T = –173 °C to T = –33 °C and measured again. In fact, the symmetry changed to monoclinic with the lattice constants a = 10.78(3) Å, b = 7.11(0) Å, c = 10.27(5) Å, β = 99.06(9)°, V = 777.39(1) Å^3, confirming those obtained from powder data.

The lattice parameters of the two modifications α-Si(NCO)$_4$ (triclinic) and β-Si(NCO)$_4$ (monoclinic) are similar and upon phase transition, one axis is halved. The molecular structure of Si(NCO)$_4$ and both crystal structures are shown in Figure 2, Figure 3 and Figure 4, further crystallographic information is listed in Table 1 and Table 2.

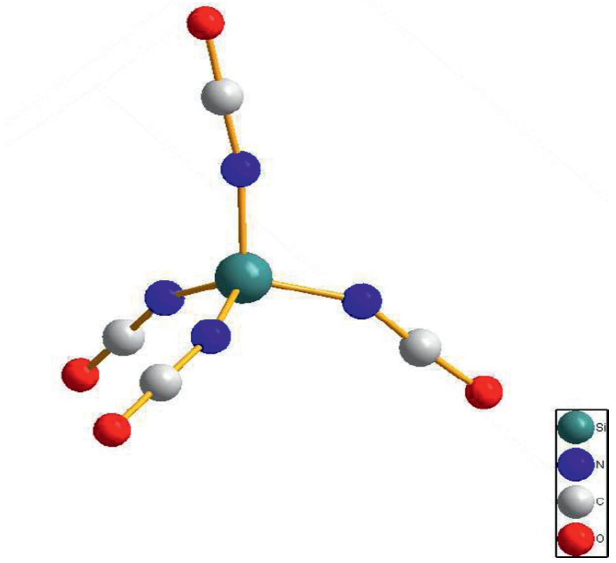

Figure 2. Molecular structure of Si(NCO)$_4$ in α-Si(NCO)$_4$.

The Si–N distances found (1.64–1.69 Å) are shorter than the values expected for a Si–N single bond of about 1.74 Å, whereas for a double bond Si=N values close to 1.56 Å have been reported.[23–25]. All remaining distances are in the expected ranges.

According to our structural studies, the Si–N=C=O group is definitely bent at the nitrogen atom in contrast to previous claims on the observation of a linear group of that kind.[8] The

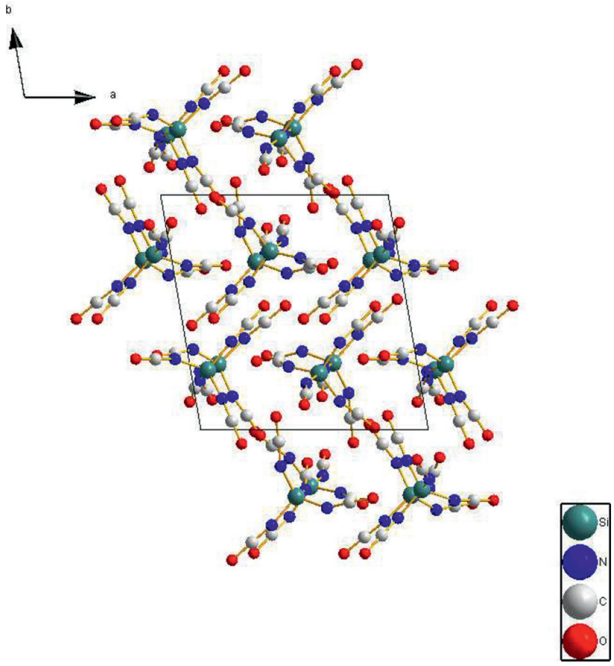

Figure 3. Crystal structure and packing of α-Si(NCO)$_4$ in the solid state (at T = –173 °C) along [001].

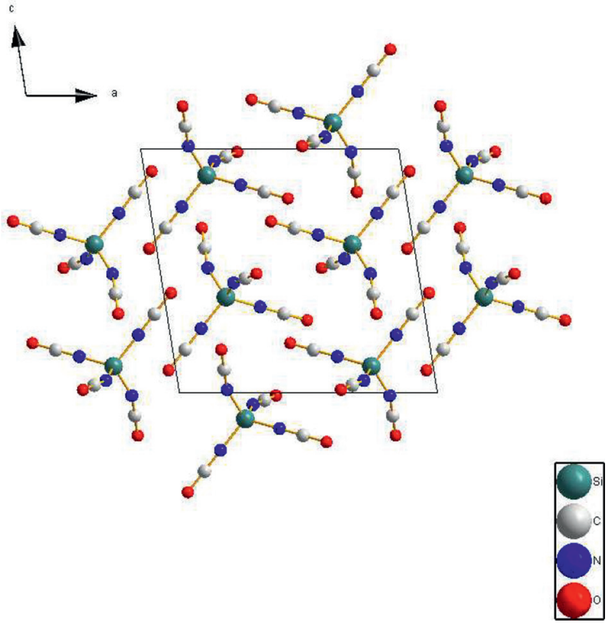

Figure 4. Crystal structure and packing of β-Si(NCO)$_4$ in the solid state (at T = –33 °C) along [010].

