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Stabilization of a Helical Water Chain in a Metal-Organic Host of a Trinuclear Schiff Base Complex

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Three heterometallic trinuclear Schiff base complexes, $[\{CuL^1(H_2O)\}_2Ni(CN)_4]\cdot 4H_2O$ (**1**), $[\{CuL^2(H_2O)\}_2Ni(CN)_4]$ (**2**), and $[\{CuL^3(H_2O)\}_2Ni(CN)_4]$ (**3**) (HL^1 = 7-amino-4-methyl-5-azahept-3-en-2-one, HL^2 = 7-methylamino-4-methyl-5-azahept-3-en-2-one, and HL^3 = 7-dimethylamino-4-methyl-5-azahept-3-en-2-one), were synthesized. All three complexes were characterized by elemental analysis, IR and UV spectroscopies, and thermal analysis. Two of them (**1** and **3**) were also characterized by single crystal X-ray crystallography. Complex **1** forms a hydrogen-bonded one-dimensional metal-organic framework that stabilizes a helical water chain into its cavity, but when any of the amine hydrogen atoms of the Schiff base are replaced by methyl groups, as in L^2 and L^3, the water chain vanishes, showing explicitly the importance of the host−guest H-bonding interactions for the stabilization of a water cluster.

Introduction

Transition-metal-directed self-assembly is a powerful approach for the construction of different supramolecular architectures with unusual and interesting properties.[1] In the past decades, much interest has been focused on the applications of using cyanide as a bridge to construct cyano-bridged homo- and heterometallic complexes with intriguing structures and interesting magnetic,[2] magneto-optical,[3] and catalytic properties.[4] A popular approach for such constructions is to employ cyano complexes[5] such as $[Ag(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[M(CN)_4]^{2-}$ (M = Cd, Ni, Pd, Pt, etc.), and $[M(CN)_6]^{3-}$ (M = Cr, Mn, Fe, etc.), which act as the bridging moiety to build multidimensional structures where $\sigma \rightarrow \pi$ back-bonding stabilizes the resulting complexes. The tetracyanonickeallate anion[5a,e,f] $[Ni(CN)_4]^{2-}$ is one of the most widely used cyanometallates, which exhibits bridging character involving either one, two, or four of the cyano groups; examples of these three possibilities have been found. However, it has been rarely used to join the Schiff base complexes of transition metals, and to our knowledge, there is only one example where the tetracyanonickellate bridges Cu(II)−Schiff base complexes.[5f] The 1:1 condensation products of 2,4-pentanedione and diamines are a group of tridentate ligands that have been used extensively for the

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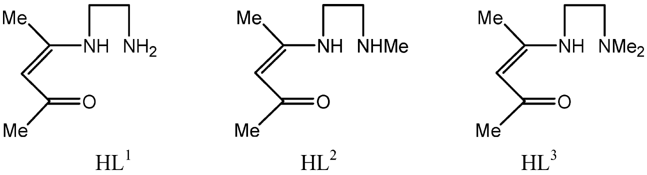
synthesis of mono-, di- and trinuclear complexes of copper(II) with the help of azido-, hydroxo-, and imidazolate-, and 4,4′-bipyridine bridges.[6] We want to synthesize heterometallic complexes by bridging the Cu(II) complexes of such Schiff bases by tetracyanonickelate. We succeeded in obtaining three trinuclear Cu(II)−Ni(II)−Cu(II) complexes, in one of which a serendipitous helical water chain is stabilized.

Water is the most studied and yet the least understood of chemical species.[7] Water has attracted considerable attention from structural chemists and biologists because of its importance in the transport of water across cells in the constricted pore of Aquaporin-1, the proton-transport mechanisms of gramicidin, the inclusion of water in zeolite-like network structures, negative thermal expansion studies of water in inorganic and organic crystals, and water conduction through carbon nanotubes.[8] The primary aim of structural studies on water clusters is to accurately characterize finite ring motifs (e.g., tetramers, pentamers, hexamers, dodecamers, etc.), one-dimensional (1D) chains, helices and tapes, and two-dimensional (2D) sheetlike water motifs by X-ray crystallography[9] for a detailed insight into related patterns in nature that control biological processes. Despite some success, it is still extremely difficult to construct water networks artificially because the structural constraints required in stabilizing these chains are not fully understood. It has been recognized that a systematic supramolecular approach, using synthetic hosts or supramolecular networks, may prove valuable.[8,9] Structures in which a water cluster is trapped in a host matrix have provided accurate and detailed information about hydrogen bonding in diverse water clusters. However, the unusual topology or architecture of hydrogen-bonded water is generally observed only in a specific host lattice. Therefore, the relationship between the water topology and the host structure is difficult to delineate. Ideally, one should synthesize different water motifs in closely related host structures to understand the relative importance of the several weak interactions that are responsible for their stabilization. Evidence to date suggests that these examples are very specific to the host system and that more structural investigations are required to give some generality to our understanding of stabilized water arrays.

