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Ya-Qi Jiang[a]; Zhao-Xiong Xie[a]
[a] Department of Chemistry and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, China

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A New Conformation of a Water Hexamer Chain and its Reversible Formation/Removal in the Host Channel by Gas–Solid Reaction

YA-QI JIANG* and ZHAO-XIONG XIE

Department of Chemistry and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

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A new type of cyclic water hexamer chain was found to occupy the host channel of a supramolecule, formulated as $[Zn(bdc)en\cdot 3(H_2O)]_n$ (1) [H_2bdc = 1,3-benzenedicarboxylic acid; en = ethylenediamine] and characterized by X-ray crystallography. As each water molecule was only involved in hydrogen bonding, facile removal of the lattice water was anticipated. The hydrogen-bonded water chain was completely removed by heating 1 at 96°C, forming the dehydrated solid $[Zn(bdc)en]_n$ (2). Interestingly, complex 1 can be regenerated in water vapor by a gas–solid reaction.

Keywords: Water cluster; Hydrogen bond; Gas–solid reaction; X-ray structure

INTRODUCTION

Small water clusters $(H_2O)_n$ $(n = 2–10)$ are currently of considerable interest and have been extensively studied both theoretically and experimentally [1–7]. A detailed understanding of the various possible structures and characteristics of water aggregates can provide an insight into the nature of water–water interactions in bulk water and in ice, as well as in biological and chemical processes. Among water clusters, the hexamer is of particular interest [8–12]. Recent studies indicate the water hexamer to be the smallest possible unit that can reveal some of the properties of liquid water [13]. Theoretical studies based on *ab initio* Hartree–Fock (HF) and density functional theory (DFT) calculations have predicted several isomers for water hexamers (see Scheme 1) [14–17], of which the three-dimensional cage structure with eight hydrogen bonds was found to be of minimum energy; this most stable form was confirmed experimentally [18]. The cyclic hexamer ('ring' in Scheme 1), almost isoenergetic with the cage isomer, was first formed in liquid helium droplets and characterized by IR spectroscopy [19]. It is particularly significant as it is the building block of ice I_h and I_c [20,21].

The lattice of the crystal host may offer an alternative environment to stabilize water clusters of various topologies. Recently, various water clusters [22–27], including cyclic water hexamers [28–31], found in a number of crystal hosts, have been structurally characterized. For example, cyclic water hexamers were found in a porous lanthanide–organic framework with both boat and chair configurations [32]; the conformation of water hexamers trapped within channels of a crystal of a dirhodium molecule was a twist boat [33]; some of the cyclic water hexamers were of high energy and displayed very different configurations from their theoretical counterparts [34]. We report here the synthesis of the coordinate polymer $[Zn(bdc)en\cdot 3(H_2O)]_n$ [$H_2bdc = 1,3$-benzenedicarboxylic acid; en = ethylenediamine] with one-dimensional channels, for which we have reported preliminary crystal data elsewhere [35]. We found planar hexamers linked with *uudd* tetramers enclathrated in the channels of the as-synthesized supramolecular complex. Furthermore, complete removal or regeneration of the water hexameric chains by moderate heating or exposure to water vapor has been successfully performed for the first time.

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*Corresponding author. Tel.: +86-592-2185667. Fax: +86-592-2183047. E-mail: yqjiang@xmu.edu.cn

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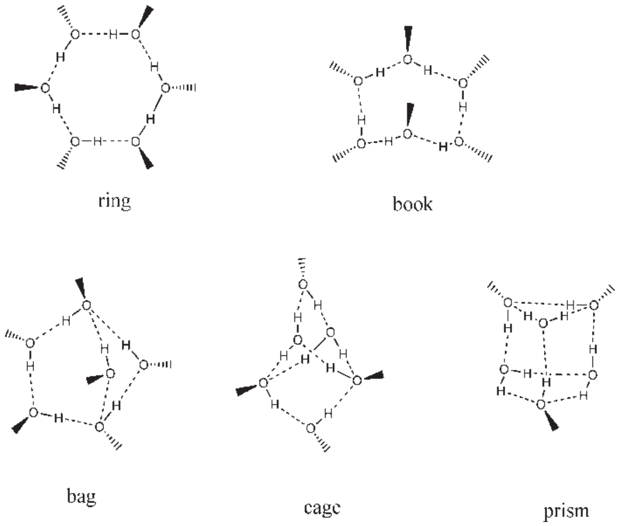

SCHEME 1 Calculated configurations of water hexamer isomers [14–17].

