Ca(SCN)$_2$ and Ca(SCN)$_2 \cdot 2$ H$_2$O: Crystal Structure, Thermal Behavior and Vibrational Spectroscopy

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Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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Thiocyanates, Vibrational Spectroscopy, Hydrogen Bonds

The dehydration of Ca(SCN)$_2 \cdot 4$H$_2$O yields single crystals of Ca(SCN)$_2 \cdot 2$ H$_2$O as well as of Ca(SCN)$_2$. Ca(SCN)$_2 \cdot 2$ H$_2$O crystallizes with a hitherto unknown structure (orthorhombic, Pnma, $Z = 4$, $a = 1280.1(2)$ pm, $b = 790.3(1)$ pm, $c = 726.9(1)$ pm, $R_{all} = 0.0430$). The Ca$^{2+}$ ions are surrounded by four SCN$^{-}$ ions and four water molecules. The polyhedra are connected to chains along [010] via common oxygen atoms. The SCN$^{-}$ ions connect these chains to a three-dimensional network so that each thiocyanate group is linked to two Ca$^{2+}$ ions. Hydrogen bonding with sulfur atoms as acceptors is observed. The crystal structure of Ca(SCN)$_2$ (monoclinic, C2/c, $Z = 4$, $a = 961.7(2)$ pm, $b = 642.4(2)$ pm, $c = 787.2(2)$ pm, $R_{all} = 0.0673$) consists of alternating layers of Ca$^{2+}$ and SCN$^{-}$ ions. The cations are surrounded by four sulfur and four nitrogen atoms in form of a square antiprism. According to $\frac{3}{2} \cdot [\text{Ca(SCN)}_{8/4}]$ each SCN$^{-}$ ion connects four Ca$^{2+}$ ions with each other. Thermal investigations show a phase transition of Ca(SCN)$_2 \cdot 4$ H$_2$O followed by dehydration to Ca(SCN)$_2$ which finally decomposes yielding CaS. IR and Raman measurements have been performed and the resulting frequencies assigned and discussed.