The Schiff bases are well-known and are very important tools for inorganic chemists, as they are widely used in biological modeling, in designing molecular ferromagnets, in catalysis, and in liquid crystals.[10] The facile method of their synthesis and the ample choice of diamines and carbonyl compounds enable the chemists to study the effect of subtle changes of steric and electronic factors as well as weak interactions in various systems. However, there have been only a few studies so far on their use in constructing artificial hosts for water clusters.[8,11]

Scheme 1



In this paper, we report an infinite 1D chain of water molecules in a metal-organic framework (MOF) of trinuclear hosts $[\{CuL^1(H_2O)\}_2Ni(CN)_4]\cdot 4H_2O$ (**1**) where HL^1 is the Schiff base, 7-amino-4-methyl-5-azahept-3-en-2-one. To demonstrate the importance of H-bonding for the stabilization of the water chain, we also synthesized two similar trinuclear complexes $[\{CuL^2(H_2O)\}_2Ni(CN)_4]$ (**2**) and $[\{CuL^3(H_2O)\}_2Ni(CN)_4]$ (**3**) where the Schiff base HL^2 (7-methylamino-4-methyl-5-azahept-3-en-2-one) contains one amine hydrogen atom and the Schiff base HL^3 (7-dimethylamino-4-methyl-5-azahept-3-en-2-one) does not contain any free amine hydrogen (Scheme 1).

Experimental Section

Materials. The reagents and solvents used were of commercially available reagent quality unless otherwise stated. ***Caution!*** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Synthesis of the Tridentate Ligands. The ligand HL^1 was prepared as a viscous oil following the literature method[12a] by using 1,2-diaminoethane and 2,4-pentanedione. A solution of 2,4-pentanedione (0.50 mL, 5 mmol) in chloroform (25 mL) was added dropwise to a solution of 1,2-diaminoethane (0.30 mL, 5 mmol) in chloroform (5 mL) at ambient temperature. The solution was stirred for an additional 3 h, and then, chloroform was subsequently evaporated under reduced pressure. The resultant viscous oil was collected and dissolved in methanol (10 mL).

The ligands HL^2 and HL^3 were prepared[12b] by refluxing *N*-methylethylenediamine (0.52 mL, 5 mmol) and *N*,*N*-dimethylethylenediamine (0.545 mL, 5 mmol), respectively, with 2,4-pentanedione (0.50 mL, 5 mmol) in methanol (30 mL) for 0.5 h.

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The resulting mixture gave the yellow solution of the respective tridentate ligands HL^2 and HL^3, which were subsequently used for complex formation.

Synthesis of $[\{CuL^1(H_2O)\}_2Ni(CN)_4]\cdot 4H_2O$ (1). A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (5 mmol, 1.853 g) in methanol (5 mL) was added to a solution of HL^1 (5 mmol) in methanol (10 mL) followed by the addition of aqueous solution (10 mL) of $K_2[Ni(CN)_4]$ (2.5 mmol, 0.603 g). To the resulting solution, triethylamine (0.7 mL, 5 mmol) was added dropwise to obtain a pH of approximately 7, and the mixture was then stirred for approximately 0.5 h and filtered to remove a small amount of precipitate that appeared immediately. The filtrate was left at room temperature. Overnight, dark-blue single crystals of **1** suitable for X-ray diffraction were obtained in ~55% yield. Anal. Calcd for $C_{18}H_{38}Cu_2N_8NiO_8$: C, 31.78; H, 5.63; N, 16.47%. Found: C, 31.90; H, 5.45; N, 16.35%. IR (KBr, cm^{-1}): 3538 (υ_{O-H}), 3414 (υ_{O-H}), 3314 (υ_{O-H} and υ_{N-H}), 3250 (υ_{O-H}), 3173 (υ_{O-H} and υ_{N-H}), 2964 (υ_{C-H}), 2167 (υ_{C-N}), 2117 (υ_{C-N}), 1597 (υ_{C-O} and υ_{C-C}), 1523 (υ_{C-N}), 1402 (υ_{C-H}).

