Inorg. Chem. **2005**, *44*, 3856–3862

Inorganic Chemistry
Article

Mn(II) Staircase Structures Stitched by Water Clusters to a 3D Metal-Organic Open Framework: X-ray Structural and Magnetic Studies

Sujit K. Ghosh,[†] Joan Ribas,*,[‡] M. Salah El Fallah,[‡] and Parimal K. Bharadwaj*,[†]

Chemistry Department, Indian Institute of Technology Kanpur, Kanpur 208016, India, and
Department de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11,
08028-Barcelona, Spain

Received January 22, 2005

4-Hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid, $cdaH_2$) reacts with $Mn(OAc)_2 \cdot 4H_2O$ to form a 1D staircase structure with dimeric Mn(II) units connected by water clusters to form a 3D framework, $\{[Mn_2(cda)_2 \cdot 4H_2O] \cdot 4H_2O\}_n$, **1**, in aqueous pyridine at room temperature. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a =$ 9.495(3), $b =$10.733(5), $c =$ 11.065(4) Å, $\alpha =$ 87.42(5), $\beta =$ 74.14(5), $\gamma =$ 80.07(2)°, $U =$ 1068.5(9) Å^3, $Z =$ 2, $\rho_{calcd} =$ 1.915 g cm^{-3}, $T =$ 100 K, $\mu =$ 1.28 mm^{-1}, $R_1 =$ 0.0453 ($I > 2\sigma(I)$), $wR_2 =$ 0.1046, GOOF = 1.282. Upon removal of the water molecules by heating, the 3D structure breaks down. Thermogravimetric analysis, infrared, X-ray powder diffraction studies, and X-ray crystallography were performed to characterize this compound. Since the coordination polymer has diaqua-bridged Mn(II) centers, it was subjected to variable-temperature magnetic studies.

Bulk water exhibits[1] a fascinating array of properties, some of which are considered anomalous. A large number of efforts have been made to develop model force fields in the quest to achieve an accurate description of liquid water capable of explaining its properties besides getting an insight into the study of solvation, cloud and ice formation, biological processes, and so forth. It is recognized that hydrogen-bonding interactions, their fluctuations, and rearrangement dynamics determine the properties of bulk water. But, none of the existing models can explain all of the properties of water, even with considerable interpretation. A major obstacle[2] to fully comprehending its behavior is that of correctly describing the cooperative nature of hydrogen-bonding interactions among a collection of water molecules; the key to tackling this will be the exploration of structural and binding properties of small water clusters in different surroundings. This realization has led to an upsurge[3−9]in the characterization of water clusters of different nuclearity in crystal hydrates. The advantage of clusters is the possibility to simply vary the size and to investigate the development of properties of the condensed phase in a step-by-step manner. Moreover, the degree of structuring of a water cluster that can be imposed by its environment and vice versa can be of importance in designing new metal-organic framework (MOF) structures.[10]

---

[*] To whom correspondence should be addressed. E-mail: pkb@iitk.ac.in (P.K.B.), joan.ribas@qi.ub.es (J.R.).

[†] Indian Institute of Technology Kanpur.

[‡] Universitat de Barcelona.

(1) (a) Ludwig, R. A*ngew. Chem*., *Int. Ed.* **2001**, *40*, 1808. (b) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, 1969.

(2) (a) Keutsch, F. N.; Saykally, R. J. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 10533. (b) Chaplin, M. F. *Biophys. Chem.* **1999**, *83*, 211.

(3) (a) Sreenivasulu, B.; Vittal, J. J. *Angew. Chem*., *Int. Ed.* **2004**, *43*, 5769. (b) Ng, M. T.; Deivaraj, T. C.; Klooster, W. T.; McIntyre, G. J.; Vittal, J. J. *Chem. Eur. J.* **2004**, *10*, 5853.

(4) Yoshizawa, M.; Kusukawa, T.; Kawano, M.; Ohhara, T.; Tanaka, I.; Kurihara, K.; Nimura, N.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 2798.

(5) (a) Liu, Q.-Y.; Xu, L. *CrystEngComm* **2005**, *7*, 87. (b) Ma, B. Q.; Sun, H. L.; Gao, S. *Angew. Chem*., *Int. Ed.* **2004**, *43*, 1374. (c) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Botar, B.; Talismanova, M. O. *Angew. Chem*., *Int. Ed.* **2003**, *42*, 2085.

(6) (a) Ghosh, S. K.; Bharadwaj, P. K.; *Angew. Chem*., *Int. Ed.* **2004**, *43*, 3577. (b) Neogi, S.; Savitha, G.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 3771.

(7) (a) Cuamatzi, P. R.; Diaz, G. V.; Hopfl, H. *Angew. Chem*., *Int. Ed.* **2004**, *43*, 3041. (b) Raghuraman, K.; Katti, K. K.; Barbour, L. J.; Pillarsetty, N.; Barnes, C. L.; Katti, K. V. *J. Am. Chem. Soc.* **2003**, *125*, 6955. (c) Pal, S.; Sankaran, N. B.; Samanta, A. *Angew. Chem*., *Int. Ed.* **2003**, *42*, 1741.

(8) (a) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Chem. Commun.* **2002**, 859. (b) Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192. (c) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671.

