

Crystal Structures of Polymerized $\text{LiCl} \cdot \text{DMSO}$ $\{2\text{LiCl} \cdot 3\text{DMSO}\}_\infty$ and $\{\text{LiCl} \cdot \text{DMSO}\}_\infty$

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Abstract

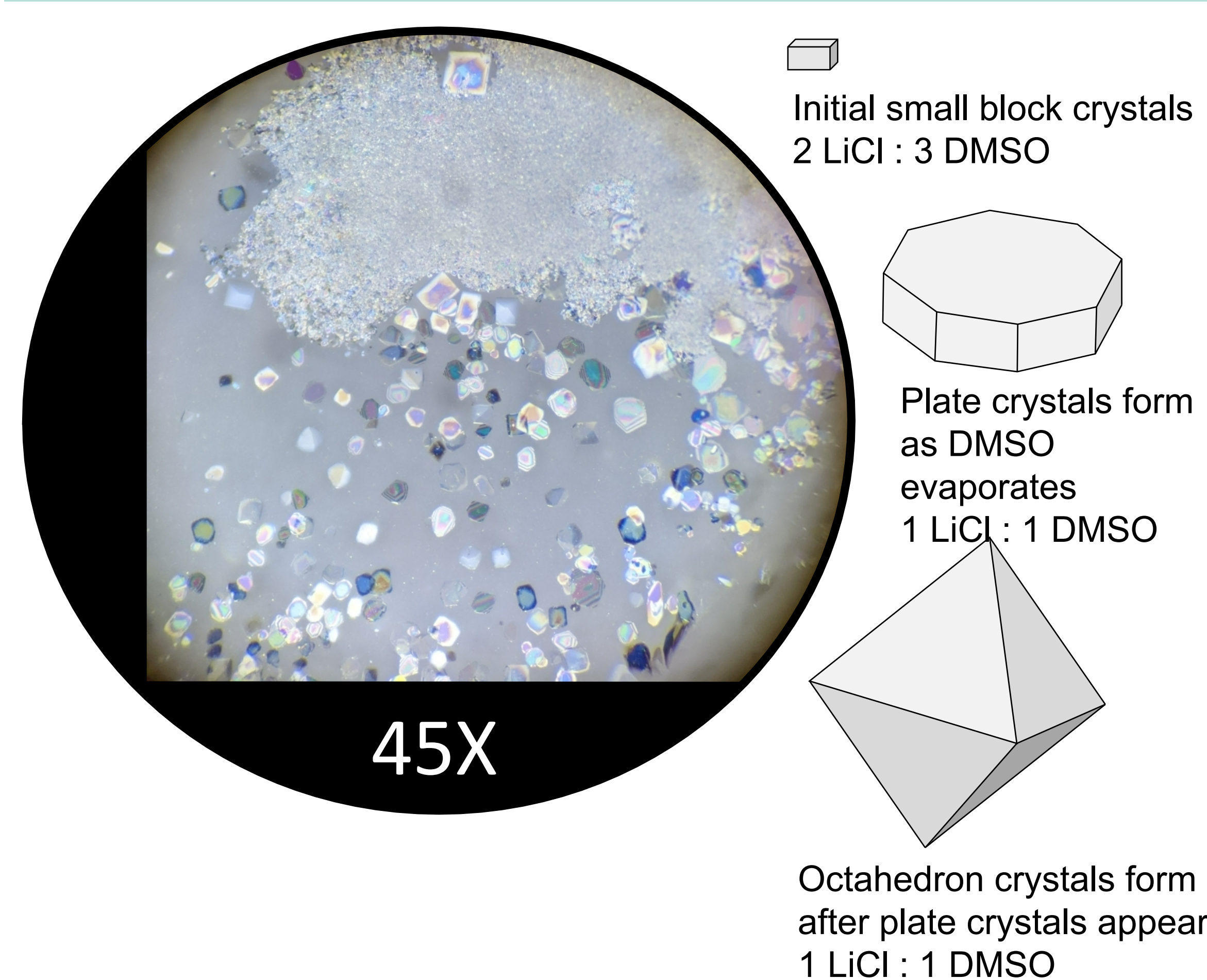
Two novel $\text{LiCl} \cdot \text{DMSO}$ polymer structures were created by combining dry LiCl salt with dimethyl sulfoxide (DMSO). The initial synthesized phase had very small block-shaped crystals (<0.08 mm) with monoclinic symmetry and a 2 LiCl : 3 DMSO ratio. As the solution evaporated, a second 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

