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A Planar Water Tetramer with Tetrahedrally Coordinated Water Embedded in a Hydrogen Bonding Network of $[Tc_4(CO)_{12}\text{-}(\mu_3\text{-}OH)_4 \cdot 4H_2O]$

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Water is the basis of life. It plays a crucial role in many biological and chemical processes.[1] Because its chemical and physical properties are primarily determined by the strong hydrogen bonds formed by oxygen and hydrogen, it is of enormous importance to understand the nature of the hydrogen bridges of bulky water,[2] not only to explain numerous anomalies of water but also to gain a better insight into the world of many biomolecules which achieve their effect by interaction with structured water.[3] The key here is to understand the bonding relationships in small water clusters.[2] The importance of these unusual compounds as model molecules for water has been emphasized in numerous theoretical[4] and experimental studies.[5−9] Here the cyclic water tetramer plays a significant role as a simple two-structure model for understanding liquid water and ice.[10] On the basis of theoretical ab initio calculations, it has been possible to calculate different configurations of the water tetramer[11] (which were also subsequently detected crystallographically) for the most part embedded in different matrixes.[12] The maximum tetrahedral coordination of the water molecule in the tetramers has, however, not yet been detected.

This study describes for the first time a virtually planar water tetramer in which the water molecules are virtually tetrahedrally coordinated in a three-dimensional network through hydrogen bonds. The network could be produced by the cocrystallization of $[Tc(CO)_3\text{-}(\mu_3\text{-}OH)]_4$ (**1**) and water.

As shown in Figure 1 the complementary components, the water tetramer (O10−O10A−O10B−O10C) and the cubic cluster **1**, independently of one another, form two interpenetrating tetragonal lattice networks held together exclusively by hydrogen bonds. The amphiphilic behavior of cluster **1** and water results in a highly ordered three-dimensional network, $[\mathbf{1} \cdot 4(H_2O)]_n$.[13] To our knowledge this constitutes the first example of a network structure formed as a result of the cocrystallization of an amphiphilic metal−organic complex and water through multiple hydrogen bridge donor and acceptor functions. As shown in Figures 1 and 2, it is also unusual that, in the water tetramers, on one hand the water molecules are linked together via hydrogen bonds in the same way as tetramers in the gas phase,[14] and on other hand the tetramer itself is embedded in a virtually tetrahedral network such as that known from ice structures.[15]

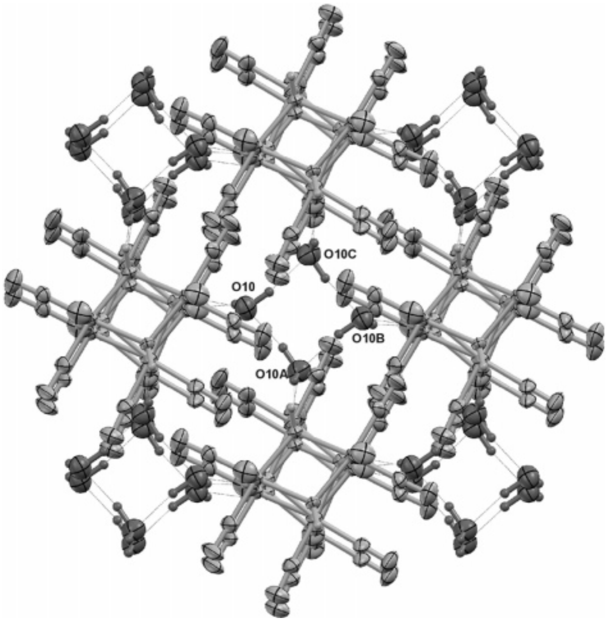

Figure 1. Network $[\mathbf{1} \cdot 4(H_2O)]_n$. View along the *c*-axis.