(9) (a) Infantes, L.; Motherwell, S. *CrystEngComm* **2002**, *4*, 454. (b) Infantes, L.; Chisholm, J.; Motherwell, S. *CrystEngComm* **2003**, *5*, 480.

(10) (a) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 5180. (b) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 6887.

10.1021/ic050102w CCC: $30.25

Synthesis of MOFs with multidentate ligands may provide voids to accommodate water clusters where both water−MOF and water−water interactions determine the overall structure. Any such exercise has the ultimate aim(s) of having novel materials with useful applications. Metal-organic hybrid structures of paramagnetic metal ions are particularly interesting as these may give rise to a series of novel framework structures with potential applications in the fields of molecular magnetism[11] and material chemistry.[12] A commonly used strategy in building such extended network structures is to employ bridging ligands capable of transmitting magnetic interactions in addition to propagate the network. We report here an MOF, built from 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid, $cdaH_2$) and Mn(II)-acetate salt. Earlier, we[13] and others[14] had used closely related pyridine-2,6-dicarboxylic acid for generating novel MOFs with transition- as well as lanthanide-metal ions. To probe the effect of the hydroxyl group at the 4-position, $cdaH_2$ was used here to afford a stairlikelike coordination polymer built through carboxylate- and aquo-bridging. Discrete tetradecameric water clusters assemble these staircases via an intricate array of hydrogen bonding into an overall 3D MOF. The water cluster takes the shape of a hexameric chair buttressed on two sides by acyclic tetramers. While no experimental report is available identifying a tetradecameric water cluster either in inorganic or in organic crystal hosts, theoretical calculations on $(H_2O)_{14}$ have revealed[15] four energy minima corresponding to four structures arising from extensions of cuboids, pentagonoids, and their combinations. The present contribution reports the synthesis, crystal structure, thermal stability, and variable-temperature magnetic susceptibility of the compound.

Experimental Section

Materials. The metal salt and 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid) were acquired from Aldrich and used as received.

Physical Measurements. Spectroscopic data were collected as follows: IR (KBr disk, 400−4000 cm^{-1}) Perkin-Elmer model 1320; X-ray powder pattern (Cu Kα radiation at a scan rate of 3°/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator; thermogravimetric analysis (heating rate of 5 °C/min) Mettler Toledo Star System. Magnetic susceptibility measurements were carried out on the polycrystalline sample at the Servei de Magnetoquímica of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-XL susceptometer apparatus working in the range 2−300 K under a magnetic field of approximately 500 G (2−30 K) and 1000 G (35−300 K). Diamagnetic corrections were estimated from Pascal Tables. The EPR spectra have been recorded on a X-band Bruker Spectrometer (ESR 300E), working with an oxford liquid helium cryostat for variable temperature. Microanalysis data for the compound were obtained from CDRI, Lucknow.

Syntheses

$\{[Mn_2(cda)_2 \cdot 4H_2O] \cdot 4H_2O\}_n$, 1. A solution containing $Mn(OAc)_2 \cdot 4H_2O$ (0.25 g; 1 mmol) and chelidamic acid (0.18 g; 1 mmol) dissolved in 25 mL of aqueous pyridine (1:1 v/v) on slow evaporation at room temperature, affords light purple crystals of **1** after 14 days in the form of a rectangular parallelepiped in 55% yield. Anal. Calcd for $C_{14}H_{22}N_2O_{18}Mn_2$: C, 27.28; H, 3.56; N, 4.54%. Found: C, 27.15; H, 3.62; N, 4.37%.

X-ray Structural Studies. Single-crystal X-ray data on **1** were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT[16] software. An empirical absorption correction was applied to the collected reflections with SADABS[17] using XPREP.[18] The structure was solved by the direct method using SHELXTL[19] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[20] program package. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters. The crystal and refinement data are collected in Table 1.

Results and Discussion

The compound is air-stable and, once formed, is insoluble in most solvents including water.The asymmetric unit of **1** contains two cda^{2-}, two Mn(II), and eight water molecules. Each Mn(II) ion exhibits heptacoordination with a distorted pentagonal bipyramidal geometry where equatorial coordination comes from the ring N and the carboxylates of a cda^{2-} ligand, one water, and one carboxylate from the neighboring cda^{2-} ligand (NO_4 donor set). Two water molecules occupy the axial positions. The hydroxyl group at the 4-position of cda^{2-} does not take part in metal coordination; it is involved in hydrogen-bonding interactions with neighboring carboxylate O atoms. The lone equatorial and one of the axial water molecules are involved in bridging another Mn(II) ion, thus

---

(11) (a) Kahn, O. *Molecular Magnetism*; Wiley-VCH: New York, 1993. (b) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. (c) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313. (d) Tasiopoulos, A. J.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117.

(12) (a) Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600. (b) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703. (c) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 375.

(13) (a) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2003**, *42*, 8250. (b) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 2293. (c) Ghosh, S. K.; Savita, G.; Bharadwaj, P. K. *Inorg. Chem.* **2004**, *43*, 5495. (d) Ghosh, S. K.; Ribas, J.; Bharadwaj, P. K. *CrystEngComm* **2004**, *45*, 250. (e) Ghosh, S. K.; Ribas, J.; Bharadwaj, P. K. *Cryst. Growth Des.* **2005**, *5*, 623.