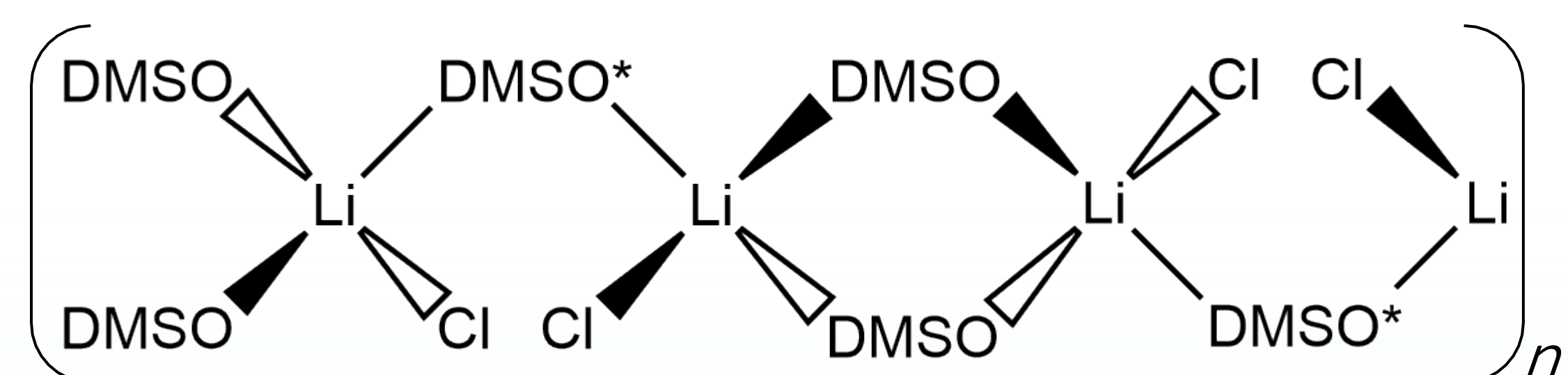
Lithium salts are soluble in a wide range of solvents and are widely used in lithium-metal and lithium-ion battery applications¹⁻³. While typically implemented as liquid electrolyte solutions, the lithium salt and solvent systems can also form complex molecular phases, including intercalating compounds⁴, 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 $\text{LiCl} \cdot \text{DMSO}$ structures are novel, and other phases likely exist in the LiCl -DMSO system as a function of temperature analogous to the LiCl - H_2O system⁹. This work aided the development of a new battery system.

