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Supporting information for article:

Hydrogen-bond network in sodium chloride tridecahydrate, analogy with ice VI

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S1. *In-situ* Single-crystal neutron diffraction of NaCl·13D₂O under high pressure

Figure S1 Representative diffraction pattern of NaCl·13D₂O described by the *STARGazer* programme (Ohhara *et al.*, 2009). The diffraction data were collected at 1.7 GPa and 298 K in the diamond anvil cell (Yamashita, Komatsu, Ohhara *et al.*, 2022) using the Laue-TOF diffractometer at BL18 (SENJU) in MLF J-PARC (Ohhara *et al.*, 2016). The diamond anvil cell was mounted in the up-side-down orientation ($\chi = 0^\circ$; see Figure 2 in Yamashita, Komatsu, Ohhara *et al.*, 2022). Diffraction patterns are extracted for time-of-flight = 10–34 ms.

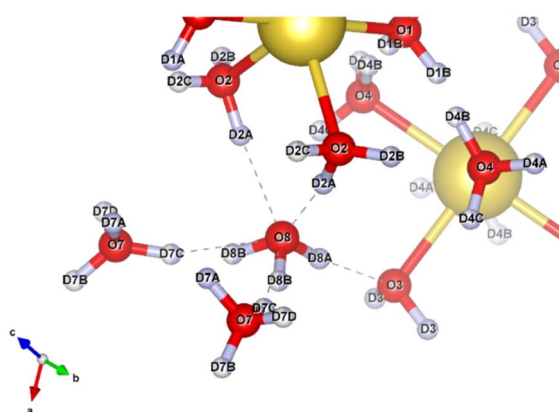
S2. Hydrogen-bond structure with violation of the ice rules

Figure S2 Close-up view around O8 in NaCl·13D₂O. Red, pale blue/white, and yellow balls correspond to oxygen, deuterium, and sodium. The two-colour divisions for deuterium represent their occupancy determined from the neutron experiments. The oxygen and deuterium are labelled.

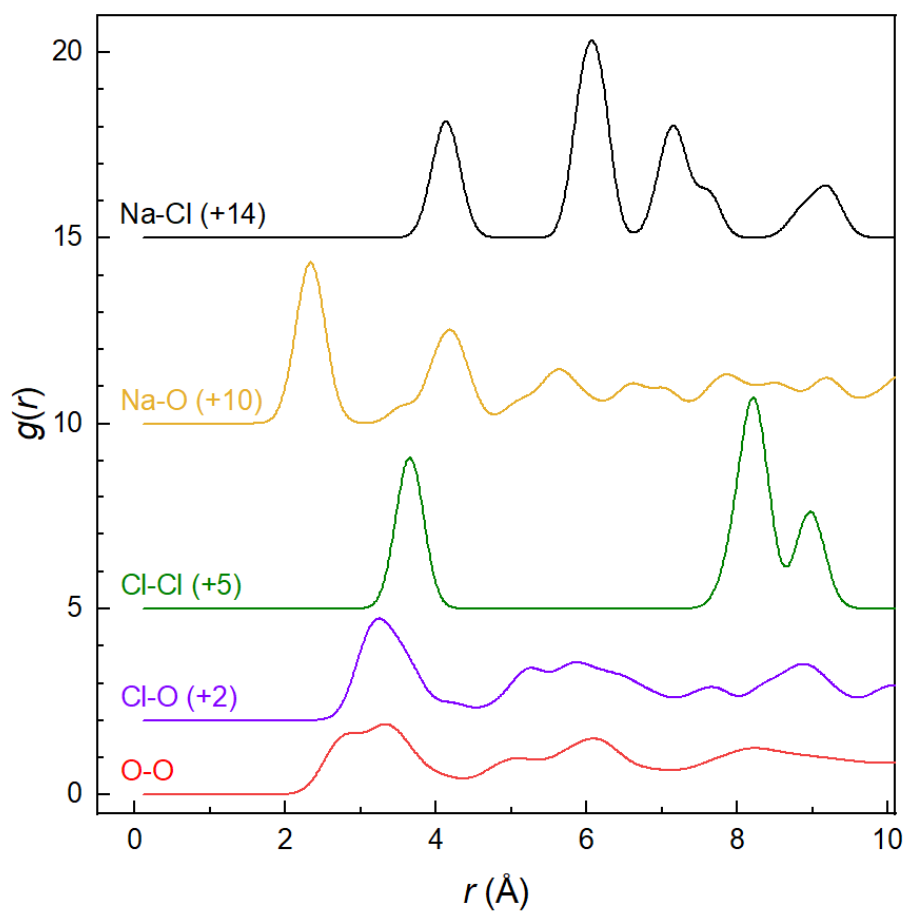
S3. Interatomic correlation in SC13 [NaCl·13H(D)₂O]