(14) (a) Nobuo, O.; Hasuyo, K.; Ayumi, F. *Acta Crystallogr. E* **2002**, *E58*, m354. (b) Zhao, B.; Yi, D.; Chen, X.-Y.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H. *Inorg. Chem.*, in press.

(15) Maheswary, S.; Patel, N.; Sathyamurthy, N.; Kulkarni, A. D.; Gadre, S. R. *J. Phys. Chem. A* **2001**, *105*, 10525.

(16) *SAINT+*, 6.02 ed.; Bruker AXS: Madison, WI, 1999.

(17) Sheldrick, G. M. *SADABS*, *Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(18) *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(19) Sheldrick, G. M. *SHELXTL*, *Reference Manual*: version 5.1: Bruker AXS; Madison, WI, 1997.

(20) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystal and Structure Refinement Data for **1**

empirical formula	$C_{14}H_{22}N_2O_{18}Mn_2$
formula weight	616.22
temperature	100 K
radiation, wavelength	Mo Kα, 0.71073 Å
crystal system	triclinic
space group	P−1
a, Å	9.495(3)
b, Å	10.733(5)
c, Å	11.065(4)
α(°)	87.425(5)
β(°)	74.143(5)
γ(°)	80.076(2)
U, Å^3	1068.5(9)
Z	2
ρ_{calc}, Mg/m^3	1.915
μ, mm^{-1}	1.280
F(000)	628
refl. collected	5096
independent refl.	4949
refinement method	full-matrix least-squares on F^2
GOOF	1.282
final *R* indices	$R_1 = 0.0453$
[$I > 2\sigma(I)$]	$wR_2 = 0.1046$
R indices	$R_1 = 0.0464$
(all data)	$wR_2 = 0.1052$

propagating the coordination polymeric chain along the crystallographic *b*-axis. Each Mn(II) in the chain is further involved in making double carboxylate bridging with another Mn(II) forming a dimeric unit that forms a step in the stairlike coordination polymeric chain (Figure 1). All Mn−O and Mn−N bond distances (Table 2) are somewhat longer compared[21] to those found in several related species. The bond angles involving a metal center are all different and deviate from an ideal pentagonal bipyramidal coordination geometry.

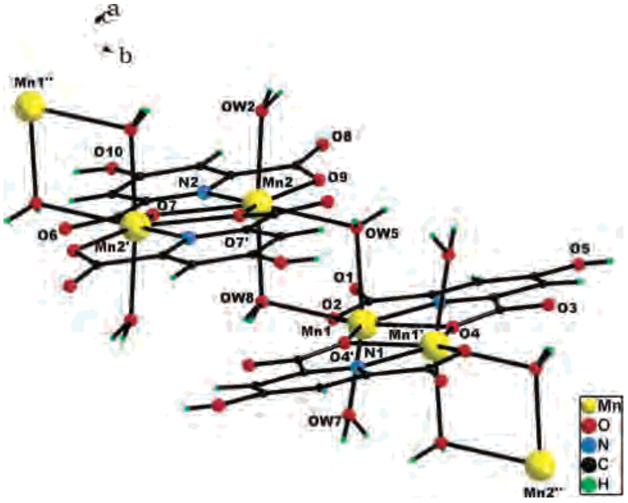

Figure 1. A view of the carboxylate-bridged Mn(II) dimeric units further joined by diaquo bridging to form a stairlike structure.

Table 2. Selected Bond Distances (Å) and Bond Angles (°) in **1**

Bond Distances (Å)			
Mn1−Ow7	2.157(3)	Mn1−Ow5	2.215(2)
Mn1−O4	2.234(2)	Mn1−N1	2.234(2)
Mn1−O2	2.330(2)	Mn1−Ow8	2.413(2)
Mn1−O4′	2.432(2)	Mn2−Ow2	2.123(2)
Mn2−N2	2.216(2)	Mn2−O7	2.232(2)
Mn2−O9	2.285(2)	Mn2−Ow8	2.308(2)
Mn2−Ow5	2.351(2)	Mn2−O7′	2.420(2)

Bond Angles (°)			
Ow7−Mn1−Ow5	171.03(10)	Ow7−Mn1−O4	89.44(9)
Ow5−Mn1−O4	84.49(8)	Ow7−Mn1−N1	91.18(11)
Ow5−Mn1−N1	97.77(9)	O4−Mn1−N1	136.95(8)
Ow7−Mn1−O2	80.77(9)	Ow5−Mn1−O2	101.60(8)
O4−Mn1−O2	151.78(7)	N1−Mn1−O2	70.11(8)
Ow7−Mn1−Ow8	97.50(10)	Ow5−Mn1−Ow8	75.18(8)
O4−Mn1−Ow8	82.33(7)	N1−Mn1−Ow8	140.01(8)
O2−Mn1−Ow8	72.91(7)	Ow7−Mn1−O4′	96.90(10)
Ow5−Mn1-O4′	87.03(8)	O4−Mn1−O4	68.55(8)
N1−Mn1−O4′	68.65(8)	O2−Mn1−O4′	138.64(7)
Mn1−O4−Mn1	111.45(8)	Ow8−Mn1−O4′	147.24(7)
Ow2−Mn2−N2	104.52(9)	Ow2−Mn2−O7	85.61(8)
N2−Mn2−O7	137.59(8)	Ow2−Mn2−O9	82.46(9)
N2−Mn2−O9	70.96(8)	O7−Mn2−O9	151.28(7)
Ow2−Mn2−Ow8	165.23(8)	Mn2−Ow8−Mn1	100.40(8)
N2−Mn2−Ow8	90.24(8)	O7′−Mn2−Ow8	83.78(7)
O9−Mn2−Ow8	102.25(8)	Ow2−Mn2−Ow5	93.80(9)
N2−Mn2−Ow5	135.68(8)	O7−Mn2−Ow5	82.89(7)
O9−Mn2−OW5	72.00(7)	OW8−Mn2−OW5	74.73(8)
OW2−Mn2−O7	100.09(9)	N2−Mn2−O7	69.01(8)
O7−Mn2−O7	68.68(8)	O9−Mn2−O7′	139.20(7)
OW8−Mn2−O7	85.56(8)	OW5−Mn2−O7′	147.02(7)
Mn2−O7−Mn2	111.32(8)	Mn1−Ow5−Mn2	105.22(9)