RESULTS AND DISCUSSION

Crystal Structure

The crystal structure of **1** [36] was reported in our previous paper [35], in which we mainly discussed the architecture of the host molecules. In brief, the chemical formula of **1** consists of one zinc ion, one bdc ligand, one en ligand and three water molecules. Each bdc or en ligand acts as doubly bridging ligand, bonding to four Zn(II) ions to form a rectangular frame. The tetrahedral coordination polyhedron of Zn(II) then allows the extension of these rectangular frames into infinite sheets as shown in Fig. 1. These sheets mutually interdigitate by π-stacking interactions between the nearest-neighbor bdc benzene rings, leading to the formation of two types of extended one-dimensional channels along the crystallographic *a* axis, with dimensions of 7.286 × 10.207 and

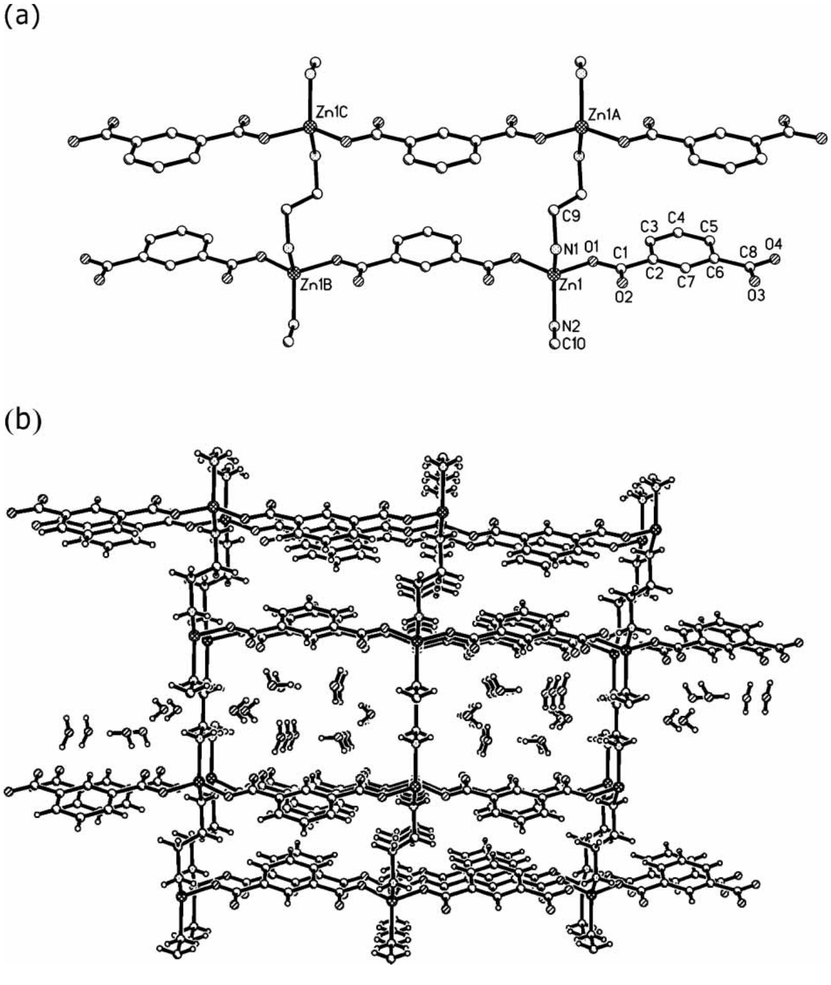

FIGURE 1 (a) The building unit present in the extended solid-state structure of complex **1** shown with nonhydrogen atoms. The displacement ellipsoids are drawn at the 50% probability level. (b) Crystal packing viewed along the *a* axis, showing water molecules trapped within the larger one-dimensional channels.

6.240 × 10.207 Å. The larger channels are occupied by water guests as shown in Fig. 1b.

