A new mineralomimetic $Cd(CN)_2$ host framework which is intermediate between H- and L-cristobalite-like frameworks

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The three-dimensional $Cd(CN)_2$ clathrate enclathrating the CH_2BrCH_2Br molecule produces a new mineralomimetic $Cd(CN)_2$ host framework (space group $I4_1/amd$) which is intermediate between H-cristobalite- (space group Fd-3m) and L-cristobalite-like species (space group $P4_12_12$).

In natural crystalline SiO_2 minerals, the SiO_4^{4-} tetrahedra are linked so that every oxygen atom is shared between two tetrahedra, giving the composition SiO_2. Likewise, the mineralomimetic $Cd(CN)_2$ host frameworks in the $Cd(CN)_2 \cdot n$G clathrates are topologically similar to the polymorphic forms of SiO_2.[1–5] The nature of the $Cd(CN)_2$ host frameworks depends on guest molecules. The H-cristobalite, L-cristobalite and H-tridymite-like hosts of $Cd(CN)_2$ were obtained using guest molecules of different properties, sizes, shapes and symmetries. For example, $CHCl_2CHCl_2$,[2,3] $CHCl_2CH_2Cl$[4] and Bu_2O[4] produce an H-cristobalite-like $Cd(CN)_2$ host framework (Fd-3m), an L-cristobalite-like species ($P4_12_12$) and an H-tridymite-like species ($P6_3/mmc$), respectively. Selecting guest molecules provides new mineralomimetic $Cd(CN)_2$ host frameworks with a body-centered tetragonal $I4_1/amd$ lattice which is intermediate between the H-cristobalite-like species (space group Fd-3m) and the L-cristobalite-like species (space group $P4_12_12$).

In nature, H-cristobalite is the high-temperature polymorph of SiO_2, existing above 1743 K. However, H-cristobalite (cubic space group Fd-3m) metastably exists up to above 540 K, where it experiences a rapid and reversible inversion to L-cristobalite (tetragonal space group $P4_12_12$).[6] A crystallograhic comparison between the two structures has been reported.[7] To the best of my knowlege, the cristobalite structure which is intermediate between H-cristobalite (Fd-3m) and L-cristobalite ($P4_12_12$) has not previously been obtained and/or found. From a crystallographic view point, an intermediate structure with a tetragonal space group $I4_1/amd$ is possible.

The new mineralomimetic framework of $Cd(CN)_2$ between the H and L-cristobalite-like types has been obtained using CH_2BrCH_2Br as guest. Treating an equimolar aqueous solution of $CdCl_2 \cdot 2.5H_2O$ and $K_2[Cd(CN)_4]$ with 1,2-dibromoethane gives colourless tetragonal crystals of $Cd(CN)_2 \cdot CH_2BrCH_2Br$. The IR spectrum indicates that the conformation of CH_2BrCH_2Br in $Cd(CN)_2$ is *trans* (1184, 594 cm^{-1}), based on the neat CH_2BrCH_2Br data.[8]

The X-ray single crystal determination† (Fig. 1) shows that the topological properties of the host framework in $Cd(CN)_2 \cdot CH_2BrCH_2Br$ are intermediate between those of H- and L-cristobalite. For example, $Cd(CN)_2 \cdot CMe_4$[3] and $Cd(CN)_2 \cdot Pr^iBr$[4] contain mineralomimetic $Cd(CN)_2$ frameworks analogous to H- and L-cristobalite SiO_2, respectively: $Cd(CN)_2 \cdot CMe_4$, space group Fd-3m, a = 12.757(2) Å, Z = 8; $Cd(CN)_2 \cdot Pr^iBr$, $P4_12_12$, a = 9.124(1), c = 11.335(3) Å, Z = 4, while the new mineralomimetic $Cd(CN)_2 \cdot CH_2BrCH_2Br$ crystalizes in the body-center tetragonal $I4_1/amd$ with lattice parameters, a = 8.116(5), c = 14.721(5) Å, Z = 4. Like the H- and L-cristobalite-like $Cd(CN)_2$ framework structures, the host framework of the present inclusion compound is composed of individual tetrahedral units linked to four neighboring tetrahedra by Cd–CN–Cd linkages. However, the new mineralominetic $Cd(CN)_2$ host framework in $Cd(CN)_2 \cdot CH_2BrCH_2Br$ does not topologically correspond to natural SiO_2 structures. Clearly, there is a large difference in the scale and orientation of the tetrahedra between the $Cd(CN)_2$ and SiO_2 structures, since organic guest species must be accommodated in the adamantane-like cavity. The Cd–CN–Cd distance is *ca*. 5.5 Å and the Cd–CN–Cd angle is 180°, whereas the Si–O–Si distance is *ca*. 3.2 Å and the Si–O–Si bond angle is more flexible.

