

Crystal Structures of Polymerized LiCl·DMSO $\{2\text{LiCl}\cdot3\text{DMSO}\}_{\infty}$ and $\{\text{LiCl}\cdot\text{DMSO}\}_{\infty}$

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Abstract

Two novel LiCl·DMSO polymer structures were created by combining dry LiCl salt with dimethyl sulfoxide (DMSO). The initial synthesized phase had very small block-shaped crystals (<0.08 mm) with monoclinic symmetry and a 2 LiCl : 3 DMSO ratio. As the solution evaporated, a second phase formed with a plate-shaped crystal morphology. After ~ 20 minutes, large (>0.20 mm) octahedron-shaped crystals formed. The plate crystals and the octahedron crystals are the same tetragonal structure with a 1 LiCl : 1 DMSO ratio.

Chemical Context

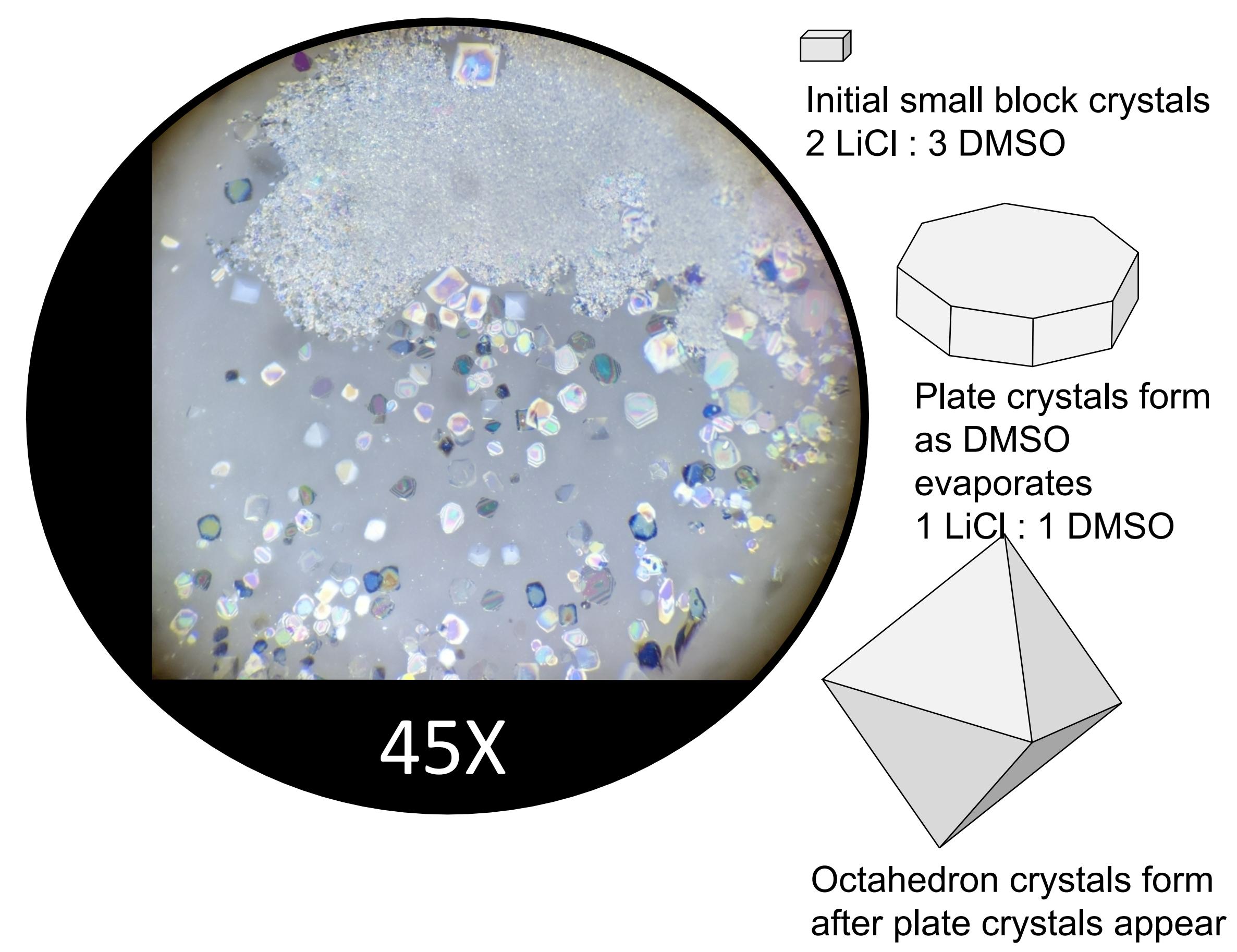
Lithium salts are soluble in a wide range of solvents and are widely used in lithium-metal and lithium-ion battery applications¹⁻³. While typically implemented as liquid electrolyte solutions, the lithium salt and solvent systems can also form complex molecular phases, including intercalating compounds⁴, crystalline solvates⁵, and polymeric structures⁶⁻⁷.