Synthesis of $[\{CuL^2(H_2O)\}_2Ni(CN)_4]$ (2). Complex **2** was obtained by following a similar procedure to that of **1** but with ligand HL^2 used in place of HL^1. After a few days of storage of the filtrate at room temperature, a green crystalline compound was obtained in ~62% yield. It was not possible to isolate suitable single crystals of **2** for X-ray diffraction. Anal. Calcd for $C_{20}H_{34}Cu_2N_8NiO_4$: C, 37.75; H, 5.39; N, 17.61%. Found: C, 37.57; H, 5.28; N, 17.79%. IR (KBr, cm^{-1}): 3388 (υ_{O-H} and υ_{N-H}), 2134 (υ_{C-N}), 2163 (υ_{C-N}), 1577 (υ_{C-O} and υ_{C-C}), 1509 (υ_{C-N}), 1402 (υ_{C-H}).

Synthesis of $[\{CuL^3(H_2O)\}_2Ni(CN)_4]$ (3). Complex **3** was obtained by following a similar procedure to that of **1** but with ligand HL^3 used in place of HL^1. After a few days of storage of the filtrate, dark-green single crystals suitable for X-ray diffraction were obtained in ~68% yield. Anal. Calcd for $C_{22}H_{38}Cu_2N_8NiO_4$: C, 39.77; H, 5.77; N, 16.87%. Found: C, 39.55; H, 5.98; N, 16.69%. IR (KBr, cm^{-1}): 3523 (υ_{O-H}), 3305 (υ_{O-H} and υ_{N-H}), 2964 (υ_{C-H}), 2160 (υ_{C-N}), 2117 (υ_{C-N}), 1601 (υ_{C-O} and υ_{C-C}), 1520 (υ_{C-N}), 1407 (υ_{C-H}).

Physical Measurements. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500−500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra were recorded in a Hitachi U-3501 spectrophotometer. PXRD were performed using an X′ Pert PRO X-ray diffractometer (PANalitical). Thermal analyses (TG-DTA) were carried out on a Mettler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate = 30 $cm^3\ min^{-1}$). The samples were heated in an alumina crucible at a rate of 10 °C min^{-1}.

Crystal Data Collection and Refinement. Crystal data for the two crystals are given in Table 1. Intensity data were measured via the Oxford X-Calibur CCD system using Mo Kα radiation at 150 K. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 3 s to give 3890 and 3972 independent reflections for **1** and **3**, respectively. Data analyses were carried out with the Crysalis program.[13] The structures were solved using direct methods with the Shelxs97 program.[14] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Empirical absorption corrections were carried out using the ABSPACK program.[15] The structures were refined on F^2 using Shelx97[14] to R1 values of 0.0551 and 0.0564 and wR2 values of 0.1383 and 0.1233 for 2690 and 1545 reflections, respectively, with $I > 2\sigma(I)$ (Table 2).

Table 1. Crystal Data and Structure Refinement of Complexes **1** and **3**

	1	3
formula	$C_{18}H_{38}Cu_2N_8NiO_8$	$C_{22}H_{38}Cu_2N_8NiO_4$
mol wt	680.35	664.39
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/n$
a/Å	8.8433(3)	8.955(1)
b/Å	14.1730(7)	16.056(2)
c/Å	11.6532(5)	10.461(1)
α/deg	(90)	(90)
β/deg	109.736(5)	106.48(1)
γ/deg	(90)	(90)
V/Å^3	1374.77(11)	1442.3(3)
Z	2	2
D_c/g cm^{-3}	1.644	1.530
μ/mm^{-1}	2.266	2.148
F (000)	704	688
R(int)	0.071	0.076
total reflns	6920	6468
unique reflns	3890	3972
$I > 2\sigma(I)$	2690	1545
R1, wR2	0.0551, 0.1466	0.0564, 0.1352
temp/K	150	150

