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Novel hydrogen-bonded two- and three-dimensional networks generated from the reaction of metal nitrate hydrates (M = Cd, Co) with the bidentate linear ligand 4,4′-bipyridine

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Two new hydrogen-bonded coordination polymers have been prepared using the transition metal nitrate hydrates $Cd(NO_3)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ in combination with the organic bidentate ligand 4,4′-bipyridine: $Cd_2(H_2O)_4(bipy)_5(NO_3)_2(PF_6)_2$ (**1**) (bipy = 4,4′-bipyridine) and $[Co(H_2O)_4(bipy)][PF_6]_2{\cdot}3bipy$ (**2**). The compounds were characterized by single crystal X-ray diffraction, IR spectroscopy, and thermogravimetric analysis. Compound **1** shows a novel hydrogen bonded brick wall motif assembled from unprecedented dimeric "H-shaped" $[Cd_2(bipy)_5]$ building blocks *via* a new complementary binary hydrogen bonding bridge. Compound **2** forms a novel three-dimensional network based on $[Co(H_2O)_4(bipy)]_n$ linear polymer chains which are cross-linked to each other by a new type of Co–H_2O(2) $\cdots$ bipy $\cdots$ H_2O(1) $\cdots$ bipy $\cdots$ H_2O(1) $\cdots$ bipy $\cdots$ H_2O(2)–Co hydrogen bonding linkage.

Introduction

Crystal engineering and the design of solid-state materials have become areas of great interest recently.[1,2] So far, however, the rational design and preparation of new materials for specific applications is still at an early evolutionary stage with the current focus mainly on understanding the factors that determine crystal packing. During the last few years, several types of forces, such as coordination bonding,[2] versatile hydrogen bonding interactions,[3] π–π stacking,[4] and electrostatic interactions[5] have been recognized and used in constructing extended networks. Up to now, the most important driving forces in crystal engineering are coordination bonding and hydrogen bonding interactions. Three main lines of study have been followed, based on coordination and hydrogen bonds: (1) extended frameworks comprised of bidentate or polydentate ligands connected *via* coordination bonds. A number of one-, two-, and three-dimensional infinite frameworks, such as diamondoid,[6] helix,[7] brick wall,[8] ladder,[8,9] honeycomb,[1,8] square grid,[10] parquet[11] and three-dimensional frameworks[12] from trigonal, tetrahedral and octahedral metal templates have been generated with linear and non-linear organic spacers. (2) Networks assembled from mono- or poly-nuclear metal complexes *via* hydrogen bonding interactions: if the hydrogen bonding functionality is combined with a coordination site for a metal ion, a bridge between coordination complexes and supramolecular assembly can be built. The materials bis(3-pyridinealdoxime)silver(I) hexafluorophosphate, bis(3-pyridinealdoxime)silver(I) perchlorate, bis(3-pyridineacetyloxime)silver(I) hexafluorophosphate and bis(3-pyridineacetyloxime)silver(I) perchlorate represent an attractive group of two-dimensional architectures formed by the combination of pyridine-oxime ligands with silver(I) salts.[13] By this approach, the geometry encoded in the coordination complexes is propagated into the architectures of the metal-containing hydrogen-bonded networks through intermolecular hydrogen bonds. (3) Extended networks assembled by both coordination and hydrogen bonds. In principle, higher dimensionality networks can be obtained by the assembly of lower dimensionality polymers (or molecules) *via* hydrogen bonding interactions. A series of such compounds, namely $[Zn(H_2O)(bipy)](NO_3)_2{\cdot}bipy$, $[Zn(H_2O)_4(bipy)](NO_3)_2{\cdot}2bipy$, $[Zn(H_2O)_4(bipy)][SO_3CF_3]_2{\cdot}2bipy$ and $[Fe(H_2O)_3(ClO_4)(bipy)](ClO_4){\cdot}1.5(bipy){\cdot}H_2O$ was reported recently.[14] The extended frameworks of these compounds are based on the one-dimensional $[M(bipy)]_n$ (M = Zn, Fe) linear chains which are cross-linked to each other by $M(H_2O)\cdots bipy\cdots H_2O$–M hydrogen bond bridges to produce two- and three-dimensional networks.

