$Ca(SCN)_2$ and $Ca(SCN)_2 \cdot 2\ H_2O$: 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 $Ca(SCN)_2 \cdot 4H_2O$ yields single crystals of $Ca(SCN)_2 \cdot 2\ H_2O$ as well as of $Ca(SCN)_2$. $Ca(SCN)_2 \cdot 2\ H_2O$ crystallizes with a hitherto unknown structure (orthorhombic, *Pnma*, $Z = 4$, $a = 1280.1(2)$, $b = 790.3(1)$, $c = 726.9(1)$ 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*, $Z = 4$, $a = 961.7(2)$, $b = 642.4(2)$, $c = 787.2(2)$ 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 $^3_\infty[Ca(SCN)_{8/4}]$ each SCN^- ion connects four Ca^{2+} ions with each other. Thermal investigations show a phase transition of $Ca(SCN)_2 \cdot 4\ H_2O$ 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.