Structural Links between Zeolite-type and Clathrate Hydrate-type Materials

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A reconsideration of crystallographic data from the literature reveals that some crystalline alkylammonium(alumino)silicate hydrates are host–guest compounds, which provides a structural link between zeolite-type and clathrate hydrate-type materials; such compounds may be of significant interest as crystalline model compounds in studies on amorphous silica hydrogels and on the atomic scale mechanisms of zeolite crystallization (*e.g.* the template effect).

Zeolites and their related materials (*e.g.* clathrasiles and zeosiles)[1,2] and clathrate hydrates and their related materials *e.g.* alkylammoniumhydroxide and alkylammoniumfluoride hydrates)[3,4] are two well-known classes of host–guest compounds in inorganic chemistry. The host structures are based on three-dimensional four-connected nets $^3_\infty[TX_{4/2}]$ with T = Si, Al and X = O in zeolite-type structures and T = O, F and X = H in clathrate hydrate-type structures. The main difference between both classes of materials is the kind of chemical bonds connecting the T atoms in the host structures, rather than the framework topologies. The bonds are strong covalent-ionic bridges T–O–T or comparatively weak hydrogen bonds $T\text{–}H\cdots T$, respectively.

Zeolite- and clathrate hydrate-type materials are commonly considered as two independent classes of host–guest compounds, which are frequency compared mainly with respect to their framework topologies.[5] However, a reconsideration of the structural data of some crystalline alkylammonium(alumino)silicate hydrates taken from the literature reveals that these compounds provide a structural link between zeolite- and clathrate hydrate-type materials. The crystal structures of the following hydrates are dealt with here: $[N(CH_3)_4]_8[Si_8O_{20}]\cdot 64.8H_2O$[6] which contains ideally 67 H_2O molecules in the formula unit (**I** hereafter), $[N(CH_3)_4]_4[Al_4Si_4O_{12}(OH)_8]\cdot 24H_2O$[7] (**II**) and $[N(C_4H_9)_4]_3[Si_8O_{12}(OH_{0.5})_8]_3[H_{41}O_{16}]$[8] (**III**). The crystals are composed of alkylkammonium cations and oligomeric silicate or aluminosilicate anions with double four-ring structures and H_2O molecules. Crystal data and the atomic parameters together with specific details of the structures are presented elsewhere.

The alkylammonium(alumino)silicate hydrates are host–guest compounds with anionic frameworks in which anions and H_2O molecules (**I** and **II**) or anions only (**III**) are linked *via* hydrogen bonds $O\text{-}H\cdots O$. Polyhedral cavities (cages) are formed by the host structures. For illustration, a part of the crystal structure of **I** is shown in Fig. 1; see also the drawings of the structures of **II** and **III** in the original papers.[7,8]

The host structures are based on three-dimensional four-connected nets if the Si and Al atoms of the anions, the O atoms of the H_2O molecules and the terminal O atoms of the double four-ring anions (except in the case of **III** where these O atoms are only two-connected) are taken as tetrahedral T atoms. The O atoms of some H_2O molecules in hydrate **I** are only three-connected, however. Then, both covalent-ionic (Si–O–Si, Al–O–Si) as well as hydrogen bonds ($Si\text{–}O\text{–}H\cdots{}^-O\text{-}Si$, $HOH\cdots{}^-O\text{-}Si$, $Al\text{-}O\text{-}H\cdots OH_2$, $HOH\cdots OH_2$) occur in the host structures. For this kind of framework the term heterogeneous tetrahedral net is suggested for distinction from the homogeneous tetrahedral net of zeolite- and clathrate hydrate-type materials, in which either only covalent-ionic bridges or only hydrogen bonds are present.

Approximately continuous change exists between the homogeneous nets of zeolite- and clathrate hydrate-type structures with intermediate heterogeneous nets of varying compositions of anions and H_2O molecules in the series of the alkylammonium(alumino)silicate hydrates. This can be seen in Fig. 2, where selected polyhedral cavities of the hydrates **I**, **II** and **III** are shown along with the $[4^66^8]$ truncated octahedral cages of the zeolite-type compound $[N(CH_3)_4]_2[Al_2Si_{10}O_{24}]$[9] and the clathrate hydrate-type compound $\beta\text{-}[N(CH_3)_4]OH\cdot 4.6H_2O$,[4,10] which both crystallize with the sodalite[2] structure type. The heterogeneous net of hydrate **II** is of the same AST[2] topology as the homogeneous net of the zeolite-type materials octadecasil[11] and $AlPO_4$-16.[12] The close structural relationship of hydrate **III** with zeolite A (LTA) has previously been discussed.[8]

H_2O molecules may be part of the host structures (**I** and **II**) or may be present as guest species as in many zeolites; *viz.* the protonated water cluster $[H_{41}O_{16}]^{9+}$ in hydrate **III** [Fig. 2(*b*)].