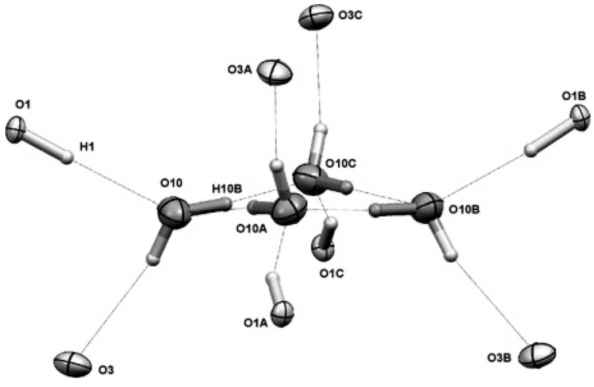

Figure 2. Water tetramer in its immediate environment. Each oxygen atom within the virtually planar water tetramer is tetrahedrally coordinated through hydrogen bonds as in ice structures.

Within the network $[\mathbf{1} \cdot 4(H_2O)]_n$ the water tetramers $(H_2O)_4$ are orientated in planes perpendicular to the main axis, C. This also applies to the midpoints of the molecules of **1**. When forming the system, the rigid μ_3-OH groups of **1** act as hydrogen bridge donors in the sense of a Lewis acid toward the free electron pairs of the oxygen in the water tetramers. At the same time, the oxygen atoms of the axial carbonyl groups behave as hydrogen bond acceptors in the sense of a Lewis base toward the free protons of the water tetramers. Thus, eight cubes are interlinked via each H_2O tetramer.

The oxygen atoms within the $(H_2O)_4$ ring are in the corners of a square that is folded by 15° along the diagonals (Figure 2). While the O−H−O bonds, with angles of 170.9°, only deviate slightly from linearity within the $(H_2O)_4$ ring, the other two hydrogen bonds with **1** form for steric reasons angles of 162.1° and 162.6° (Table 1). The O−O distance of approximately 294 pm for the hydrogen

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10.1021/ja057142j CCC: $33.50

Table 1. Summary of the Distances and Angles in the $(H_2O)_4$ Ring

bond	distance [pm]	angle	[deg]
O10−O10A	294.0	O10A−O10−O10C	89.54
O10−O3	302.5	O3−O10−O10A	118.62
O10−O1	292.8	O1−O10−O10A	124.78
O10−H10A	87.0	O10−H10B−O10C	170.9
O1−H1	96.7	O1−O10−O3	84.11
O10−H10B	101.2	O1−H1−O10	162.6
		O3−H10A−O10	162.1

Table 2. Experimentally Determined O−O Distances and IR Absorptions of the Bound OH Stretching Vibrations in Small Cyclic Water Clusters

cluster	distance [pm]	IR absorption[19] [cm^{-1}]
$(H_2O)_4$ in this study	294	3598
trimer[6c]	291	3533
tetramer[16]	281	3416
pentamer[20]	272	3360
water[1]	285	3280
ice I_h[1]	276	3220

bonds within the $(H_2O)_4$ ring is considerably greater than the O−O distances measured in the solid phase for the water tetramer[16] and for the water trimer[6c,17] of 281 and 291 pm, respectively (Table 2). As is known, the O−O distance in small cyclic water clusters ($n = 3-6$) decreases almost exponentially with increasing cluster size.[2] In this respect our measured distance of 294 pm is unusual. Also, the infrared absorptions of small water clusters $(H_2O)_n$ ($n = 3-10$) show a dependence on the number of water molecules in the cluster in the gas phase. As the size increases, the wavenumber of the OH stretching vibrations continuously decreases in the range from 3720 to 2935 cm^{-1}.[19] The broad IR band of $[\mathbf{1}\cdot 4(H_2O)]_n$ at 3598 cm^{-1} for the bound OH stretching vibrations also fits in this scheme over the IR absorptions of the water tetramer at 3416 cm^{-1} and the water trimer at 3533 cm^{-1}. Unlike water and ice, cyclic clusters in the gas phase show a sharp single contribution of the vibrational bands. Because of cooperative effects in the tetrahedrally coordinated cluster the wavenumber may be higher than in the gas-phase cluster. In addition, with an O−O distance of 303 pm, the hydrogen bonds in the water tetramer are critically weakened by the hydrogen bonds between the tetramer and the CO groups.