The unique strength, directionality, and complementarity of non-covalent hydrogen and coordinative bonding play a central role in the creation of a variety of architectures for molecular self-assembly and recognition in chemical, physical and biological sciences;[15] however, networks constructed by incorporation of metal ions within ordered hydrogen-bonded systems by the concurrent action of both extended coordination and hydrogen bonds have not yet attracted great attention.[13,14] Herein, we report the synthesis and the structures of two such materials: $Cd_2(H_2O)_4(bipy)_5(NO_3)_2(PF_6)_2$ (**1**) (bipy = 4,4′-bipyridine) and $[Co(H_2O)_4(bipy)][PF_6]_2{\cdot}3bipy$ (**2**). In the solid state, compound **1** features a novel hydrogen bonded two-dimensional network which consists of "H-shaped" $Cd_2(H_2O)_4(bipy)_5(NO_3)_2(PF_6)_2$ building block molecules linked by intermolecular O–H $\cdots$ N hydrogen bonds, while compound **2** exhibits a novel three-dimensional network which results from inter-polymer hydrogen bonding interactions (O–H $\cdots$ N) between one-dimensional $[Co(H_2O)_4(bipy)][PF_6]_2$ linear polymer chains.

Experimental

Materials and methods

$Cd(NO_3)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, 4,4′-bipyridine and pyrazine were purchased from Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer as KBr pellets in the 4000–400 cm^{-1} range. Elemental analyses were carried out by National Chemical Consulting. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA in a helium atmosphere at a heating rate of 10 °C min^{-1}.

Synthesis

Synthesis of $Cd_2(H_2O)_4(bipy)_5(NO_3)_2(PF_6)_2$ (1). To an aqueous solution (7 mL) of $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol), an ethanol

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Table 1 Crystallographic data for **1** and **2**

	1	**2**
Formula	$CdC_{25}H_{24}N_6O_5PF_6$	$CoC_{40}H_{40}N_8O_4P_2F_{12}$
Formula weight	745.88	1045.67
Crystal system	Monoclinic	Monoclinic
a/Å	20.669(3)	17.918(2)
b/Å	23.430(5)	11.397(1)
c/Å	7.533(1)	23.071(2)
β/°	104.61(1)	101.286(9)
V/Å^3	3530(1)	4620.3(8)
Space group	$C2/m$ (no. 12)	$C2/c$ (no. 15)
Z	4	4
ρ calc/g cm^{-3}	1.403	1.503
μ (Mo-Kα)/cm^{-1}	7.353	5.385
T/°C	23	23
No. reflections ($I > 3\sigma$)	1774	2297
Residuals[a]: R; R_w	0.060; 0.082	0.052; 0.062

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|^2)/\Sigma_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$.

solution (8 mL) of pyrazine (2.0 mmol) was added slowly. The mixture was heated at 50 °C for 10 min, and allowed to cool. An ethanol solution (7 mL) of bipy (2.0 mmol) was then added in very slowly, followed by addition of solid $NaPF_6$ (1.30 mmol). Initially a small amount of fine precipitate formed, which was filtered off. The clear filtrate was allowed to stand for three weeks at room temperature, resulting in the formation of colorless crystals (yield 69%, based on $Cd(NO_3)_2{\cdot}6H_2O$). IR(cm^{-1}, KBr): 1598.70(s), 1531.21(s), 1490.71(s), 1467.57(w), 1456.00(m), 1413.57(s), 1383.64(s), 1324.86(m), 1220.72(s), 1076.09(s), 1045.23(s), 1006.66(s), 999.00(s), 835.00(s), 808.03(s), 736.67(s), 725.10(w), 630.61(s), 615.18(s), 561.18(s), 507.10(s), 491.76(s). Anal. Calc. for $Cd_2C_{50}H_{48}N_{12}O_{10}P_2F_{12}{\cdot}3H_2O$: C, 38.84; H, 3.50; N, 10.87%. Found: C, 38.87; H, 4.00; N, 10.59%.