One bridging and two nonbridging axial water molecules belong to a staircase unit and are connected to a similar set of water molecules belonging to another staircase through eight other intervening water molecules forming an overall tetradecameric cluster. Atom Ow6 or Ow6′, present at either end of this cluster (Figure 2), is within a hydrogen-bonding distance (2.702 Å) from the terminal atom of the next cluster. However, they are related by a center of symmetry, and so their corresponding H-atoms are oriented either face to face (that is, angle, O−H···H 177°) or away from each other and are not considered hydrogen-bonded. The H···H separation of 1.144 Å is, however, shorter compared to the shortest intermolecular H···H separation (1.949 Å) found in the polymorph A of 1,2,3,5-tetra-*O*-acetyl-*β*-D-ribofuranose.[22] The repulsive interaction associated with this short distance is compensated by strong nonbonding water−MOF interactions. Also, atoms Ow5 and Ow8 show a distance of 2.827 Å, although their H-atoms are pointing away from each other leaving the two O atoms face to face and so are not considered as hydrogen-bonded. Therefore, the group of 14 water molecules are regarded as a discrete water cluster. These water clusters assemble the staircases along the crystallographic *a*-axis (Figure 3) while other $(H_2O)_{14}$ clusters extend the polymeric chain in the crystallographic *c*-axis to form an overall 3D structure (Figure 4). An approximate distance of 9.50 Å is maintained between the staircases by these clusters acting as pillars.

Various nonbonding distances and angles relevant to the water cluster are collected in Table 3. Its structure can be described as an ice-like (I_h) hexameric chair with two acyclic tetramers dangling from two opposite ends (Figure 2). The hexameric part shows a wide variation in the O···O nonbonding distances (Table 3) that range from 2.669 to 2.938

---

(21) (a) Tynan, E.; Jensen, P.; Kruger, P. E.; Lees, A. C. *Chem. Commun.* **2004**, *23*, 2660. (b) Marioni, P.-A.; Marty, W.; Stoeckli-Evans, H.; Whitaker, C. *Inorg. Chem. Acta* **1994**, *219*, 161.

(22) Bombicz, P.; Czugler, M.; Tellgren, R.; Kálmán, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1957.

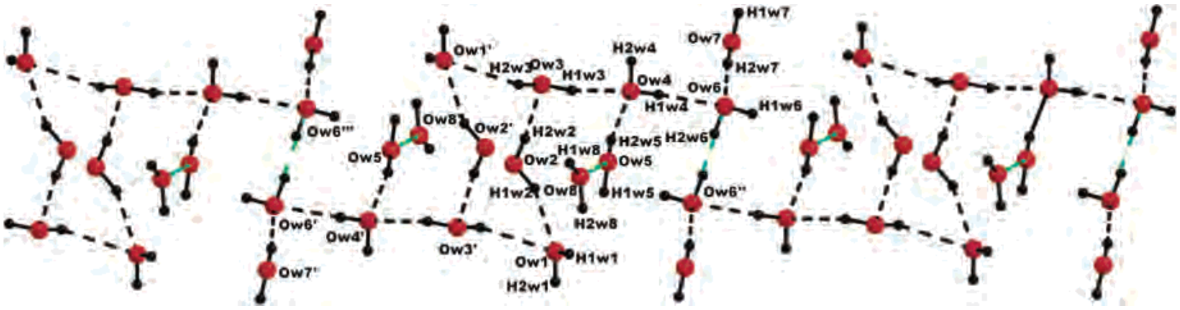

Figure 2. A perspective view of the $(H_2O)_{14}$ cluster illustrating the hydrogen bonding scheme. The O atoms connected by blue-colored bonds are related by center of symmetry and even though their distances lie within normal hydrogen-bonding distances, they are considered nonbonded as the H-atoms are not pointing in the right directions.