In diamagnetic **1** the μ_3-OH group can be formally considered a 5-electron donor, as in the homologous compounds $[M(CO)_3(\mu_3\text{-}OH)]_4$ ($M = Mn, Re$).[21] The structure of **1** is based on a distorted heterocubane system, the corners of which are occupied alternately by Tc and O atoms. Because in **1** there is only one independent $Tc(CO)_3OH$ fragment crystallographically, all four $Tc(CO)_3OH$ units are equivalent in terms of the bond angles and bond order.

The angles between pairs of adjacent carbonyl groups are identical within the limit of error (average value = 86.8° ± 0.3). Very comparable values were measured for the Tc−C distances, the C−O bond lengths of the carbonyl groups and the Tc−O bond distances to the hydroxyl groups. On average these are 190 ± 0.6 pm for the Tc−C bonds, 114.4 ± 0.8 for the C−O bond lengths, and 219.3 ± 0.4 pm for the Tc−O distances.

Supporting Information Available: Crystallographic data of $\mathbf{1}\cdot 4H_2O$ in CIF format and experimental details.This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808.
(2) Keutsch, N. K.; Saykally, R. *J. Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 10533.
(3) (a) Pomes, R.; Roux, B. *J. Biophys.* **2002**, *82*, 2304. (b) Cukierman, S. *J. Biophys.* **2000**, *78*, 1825. (c) Westhoff, E. *Water and Biological Macromolecules;* ED., CRC Press: Boca Raton, Fl, 1993.
(4) (a) Kim, J.; Kim, K. S. *J. Chem. Phys.* **1998**, *109*, 5886−5895. (b) Kim, J.; Majumbur, D.; Lee, H. M.; Kim, K. S. *J. Chem. Phys.* **1999**, *110*, 9128−9134. (c) Xantheas, S. S. *J. Chem. Phys.* **1995**, *102*, 4505−4517. (d) Xantheas, S. S. *J. Chem. Phys.* **1994**, *100*, 7523−7534. (e) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568−11569.
(5) (a) Ma, B.-Q.; Sun, H.-L.; Gao, S. *J. Chem. Soc.* **2005**, *18*, 2336. (b) Ma, B.-Q.; Sun, H.-L.; Gao, S. *J. Chem. Soc.* **2004**, *19*, 2220. (c) Ma, B.-Q.; Sun, H.-L.; Gao, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1374. (d) Ghosh, S. K.; Bharadwaj, P. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3577. (e) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 5180. (f) Neogi, S.; Savitha, G.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 3771.
(6) (a) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192−7193. (b) Blanton, W. B.; Gordon-Wylie, S. W.; Clark, G. R.; Jordan, K. D.; Wood, J. T.; Geiser, U.; Collins, T. J. *J. Am. Chem. Soc*. **1999**, *121*, 3551−3552. (c) MacGillivray, L. R.; Wood, J. T. *J. Am. Chem. Soc.* **1997**, *119*, 2592−2593. (d) Doedens, R. J.; Yohannes, E.; Khan, M. I. *Chem. Commun.* **2002**, *62*−63.
(7) (a) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671−673. (b) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed*. **2000**, *39*, 3094−3096. (c) Moorthy, J. N.: Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3417−3420.
(8) (a) Raghuraman, K.; Katti, K. K.; Barbour, L. J.; Pillarsetty, N.; Barnes, C. L.; Katti, K. V. *J. Am. Chem. Soc*. **2003**, *125*, 6955−6961. (b) Janiak, C.; Scharamann, T. G. *J. Am. Chem. Soc*. **2002**, *124*, 14010−14011.