Table 2. Bond Lengths (Å) and Angles (deg) in the Cu(II) Coordination Spheres in **1** and **3**

atom	1	3
Cu(1)−O(11)	1.927(2)	1.938(3)
Cu(1)−N(15)	1.944(3)	1.947(4)
Cu(1)−N(18)	2.008(3)	2.059(3)
Cu(1)−N(2)	1.972(3)	1.971(5)
Cu(1)−O(100)	2.530(3)	2.328(3)
Ni(2)−C(2)	1.867(4)	1.857(5)
Ni(2)−C(1)	1.873(4)	1.867(5)
C(1)−Ni(2)−C(2)	91.5(2)	91.5(2)
O(11)−Cu(1)−N(15)	93.9(1)	93.3(2)
O(11)−Cu(1)−N(2)	88.7(1)	88.8(2)
N(15)−Cu(1)−N(2)	172.6(1)	167.0(2)
O(11)−Cu(1)−N(18)	176.5(1)	174.0(2)
N(15)−Cu(1)−N(18)	85.0(1)	84.8(2)
N(2)−Cu(1)−N(18)	91.9(1)	91.8(2)
O(11)−Cu(1)−O(100)	98.15(9)	96.5(1)
N(15)−Cu(1)−O(100)	92.8(1)	97.6(2)
N(2)−Cu(1)−O(100)	93.7(1)	95.0(2)
N(18)−Cu(1)−O(100)	85.2(1)	89.4(1)

Results and Discussion

Synthesis of the Complexes. It is well-known that tridentate Schiff base ligands such as HL^1, HL^2, or HL^3 react readily with Cu(II) to occupy three coordination sites of a square planar environment, thus leaving one site vacant so that various anionic or neutral ligands can be coordinated to yield different types of complexes.[6] Thus, there is a possibility that the cyanide groups of tetracyanonickelate(II) can bridge two to four $[CuL]^+$ units, and with this expectation, we added the Schiff base (HL) to a methanol solution of Cu(II) perchlorate followed by potassium tetracyanonickelate(II) and triethylamine. For all three ligands, the heterotrinuclear complexes **1**, **2**, and **3**, in which the two *trans* cyanide of tetracyanonickelate(II) bridged two $[CuL]^+$ units,

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(13) *Crysalis*, version 1; Oxford Diffraction Ltd.: Oxford, U.K., 2005.

(14) Sheldrick, G. M. *SHELXS-97 and SHELXL-97, Programs for Crystallographic Solution and Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(15) *ABSPACK*; Oxford Diffraction Ltd.: Oxford, U.K., 2005.

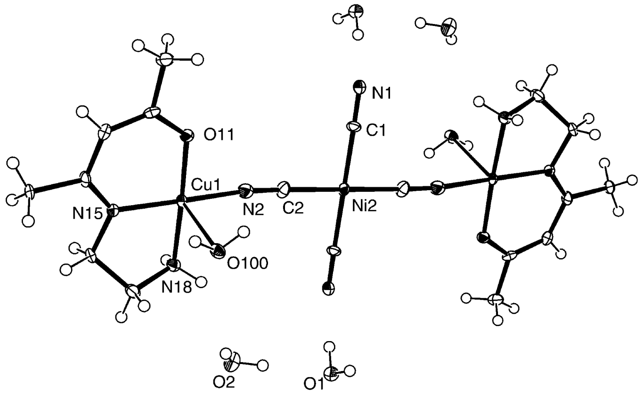

Figure 1. Structure of **1** with ellipsoids at 50% probability.

were obtained from the solutions. For the syntheses of these complexes, the amount of triethylamine that was used proved to be crucial. The desired trinuclear complexes were obtained only when the triethylamine (1:1 molar ratio with ligand) was added so that the reaction mixture was just neutralized (pH about 7). The addition of more triethylamine makes the solution alkaline, and the hydroxo-bridged trinuclear complexes, $[(CuL)_3OH]^{2+}$, were formed as was observed by us earlier.[6d] On the other hand, when no triethylamine was added, the Schiff bases underwent hydrolysis, and no desired products were obtained. Previously, we also observed that the proton, liberated from the Schiff base during complex formation, caused the hydrolysis of the Schiff base ligand.[6a]