Interestingly, a close examination of the molecular packing indicates that the water molecules are associated by O—H···O hydrogen bonds into cyclic centrosymmetric hexamers that adopt a planar conformation (Fig. 2a). Geometric parameters for the cyclic water hexamers are summarized in Table I. The average O···O distance of 2.781(3) Å within the hexamers is slightly longer than the corresponding value of 2.759 Å found in ice I$_h$ at −90°C. The torsion angles of O1w···O2w···O3w···O1w^a and O2w···O3w···O1w^a···O2w^a are 1.2(2) and −1.1(2)°, respectively [symmetry code: (a) $2 - x, -y, 2 - z$], indicating that the water hexamer is an approximate planar structure. The water hexameric rings are almost parallel to the bdc benzene rings, and self-assemble along the channels by an O3w—H···O2w hydrogen bond into infinite ladder-like chains that consist of alternate four- and six-membered rings (Fig. 2b). The water tetramers (the four-membered ring) adopt the well-known *uudd* [37–39] configuration with an average O···O distance of 2.774 Å. They are nearly perpendicular to the water hexameric rings. The torsion angle of O1w···O2w···O3w···O2w^b is 93.3(1)° [symmetry code: (b) $1 - x, -y, 2 - z$]. To the best of our knowledge, this is a new conformation for the one-dimensional water chain.

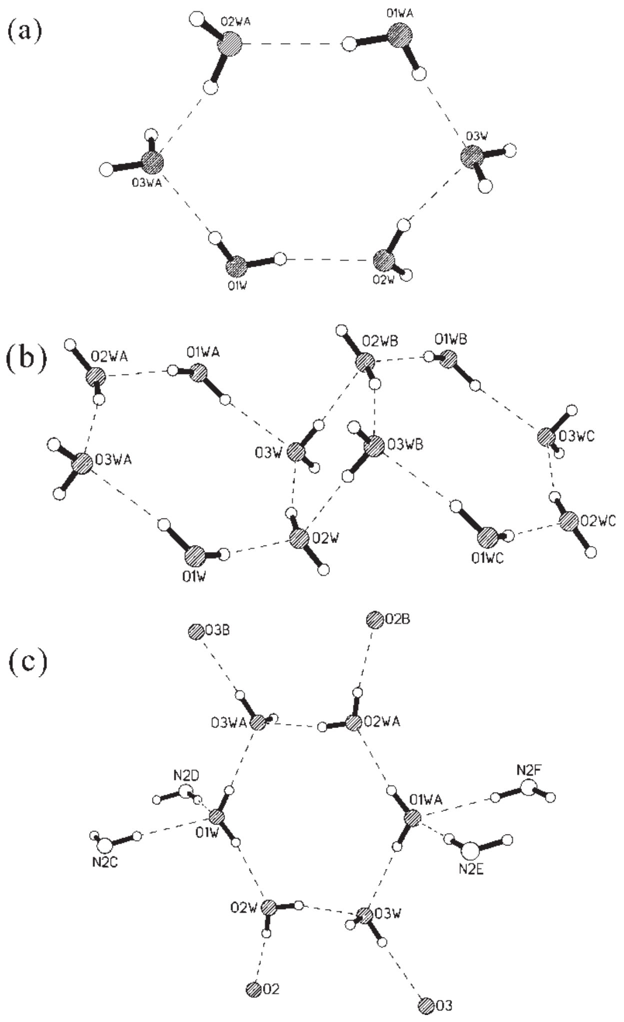

FIGURE 2 (a) Representation of the planar configuration of the cyclic water hexamer found in the channels of complex **1**. (b) Self-assembly of the water hexamers into a one-dimensional ladder-like chain. (c) View of the water hexamer and its immediate environment, showing hydrogen bonds between water cluster and host organic ligands. Other water molecules in adjacent rings are omitted for clarity.

As shown in Fig. 2c, hydrogen bonds also exist between the water clusters and host organic ligands, with average distances of 2.985(3) and 2.749(2) Å for Ow···N and Ow···O, respectively. These cooperative interactions between guest water molecules and crystal host help not only to form the less stable *uudd* tetramer and planar cyclic hexamer of the water clusters in the channels but also to stabilize the whole structure. Each water molecule in the water chain is involved in the formation of four hydrogen bonds in an almost tetrahedral arrangement. O2w and O3w are hydrogen bonded to three other water molecules and one oxygen atom from the neighboring organic ligand bdc, respectively, while O1w is hydrogen bonded to two other water molecules and two nitrogen atoms from the neighboring organic ligand en. Each water molecule servers as both a hydrogen bond donor and acceptor.