The orientation of the cationic guest species $[N(CH_3)_4]^+$ within the different large polyhedral cavities of the compounds under consideration varies with the composition of the homogeneous/heterogeneous nets, *i.e.* the orientation depends significantly on the weak guest–host interactions $C\text{–}H\cdots O$; compare the cages (*a*), (*c*), (*d*), (*e*) and (*f*) in Fig. 2.

From the examples presented in this paper it is concluded that crystalline structural links with heterogeneous nets exist between zeolite- and clathrate hydrate-type materials. Heterogeneous but amorphous net structures also occur in silica

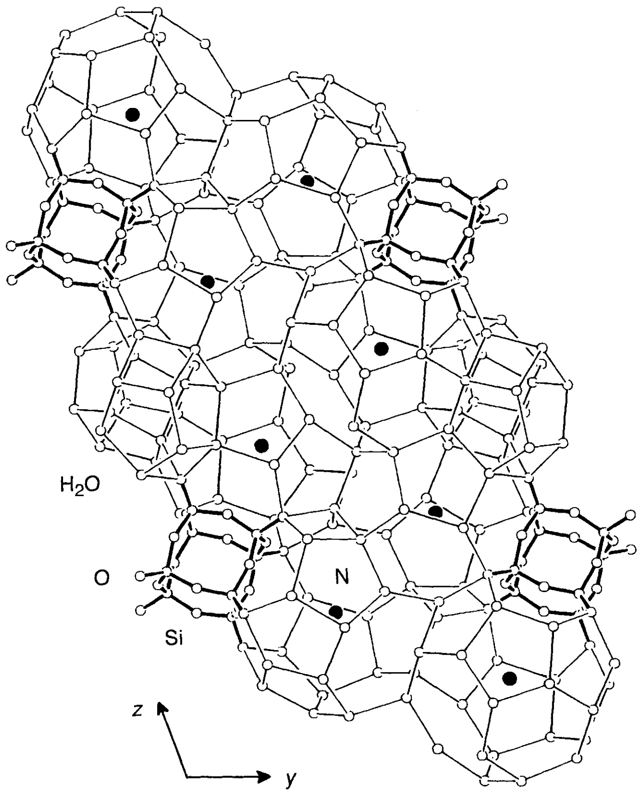
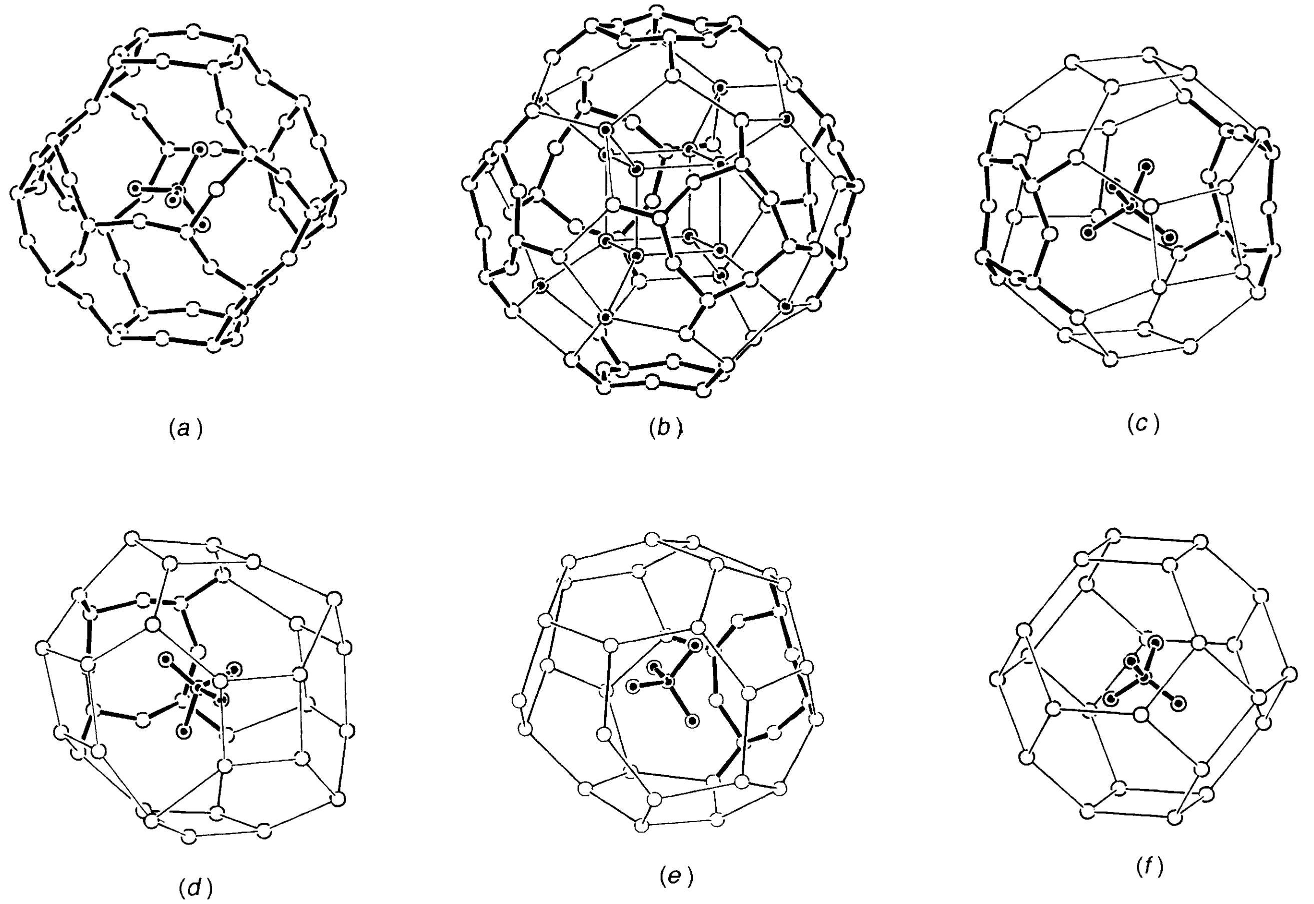