Table 1. Crystal data (single-crystal X-ray diffraction) and structure refinement for both polymorphs of Si(NCO)$_4$.

	α-Si(NCO)$_4$	β-Si(NCO)$_4$
Space group	$P\bar{1}$ (triclinic)	$P2_1/c$ (monoclinic)
Cell parameters /Å;°	a = 10.05(6)	a = 10.75(5)
	b = 10.50(6)	b = 7.24(4)
	c = 14.32(8)	c = 10.42(6)
	α = 91.62(0)	
	β = 92.31(6)	β = 99.72(9)
	γ = 99.68(3)	
Cell volume /Å^3	1488.6(1)	799.0(9)
Z	8	4
T /K	173	250
Formula weight /g·mol^{-1}	196.17	196.17
ρ_{calc} /g·cm^{-3}	1.75	1.63
Radiation source/λ /Å	0.71073	0.71073
Absorption coefficient /mm^{-1}	0.303	0.282
F (000)	784	392
θ-range /°	1.42 to 21.01	1.92 to 14.85
Index range	$-10 \le h \le 10$	$-7 \le h \le 7$
	$-10 \le k \le 10$	$-5 \le k \le 5$
	$-14 \le l \le 14$	$-7 \le l \le 7$
Reflections collected	8232	1246
Independent reflections	8232	301
Parameters/Restrains	470/0	118/0
GooF	1.152	0.814
min/max e-density /e·Å^{-3}	–0.387/0.401	–0.095/0.087
Final R indices $I > 2\sigma(I)$	R_1 = 0.0847	R_1 = 0.0355
	wR_2 = 0.2027	wR_2 = 0.0859
Final R indices (all data)	R_1 = 0.1354	R_1 = 0.0481
	wR_2 = 0.2386	wR_2 = 0.0983

Table 2. Bond lengths /Å and angles /° for both polymorphs of Si(NCO)$_4$.

	α-Si(NCO)$_4$	β-Si(NCO)$_4$
Si–N	1.64(7)–1.68(8)	1.65(2)–1.67(2)
C–N	1.17(1)–1.21(1)	1.10(2)–1.16(2)
C–O	1.16(1)–1.21(1)	1.12(2)–1.13(2)
N–Si–N	106.3(4)–112.5(4)	106.0(8)–112.3(1)
N–C–O	174.9(9)–178.8(1)	178.7(4)–179.2(2)
C–N–Si	150.1(8)–169.8(8)	157.4(2)–179.6(1)

bending angles are found to range from 149° to 170° in α-Si(NCO)$_4$.

In order to shed further light on this issue, we have performed a charge distribution analysis on solid Si(NCO)$_4$. The total energy calculation for both polymorphs have revealed that α-Si(NCO)$_4$ is about 12.3 eV more stable than the high-temperature form β-Si(NCO)$_4$. The calculated atomic charges for α-Si(NCO)$_4$ are Si: +1.81, N: –0.83, C: +0.87, O: –0.50, quite similar to those for β-Si(NCO)$_4$ with Si: +1.78, N: –0.89, C: +0.95, O: –0.49. Thus, silicon seems to bear a rather high positive charge compared to other compounds studied in a similar way.[26] According to these results, the previously assumed substantial charge transfer from nitrogen to silicon, which would be associated to a linear Si–N–C configuration, cannot be confirmed.

As a summary, we conclude that silicon tetraisocyante Si(NCO)$_4$ can be prepared in a very pure state as has been monitored by several experimental techniques. In neither of the solid-state polymorphs studied, indications for a linear Si–N=C=O arrangement was found. However, Si–N distances as observed turned out to be smaller than known for silicon-nitrogen single bonds.

Concerning chemical reactivity, nucleophiles (as H_2O or NH_3) will most likely attack at the Si–N single bond and not at the isocyanate function. Thus the respective reaction paths will be quite different to these encountered in the case of organic isocyanates.

The 3D molecular arrangement is reminiscent of a *bcc* packing.

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