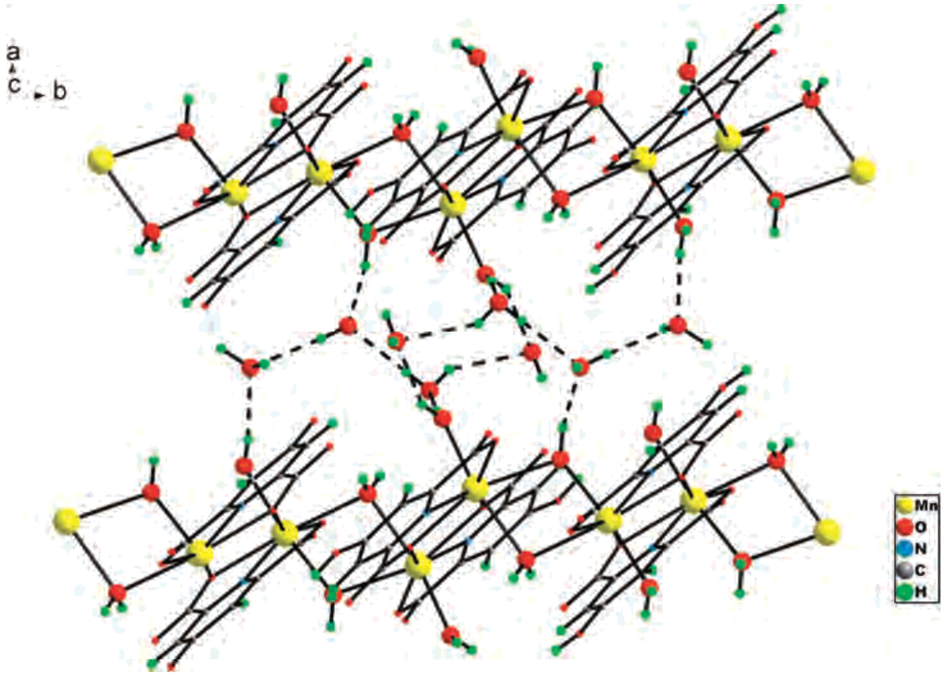

Figure 3. A view showing a tetradecameric water cluster connecting two staircases.

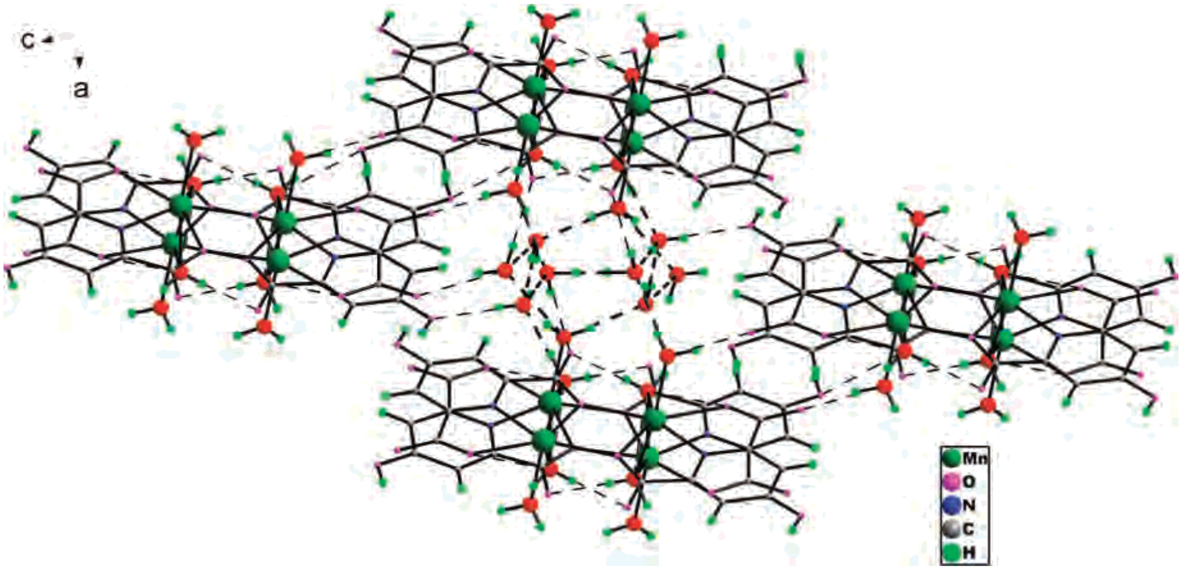

Figure 4. A perspective view showing how the water clusters form the overall 3D MOF.

Å compared[23] to 2.759 Å in ice I_h at −90° C or 2.85 Å in liquid water. The O···O···O angles in the hexamer also vary widely with an average of 93.57° that is considerably different from the corresponding value of 109.3° in hexagonal

Table 3. Nonbonding Distances (Å) and Angles (°) Pertaining to the Tetradecameric Cluster