Fig. 1 ORTEP[14] diagram of the crystal structure of $[N(CH_3)_4]_8[Si_8O_{20}]\cdot 67H_2O$, illustrating the infinite heterogeneous net assembly of hydrogen-bonded double four-ring anions $[Si_8O_{20}]^{8-}$ and H_2O molecules (host structure). Thick lines represent covalent-ionic bonds Si–O, thin lines represent contacts between donor and acceptor atoms in hydrogen bonds $O\text{-}H\cdots O$. Of the cationic guest species $[N(CH_3)_4]^+$ within the large polyhedral cavities only the N atoms are shown by ●, Si and O atoms are shown as ○ with arbitrary radii.



(a) (b) (c)

(d) (e) (f)

Fig. 2 ORTEP[14] drawings of selected cages with entrapped cationic guest species of the host–guest compounds (*a*) $[N(CH_3)_4]_2[Al_2Si_{10}O_{24}]$, (*b*) $[N(C_4H_9)_4]_3[Si_8O_{12}(OH_{0.5})_8]_3[H_{41}O_{16}]$, (*c*) and (*d*) $[N(CH_3)_4]_4[Al_4Si_4O_{12}(OH)_8]\cdot 24H_2O$, (*e*) $[N(CH_3)_4]_8[Si_8O_{20}]\cdot 67H_2O$, and (*f*) β-$[N(CH_3)_4]OH\cdot 4.6H_2O$. The $[N(CH_3)_4]^+$ cations are shown in one orientation only, although they are orientationally disordered in most polyhedral cavities. Atoms are represented by ○, the atoms of the guest species are marked by ◉, H atoms are omitted for clarity. Thick lines represent covalent–ionic bonds, thin lines represent hydrogen bonds.

hydrogels and the intermediate gel phases formed during most hydrothermal zeolite syntheses. Host–guest compounds such as those discussed above may be considered as crystalline model compounds in studies on amorphous materials and may contribute to a deeper understanding of the structure-directing (templating) or void-filling role of organic cations and molecules in zeolite crystallization.[13]

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