

Crystal Structure and Thermal Solid-State Reactivity of Ammonium Cyanoureate $\text{NH}_4[\text{H}_2\text{NC}(=\text{O})\text{NCN}]$

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The ammonium salt of cyanourea $\text{NH}_4[\text{H}_2\text{NC}(=\text{O})\text{NCN}]$ has been synthesised *via* an acid-base route from the parent acid and characterized by single-crystal and powder X-ray diffraction, NMR and vibrational spectroscopy, mass spectrometry as well as thermal analysis. The molecular salt ($P2_1/c$, $a = 388.95(8)$, $b = 1121.0(2)$, $c = 1096.4(2)$ pm, $\beta = 92.57(3)^\circ$, $V = 477.5(2) \cdot 10^6$ pm³, $Z = 4$, $T = 140$ K) which may formally be derived from the related compound ammonium dicyanamide $\text{NH}_4[\text{N}(\text{CN})_2]$ by addition of one molecule water, consists of isolated ammonium and cyanoureate ions which are assembled *via* $\text{H} \cdots \text{N}$ and $\text{H} \cdots \text{O}$ hydrogen bonds, forming a three-dimensional arrangement. At elevated temperatures, ammonium cyanoureate undergoes a complex transformation affording the formation of urea and cyanoguanylurea $\text{H}_2\text{NC}(=\text{O})\text{NHC}(\text{NH}_2)=\text{NCN}$ or the isomeric ammeline $(\text{C}_3\text{N}_3)(\text{NH}_2)_2(\text{OH})$ as the main products, depending on the reaction conditions. The transformation is accompanied by consecutive reactions such as proton transfer and the dis- and re-assembly of molecular fragments, yielding a macroscopic segregation of the reaction products. The conversion represents yet another example of a complex reaction proceeding in the solid-state.

Key words: Solid-State Reaction, Crystal Structure, Cyanourea, Thermal Reactivity