Nonbonding Distances (Å)			
Ow1···Ow2	2.777(6)		
Ow2···Ow3	2.669(4)		
Ow3···Ow1	2.938(4)		
Ow3···Ow4	2.812(6)		
Ow4···Ow5	2.696(6)		
Ow4···Ow6	2.810(6)		
Ow6···Ow7	2.699(6)		
Ow1···O6	2.840(4)		
Ow1···O8	2.727(6)		
Ow4···O5	2.770(3)		
Ow6···O3	2.811(4)		
Ow7···O1	2.687(4)		
H1w1···Ow1	0.826(4)	H1w1···O8	1.929(3)
H2w1···Ow1	0.826(3)	H2w1···O6	2.050(4)
H1w2···Ow2	0.834(4)	H1w2···Ow1	2.017(4)
H2w2···Ow2	0.849(2)	H2w2···OW3	1.824(2)
H1w3···Ow3	0.855(1)	H2w3···OW1	2.173(3)
H2w3···Ow3	0.844(4)	H1w3···OW4	1.983(3)
H1w4···Ow4	0.841(2)	H1w4···O6	1.970(3)
H2w4···Ow4	0.828(3)	H2w4···O5	1.945(4)
H1w5···Ow5	0.888(4)	H1w5···O6	1.794(2)
H2w5···Ow5	0.841(1)	H1w6···Ow6	0.781(4)
H2w6···Ow6	0.821(3)	H1w7···Ow7	0.857(2)
H2w7···Ow7	0.841(4)	H1w4···OW4	1.865(3)
H2w6···O3	2.096(3)	H1w7···O1	1.844(2)
H1w7···OW6	1.863(3)		
Angles (°)			
Ow1···H−Ow2	151.2(2)	Ow3···H−Ow2	173.1(1)
Ow3···H−Ow1	150.7(2)	Ow4···H−Ow3	163.3(2)
Ow4···H−Ow5	169.4(2)	Ow6···H−Ow4	177.0(2)
Ow6···H−Ow7	172.2(2)	Ow1−H···O6	159.9(1)
Ow1−H···O8	161.9(2)	Ow4−H···O5	174.6(2)
Ow6−H···O3	145.5(1)	Ow7−H···O1	167.1(2)
Ow1···Ow2···Ow3	104.1(2)	Ow2···Ow3···Ow1′	102.5(1)
Ow3′···Ow1···Ow2	73.9 (3)	Ow3···Ow4···Ow5	106.5(2)
Ow3···Ow4···Ow6	113.6(2)	Ow4···Ow6···Ow7	111.7(3)

ice. Theoretical calculations on the water hexamer revealed[24] the existence of several "cage", "prism", "book", "boat", and "cyclic" conformers which are almost isoenergetic to within ∼0.7 kcal mol^{-1}. The "cage" conformer is the most stable one at very low temperature and has been observed[25] by vibration−rotation tunneling spectroscopy, while a quasi-planar cyclic hexamer was detected[26] in a helium droplet. However, the lattice of a crystal host offers an environment where a higher-energy conformer can be stabilized via water−water and water−host interactions, and chair,[7a,13a,27] boat,[28] and planar[29] conformers have been characterized crystal hosts.

Supramolecular association of water molecules to form a chair conformation and their self-assembly into a 1D tape had been identified[30] in an organic host constructed from 2,4-dimethyl-5-aminobenzo[*b*]-1,8-naphthyridine. A discrete chair conformer has recently been found[13a] in the zigzag voids of an MOF constructed from pyridine-2,6-dicarboxylic acid and Ce(III) or Pr(III), while 1D chains consisting of chair conformers connected by Zn(II) or Co(II) have been found[31] in the complexes, $[M(H_2biim)_2(OH_2)_2](ina)_2\cdot 4H_2O$ [M = Zn(II) or Co(II), H_2biim = 2,2′-biimidazole, ina = isoniconate]. In the present structure, the chair conformation is slightly different from the reported structures with respect to the O···O distances or O···O···O angles, and the hydrogen-bonding interactions are strong and highly directional (Table 3) commensurate with the environment the cluster is in. Each acyclic tetramer is bound to the hexameric unit quite strongly (Ow3···Ow4, 2.812 Å), while the O···O distances in the tetrameric part span a wide range (2.696−2.810 Å). It follows, therefore, that the structure of the cluster is sufficiently flexible to be accommodated in the voids between the polymeric chains and at the same time maximizing the interactions among water molecules themselves and between water and carboxylate or hydroxyl O of the coordination polymeric chains (Figure 3). Every O atom in the cluster does not show four coordination just like water molecules[32] at the surface of ice or liquid water. Theoretical calculations[15] for the $(H_2O)_{14}$ cluster have revealed the existence of four energy minima in the potential energy surface corresponding to four different structures arising from extensions of cuboids, pentagonoids, and their combinations. The minimum energy structure is suggested to result from a cube with two parallel pentamers sharing two edges of the cube, while higher-energy structures include extended cuboid, two edge-sharing cuboids, and two parallel fused pentamers attached to a cyclic tetramer on one side (Figure 5). The structure of the cluster described herein is very different from these predicted ones due to the chemical environment.

Thermal gravimetric analysis of **1** further corroborates the existence of strong hydrogen-bonding interactions between the MOF and the water cluster. Weight loss in air due to exclusion of water begins[33] only after 140 °C, and the loss of 23.1% corresponding to all of the water (calculated 23.4%) takes place above 300 °C. Complete decomposition of the compound is achieved above 450 °C. The FTIR spectrum of **1** shows a broad band centered around 3405 cm^{-1} without showing any resolution. This band is not seen in the spectrum taken after heating the compound under vacuum (0.1 mm) at 300 °C for 4 h due to escape of water from the lattice. Deliberate exposure to water vapor for 3 days does not lead to reabsorption of water into the lattice as monitored by FTIR spectroscopy. The powder X-ray diffraction pattern of **1** simulated from the single-crystal data shows several prominent peaks which match with the diffraction peaks on the powdered sample before heating.[33] However, after water

---

(23) (a) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863. (b) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, 1969.

