

Poster Presentations

[MS25-P12] Air-Stable Cyclohexasulphur as Cocrystal.

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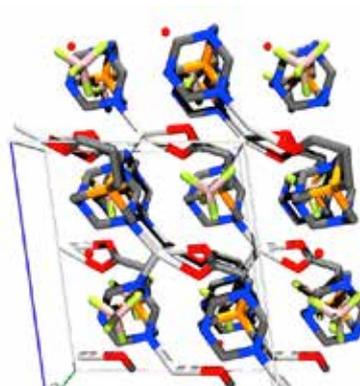
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Sulphur is an important element in industrial applications, such as sulphuric-acid synthesis and vulcanization of rubbers, as well as an essential element in living organisms; however, it is an undesirable contaminant in fossil fuels. Sulphur has more than 30 allotropes and shows a wide range of oxidation states from -2 to +6, resulting in a variety of physical and chemical properties. The control of the chemical states of sulphur is, therefore, crucial in its applications. In particular, studies on the stability and controllability of allotropes of sulphur are vital in both basic and applied sciences. In nature, the cyclooctasulphur form is the most commonly found solid-state and smallest air-stable allotrope. Although cyclohexasulphur (cyclo-S₆) has been synthesized and characterized in studies using single-crystal X-ray diffraction experiments, the crystals of this molecule become non-crystalline within a few days.[1] Recently, we discovered new air-stable cyclo-S₆ molecules in the solid state via crystallization of cocrystals with 3,5-diphenyl-1,2,4-dithiazol-1-ium (dpdti) iodide, which was stored in cocrystals for at least half a year.[2]

A new air-stable cyclo-S₆ was discovered in the crystal of dpdti iodide, formed by cocrystallization. The dpdti was synthesized via an oxidation reaction of thiobenzamide with iodine in benzene. The cyclo-S₆ molecule obtained after the recrystallization of dpdti iodide from acetonitrile solvent. A single-crystal X-ray



structure analysis using a synchrotron X-ray characterizes all molecules, cyclo-S₆, dpdti, and iodide, in cocrystal. The conformation of the cyclo-S₆ molecule was discovered as a chair structure. The average S–S distance (2.062 Å) in the cyclo-S₆ molecule of cocrystal was in the range of the bond lengths in neutral sulphur rings, which is characteristic for a normal S–S single bond.[3] In the crystal packing of cocrystal, the cyclo-S₆ molecule is a self-assembly, surrounded by the dpdti cation and iodide anion. The short contact distances among cyclo-S₆, dpdti, and iodine, S···H, S···S, and S···I, were found to be lower than the summation of the van der Waals radius of nearest-neighbor atoms. The high stability of cyclohexasulphur may be enhanced by weak intermolecular effects such as van der Waals forces, akin to the Sn ring in zeolites and sodalites.[4]

In thermal analysis, we clarified the thermal stability of cyclo-S₆ in cocrystal. The differential thermal analysis curve of cocrystal displayed an endothermic peak at 446 K owing to thermal decomposition of cyclo-S₆, though an unstable cyclohexasulphur molecule decomposes at 323 K. The thermal decomposition temperature of cyclo-S₆ was found to increase significantly because of cocrystallization.

We achieved a method to turn an unstable molecule into a stable crystalline molecule of cyclo-S₆ that maintains its origin structure by cocrystallization. Crystal engineering of cocrystals resulted in air-stable cyclo-S₆, though the stability of allotropes of sulphur has not yet been completely elucidated. Cocrystallization

is effectively used as a method to control the stability and activity of sulphur, for improved utilization.

[1] Steidel, J., Pickardt, J., Steudel, R. (1978). *Zeitschrift für Naturforschung. Teil B, Anorganische Chemie, organische Chemie* **33**, 1554–1555.