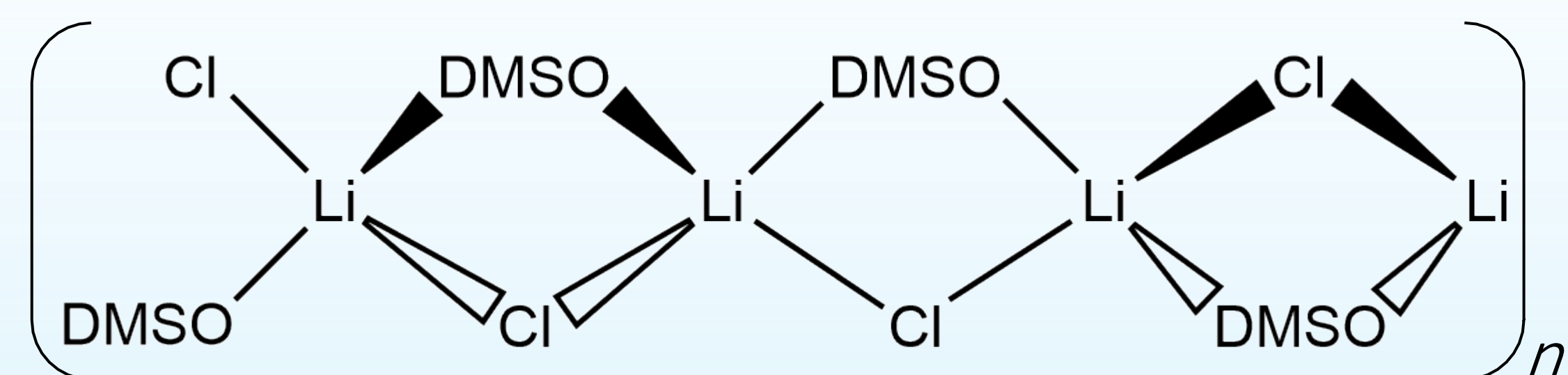
Phase Change



Polymer Schematics

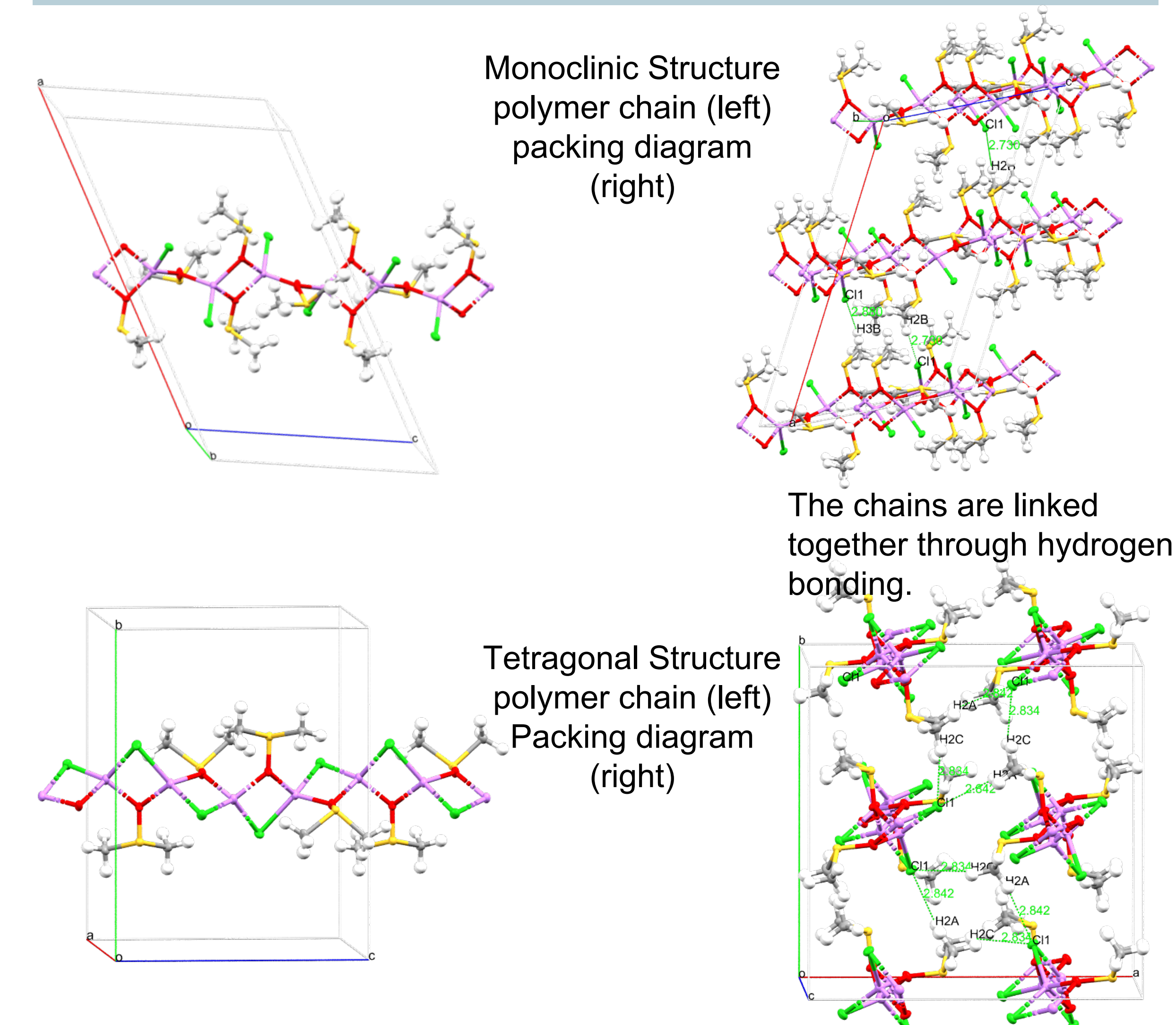


Monoclinic structure. The repeating unit of the polymer has 4 LiCl and 6 DMSO. The disordered DMSO molecule is marked with an asterisk.



Tetragonal structure. The repeating unit of the polymer has 4 LiCl and 4 DMSO.

Crystal Structure



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 (SIWFOT^{10}), and the other is a crown ether complex (XEGBIX^{11}). An extensive list of LiCl structures with various other ligands can be found in Ref. 7.

- References
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