

Quadratate und Hydrogenquadratate cyclischer Stickstoffbasen mit Schicht-, Ketten- und Leiterstrukturen

Squarates and Hydrogensquarates of Cyclic Nitrogen Bases with Layer-, Chain- and Ladder-Structures

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The synthesis and single crystal X-ray structures of four adducts of squaric acid with cyclic nitrogen bases are reported. Extensive hydrogen bonding, ionic interactions and (in one case) π - π -interactions lead to layered, and to two- and three-dimensional assemblies. [Pyrimidinium][hydrogenquadratate] (**1**) has a layer structure, consisting of head-to-tail infinite chains of pyrimidinium and $[\text{HC}_4\text{O}_4]^-$ ions, which are cross-linked by short $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. $[\text{C}_9\text{H}_{11}\text{N}_2][\text{HC}_4\text{O}_4]\cdot 0.5\text{H}_2\text{C}_4\text{O}_4$ (**2**), the adduct of a benzodiazepin and squaric acid, has a ladder-structure. Chains of $[\text{HC}_4\text{O}_4]^-$ ions and $\text{H}_2\text{C}_4\text{O}_4$ molecules in alternating order form the ladder-beam. Layers of cations and anions in the ratio 2:1 build the crosspieces at an angle of 49° to the beam. The layers contain dimers of $[\text{HC}_4\text{O}_4]^-$ ions. $[\text{H}_2\text{L}^2][\text{HC}_4\text{O}_4]_2$ (**3**) with $\text{L}^2 = 5,6,7,8,9,14,15,16,17,18$ -decahydrodibenzo[e,l]-1,4,8,11-tetraaza-cyclotetradecine shows zigzag chains made of $[\text{HC}_4\text{O}_4]^-$ ions. Between the $[\text{H}_2\text{L}^2]^{2+}$ and the $[\text{HC}_4\text{O}_4]^-$ ions π - π interactions exist besides up to four $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. The $[\text{H}_2\text{L}^2]^{2+}$ ions possess two different conformations. $[\text{H}_2\text{cyclam}][\text{C}_4\text{O}_4]\cdot 4\text{H}_2\text{O}$ (**4**) contains strongly undulated layers of the composition $[\text{C}_4\text{O}_4\cdot 4\text{H}_2\text{O}]^{2-}$. The cations, which show two intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds with $\text{N}\cdots\text{N}$ distances of 2.870 (3) Å, are interlinked at an angle of 41.5° .

Key words: Hydrogen Bonds, Squaric Acid Adducts, Cyclic Nitrogen Bases