In preparation for battery research, dry LiCl was added to a jar of DMSO at a ratio of 5 g LiCl per 25 g DMSO (approximately twice the saturation limit⁸ at 25°C). The solution quickly becomes viscous unless stirred vigorously for a prolonged time, about three days. The small crystals that form from this process were collected for analysis. During sample preparation for single crystal X-ray diffraction[†], DMSO from the solution evaporated, resulting in a second, likely metastable, phase with different crystal morphology. These two LiCl·DMSO structures are novel, and other phases likely exist in the LiCl-DMSO system as a function of temperature, analogous to the LiCl-H₂O system⁹. This work aided the development of a new battery system.

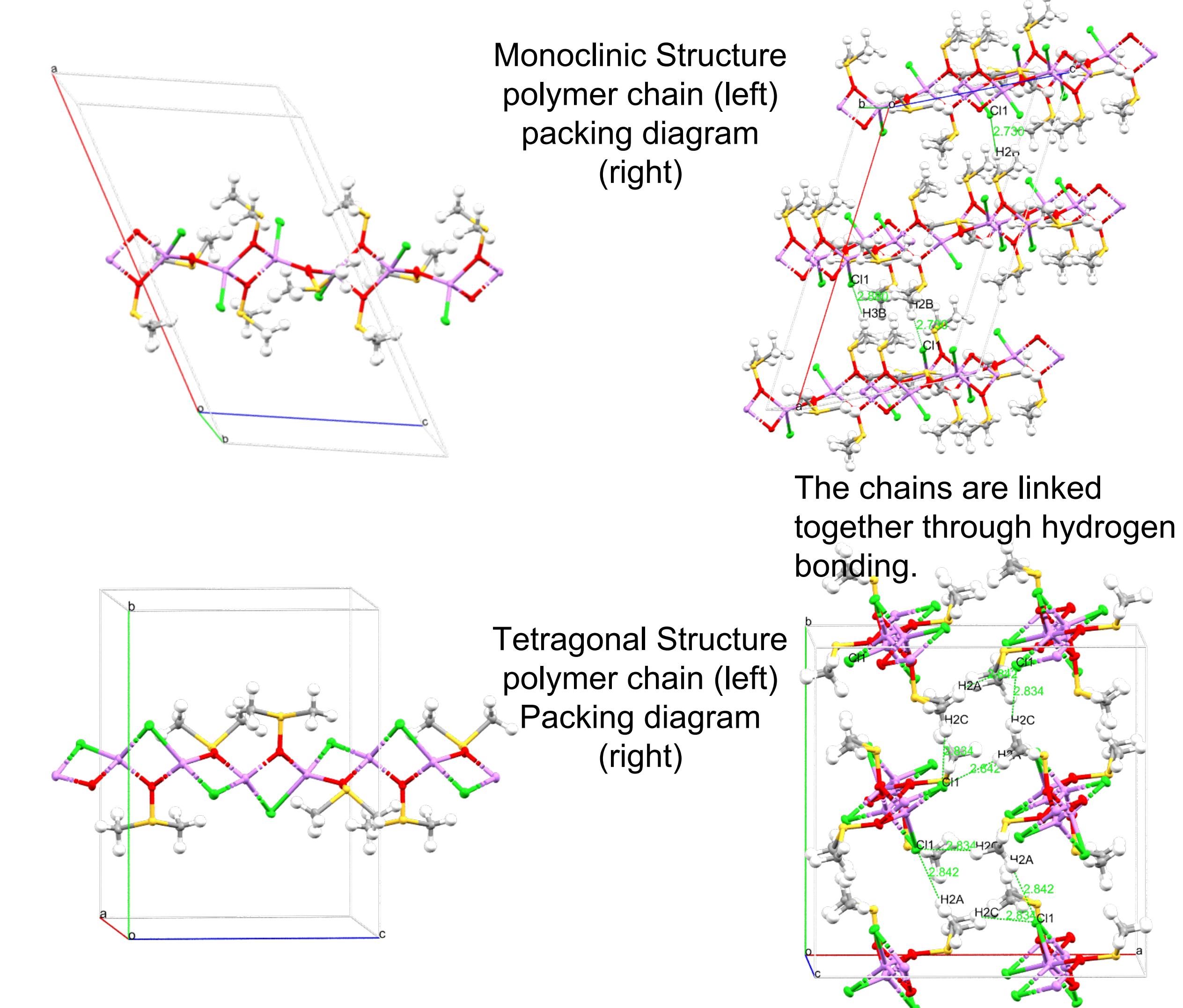
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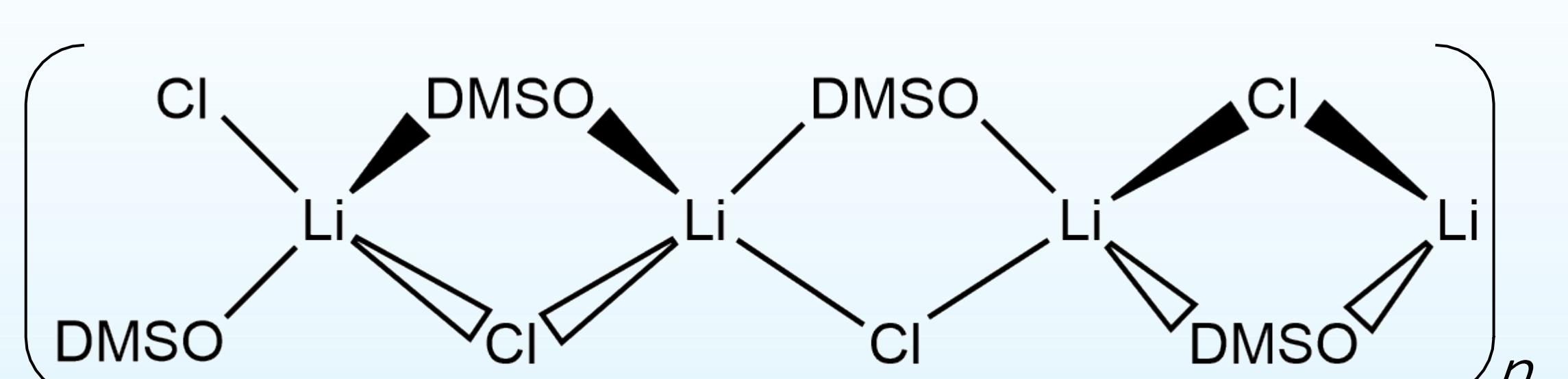
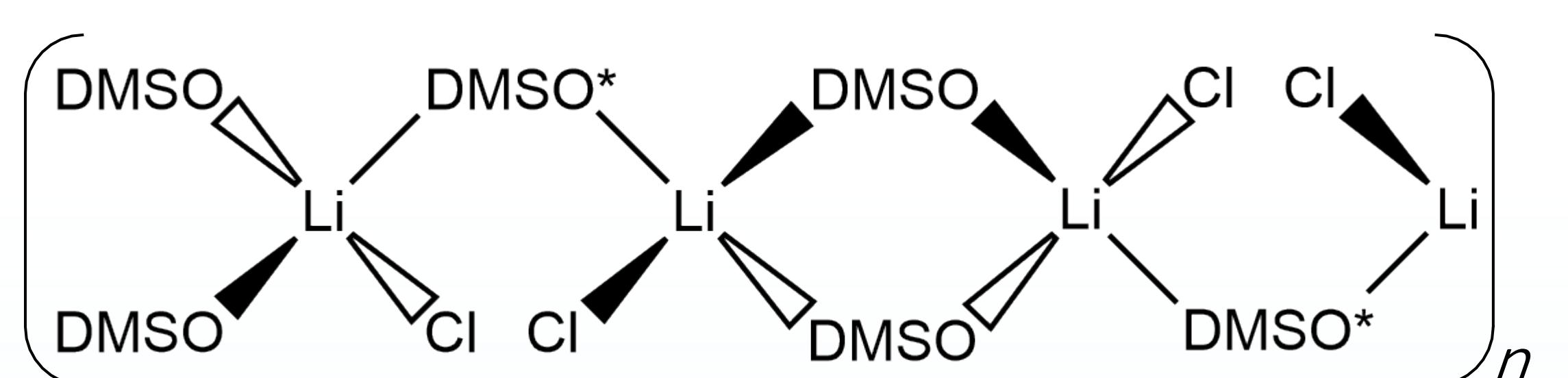
Phase Change



