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Mendeleev Commun., 2004, 14(6), 266–268
Mendeleev Communications

Small water clusters

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DOI: 10.1070/MC2004v014n06ABEH001906

An analysis of the structures of compounds presented in the Cambridge Structural Databank allowed us to discover nine hitherto unknown small isolated 3D water clusters.

Water is a versatile solvent. When compounds crystallise from aqueous solutions, water molecules are often involved in the solid phase as ligands and/or solvate molecules. Systems of hydrogen bonds involving water molecules play an important role in the stabilisation of the crystals formed. In a number of structures, crystallisation water molecules form hydrogen bonds between each other. This may result in isolated water clusters or one-, two- or three-dimensional water associates. The structure of water clusters has been attracting considerable attention;[1–7] the clusters themselves are often used as models for studying the processes of water self-organisation. A study of the structures of the known crystal hydrates presented in the Cambridge Structural Databank[7,8] has shown that the formation of small water clusters is a rare phenomenon. In this work, we report on a systematic search for isolated 3D water clusters in the structures of compounds available in the Cambridge Structural Databank (version 5.24, February 2003).[9] A number of restrictions has been imposed on the structures under consideration.

– All the water molecules contained in a cluster are solvate molecules.

– Isolated water clusters are considered. Water molecules from a cluster may be involved in hydrogen bonds with other structural units but may not be involved in infinite water associates or chains of water clusters (in particular, we do not consider clathrate fragments).

– A cluster is three-dimensional (3D). Closed chains of water molecules are not taken into consideration.

– Crystallisation water molecules in the structures of crystal hydrates are ordered, and their positions in the structure are completely populated.

– The oxygen–oxygen distances range from 2.6 to 3.0 Å.

Note that a considerable number of water clusters, the existence of which has been reported previously,[1,3–5] do not comply with some of the above conditions. Table 1 presents data on water clusters that satisfy the above requirements; they are ordered in accordance with the codes of compounds in the Cambridge Structural Databank.

The cluster that contains the smallest number of water molecules has been found in the structure of $([C_{12}H_{24}Bi_3ClN_6O_6]Cl_2 \cdot 6H_2O)_n$ [PERRAF, space group *R*3, Figure 1(*a*)]. The $(H_2O)_5$ cluster is arranged on the 3 axis (distorted trigonal bipyramid); the hydrogen atoms have not been located. The water cluster in $[C_{58}H_{68}Fe_2N_{12}O_5](ClO_4)_4 \cdot 7H_2O$ (POZCUC, space group *Cmcm*) is formed from seven water molecules; two of them are terminal molecules and do not belong to the cluster. The cluster symmetry is *mm*2; the hydrogen atoms have not been located. However, the high thermal parameters of the oxygen atoms in water molecules ($U_{equiv.}$ = 0.2–0.4 Å^2) and the disordering of two of the three perchlorate ions allow us to assume that the symmetry of the space group in this compound is overestimated and that the authors have dealt with centrosymmetric twinning.

The structures of the majority of the water clusters discovered are the derivatives of a cubic structure. The $(H_2O)_8$ clusters with a distorted cubic structure have been found in $[C_{18}H_{22}CoN_6O_4]$-

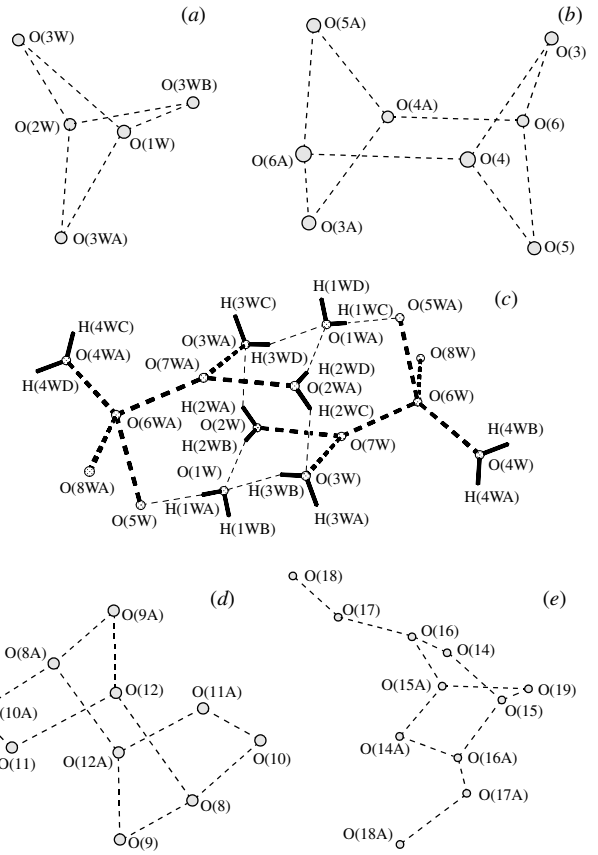

Figure 1 The structures of water clusters in (*a*) PERRAF, (*b*) ROLNEL, (*c*) HOWPUE, (*d*) QAMMIA and (*e*) QAPREE.