Figure S3 Partial atomic pair correlation function $g(r)$ of the O-O, Cl-O, Cl-Cl, Na-O, and Na-Cl in SC13 simulated by *PDFGUI* (Farrow *et al.*, 2007). The latter three are displayed with vertical offsets of 2, 5, 10, and 15, respectively for clarity. The structure model determined by the neutron diffraction at 1.7 GPa and 300 K is used.

S4. Powder neutron diffraction

Powder neutron diffraction measurements of NaCl·13D₂O were also carried out on the BL11 beamline (PLANET; Hattori *et al.*, 2015) in the Material and Life Science Experimental Facility (MLF) of J-PARC, Ibaraki, Japan. Pressure and temperature were controlled using a *P-T* variable cell, the so-called MITO system (Komatsu *et al.*, 2013). The NaCl + 9D₂O solution was loaded into a pair of TiZr gaskets (Marshall & Francis, 2002) and they were set in an aluminium ring. No additional pressure marker was enclosed, the pressure was determined from the equation of state of NaCl which precipitated from the solution with increasing pressure (Skelton *et al.*, 1984). The sample was encapsulated by compressing to 3 tonnes and cooled to 200 K by 5 K min⁻¹. Then the sample was compressed up to 24 tonnes, and heated to 250 K. After heating, the sample was transformed into the mixture of NaCl·13D₂O, ice VIII and NaCl. We collected the neutron diffraction data at 2.2 GPa and 250 K.

S4.1. Structure refinement

The crystal structure of NaCl·13D₂O was refined using *GSAS* (Larson & Von Dreele, 2004) + *EXPGUI* (Toby, 2001). The initial structure was derived from the results of single-crystal neutron diffraction. Rietveld method was used for powder data optimization of NaCl·13D₂O and ice VIII, NaCl. It is likely that NaCl partially became coarse crystals when the sample first crystallised and it remained during measurements. The deuterium occupancies are restricted to follow the ice rules (Details in the main text). The number of parameters to be refined is reduced by constraints of U_{iso} to be identical among all deuterium atoms, oxygen atoms coordinating on the same sodium atom, or oxygen atoms of interstitial water. To avoid divergence of some deuterium positions, covalent O-D and hydrogen-bonded D··O are restrained to be 0.966 Å and 1.8 Å. The covalent O-D length is from a precise structure analysis of ice VII at 2.2 GPa and 274 K (Yamashita, Komatsu, Klotz *et al.*, 2022). The hydrogen-bonding distance is from the average of the single-crystal neutron results. The diffraction patterns with refinement results are shown in Figure S4. Details of refinement are given in Table S1. The derived deuterium occupancies are Occ. (D4A) = 0.886 (10) and Occ. (D6A) = 0.835 (12).

Table S1 Details of the refinement of powder neutron experiment

| | |
|--|--|
| Crystal data | |
| Chemical formula | NaCl·13D ₂ O |
| M_r | 318.85 |
| Temperature (K) | 250 |
| Pressure (GPa) | 2.2* |
| Crystal system, space group | Monoclinic, <i>C2/m</i> |
| a, b, c (Å) | 11.3121 (4), 11.7688 (7), 10.8106 (5) |
| β (°) | 119.653 (3) |
| V (Å ³) | 1250.73 (5) |
| Z | 4 |
| Calculated density (g cm ⁻³) | 1.693 |
| | |
| Data collection | |
| Radiation type | Pulsed white neutron |
| Diffractometer | PLANET (BL11), MLF, J-PARC |
| Specimen mounting | The MITO system |
| Data collection mode | Time-of-flight |
| 2θ values | $2\theta_{\min} = 79^\circ$, $2\theta_{\max} = 101^\circ$ |
| d range/Å | 0.5–6.0 |
| R factors and goodness of fit | $R_p = 0.0523$, $wR_p = 0.0415$, $R(F^2) = 0.1098$, $\chi^2 = 7.334$ |
| Number of data points | 4328 |
| Number of refined parameters, restraints | 133, 44 |

Note: (*) estimated from the lattice parameter of NaCl (Skelton *et al.*, 1984).