Reversible Removal/Formation of the Water Chain

Crystal structure study reveals that none of the water molecules is covalently bonded to the host metal ion. The relatively weak interactions with the host framework suggest that the water chains are fairly loosely held in the host channels. Therefore, facile removal of these water molecules under moderate heating is anticipated. Thermogravimetric analysis (TGA) shows a first weight loss of 15.1% at 96°C, corresponding to the removal of all three water molecules (theor. 15.7%) per formulae unit. The elemental analysis (see Experimental) supports the formation of [Zn(bdc)(en)] (**2**). It should be pointed out that there is a phase change after the removal of lattice water, as the dehydrated solid **2** shows a very different X-ray diffraction (XRD) pattern from that of the initial complex **1** (see Fig. 3a,b). The phase change could be due to the movement of the two-dimensional framework on the *bc* plane.

Interestingly, when the dehydrated material **2** was exposed to a moist environment, the product **3** had almost the same XRD pattern as **1** (see Fig. 3). Therefore, **1** has been successfully regenerated, which has also been supported by elemental analysis (see Experimental). In the XRD pattern of **3**, the diffraction peaks are slightly lower and wider than that of **1**, which indicates that the particle size of the regenerated product **3** becomes smaller. To further

TABLE I Geometrical parameters (Å, °) for the cyclic water hexamers in **1**

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1w2···O2w	0.84(1)	1.97(1)	2.786(2)	166(3)
O1w—H1w1···O3w^a	0.84(1)	1.95(1)	2.787(3)	171(3)
O2w—H2w1···O2	0.84(1)	1.91(1)	2.743(2)	174(2)
O2w—H2w2···O3w	0.83(1)	1.96(1)	2.774(3)	165(3)
O3w—H3w2···O2w^b	0.85(1)	1.94(1)	2.778(2)	171(2)
O3w—H3w1···O3	0.84(1)	1.93(1)	2.755(3)	164(3)
N2—H2n1···O1w^c	0.86(1)	2.15(1)	3.001(3)	169(2)
N2—H2n2···O1w^d	0.85(1)	2.12(1)	2.968(2)	171(2)
O···O···O			O···O···O···O	
O1w···O2w···O3w	125.2		O1w—O2w—O3w—O1w^a	1.2(2)
O2w···O3w···O1w^a	118.2		O2w—O3w—O1w^a—O2w^a	−1.1(2)
O3w···O1w^a···O2w^a	116.6		O1w—O2w—O3w—O2w^b	93.3(1)

Symmetry codes: a $(-x+2, -y, -z+2)$; b $(1-x, -y, 2-z)$; c $(x-1, y, z)$; d $(-x+1, -y+1, -z+2)$.

check whether the water chain had been regenerated in product **3**, FTIR analyses were performed. Figure 4 shows the FTIR spectra of the original complex **1**, the dehydrated solid **2** and the regenerated product **3**. The intensity of the bands at 3348, 3290 and 3223 cm^{-1} decrease significantly in the dehydrated solid **2** in comparison with that of the original complex **1**. These adsorption bands correspond to the O—H stretching, which theoretically should disappear when all the water had been removed. However, we could not avoid the adsorption of water when preparing the sample for IR analysis. Meanwhile, a series of bands centered at 2580 cm^{-1} and ranging from 2958 to 1890 cm^{-1} in the original complex **1** disappeared upon heating (for the dehydrated solid). Because similar IR bands at 2528 cm^{-1} were thought to be the results of Fermi resonance of ν_{OH} with the in-plane δ_{OH} and out-plane γ_{OH} bending modes [26] in the cyclic water tetramer, we assigned the bands centered around 2580 cm^{-1} as the characteristic O—H bending mode in the water hexamers and tetramers. In the product **3**, the characteristic bands of the water hexamer and tetramer reappear in the IR spectrum, which is almost identical to that of **1** (see Fig. 4), strongly suggesting that the water chains have been successfully regenerated.