$[C_{16}H_{20}CoN_2O_6]_2{\cdot}8H_2O$ (CIGGAA, space group $C2/c$) and $(C_4H_{12}N)_4[H_8Al_4O_{20}Si_4]{\cdot}24H_2O$ (GIHDOQ, space group $I\bar{4}2m$, two crystallographically independent clusters); the cluster symmetry was $\bar{1}$ or $\bar{4}$, $\bar{4}2m$, respectively. In all the cases, the hydrogen atoms have not been located. Note that it has been reported in 1987 that 'water molecules form groups in the shape of a cube consisting of eight molecules' in GIHDOQ.[11]

The cleavage of two hydrogen bonds in the cubic cluster results in clusters shown in Figure 1(*b*). In $(C_{24}H_{20}As)(C_6H_6N_3O_2S){\cdot}4H_2O$ (ROLNEL, space group $P2_1/n$), $[C_{48}H_{32}N_8O_9S_2V_2]{\cdot}8H_2O$ (YIPXUQ, space group $C2/c$) and $[C_{22}H_{40}Cu_2N_6O_{10}]{\cdot}8H_2O$ (ZITVON, space group $P\bar{1}$), water clusters are of the $\bar{1}$ symmetry; all the hydrogen atoms have been located. It is interesting that hydrogen bonds in all of the three clusters have different directions [Figure 2(*a*)–(*c*)], which indicates that the direction of hydrogen bonds in water clusters depends considerably on their environments. The symmetry of a similar water cluster in $[C_{60}H_{86}Cl_2O_2Ru_8](BF_4)_2{\cdot}8H_2O$ (IDOYAB, space group $C2/m$) is $2/m$; the hydrogen atoms have been partially located. However, judging by the geometry of hydrogen bonds, either the positions of some hydrogen atoms are determined incorrectly, or the water molecules are disordered. The centrosymmetric cluster in $C_{24}H_{44}Cu_2N_6O_9{\cdot}MeCN{\cdot}7H_2O$ (JOQKAB, space group $P\bar{1}$) also contains a central fragment analogous to those considered above. However, the positions of the hydrogen atoms reported are also doubtable. Another similar fragment containing a water cluster is found in $[C_{22}H_{29}N_{14}O_4Pt]ClO_4{\cdot}8H_2O$ [HOWPUE, space group $P\bar{1}$, Figure 1(*c*)]. The cluster symmetry is $\bar{1}$; the hydrogen atoms have been partially located. The positions of lacking hydrogen atoms are easily determined from geometric considerations [Figure 2(*d*)].

Table 1 Small isolated water clusters in the structures of organic compounds.

Compound code	Number of water molecules in the cluster / of these, independent molecules	A water cluster mentioned or not mentioned	Ref.
CIGGAA	8/4	yes	2
DOQSIL	12/6	no	10
GIHDOQ	8/2 (two clusters)	yes	11
HOWPUE	12/6	no	12
IDOYAB	8/3	no	13
JOQKAB	8/4	no	14
PERRAF	5/3	no	15
POZCUC	5/3	no	16
QAMMIA	10/5	no	17
QAPREE	7/4	no	18
ROLNEL	8/4	yes	19
YIPXUQ	8/4	yes	6
ZITVON	8/4	no	20

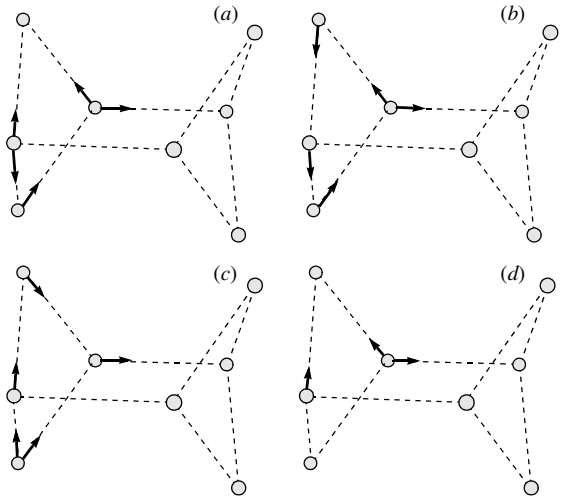

Figure 2 The graphs of water clusters in (*a*) ROLNEL, (*b*) YIPXUQ, (*c*) ZITVON and (*d*) HOWPUE. All the clusters have the $\bar{1}$ symmetry. The arrows indicate the direction of the O–H···O hydrogen bonds.