Description of the Structures of $[(CuL^1)_2Ni(CN)_4(H_2O)_2]\cdot 4H_2O$ (1) and $[(CuL^3)_2Ni(CN)_4(H_2O)_2]$ (3). The two structures show equivalent centrosymmetric trinuclear complexes, and they are shown in Figures 1 and S1 (Supporting Information). In both complexes, the nickel(II) atoms are situated on centers of symmetry and bonded to four cyanide groups through the carbon atoms with equivalent distances of 1.873(4) and 1.867(4) Å in **1** and 1.857(5) and 1.867(5) Å in **3**. The nickel(II) has a square planar environment in which two of the cyanides are terminal and the other two bridge to copper atoms. This bridging N(2) atom completes an equatorial square plane together with the tridentate ligand around the copper atom. Although the dimensions in the two molecules are similar, one significant difference in the bond lengths is that Cu(1)−N(18) is 2.059(3) Å in **3** where N(18) is bonded to two methyl groups but only 2.008(3) Å in **1** where N(18) is bonded to two hydrogen atoms. Water molecules occupy one axial position in the copper coordination spheres in both structures at 2.530(3) Å in **1** but 2.328(3) Å in **3**. The H-bonded one-dimensional chain structure of the trinuclear complex moieties is illustrated in Figures S2 and S3 (Supporting Information). Two hydrogen bonds are formed from the hydrogen atoms of the coordinated water molecule O(100) to $N(1)^{i}$ and with $O(11)^{i}$ (Table 3), leading to the formation of a one-dimensional H-bonded metal-organic framework along the [001] direction. In complex **1**, the voids that are created between these supramolecular one-dimensional chains are not empty; rather, an infinite chain of hydrogen-bonded water molecules weaves through them (Figure 2a), which is absent in complex **3** (Figure 3a). The complete water-helical chain structure is built up from only two crystallographically independent water molecules O1 and O2 (Figure 4). Each water molecule in the chain participates in four hydrogen bonds in a tetrahedral arrangement. The O2 water molecule forms two donor hydrogen bonds to O1 at 2.842(4) Å and with another $O1^{ii}$ at 2.790(4) Å to form the one-dimensional water chain (Table 3). The O···O distances are within the range of the other reported water chains.[9] The amine nitrogen atom N(18) forms two donor hydrogen bonds to two different O(2) water molecules, with O2 at 3.144(4) Å and with another $O2^{iii}$ at 2.949(4) Å.

Table 3. Geometrical Parameters of Hydrogen Bonds (Å, deg) for **1** and **3**[a]

D−H···A	d(D−H)	d(H···A)	d(D···A)	(D−H···A)
		compd **1**		
$O100-H1\cdots O11^{i}$	0.85(2)	1.94(3)	2.767(3)	164(4)
$O100-H2\cdots N1^{i}$	0.84(2)	2.37(2)	3.132(5)	150(3)
$O2-H3\cdots O1$	0.86(4)	1.99(4)	2.842(4)	175(4)
$O2-H4\cdots O1^{ii}$	0.82(4)	2.02(4)	2.790(4)	155(4)
$O1-H5\cdots O100^{iv}$	0.85(3)	2.06(3)	2.864(3)	158(4)
$O1-H6\cdots N1^{v}$	0.85(3)	2.04(3)	2.887(4)	173(4)
$N18-H19A\cdots O2^{iii}$	0.90	2.16	2.949(4)	147
$N18-H19B\cdots O2$	0.90	2.38	3.144(4)	143
		compd **3**		
$O100-H1\cdots O11^{i}$	0.85(3)	1.97(2)	2.791(4)	163(3)
$O100-H2\cdots N1^{i}$	0.83(4)	2.27(4)	3.068(6)	164(4)

[a] Symmetry operators: $^{i} = (1 - x, 1 - y, 1 - z)$, $^{ii} = (x - {}^{1}/_{2}, -y + {}^{1}/_{2}, z)$, $^{iii} = (-x + 1, -y + 1, -z)$, $^{iv} = (x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z)$, $^{v} = (-x + 2, -y + 1, -z + 1)$.