As shown in Fig. 2, the adamantane-like cavity in the new $Cd(CN)_2 \cdot CH_2BrCH_2Br$ clathrate is occupied by the guest CH_2BrCH_2Br molecule, like the H- and L-cristobalite-like cadmium cyanide clathrates. However, the accommodation mode of CH_2BrCH_2Br is completely different from that of the guest molecules in the H- and L-cristobalike-like clathrates. The shape, size and conformation of CH_2BrCH_2Br is associated with forming the $I4_1/amd$ $Cd(CN)_2$ host framework. The orientation of the guest CH_2BrCH_2Br molecules is along the c axis. The Br atom projects toward a branch consisting of one Cd atom and two cyanide groups in the adamantane-like cavity, while each methyl group of CMe_4 in H-cristobalite-like $Cd(CN)_2 \cdot CMe_4$ projects toward a tripod consisting of one Cd atom and three cyano groups,[3] and the two methyl groups of Pr^iBr in the L-cristobalite-like $Cd(CN)_2 \cdot Pr^iBr$ project towards two tripods.[4] The guest CH_2BrCH_2Br as a template allows the new mineralomimetic $Cd(CN)_2$ host framework, which can be obtained by expanding the c axis and depressing the a and b axes in the H-cristobalite-like Fd-3m host framework. The insertion into the branch induces an expansion of the host framework along the c axis. The affinity of the guest molecules in the polymeric host framework varies depending on the

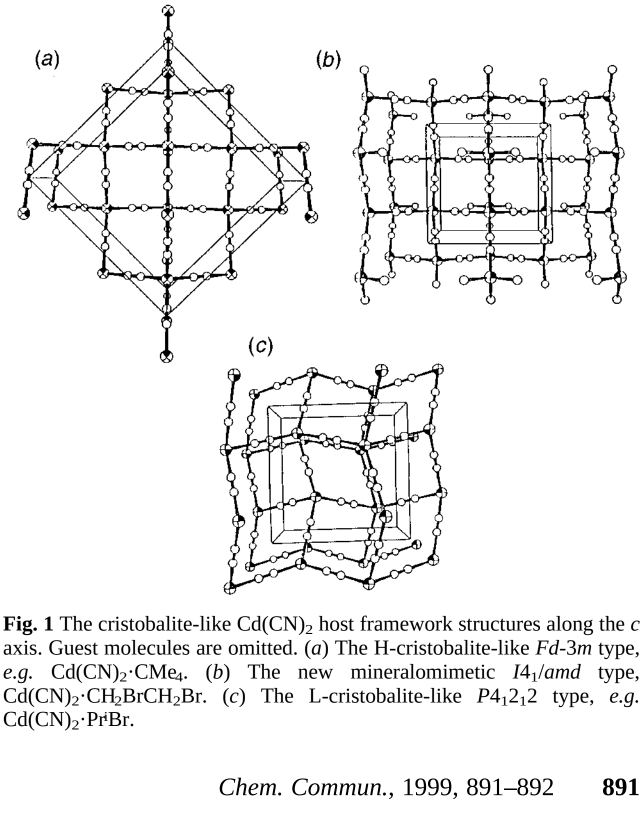

Fig. 1 The cristobalite-like $Cd(CN)_2$ host framework structures along the c axis. Guest molecules are omitted. (*a*) The H-cristobalite-like Fd-3m type, *e.g.* $Cd(CN)_2 \cdot CMe_4$. (*b*) The new mineralomimetic $I4_1/amd$ type, $Cd(CN)_2 \cdot CH_2BrCH_2Br$. (*c*) The L-cristobalite-like $P4_12_12$ type, *e.g.* $Cd(CN)_2 \cdot Pr^iBr$.