Synthesis of $[Co(H_2O)_4(bipy)][PF_6]_2{\cdot}3bipy$ (2). The procedure is similar to the synthesis of compound **1**, except that $Co(NO_3)_2{\cdot}6H_2O$ was used instead of $Cd(NO_3)_2{\cdot}4H_2O$ (yield, 75% based on $Co(NO_3)_2{\cdot}6H_2O$). IR(cm^{-1}, KBr): 1596.78(s), 1536.99(s), 1488.78(m), 1407.78(s), 1321.00(m), 1222.65(s), 1064.52(s), 1043.30(m), 998.95(m), 835.03(s) 804.17(s), 738.60(m), 678.82(w), 619.04(s), 557.33(s), 526.47(m), 460.90(w). Anal. Calc. for $CoC_{40}H_{40}N_8O_4P_2F_{12}$: C, 45.90; H, 3.83; N, 10.71%. Found: C, 45.82; H, 4.19; N, 11.01%.

Single crystal structure determination

The single crystals used for data collection were attached onto thin glass fibers using epoxy glue in air. Intensity measurements were made at 20 °C on a Rigaku AFC6S four-circle diffractometer using Mo-Kα radiation ($\lambda = 0.71069$ Å). Unit cells for each compound were determined from 25 randomly selected reflections obtained using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and refinement statistics for **1** and **2** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1** and **2** are collected in Tables 2 and 3, respectively. All data processing was performed on a Silicon Graphics INDIGO[2] computer using the TEXSAN structure solving program library obtained from the Molecular Structure Corporation, The Woodlands, TX. Lorentz-polarization (Lp) and absorption corrections (DIFABS)[16] were applied to each data set. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o{}^2)/2F_o$ and $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (0.02\ I_{net})^2]^{1/2}/\mathrm{Lp}$.

The intensities of three standard reflections measured every 150 reflections for each compound showed no significant deviations during data collection. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters; the hydrogens were calculated and therefore not refined.

CCDC reference number 186/1800.

See http://www.rsc.org/suppdata/dt/a9/a909014b/ for crystallographic files in .cif format.

Table 2 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **1**

Cd–O(1)	2.425(9)	Cd–O(5)	2.321(8)
Cd–O(4)	2.377(8)	Cd–N(2)	2.382(8)
Cd–N(3)	2.306(7)		
O(1)–Cd–O(4)	70.0(3)	O(1)–Cd–O(5)	147.2(3)
O(1)–Cd–N(2)	127.9(3)	O(1)–Cd–N(3)	87.9(2)
O(4)–Cd–O(5)	77.2(3)	O(4)–Cd–N(2)	162.1(3)
O(4)–Cd–N(3)	90.7(2)	O(5)–Cd–N(2)	84.9(3)
O(5)–Cd–N(3)	92.6(2)	N(2)–Cd–N(3)	90.1(2)
N(3)–Cd–N(3)	174.8(3)		

Table 3 Interatomic distances (Å) and bond angles (°) with esds in parentheses for **2**

Co–O(1)	2.054(3)	Co–O(2)	2.144(3)
Co–N(1)	2.150(5)	Co–N(2)	2.170(5)
O(1)–Co–O(1)	179.1(2)	O(1)–Co–O(2)	90.0(1)
O(1)–Co–N(2)	89.56(9)	O(2)–Co–O(2)	177.9(2)
O(2)–Co–N(2)	91.03(8)	N(1)–Co–N(2)	180.00