(9) (a) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Botar, B.; Talismanova, M. O. *Angew. Chem., Int. Ed*. **2003**, *42*, 2085−2090. (b) Pal, S.; Sankaran, N. B.; Samanta, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1741−1743.
(10) Benson, S. W.; Siebert, E. D. *J. Am. Chem. Soc*. **1992**, *114*, 4269−4276.
(11) (a) Owicki, J. C.; Shipman, L. L.; Scheraga, H. A. *J. Phys. Chem.* **1975**, *79*, 1794−1810. (b) Lentz, B. R.; Scheraga, H. A. *J. Chem. Phys.* **1973**, *58*, 5296−5308. (c) Radhakrishnan, T. P.; Herndon, W. C. *J. Phys. Chem.* **1991**, *95*, 10609−10617. (d) Dykstra, C. *J. Chem. Phys.* **1989**, *91*, 6472−6476. (e) Udalde, J. M.; Alkorta, I.; Elguero, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 717−720.
(12) (a) Chacko, K. K.; Saenger, W. *J. Am. Chem. Soc.* **1981**, *103*, 1708−1715. (b) Zabel, V.; Saenger, W.; Mason, S. A. *J. Am. Chem. Soc*. **1986**, *108*, 3664−3673. (c) Stephens, F. C.; Vagg, R. S. *Inorg. Chim. Acta* **1982**, *57*, 43. (d) Xu, J.; Radkov, E.; Ziegler, M.; Raymond, K. N. *Inorg. Chem.* **2000**, *39*, 4156−4164. (e) Favas, M. C.; Kepert, D. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans*. **1980**, *454*. (f) Supriya, S.; Das, S. K. *New J. Chem.* **2003**, *27*, 1568−1574. (g) Long, L.; Wu, Y. R.; Huang, R.; Zheng, L. *Inorg. Chem.* **2004**, *43*, 3798−3800.
(13) Structure analysis of $\mathbf{1}\cdot 4H_2O$: see Supporting Information.
(14) (a) Cruzan, J. D.; Barly, L. B.; Liu, K.; Brown, M. G.; Loeser, J. G.; Saykally, R. *J. Science* **1996**, *271*, 59−62. (b) Liu, K.; Cruzan, J. D.; Saykally, R. *J. Science* **1996**, *271*, 929−933. (c) Cruzan, J. D.; Viant, M. R.; Brown, M. G.; Saykally, R. *J. Phys. Chem.* **1997**, *101*, 9022−9031.
(15) (a) Peterson, S. W.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 70. (b) Fletscher, N. H.: *The Chemical Physics of Ice*; Cambridge University Press: Cambridge, 1970.
(16) Sun, J.-Q.; Zang, J.; Ju, Z.-F.; Yang, G.-Y. *Aust. J. Chem.* **2005**, *58*, 572−577.
(17) (a) Xantheas, S. S.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 8774. (b) Viant, M. R.; Brown, M. G.; Cruzan, J. D.; Saykally, R. J.; Geleijns, M.; Van der Avoird, A. *J. Chem. Phys.* **1999**, *110*, 4369−4381.
(18) (a) Dyke, T. R.; Mack, K. M.; Muenter, J. S. *J Chem. Phys.* **1977**, *66*, 498−510. (b) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press. Oxford, 1969.
(19) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863.
(20) Zheng, J.-M.; Batten, S. R.; Du, M. *Inorg. Chem*. **2005**, *44*, 3371−3373.
(21) (a) Heberhold, M.; Wehrmann, F.; Neubauer, D.; Huttner, G. *J. Organomet. Chem.* **1978**, *152*, 329. (b) Clerk, M. D.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* 1991, 1283. (c) Heberhold, M.; Süss, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *24*, 700. (d) Heberhold, M.; Süss, G.; Ellermann, J.; Gäbelein, H. *Chem. Ber.* **1978**, *111*, 2931.

JA057142J