Niedere Hydrate aliphatischer primärer Amine. Neue Untersuchungen zu Bildung und Struktur [1]

Lower Hydrates of Aliphatic Primary Amines.
New Studies of Formation and Structure [1]

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Amine Hydrates, Hydrates, Melting Diagram, Crystal Structure, Hydrogen Bonding

After earlier work in this laboratory on lower hydrates of amines, the melting diagram of the system 1,8-diaminooctane/water and six new crystal structures of hemi- and monohydrates of terminal primary n-alkylamines and diamines have been determined. In the hydrates 1-$PrNH_2 \cdot 0.5\ H_2O$ (space group $C\ 2/m$ with $Z = 4$ formula units per unit cell), $1\text{-}HexNH_2 \cdot 0.5\ H_2O$ ($P1$, $Z = 2$) and $H_2N(CH_2)_nNH_2 \cdot H_2O$ with $n = 4, 6, 8$ ($P\ 2_1/c$, $Z = 4$), the O and N atoms are hydrogen-bonded into a two-dimensional array analogous to the mutual coordination of cations and anions in the CdI_2 structure type: $[ON_{6/3}] \sim [CdI_{6/3}]$. In the hydrate $H_2N(CH_2)_2NH_2 \cdot H_2O$ ($C\ 2/c$, $Z = 4$), the H_2O/NH_2 partial structure is three-dimensional but can be reduced, by neglecting the longest H bond, to an array which is again just two-dimensional and related now to the red HgI_2 structure type: $[ON_{4/2}] \sim [HgI_{4/2}]$. In all the monohydrates, the arrays as defined are crosslinked by the alkylene chains of the bifunctional amine molecules.

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