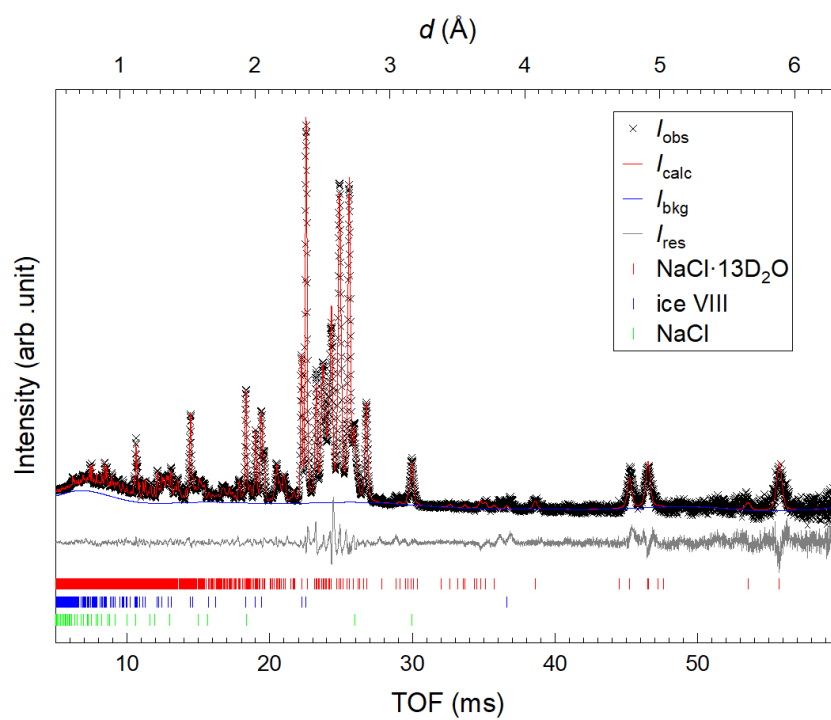


Figure S4 Powder neutron diffraction pattern of NaCl·13D₂O at 2.6 GPa and 250 K at the BL11 (PLANET) in the MLF J-PARC.

S5. Construction of completely ordered configurations in SC13

To figure out possible configurations in the hydrate, the disordered hydrogen-bond sub-network is extracted from the unit cell by eliminating other than disordered hydrogen bonds from Figure 5d. The internetwork hydrogen bonds between O7 and O8 are unicursal because other hydrogen bonds from and to O8 are unidirectional. Therefore, one of the two equivalent but independent subnetworks, related by *C*-centring, is enough to count up the configurations. Figure S5 represents the reduced topology of the disordered hydrogen-bond subnetwork in SC13 by omitting ordered bonds and oxygen nodes on unicursal chains. The disordered sub-network is completed within itself. Topological analyses revealed that the single subnetwork can have 28 types of configurations. A combination of two subnetworks in a unit cell results in 784 possible configurations. From a symmetric analysis, 128 unique configurations were finally found.