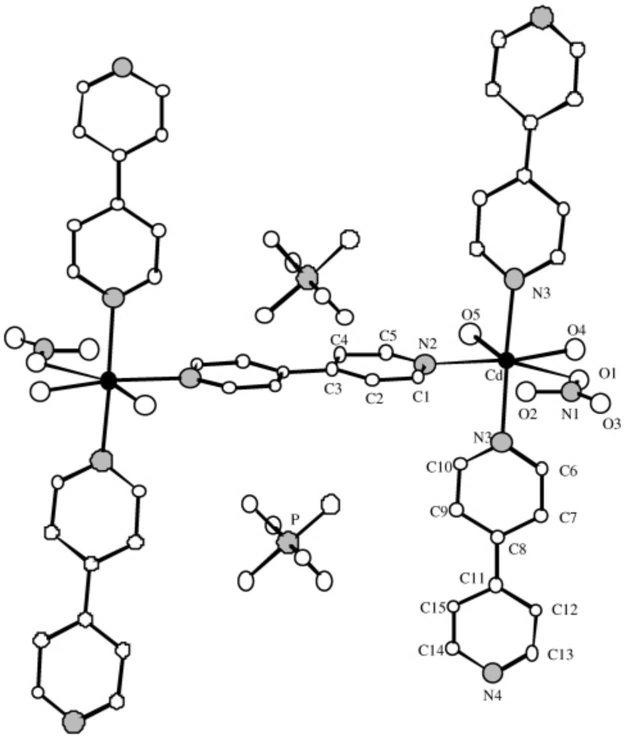

Fig. 1 View of the H-shaped $Cd_2(bipy)_5$ building block molecules in **1**, with partial atom labeling. The hydrogen atoms are omitted for clarity.

Results and discussion

Synthesis and structural analysis

When $Cd(NO_3)_2{\cdot}4H_2O$ was treated with bipy in H_2O–EtOH in the presence of pyrazine and $NaPF_6$ at ambient temperature, compound **1** was obtained as an "H-shaped" molecular complex within one month. As shown in Fig. 1, the molecular structure of **1** features six-coordinate cadmium in a pseudo-octahedral geometry defined by three nitrogen donors from three bipy ligands [Cd–N(2) = 2.382(8) Å (×2) and Cd–

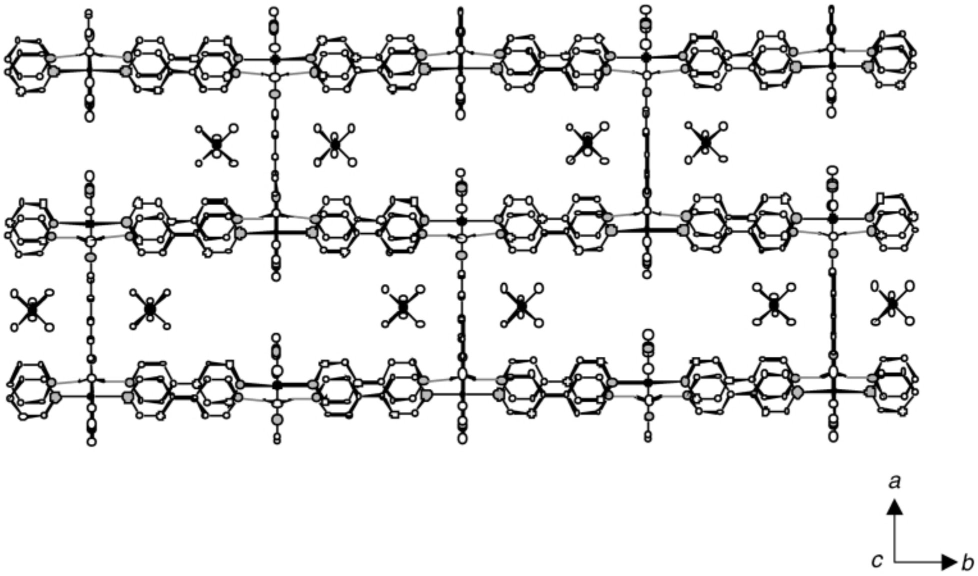

Fig. 2 Crystal packing in compound **1** (view down the crystallographic *c* axis). The bridging bipyridine ligand is vertical in this view. Hydrogen bonds are shown as dotted lines. Cadmium centers are shown as black circles, nitrogen atoms as gray circles. Oxygen, carbon and hydrogen atoms are shown as the large, medium, and small open circles, respectively. The hydrogen atoms on the bipy ligands are omitted for clarity. The PF_6^- anions are located in the rectangular cavities.

