

Poster Presentations

[MS25-P24] Formation of Bifurcated S-H...O Hydrogen Bonds in Cysteine Containing Crystal Structures on Increasing Pressure.

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In a series of recent publications, the crystals of L- and DL-cysteine were shown to undergo multiple phase transitions upon variation of temperature and pressure. All these transitions are related to rotation of the amino acid side chain accompanied by switching the weak S-H...X hydrogen bonds. Accordingly, cysteine-containing crystal structures should be stabilized with respect to phase transitions by measures that reduce the mobility of the side chain in the crystalline environment. In the recent work, we show that this can be achieved by increasing the significance of the side chain -SH group as a participant in intermolecular hydrogen bonds, either by N-acetylation, which removes the strong -NH₃⁺ donor of cysteine and leaves a system without strong charge-assisted interactions, or by co-crystallization with an acid (oxalic acid) that converts the amino acid to a cation and itself forms a strong anion H-bond acceptor, thus boosting the importance of potential -SH donors. The crystal structures of the three compounds N-acetyl-L-cysteine, DLcysteinium semioxalate, and bis(DL-cysteinium) oxalate have thus been studied with variation of temperature and pressure. Cooling down to 4 K and increasing pressure up to 9.5 GPa did not result in any structural phase transitions in N-acetyl-L-cysteine and bis(DL-cysteinium) oxalate. In case of DL-cysteinium semioxalate, increasing pressure caused a phase transition at a much higher pressure (~6 GPa), compared to the ranges of pressure-induced phase transitions observed earlier for both monoclinic and orthorhombic L-cysteine (2.5–3.9 GPa

and 1.1–2.5 GPa, respectively) or DL-cysteine (0.1–5 GPa). This phase transition had a large hysteresis, so that the reverse transformation on decompression was observed at ~3.7 GPa only, and was accompanied by a change in molecular conformations, as well as by the reorganization in the N-H... O hydrogen bonds in the crystal structure. The precise polarized Raman spectroscopy from oriented single crystals and single crystal X-ray diffraction study of N-acetyl-L-cysteine reveals continuous changes in S-H...O hydrogen bond on increasing pressure resulting in formation of bifurcated SH...O hydrogen bond where oxygens from carbonyl and carboxyl groups act as acceptors. The blue shift of stretching vibrations of -SH group in orthorhombic and monoclinic L-cysteine on increasing pressure at the shortening of S...O distance may be explained by formation of the bifurcated hydrogen bonds in crystal structures. The work was partly supported by Integration Project of SB RAS No. 108 and the Ministry of Education and Science of the Russian Federation (agreement No. 14.B37.21.1093).

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