(24) (a) Tsai, C. J.; Jordan, K. D. *Chem. Phys. Lett.* **1993**, *213*, 181. (b) Kim, K.; Jordan, K. D.; Zwier, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 11568.

(25) Liu, K.; Brown, M. G.; Carter, C.; Saykally, R. J.; Gregory, J. K.; Clary, D. C. *Nature* **1996**, *381*, 501.

(26) Nauta, K.; Miller, R. E. *Science* **2000**, *287*, 293.

(27) (a) Foces-Foses, C.; Cano, F. H.; Martinez-Ripoli, M.; Faure, R.; Roussel, C.; Claramunt, R. M.; Lopez, C.; Sanz, D.; Elguero, J. *Tetrahedron*: *Asymmetry* **1990**, *1*, 65. (b) Michaelides, A.; Skoulika, S.; Bakalbassis, E. G.; Mrozinski, J. *Cryst. Growth Des.* **2003**, *3*, 487.

(28) Ren, Y.-P.; Long, L.-S.; Mao, B.-W.; Yuan, Y.-Z.; Huang, R.-B.; Zheng, L.-S. *Angew. Chem., Int. Ed.* **2003**, *42*, 532.

(29) Moorthy, J. N.; Natarajan, R.; Venugopalan, P. *Angew. Chem., Int. Ed.* **2002**, *41*, 3417.

(30) Custecean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094.

(31) Ye, B.-H.; Ding, B.-B.; Weng, Y.-Q.; Chen, X.-M. *Inorg. Chem.* **2004**, *43*, 6866.

(32) Gruenloh, C. J.; Carney, J. R.; Arrington, C. A.; Zwier, T. S.; Fredericks, S. Y.; Jordan, K. D. *Science* **1997**, *276*, 1678.

(33) See Supporting Information.

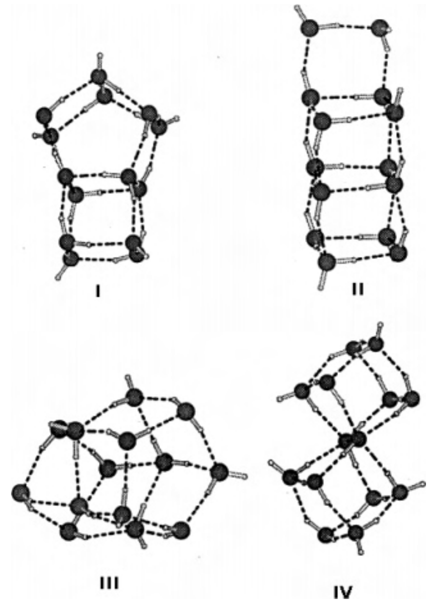

Figure 5. Schematic representation of theoretically calculated low-energy structures of $(H_2O)_{14}$ cluster.

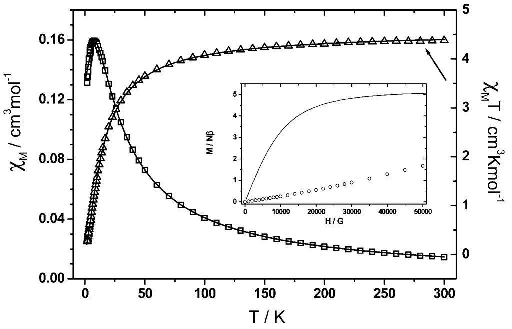

Figure 6. Plot of the $\chi_M T$ vs T for complex **1**. The open points are the experimental ones, and the solid lines correspond to the best fit obtained. Inset: Plot of the magnetization in 2S units measured at 2 K (open circles). Continuous line corresponds to the Brillouin function for an isolated $S = 5/2$.

expulsion by heating, a total change in the pattern is observed, suggesting complete breakdown of the host lattice. This is expected, as the water cluster acts as a “glue” to assemble the overall structure.

Magnetic Properties

The existence of diaquo-bridged Mn(II) centers in the structure prompted us to carry out variable-temperature magnetic studies. The magnetic susceptibility measurements were carried out from 300 to 2 K. Diamagnetic corrections were estimated[34] from Pascal’s Table. The magnetic behavior of **1** is illustrated in Figure 6 by means of a plot of $\chi_M T$ vs the temperature. At room temperature, $\chi_M T$ gives a value of 4.37 cm^3 K mol^{-1} which is as expected for one Mn(II) ion (4.375 cm^3 mol^{-1} K per Mn(II) with $g = 2.0$). When the sample is cooled, the $\chi_M T$ decreases slowly; below approximately 100 K, it decreases more quickly and reaches 0.271 cm^3 K mol^{-1} at 2 K. The χ_M value increases continuously on cooling to reach a maximum of 0.1595 cm^3 mol^{-1} at 7.5 K and decreases to a value of 0.1354 cm^3 mol^{-1} at 2 K. As shown in the Figure 1, the structure consists of Mn(II) ions linked by two 4-hydroxy-2,6-pyridynedicarboxylate groups and two asymmetric diaqua bridge alternatively to give an alternating 1D system. Thus, two coupling parameter J_1 and J_2 must be considered to interpret the two possible magnetic interactions in this complex (Figure 7). In the first approach and taking into account the above consideration, the experimental magnetic data have been fitted using the Drillon’s equation[35] based upon the spin Hamiltonian $H = -J_1\Sigma(S_{2i}S_{2i+1}) - J_2\Sigma(S_{2i+1}S_{2i+2})$, where the Mn(II) ion and the J_1 and J_2 values are isotropic.