N(3) = 2.306(7) Å], two oxygen donors from two coordinated water molecules [Cd–O(5) = 2.321(8) Å and Cd–O(4) = 2.377(8) Å] and one oxygen donor from one monodentate nitrate anion [Cd–O(1) = 2.425(9) Å]. The Cd–O distance of 2.425 Å for the monodentate nitrate group is comparable to those of other known Cd complexes containing monodentate nitrate groups.[17] There are two different types of bipy ligand in molecule **1**. The first type uses only one terminal nitrogen [N(3)] atom to coordinate the Cd(II) center to give two linear bipy–Cd(II)–bipy subunits, while the second type of bipy acts as a bridge, connecting both linear bipy–Cd(II)–bipy subunits using both terminal nitrogen atoms [N(2)] to generate a novel "H-shaped" molecule based on the $[Cd_2(bipy)_5]$ moiety. To the best of our knowledge, this "H-shaped" moiety has not been observed previously. Two nitrate anions are replaced by two PF_6^- anions in **1**. The two uncoordinated PF_6^- counterions are located on both sides of the bridging bipy, the two pyridyl rings of which are strictly coplanar. Compound **1** crystallizes in the centrosymmetric space group *C*2/*m*; the cadmium atoms, O(4), O(5), both monodentate nitrates as well as the bridging bipy ligand all reside in a crystallographic mirror plane.

This result is really unexpected and quite different from the result obtained by Fujita *et al.*, where the square grid network structure $Cd(bipy)_2(NO_3)_2$ was obtained when $Cd(NO_3)_2{\cdot}4H_2O$ was treated with bipy (1 : 2 metal-to-ligand ratio) in H_2O–EtOH.[10] It is not clear from this study why **1** exists in the "H-shaped" molecular complex rather than another likely motif, such as a square grid, ladder or even linear chain motif. It appears that the (unincorporated) pyrazine molecules and non-coordinating PF_6^- counterions used in our synthesis (but not in Fujita's) are critical in influencing the product. When the experiment was performed in the absence of pyrazine, extremely unstable crystals which turned opaque immediately under ambient atmosphere were obtained, a property distinctly different from the air-stable **1**.

It is tempting to view compound **1** as a "one-rung" $[Cd_2(bipy)_5]$ fragment of a ladder-type structure that might be considered a molecular intermediate on the route to the ladder polymeric motif. However, an extensive and interesting hydrogen-bonding network is present which links **1** into a two-dimensional structure, as follows. In the solid state, the cationic "H-shaped" building blocks are bound together by hydrogen bonds to create a brick wall pattern when projected onto the crystallographic *ab* plane (Fig. 2). Each "H-shaped" molecule, as a hydrogen bond acceptor, forms four equivalent N · · · H–O hydrogen bonds between the four terminal N(4) nitrogen atoms on the four mono-coordinated bipy ligands with the hydrogen atoms from four coordinated water molecules [O(5)] on four neighbor molecules [N(4) · · · O(5) = 2.831(5) Å, N(4) · · · H(13) = 1.905(4) Å, and N(4) · · · H(13)–O(5) = 169.13(3)°]. On the other hand, each "H-shaped" molecule also acts as a hydrogen bond donor, forming four additional equivalent O–H · · · N hydrogen bonds between its two coordinated water molecule hydrogens [O(5)] with four nitrogen atoms [N(4)] on four mono-coordinated bipy ligands from four neighbor molecules. The structure, therefore, features a complementary binary hydrogen bonding system (Fig. 3), which serves as a connector to double bridge the intermolecular Cd(II) centers. It is noteworthy that the mono-coordinated bipy ligands in the "H-shaped" cationic building block bend outward toward the coordinated water molecules on neighboring Cd(II) centers due to the formation of the hydrogen bonds (Fig. 3). In the hydrogen-bonded brick wall pattern thus created in **1**, each "brick" is enclosed by six Cd(II) centers, two coordinated bipy ligands and four sets of complementary binary hydrogen bonding linkages, and has a cross-sectional area of *ca.* 35 × 12 Å. The two-dimensional brick wall sheets stack along the crystallographic *c* axis and give rise to large rectangular channels in which the PF_6^- counterions are located (Fig. 2). So far, several Co-, Cd- and Ni-containing brick wall networks comprised of "T-shaped" building blocks connected *via* extended coordination bonds have been reported in the literature.[8] However, the brick wall motif in **1**, generated from cationic "H-shaped" building blocks *via* complementary binary extended hydrogen bonds is, to the best of our knowledge, unprecedented.