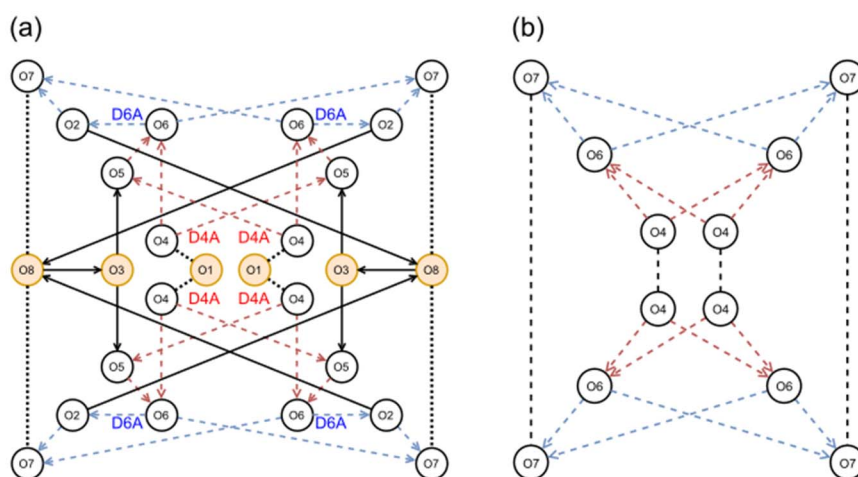


Figure S5 (a) Topological graph of the hydrogen-bond network in SC13 represented by nodes for oxygen and edges for hydrogen bonds. Nondirectional dot lines and unidirectional solid arrows correspond to fully-disordered and completely-ordered hydrogen bonds, respectively. Partially-disordered hydrogen bonds are described as coloured dashed arrows. Red and blue colours of partially-disordered hydrogen bonds correspond to those in which deuterium occupancies can be derived from Occ. (D4A) and Occ. (D6A), respectively. Orange nodes represent oxygen atoms on the mirror plane. A single network in the unit cell was extracted from the two interpenetrated networks except for the internetwork hydrogen bonds between O7 and O8. (b) Extracted graph from (a) for reduced representation of the disordered hydrogen-bond subnetwork in SC13. Directional and nondirectional edges between nodes correspond to completely- and partially-disordered hydrogen-bond chains, respectively, derived by the neutron diffraction data. From the ice rules, O4, O6, and O7 respectively accept 2, 2, and 1 hydrogen bonds from the neighbouring nodes and donate 1, 2, and 2 hydrogen bonds to the other neighbouring nodes.

Table S2 Selected geometric parameters (Å, °)

| | | | |
|--|------------|--------------------------|------------|
| Na1—O1 | 2.305 (18) | O5—D5A | 0.913 (19) |
| Na1—O2 ⁱ | 2.381 (19) | O5—D5C | 0.94 (13) |
| Na2—O3 | 2.365 (16) | O5—D5B | 1.02 (3) |
| Na2—O4 ⁱⁱ | 2.388 (19) | O6—D6B | 0.91 (4) |
| O1—D1A | 0.929 (16) | O6—D6C | 0.95 (3) |
| O1—D1B | 0.93 (3) | O6—D6D | 1.0 (2) |
| O2—D2C | 0.93 (8) | O6—D6A | 0.98 (3) |
| O2—D2B | 0.93 (3) | O7—D7D | 0.83 (17) |
| O2—D2A | 0.974 (18) | O7—D7B | 0.94 (4) |
| O3—D3 | 0.962 (16) | O7—D7C | 0.96 (5) |
| O4—D4A | 0.93 (3) | O7—D7A | 0.97 (2) |
| O4—D4C | 0.97 (3) | O8—D8B | 0.96 (4) |
| O4—D4B | 0.99 (4) | O8—D8A | 1.00 (2) |
| O1—Na1—O2 ⁱⁱⁱ | 93.4 (5) | D4C—O4—Na2 ^{vi} | 107 (2) |
| O2 ⁱⁱⁱ —Na1—O2 ⁱ | 90.7 (10) | D4B—O4—Na2 ^{vi} | 99 (3) |
| O3—Na2—O4 ^{iv} | 88.0 (5) | D5A—O5—D5C | 116 (6) |
| O4 ^{iv} —Na2—O4 ⁱ | 85.5 (10) | D5A—O5—D5B | 100 (2) |
| D1A—O1—D1B | 112 (2) | D5C—O5—D5B | 99 (6) |
| D1B ^v —O1—D1B | 98 (4) | D6B—O6—D6C | 123 (5) |
| D1A—O1—Na1 | 107.6 (17) | D6B—O6—D6D | 93 (9) |
| D1B—O1—Na1 | 113.9 (19) | D6C—O6—D6D | 108 (8) |
| D2C—O2—D2B | 122 (7) | D6B—O6—D6A | 107 (3) |
| D2C—O2—D2A | 104 (5) | D6C—O6—D6A | 103 (2) |
| D2B—O2—D2A | 113 (2) | D6D—O6—D6A | 124 (10) |
| D2C—O2—Na1 ^{vi} | 92 (6) | D7D—O7—D7B | 101 (8) |
| D2B—O2—Na1 ^{vi} | 117.8 (15) | D7D—O7—D7C | 103 (7) |
| D2A—O2—Na1 ^{vi} | 104 (2) | D7B—O7—D7C | 128 (4) |
| D3 ^v —O3—D3 | 104 (3) | D7D—O7—D7A | 111 (5) |
| D3—O3—Na2 | 106.4 (14) | D7B—O7—D7A | 109 (3) |
| D4A—O4—D4C | 98 (3) | D7C—O7—D7A | 104 (4) |
| D4A—O4—D4B | 109 (3) | D8B—O8—D8B ^v | 88 (5) |
| D4C—O4—D4B | 129 (3) | D8B—O8—D8A | 101 (3) |
| D4A—O4—Na2 ^{vi} | 116.6 (16) | | |

Symmetry code(s): (i) $x-1, y, z$; (ii) $x-1, -y, z$; (iii) $-x+1, y, -z$; (iv) $-x+1, y, -z+1$; (v) $x, -y, z$; (vi) $x+1, y, z$.