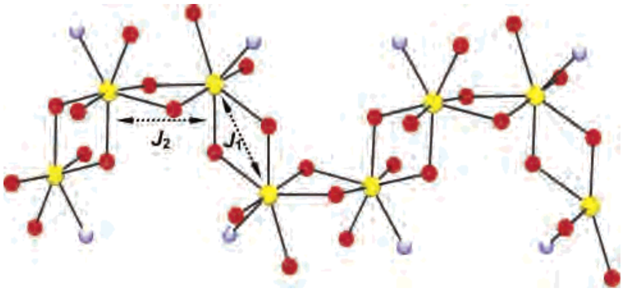

Figure 7. Schematic exchange interactions within **1**.

$$\chi = [Ng^2\beta^2/3kT][S(S+1)][(1 + u_1 + u_2 + u_1u_2)/(1 - u_1u_2)] \quad (1)$$

Here, $u_1 = \coth[J_1[S(S+1)]/kT] - kT/J_1[S(S+1)]$ and $u_2 = \coth[J_2[S(S+1)]/kT] - kT/J_2[S(S+1)]$.

The J_1 and J_2 are obtained by minimizing the function $R = \Sigma[(\chi_M)_{exp} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{exp}]^2$. The best-fit parameters from 300 down to 2 K are found as follows: $J_1 = -1.57$ cm^{-1}, $J_2 = -1.17$ cm^{-1}, and $g = 2.05$ with an error $R = 2.3 \times 10^{-5}$. The bridging angles involving carboxylate and water lie in the range 105−110°, leading to small antiferromagnetic coupling. On the other hand, the diaqua bridging that gives nonplanarity favors ferromagnetic coupling.[36] Taking these two factors together, we can attribute the greater value $J_1 = -1.57$ cm^{-1} to the double 4-hydroxy-2,6-pyridynedicarboxylate bridging with the large angle, Mn1−O4−Mn2 = 111.44(8)° and the lower value $J_2 = -1.17$ cm^{-1} to the asymmetric diaqua angle, Mn1−Ow2−Mn2 = 100.44(8)° and Mn1−Ow4−Mn2 = 105.26(9)°. On the other hand, considering that the two J_1 and J_2 values are weak and are close in value, we have also interpreted the experimental data to the reduced classical uniform chain, taking $u_1 = u_2$, and following the Fisher’s equation[37]

$$c = [Ng^2b^2/3kT][S(S+1)][(1+u)/(1-u)] \quad (2)$$

with $u = \coth[J[S(S+1)]/kT] - kT/J[S(S+1)]$) and $J_1 = J_2 = J$. The new fitting leads to the following values: $J = -1.38$ cm^{-1}, $g = 2.05$, and $R = 7.1 \times 10^{-5}$.

The weak, yet nonnegligible, antiferromagnetic interaction between the Mn(II) centers is confirmed by magnetization measurements at 2 K up to an external field of 5 T. At higher

---

(34) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, 1993.

(35) Drillon, M. *Inorg. Chem.* **1997**, *36*, 677.

(36) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297 and references therein.

(37) Fisher, A. *J. Phys.* **1964**, *32*, 343.

field, the magnetization corresponds to a nonsaturated $S = {}^5/_2$ system (Figure 4, inset). Comparison of the overall shape of the plot with the Brillouin plot for a fully isolated $S = {}^5/_2$ system indicates slower magnetization, consistent with a weak antiferromagnetic interaction. The solid-state EPR spectrum of **1** at room temperature exhibits an isotropic signal without revealing any fine structure indicative of the coordination geometry. The g_{av} is found to be 2.02 with a peak-to-peak line width of 357 G.[33]

In conclusion, we have shown that supramolecular association of water molecules joins stairlike coordination polymers into an overall 3D MOF. The association of water molecules is best described as a discrete tetradecameric cluster in the form of a chair conformer with two acyclic tetramers dangling at two opposite ends. A wide variation in the hydrogen-bonding distances and angles are found commensurate with the MOF. The resulting material exhibits weak antiferromagnetic coupling between Mn(II) centers. Water clusters of different sizes and shapes in diverse environments are presently being investigated in our laboratory with the ultimate aim to know how the degree of structuring of a cluster can be imposed by its environment and vice versa besides facilitating our understanding the properties of liquid water in a stepwise manner.

Acknowledgment. We gratefully acknowledge the financial support received from the Council of Scientific and Industrial Research, New Delhi, India (Grant No.1638/EMR II) and a SRF to S.G. Authors from Barcelona acknowledge the financial support from Ministerio de Educación y Ciencia (Programa Ramón y Cajal, Grant No. BQU2003/ 00539).

Supporting Information Available: Crystallographic data (CIF), binding mode of ligand with Mn(II), binding mode of waters, thermogram and X-ray powder diffraction patterns for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC050102W