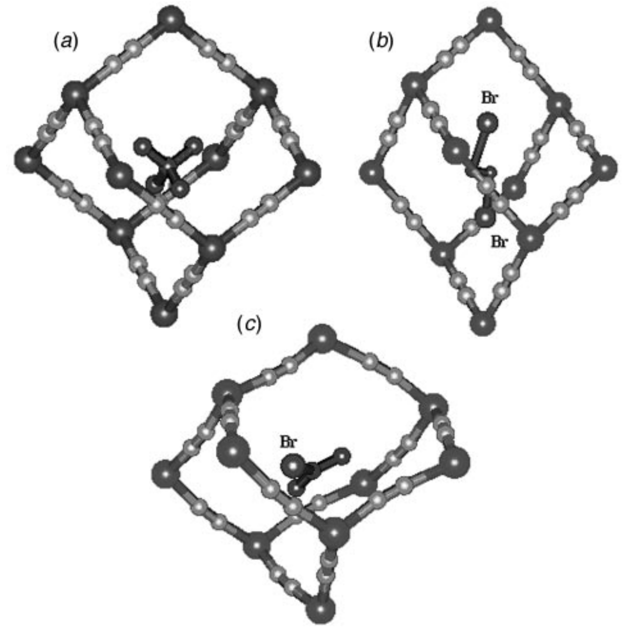

Fig. 2 The adamantane-like cavities of the $Cd(CN)_2\cdot G$ clathrates. (*a*) The cavity of the H-cristobalite-like $Cd(CN)_2\cdot CMe_4$ clathrate. (*b*) The cavity of the new mineralomimetic *I*4$_1$/*amd* type, $Cd(CN)_2\cdot CH_2BrCH_2Br$ clathrate. Since the C atoms of the CH_2BrCH_2Br are highly disordered, one possible conformation is shown. (*c*) The cavity of the L-cristobalite-like $Cd(CN)_2\cdot Pr^iBr$.

proprieties of the guest molecules. The guest structure serves as a template for the solid host lattice.

These results indicate that the cadmium cyanide host is flexible depending on the guest molecules. To the best of my knowledge, a SiO_2 structure topologically similar to the host in $Cd(CN)_2\cdot CH_2BrCH_2Br$ has not been previously found. The new mineralomimetic $Cd(CN)_2$ host framework with a *I*4$_1$/*amd* space group has implications for the natural and/or synthetic SiO_2 systems. The formation of the mineralomimetic *I*4$_1$/*amd* $Cd(CN)_2$ host structure suggests the formation of *I*4$_1$/*amd* type SiO_2 under special conditions. This new cadmium cyanide clathrate may be of significant interest as a crystalline model compound for studies of the transformation of SiO_2 and nanoscale control of host frameworks.

Notes and references

† *Crystal data*: $Cd(CN)_2\cdot CH_2BrCH_2Br$, $M = 352.31$, *I*4$_1$/*amd* (No. 141), $a = 8.116(5)$, $c = 14.721(5)$ Å, $U = 969.7(9)$ Å^3, $Z = 4$, $D_x = 2.41$ g cm^{-3}, μ(Mo-Kα) = 10.423 mm^{-1}; 322 reflections observed, 2 restrains and 18 parameters refined: $R = 0.0629$ [$I > 2\sigma(I)$], goodness of fit (gof) = 1.056. The collection of X-ray diffraction intensity data was carried out on a Rigaku AFC5S diffractometer (Mo-Kα: $\lambda = 0.71069$ Å) at 180 K. The structure was solved using the TEXSAN software package installed on the diffractometer system and refined by full-matrix least-squares methods with the program SHELXL-93. After refinement of the host lattice $Cd(CN)_2$, the difference map suggested that the guest CH_2BrCH_2Br molecules displayed considerable positional disorder due to the large thermal motion and pseudo-symmetry associated with the space group. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms have not been located. Since disorder in the orientation of the cyanide group between tetrahedral Cd atoms has been found by solid state ^{113}Cd NMR spectroscopy in $Cd(CN)_2$ host–guest materials (ref. 9), all the relevant C and N atoms were assumed to have 50% probability of being C and N. CCDC 182/1217. See http://www.rsc.org/suppdata/cc/1999/891/ for crystallographic files in .cif format.

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