When $Co(NO_3)_2{\cdot}6H_2O$ was used instead of $Cd(NO_3)_2{\cdot}4H_2O$ to perform the experiment, needle-shaped orange crystals of compound **2** formed within one month. Single crystal X-ray analysis revealed that the structure of **2** is a coordination polymer distinctly different from **1**. As shown in Fig. 4, the coordination environment of each cobalt atom consists of two pyridyl nitrogen donors [N(1) and N(2)] from two bipy ligands and four aquo oxygen donors [O(1), O(2) and their symmetry equivalents]. The pseudo-octahedral coordination geometry may be described as a basal plane associated with O(1) and O(2) from the coordinated water molecules [O(1)–Co–N(1) = 90.44(9)° and O(2)–Co–N(2) = 91.03(8)°], with Co–O bond lengths of 2.054(3) and 2.144(3) Å, respectively. The axial positions are

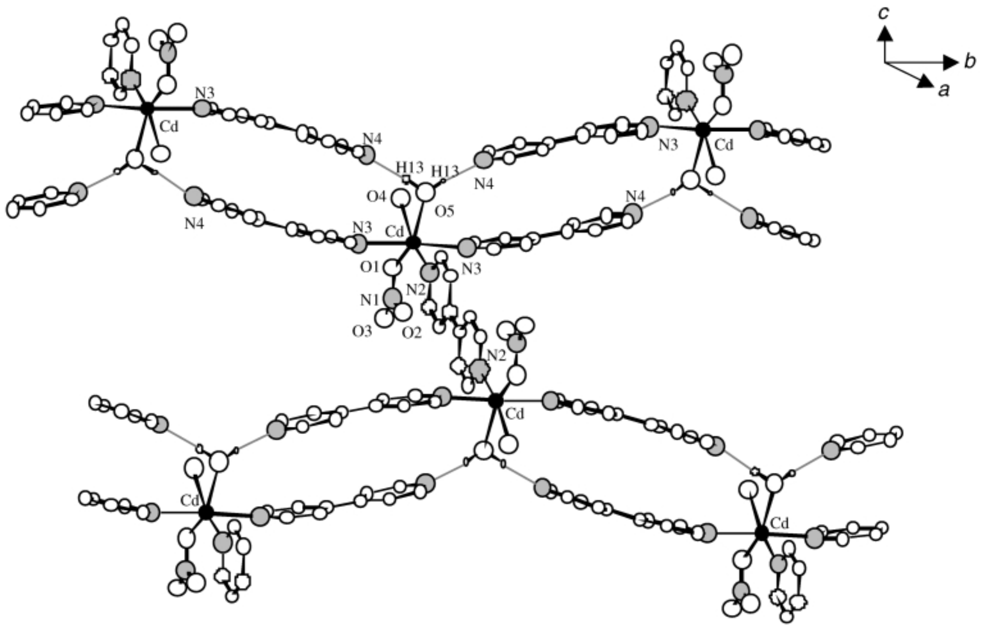

Fig. 3 The hydrogen bonding system in **1**. Hydrogen bonds are shown as dotted lines. The hydrogen atoms on the bipy molecules and O(4) are omitted for clarity.