Crystal Structure



Polymer Schematics



Novel Phases

Only two compounds are in the CCDC Structural Database with the relevant chemistry, and neither have DMSO. One is a LiCl sulfolane adduct (SIWFOT¹⁰), and the other is a crown ether complex (XEBGIX¹¹). An extensive list of LiCl structures with various other ligands can be found in Ref. 7.

References

- 1 Bushkova, O. V., Yaroslavtseva, T. V., & Dobrovolsky, Y. A. (2017). *Russian Journal of Electrochemistry*. **53**(7), 677-699.
- 2 Mauger, A., Julien, C. M., Paoella, A., Armand, M., & Zaghib, K. (2018). *Materials Science and Engineering R*. **134**, 1-21.
- 3 Younesi, R., Veith, G. M., Johansson, P., Edström, K., & Vegge, T. (2015). *Energy Environ. Sci.* **8**(7), 1905-1922.
- 4 Yamada, Y., Takazawa, Y., Miyazaki, K., & Abe, T. (2010). *J. Phys. Chem. C*. **114**(26), 11680-11685.
- 5 Ugata, Y., Shigenobu, K., Tatara, R., Ueno, K., Watanabe, M., & Dokko, K. (2021). *Phys. Chem. Chem. Phys.* **23**(38), 21419-21436.
- 6 Rao, C. H., Rao, A. M., & Rao, C. N. R. (1984). *Inorg. Chem.* **23**(14), 2080-2085.
- 7 Chivers, T., Downard, A., Parvez, M., & Schatze, G. (2001). *Inorg. Chem.* **40**(8), 1975-1977.
- 8 Xin, N., Sun, Y., He, M., Radke, C., & Prausnitz, J. (2018). *Fluid Phase Equilibria*. **461**, 1-7.
- 9 Perron, G., Brouillet, D., & Desnoyers, J. E. (1997). *Can. J. Chem.* **75**(11), 1608-1612.
- 10 Harvey, S., Skelton, B. W., & White, A. H. (1991). *Aust. J. Chem.* **44**, 309-312.
- 11 Reuter, K., Rudel, S. S., Buchner, M. R., Kraus, F., & von Hänisch C. (2017). *Chem. Eur. J.* **23**, 9607-9617.