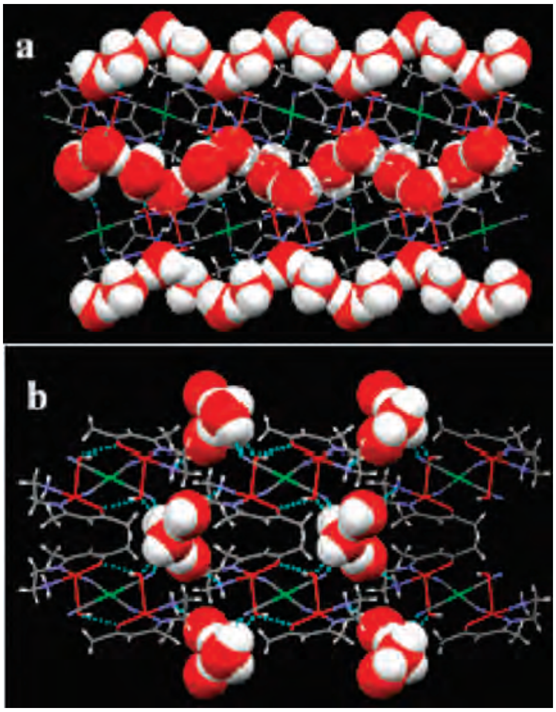

Figure 2. Depiction of the alternating helical columns that make up the water clusters in **1**: (a) viewed down the crystallographic *c* axis; (b) viewed down the crystallographic *a* axis.

In addition, O1 also forms two donor hydrogen bonds to $O(100)^{iv}$ at 2.864(3) Å and $N(1)^{v}$ at 2.887(4) Å (Figure 4). A view along the *c* axis reveals 2D sheets of alternating Cu−Ni−Cu MOFs and helical water chains, as depicted in Figure 2a. This assembly of helical water chains in the

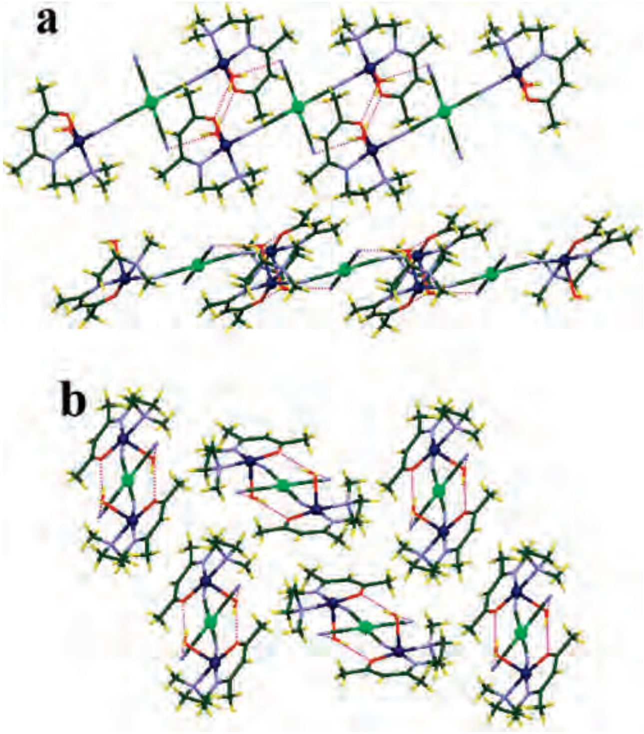

Figure 3. Perspective view of the one-dimensional MOF layers in **3**: (a) down the crystallographic *c* axis; (b) down the crystallographic *a* axis.

cavities formed by the one-dimensional chains of the Schiff base containing MOF appears to be a particularly rare event; to our knowledge, very few other examples of this arrangement exist.[8,11] The pitch of each water helix is 8.843 Å and corresponds to the *a* axis unit cell length. The unit cell packing diagram shows the presence of four helices located near the four corners of the cell axes (Figure S4 of the Supporting Information). The helices exhibit both left and right handedness in a 1:1 ratio (Figure S4 of the Supporting Information).

The packing of the hydrogen-bonded one-dimensional MOFs in **3** is different from that of **1**. In **1**, four parallel chains of MOFs create the cavities to hold the water chain (Figure 2b), whereas in **3**, the neighboring MOF chains are not parallel (Figure 3b). The different orientation of the chains is apparently to achieve better crystal packing. The size of the cavity channel between the neighboring one-dimensional MOF chains in **3** is comparable to that of **1**. But, there are no guest molecules, which must be due to the absence of the H-bond donor primary amine group, as other parts of complex **3** are identical to those of complex **1**. So, the stability of the water chains in **1** is derived from strong hydrogen-bonding interactions between neighboring amine hydrogen and water molecules.

