Supplementary Material (ESI) for Chemical Communications

Supplementary Material

for the paper

Solvent-Free Methylthiomethyllithium $[LiCH_2SMe]_\infty$: Solid State Structure and Thermal Decomposition.

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1. Thermolysis Details:

The capillaries were dried by repeated cycles of heating followed by application of a dynamic vacuum and subsequent storage of the capillary in vacuo overnight. Since the screw-cap of the vial was made of plastic, higher temperatures could not be applied; the vials were thus dried just by storing them at room temperature in a dynamic vacuum for four hours.

2. Structure Solution and Refinement Details:

A high resolution X-ray powder diffraction pattern of $[LiCH_2SMe]_\infty$ was recorded at room temperature on a laboratory powder diffractometer (D-8, Bruker, Cu-Kα_1 radiation from primary Ge(111)-Johanson-type monochromator; Våntag-1 position sensitive detector) in Debye-Scherrer geometry with the sample sealed in a lithium borate glass capillary of 0.5 mm diameter (Hilgenberg glass No. 50). Data were taken from 8.0 – 68.0° 2Θ at a speed of 0.05°/minute. The step width was 0.017° 2Θ. The sample was spun during measurement for better particle statistics.

Data reduction on the powder diffraction pattern was performed using GUFI.[1] Indexing with ITO[2] led to a primitive monoclinic unit cell for $[LiCH_2SMe]_\infty$. Application of the extinction rules revealed $P2_1/c$ as the most probable space group. The number of formula units per unit cell was calculated to be $Z = 4$ from volume increments. The peak profiles and precise lattice parameters for all powder patterns were determined by LeBail-type fits[3] using the program GSAS[4]. The background was modeled manually using GUFI. The peak-profile was described by a pseudo-Voigt function in combination with a special function that accounts for the asymmetry due to axial divergence[5, 6]. The powder pattern of $[LiCH_2SMe]_\infty$ exhibits severe anisotropic peak broadening caused by lattice strain. The phenomenological strain model of Stephens[7] as implemented in GSAS was used to model the anisotropy of the FWHM. Nine parameters were refined for the monoclinic phase.

The crystal structure of $[LiCH_2SMe]_\infty$ was solved by global optimization in direct space using the DASH structure solution package[8]. The measured powder pattern at room temperature was subjected to a Pawley refinement[9] in space group $P2_1/c$, in order to extract correlated integrated intensities from the pattern. Good fits to the data were obtained. An internal coordinate description of the CH_2SMe moiety was constructed using bond lengths and angles from ref[3]. The positions of the lithium cation as well as the position and orientation and torsion angles of the CH_2SMe molecule in the unit cell were postulated and the trial structure

was subjected to a global optimization. The structures giving the best fit to the data in space group $P2_1/c$ was validated by Rietveld refinement[10] of the fractional coordinates obtained at the end of the simulated annealing run using the GSAS program. To stabilize the refinement of the CH_2SMe molecule, slack soft constraints for the bond lengths (C-S, C-H) and bond angles (H-C-S) were introduced.

1 R. E. Dinnebier and L. Finger, *Z. Krist.*, 1998, Supplement Issue **15**, 148.

2 J. W. Visser, *J. Appl. Crystallogr.*, 1969, **2**, 89.

3 A. Le Bail, H. Duroy and J. L. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447.

4 A. C. Larson and R. B. von Dreele, Los Alamos National Laboratory Report LAUR 86-748, *GSAS 1994, Version 2002* V, 2002.

5 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79.

6 L. W. Finger, D. E. Cox and A. P. Jephcoat, *J. Appl. Crystallogr.*, 1994, **27**, 892.

7 P. W. Stephens, *J. Appl. Crystallogr.*, 1999, **32**, 281.

8 W. I. F. David, K. Shankland and N. Shankland, *Chem. Commun.*, 1998, 931.

9 G. S. Pawley, *J. Appl. Crystallogr.*, 1981, **14**, 357.

10 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.

3. Rietveld Plot