EXPERIMENTAL

Preparation

1,3-Benzenedicarboxylic acid (H$_2$bdc, 5 mmol) was dissolved in ethanol (20 ml) in the presence of ethylenediamine (en, 20 ml). A solution of zinc nitrate (10 mmol, 20 ml) in water was added dropwise and the mixture was refluxed for 4 h,

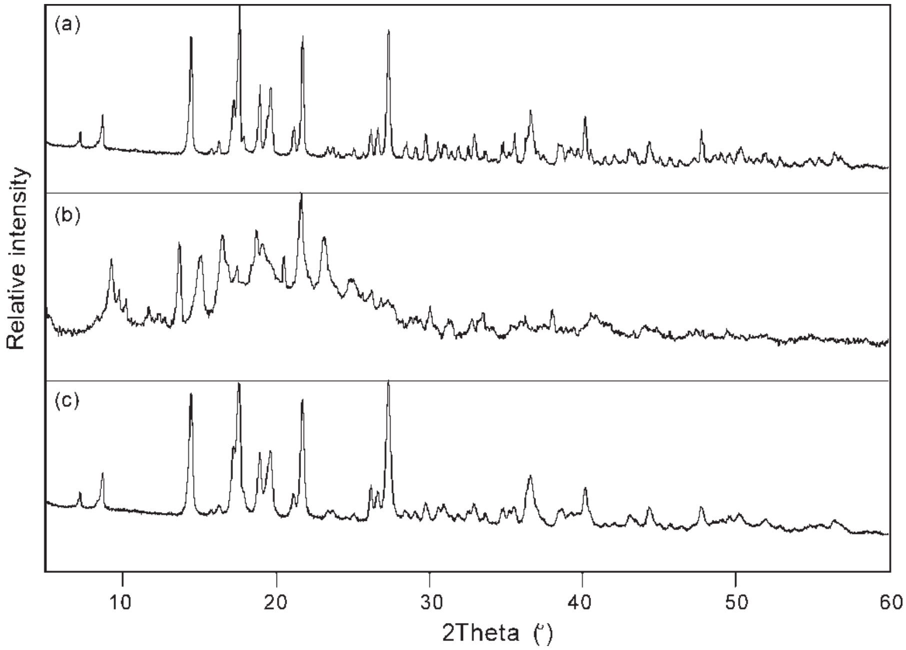

FIGURE 3 X-ray powder diffraction patterns of (a) the original complex **1**, (b) the dehydrated solid **2**, and (c) the regenerated solid **3**.