Thermal and Powder Diffraction Analyses. The thermogravimetric analyses were carried out in air on powder samples of **1**−**3**. In **1**, the first endothermic weight loss of 16.3% corresponding to the departure of all six water molecules per trinuclear unit (calcd = 15.9%) was observed between 50 and 80 °C (Figure S5 of the Supporting Information). In a separate experiment, the sample of **1** was heated in air at 80 °C, and then it was exposed to the open atmosphere for 24 h at room temperature; the resulting sample on reheating showed a weight loss of 16.2% between 50 and 80 °C. Similarly, complexes **2** and **3** showed a weight loss of 5.9% (theoretical = 6.0%) and 5.3% (theoretical = 5.4%) between 75−150 °C and 60−145 °C, respectively (Figures S6 and S7 of the Supporting Information). The dehydrated samples of both **2** and **3** also reabsorbed the water molecules on exposure in the open atmosphere. Thus, the departure and absorption of water of complexes **1**−**3** are reversible processes. As the dehydrated species absorb the water molecules readily from the atmosphere, we were not able to record the IR spectra and PXRD patterns of the dehydrated species. The FT-IR spectra of the rehydrated species are identical to the original complexes. The powder XRD pattern of **1** (Figure S8 of the Supporting Information) resembles closely that of the rehydrated sample (Figure S9 of the Supporting Information), obtained after exposing the dehydrated species to open atmosphere. Thus, the metal-organic host functions like a supramolecular sponge:[9e] it readily uptakes moisture and releases the guest under relatively mild conditions (<80 °C).

Infrared and Electronic Spectra. Spectroscopic data and their assignments are given in the Experimental Section. Assignments are based on the structures of **1** and **3** and related complexes previously reported. The FT-IR spectrum of **1** shows a number of peaks in the region 3550−3150 cm^{-1} due to free amine at 3250 and 3173 cm^{-1} and for water molecules at 3538, 3414, and 3314 cm^{-1}. The FT-IR spectrum of ice[16] shows the O−H stretching at 3220 cm^{-1}, whereas the stretching vibration in liquid water[16] appears at 3490 and 3280 cm^{-1}. Hence, the water chain in **1** shows O−H stretching vibrations for the liquid water. Water clusters identified in other MOFs show[17] O−H stretching vibrations in the range 3400−3500 cm^{-1}. On the other hand, the FT-IR spectrum of **2** shows just one broad band centered at 3388 cm^{-1} due to both water and N−H stretching vibrations; complex **3** shows two sharp bands at 3523 and 3305 cm^{-1} for coordinated water molecules.

IR spectroscopy is a very sensitive tool for the determination of bonding variations in M−CN−M′ arrays.[18] Previously, it was observed for LM′−Ni(CN)$_4$−LM′ systems with organometallic building blocks M′ that the increase of ν(CN) upon the coordination of the second metal (which is a general phenomenon due to the kinematic effect) is modulated in a typical way by the π-donor and σ-acceptor properties of the attached metals.[18] As a rule, electron withdrawal by the σ-acceptor at the N terminus of the CN is compensated by an increased π-donation from the metal at the C terminus, resulting in a reduction in the increase in ν(CN).[18b] For all three trinuclear complexes (**1**−**3**), the IR bands of the

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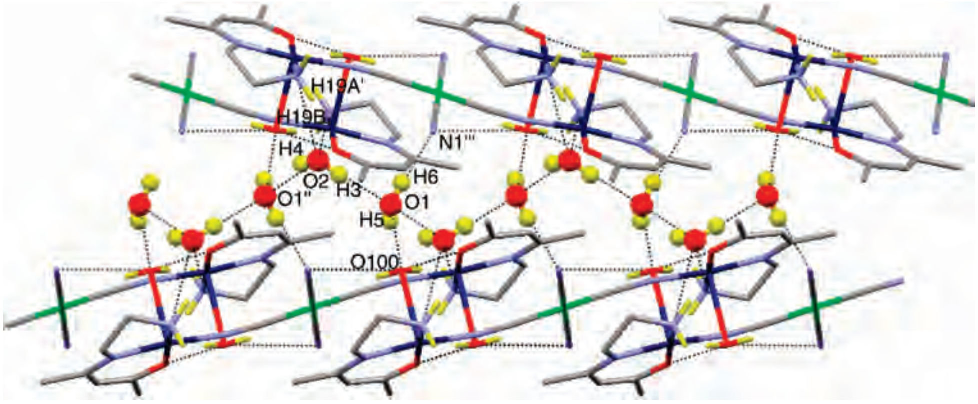

Figure 4. Depiction of an individual water helix displaying the hydrogen bonds both within the helix and provided by the metal-organic framework in **1**.