The structures of water clusters in ROLNEL, YIPXUQ and ZITVON can be found in different ways. Instead of a cubic cluster, let us take as the base a ring of six water molecules in the chair conformation and two bridges of one water molecule in each. HOWPUE [Figure 1(*c*)] contains two bridges of three water molecules. Two bridges of two water molecules added to a ring of six water molecules give the central fragment of the water cluster in $[C_{32}H_{24}Cl_2N_4O_7P_2Zn]{\cdot}5H_2O$ [QAMMIA, space group $P2_1/n$, Figure 1(*d*)]. The cluster symmetry is $\bar{1}$; the hydrogen atoms have not been located. The addition of four bridges (2×2+2×1) to the six-membered ring allows us to describe the structure of $[C_{18}H_{18}N_2O_7Ti]{\cdot}3.67H_2O$ (DOQSIL, space group $C2/c$; the cluster symmetry is $\bar{1}$; the hydrogen atoms have been partially located). The central fragment of the cluster in $[C_6H_8N_{12}O_{13}Yb]{\cdot}6H_2O$ (QAPREE, space group $C2/c$) consisting of seven water molecules is also derived from the $(H_2O)_6$ fragment [Figure 1(*e*)] (the cluster symmetry is 2; the hydrogen atoms have not been located).

In conclusion, small isolated water clusters have been discovered only in 13 of the 27056 structures containing solvate water. The small number of the set prevents us from finding the regularities of the formation of water clusters *vs.* the composition of crystal hydrates. However, the existence of ordered water associates in the crystalline phase makes it possible to use the structures of water clusters as models in the study of aqueous systems.

References

1 L. J. Barbour, G. W. Orr and J. L. Atwood, *Nature*, 1998, **393**, 671.
2 W. B. Blahton, S. W. Gordon-Wylie, G. R. Clark, K. D. Jordan, J. T. Wood, U. Geiser and T. J. Collins, *J. Am. Chem. Soc.*, 1999, **121**, 3551.
3 L. J. Barbour, G. W. Orr and J. L. Atwood, *Chem. Commun.*, 2000, 859.
4 J. L. Atwood, L. J. Barbour, T. J. Ness, C. L. Raston and P. L. Raston, *J. Am. Chem. Soc.*, 2001, **123**, 7192.
5 M. Yu. Antipin, A. B. Ilyukhin and V. Yu. Kotov, *Mendeleev Commun.*, 2001, 210.
6 R. J. Doedens, E. Yohannes and M. I. Khan, *Chem. Commun.*, 2002, 62.
7 L. Infantes and S. Motherwell, *Cryst. Eng. Commun.*, 2002, **4**, 454.

8 L. Infantes, J. Chisholm and S. Motherwell, *Cryst. Eng. Commun*., 2003, **5**, 480.
9 F. H. Allen, *Acta Crystallogr., Sect. B*., 2002, **58**, 380.
10 M. Guo, H. Sun, S. Bihary, J. A. Parkinson, R. O. Gould, S. Parsons and P. J. Sadler, *Inorg. Chem*., 2000, **39**, 206.
11 Yu. I. Smolin, Yu. F. Shepelev, A. S. Ershov and D. Knobbel, *Proc. Nat. Acad. Sci. USSR*, 1987, **297**, 1377.
12 M. B. L. Janik, A. Hegmans, E. Freisinger and B. Lippert, *J. Biol. Inorg. Chem.*, 1999, **4**, 130.
13 M. Faure, H. Stoeckli-Evans and G. Suss-Fink, *Inorg. Chem. Commun*., 2002, **5**, 9.
14 M. Lockwood, T. J. Blubaugh, A. M. Collier and J. M. Mayer, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 225.
15 K. Hegetschweiler, M. Ghisletta and V. Gramlich, *Inorg. Chem*., 1993, **32**, 2699.
16 K. B. Jensen, C. J. McKenzie, O. Simonsen, H. Toftlund and A. Hazell, *Inorg. Chim. Acta*, 1997, **257**, 163.
17 A. Muller-Hartmann and H. Vahrenkamp, *Eur. J. Inorg. Chem*., 2000, 2355.
18 S. Jirong, H. Rongzu, K. Bing and L. Fuping, *Thermochim. Acta*, 1999, **331**, 49.
19 K. V. Domasevich, A. A. Mokrih and E. B. Rusanov, *Zh. Obshch. Khim.*, 1996, **66**, 1501 (*Russ. J. Gen. Chem*., 1996, **66**, 1463).
20 W. Chen, N. H. Tioh, J.-Z. Zou, Z. Xu and X.-Z. You, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., 1996, **52**, 43.

Received: 18th February 2004; Com. 04/2232