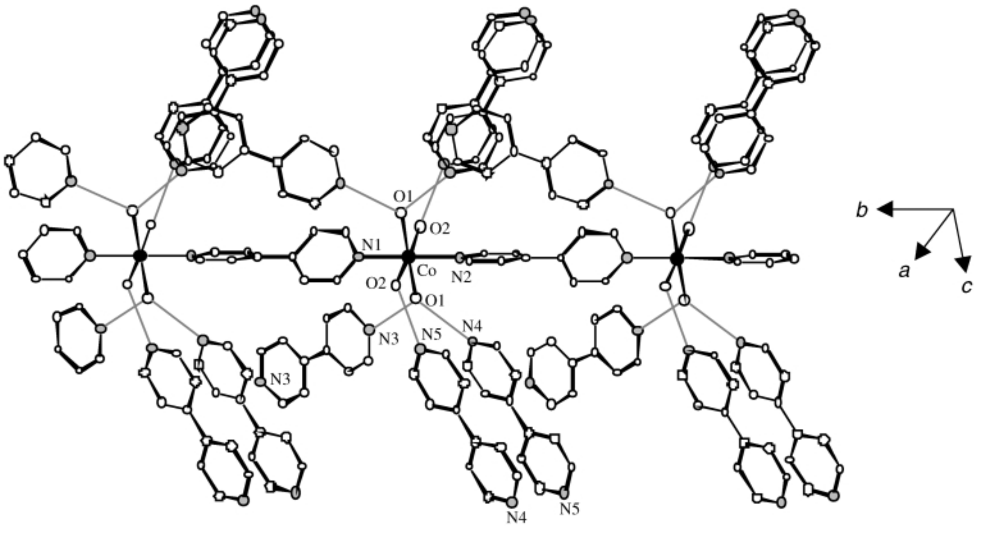

Fig. 4 The one-dimensional $[Co(H_2O)_4(bipy)]_n$ chain in compound **2** along with the hydrogen bonded uncoordinated bipy spacers. The hydrogen atoms are omitted for clarity.

occupied by *trans* nitrogen donors N(1) and N(2), with Co–N distances of 2.150(5) and 2.170(5) Å, respectively. The cobalt atom and the N(1) and N(2) atoms all reside on a crystallographic two-fold axis. In addition, there are three uncoordinated bipy molecules in the asymmetric unit, which are hydrogen bonded with the coordinated water molecules.

In **2**, all the NO_3^- ions have been replaced by uncoordinated PF_6^- counterions, while in **1** only half of nitrate anions per formula unit were replaced. As shown in Fig. 4, the structure of **2** features hexacoordinate Co(II) centers assembled into a linear polymer chain through intervening bipy ligands. The linear $(–Co–bipy–Co–bipy–)_n$ chains run parallel to the crystallographic *b* axis. Interchain connections are formed through O–H···N hydrogen bonds (O···N range 2.72–2.84 Å), involving coordinated water and uncoordinated bipy molecules. This extended hydrogen bonding system generates a three-dimensional network, illustrated in Fig. 5. The novel hydrogen bonding linkage system found in **2**, we believe, is new. It is comprised of four coordinated water molecules and three uncoordinated bipy molecules, and can be formulated as Co–H_2O(2)···bipy···H_2O(1)···bipy···H_2O(1)···bipy···H_2O(2)–Co. The H_2O(1) molecules are also anchored on the cobalt centers. Such a hydrogen bonding linkage extends periodically in the crystallographic *ac* plane in a zigzag fashion and acts as a connector to bind interchain cobalt atoms together. The lengths of the hydrogen bonded interchain Co–H_2O(1)···bipy···H_2O(1)–Co and Co–H_2O(1)···bipy···H_2O(2)–Co segments are 17.011(7) and 16.887(6) Å, respectively, significantly longer than the intrachain Co···Co distance of 11.397(7) Å. It is worth noting that there are two types of hydrogen bonding donors in this linkage, H_2O(1) and H_2O(2) (Fig. 5) due to H_2O(1) forming two symmetrical hydrogen bonds with two nitrogen atoms [N(3) and N(4)] on two uncoordinated bipy ligands [O(1)···N(3) = 2.831(7) Å, O(1)–H(22)···N(3) = 172.38(7)°, and N(3)···H(22) = 2.079(4) Å; O(1)···N(4) = 2.834(3) Å, O(1)–H(23)···N(4) = 171.77(7)°, and N(4)···H(23) = 2.150(4) Å] and due to H_2O(2) forming one hydrogen bond with only one nitrogen atom [N(5)] on one uncoordinated bipy spacer [O(2)···N(5) = 2.736(7) Å, O(2)–H(25)···N(5) = 172.153(7)°, and N(5)···H(25) = 1.818(3) Å]. The positive charge of this metallo-ligand lattice is balanced by PF_6^- counterions located between the uncoordinated bipy spacers (Fig. 5). Interestingly, within the chains, the two pyridyl groups of the bipy molecules are rotated by *ca.* 60° with respect