terminal and bridging CN ligands can be clearly discerned. The band positions for the terminal cyanides are only slightly different from the $K_2[Ni(CN)_4]$ complex. In contrast, ν(CN) for the bridging cyanides rises. The FT-IR spectrum in the CN stretching region of **1** consists of two sharp bands at 2167 and 2117 cm^{-1}. The band at 2117 cm^{-1} is assigned to terminal CN ligands and is in agreement with the CN stretch of $K_2[Ni(CN)_4]$ at 2121 cm^{-1}, and the band at 2167 cm^{-1} is assigned to the bridge CN stretch. Similarly, the FT-IR spectra of **2** and **3** show two sharp bands at 2134 and 2117 cm^{-1} for the terminal CN and at 2163 and 2160 cm^{-1} for the bridging CN, respectively. The characteristic bands of the ligands (HL^1, HL^2, and HL^3) are easily located at 1597 cm^{-1} for υ(CO) and υ(CC) and at 1523 cm^{-1} for υ(CN) in complex **1**, at 1577 cm^{-1} for υ(CO) and υ(CC) and at 1509 cm^{-1} for υ(CN) in complex **2**, and at 1601 cm^{-1} for υ(CO) and υ(CC) and at 1520 cm^{-1} for υ(CN) in complex **3**.

Cu(II) in a trigonal-bipyramidal environment gives rise to two d-d transitions in the visible or NIR range which are the origin of its bluish colors. In practice, one broadband at 700−800 nm with a more or less pronounced shoulder on the higher energy side is observed. This is also the case here. The d-d transition for square pyramidal Cu(II) ions appear at 698 nm for complex **1,** 695 nm for complex **2** and at 697 nm for complex **3** where as d-d band for square planar Ni(II) ions are found at 420, 422 and 425 nm for complex **1, 2** and **3** respectively.

Importance of the H-bond for Stabilization of the Water Chain. The three Schiff base ligands HL^1, HL^2, and HL^3 differ in the number of amine hydrogen atoms that can potentially take part in H-bond formation. The crystal structures of **1** and **3** clearly show that a water chain is stabilized in **1** but not in **3**, presumably because of the participation of a NH_2 group in extensive H-bonding. It was not possible to isolate suitable single crystals of **2** for X-ray diffraction, but the presence of only two water molecules per trinuclear unit suggests that its structure should be similar to that of **3**. It should be emphasized that in the previously reported water clusters, the X-ray crystal structures of both hydrated and anhydrous forms have been obtained on very few occasions.[9e,19] On the other hand, in a recent paper,[11] the role of water clusters in the crystallization process has been investigated by introducing other solvent molecules such as methanol and DMSO. The authors have also tried to evaluate the strength and flexibility of the guest water cluster by altering the number of sites available for hydrogen-bonding interactions in the host molecules and rather surprisingly found that the number of host water molecules and their hydrogen-bonding patterns remain unaffected. Thus, the importance of H-bond formation between the host and guest molecules in stabilizing the water cluster remained unproven from that example. On the other hand, the importance of hydrogen bonding in connecting coordination complexes to result in the directed assembly was demonstrated recently.[20] In that paper, it was shown in the structures of several halo-metallates that a well-defined supramolecular motif is formed only when the cations are capable of forming directional hydrogen bonds to overcome the influence of a collection of less directional packing forces. Although it is common knowledge that supramolecular hydrogen bonding interactions must be very important for the construction of a water cluster, until now, there has been no direct comparison of similar metal complexes that shows that when the metal complex can form H-bonds then a water cluster is created but when the metal complex cannot form H-bonds then no water cluster exists. The present report is therefore the first one in which it is clearly shown that the number of hydrogen bonding sites in the host molecule is the key factor in obtaining the water chains.

Conclusions

This report presents three new trinuclear Cu−Ni−Cu Schiff base complexes that form one-dimensional MOFs by H-bonding. One of the MOFs stabilizes a water chain in its cavity by forming H-bonds. When the amine hydrogen atoms of the Schiff base ligand are replaced by methyl groups to remove the potential for H-bond formation, the H-bonded one-dimensional MOF structure is not affected, but the water

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chain loses its stability. Thus, the present system clearly demonstrates the importance of H-bonding interactions between host and guest molecules in the stabilization of water clusters through the absence of hydrogen bonds.

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Supporting Information Available: Crystallographic data in CIF format for the structures reported, structures of **1** and **3**, unit cell diagram of **3**, thermogravimetric plots of **1**−**3**, PXRD curves of **1**, and IR spectra of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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