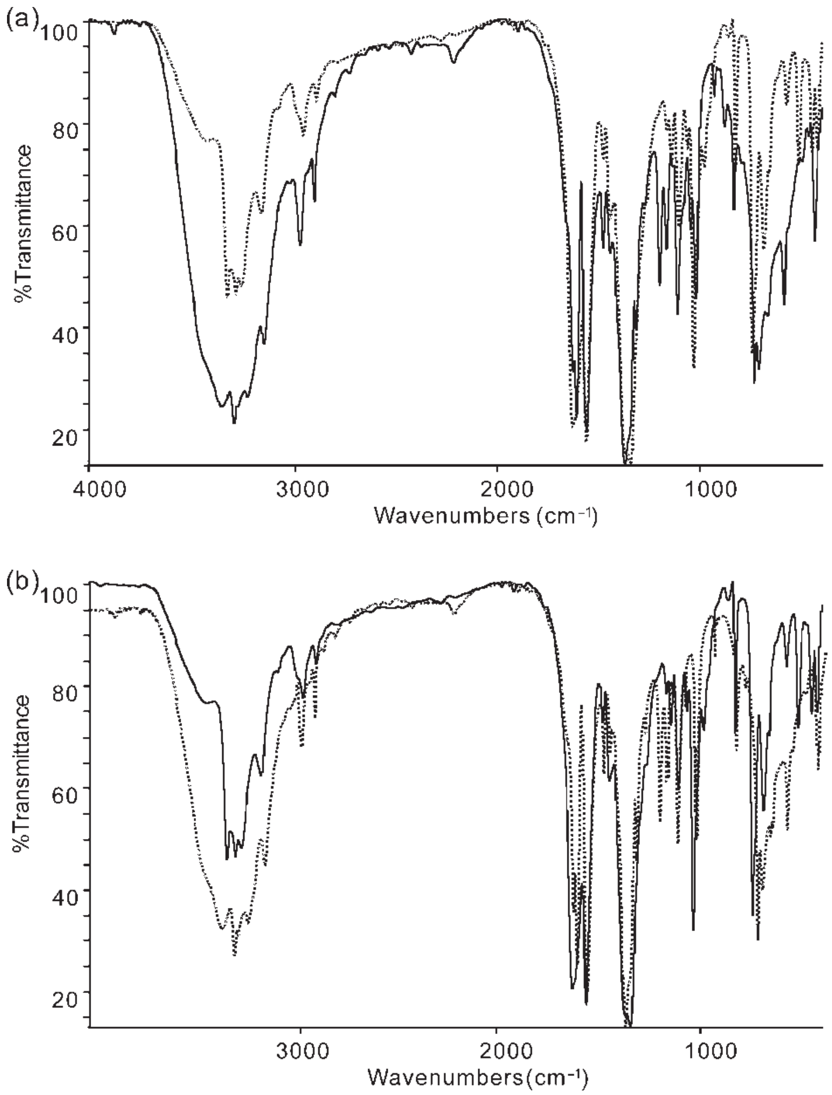

FIGURE 4 (a) FTIR spectrum of the initial complex **1** (solid line) and the dehydrated solid **2** (broken line). (b) FTIR spectrum of the dehydrated solid **2** (solid line) and the regenerated solid **3**.

then filtered to remove the white precipitate formed. Colorless products were crystallized from pale yellow filtrations 2 days later. They were collected and washed sequentially with water and ethanol. Yield: *ca*. 78%. IR (KBr pellet, cm^{-1}) 3348s, 3290s, 3223s, 3141s, 2959m, 2895m, 2793w, 2716w, 2650w, 2580w, 2525w, 2420w, 2212w, 1942w, 1892w, 1626s, 1606s, 1557s, 1476m, 1445m, 1369s, 1313m, 1199m, 1166m, 1111s, 1078s, 1019s, 933w, 880w, 836m, 732s, 711s, 671m, 590m, 493w, 468w, 438m. Anal. Calcd for $ZnC_{10}H_{18}N_2O_7$ (*M* 343.65): C 34.95%, H 5.28%, N 8.15%. Found: C 34.87%, H 5.44%, N 8.36%.

Dehydration

A freshly prepared sample of **1** (182 mg) was heated at 96°C in a conventional oven for 4 h. The measured weight loss (28.4 mg) was equivalent to the loss of three water molecules per formula unit of $[Zn(bdc)(en)(H_2O)_3]$ (**1**) (calcd 28.6 mg). The weight loss supported the formulation of the dehydrated compound as [Zn(bdc)(en)] (**2**). This is consistent with the elemental analysis. Calcd for $ZnC_{10}H_{12}N_2O_4$ (*M* 289.61): C 41.47%, H 4.18%, N 9.67%. Found: C: 40.86%, H 4.20%, N 9.62%.

Regeneration of the Water Hexamer Chain

Dehydrated material **2** (153.6 mg) was exposed to a moist environment (by keeping the sample in the upper part of a desiccator that contained water in the lower part). Two days later, **1** was regenerated from dehydrated material **2** by absorbing water vapor. The increase in the weight (28.9 mg) was equivalent to the gain of three water molecules per formula unit of [Zn(bdc)(en)] (**2**) (calcd 28.6 mg). The regenerated solids showed an identical XRD pattern and IR spectrum to those of the original complex **1**. Anal.

Calcd for regenerated solid **3** $ZnC_{10}H_{18}N_2O_7$ (*M* 343.65): C 34.95%, H 5.28%, N 8.15%. Found: C 34.67%, H 5.58%, N 8.34%.

Instrumentation

Microanalysis (C, H, N) data were obtained with an EA1110 CHNS-O elemental analyzer. The infrared spectrum was recorded by using KBr pellets on a Nicolet Avatar 360 FTIR spectrophotometer in the range 4000–400 cm^{-1}. XRD powder patterns were collected on a Panalytical X'pert X-ray diffractometer using nickel-filtered Cu Kα radiation in the angular range $2\theta = 5–60°$ with a step size of 0.008° and a scan step time of 10.16 s. TGA and DSC were performed on a NTTZSCH STA 449C thermal analyzer at a heating rate of 1°C/min under a nitrogen atmosphere.

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References

[1] Ming, Y.; Lai, G. L.; Tong, C. H.; Wood, R. H.; Doren, D. J. *J. Chem. Phys.* **2004**, *121*, 773.
[2] Keutsch, F. N.; Cruzan, J. D.; Saykally, R. J. *Chem. Rev.* **2003**, *103*, 2533.
[3] Wales, D. J.; Walsh, T. R. *J. Chem. Phys.* **1997**, *106*, 7193.
[4] Lee, H. M.; Kim, D.; Kim, K. S. *J. Chem. Phys.* **2002**, *116*, 5509.
[5] Mhin, B. J.; Kim, H. S.; Yoon, C. W.; Kim, K. S. *Chem. Phys. Lett.* **1991**, *176*, 41.
[6] Severson, M. W.; Buch, V. *J. Chem. Phys.* **1999**, *111*, 10866.
[7] Ludwig, R. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1808.
[8] Liu, K.; Brown, M. G.; Saykally, R. J. *J. Phys. Chem. A* **1997**, *101*, 8995.
[9] Fajardo, M. E.; Tam, S. J. *Chem. Phys.* **2001**, *115*, 6807.
[10] Morgenstern, K.; Rieder, K. H. *J. Chem. Phys.* **2002**, *116*, 5746.
[11] Kelley, J. A.; Weddle, G. H.; Robertson, W. H.; Johnson, M. A. *J. Chem. Phys.* **2002**, *116*, 1201.
[12] Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M.; Faure, R.; Roussel, C.; Claramunt, R. M.; Lopez, C.; Sanz, D. *Tetrahedron: Asymmetry* **1990**, *1*, 65.
[13] Gregory, J. K.; Clary, D. C.; Liu, K.; Brown, M. G.; Saykally, R. J. *Science* **1997**, *275*, 814.
[14] Kozmutza, C.; Kryachko, E. S.; First, E. T. *J. Mol. Struct. Theochem.* **2000**, *501*, 435.
[15] Mhin, B. J.; Kim, J. S.; Lee, S.; Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1994**, *100*, 4484.
[16] Lee, C. T.; Chen, H.; Fitzgerald, G. *J. Chem. Phys.* **1994**, *101*, 4472.
[17] Gregory, J. K.; Clary, D. C. *J. Phys. Chem. A* **1997**, *101*, 6813.
[18] Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J. *Nature* **1996**, *381*, 501.
[19] Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293.
[20] Speedy, R. J.; Madura, J. D.; Jorgensen, W. L. *J. Phys. Chem.* **1987**, *91*, 909.
[21] Belch, A. C.; Rice, S. A. *J. Chem. Phys.* **1987**, *86*, 5676.
[22] Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671.
[23] 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.
[24] Long, L.-S.; Wu, Y.-R.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem.* **2004**, *43*, 3798.
[25] Supriya, S.; Das, S. K. *N. J. Chem.* **2003**, *27*, 1568.
[26] Cheruzel, L. E.; Pometun, M. S.; Cecil, M. R.; Mashuta, M. S.; Wittebort, R. J.; Buchanan, R. M. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 5452.
[27] Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192.
[28] Custelcean, R.; Afouroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3094.
[29] Bernal, I.; Bear, J. L. *J. Chem. Crystallogr.* **2002**, *32*, 485.
[30] Doedens, R. J.; Yohanne, E.; Khan, M. I. *Chem. Commun.* **2002**, 62.
[31] Venkataramanana, B.; James, W. L. G.; Vittal, J. J.; Suresh, V. *Cryst. Growth Des.* **2004**, *4*, 554.
[32] Michaelides, A.; Sloulika, S.; Bakalbassis, E. G.; Mrozinski, J. *Cryst. Growth Des.* **2003**, *3*, 487.
[33] Rother, I. B.; Willermann, M.; Lippert, B. *Supramol. Chem.* **2002**, *14*, 189.
[34] Moorthy, J. N.; Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 3417.
[35] Jiang, Y. Q.; Xie, Z. X.; Ng, S. W. *Acta Cryst.* **2003**, *E59*, m947.
[36] Detailed crystallographic data for complex **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 225688. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (tel: +44-1223-336031; fax: +44-1223-336003; mailto: deposit@ccdc.cam.ac.uk).
[37] Udade, J. M.; Aldorta, I.; Elgero, J. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 717.
[38] Dykstra, C. J. *Chem. Phys.* **1989**, *91*, 6472.
[39] Radhakrishnan, T. P.; Hemdon, W. C. *J. Phys. Chem.* **1991**, *95*, 10609.