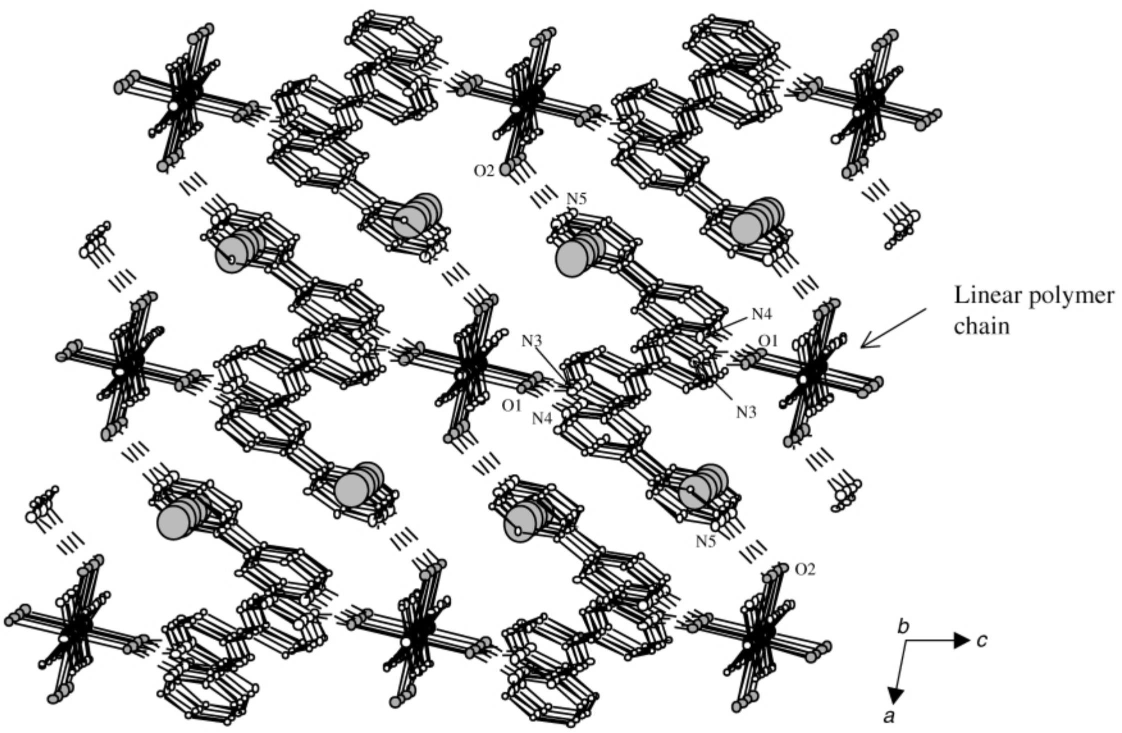

Fig. 5 Crystal packing pattern of **2**, viewed down the crystallographic *b* axis (parallel to the $[Co(H_2O)_4(bipy)]_n$ polymer chains) showing the extended 3-D network formed by $Co–H_2O(2)\cdots bipy\cdots H_2O(1)\cdots bipy\cdots H_2O(1)\cdots bipy\cdots H_2O(2)–Co$ hydrogen bonding linkages. Cobalt centers are shown as black circles. PF_6^- anions and coordinated aquo oxygen atoms are shown as the large and small gray circles, respectively. Nitrogen and carbon atoms are shown as the large and small open circles, respectively. All hydrogen atoms are omitted for clarity.

to one another, while the pyridyl groups in the uncoordinated bipy molecules are strictly coplanar.

Several types of hydrogen bonding linkages involving 4,4′-bipyridine and coordinated water molecules in inorganic/organic polymers have recently been reported, such as single $(M–H_2O\cdots bipy\cdots H_2O–M)$[14,18] and double $[M–(H_2O)_2\cdots(bipy)_2\cdots(H_2O)_2–M]$[14] and alternating single and double $[M–H_2O\cdots bipy\cdots H_2O–M–(H_2O)_2\cdots(bipy)_2\cdots(H_2O)_2–M]$[14] hydrogen bonding bridges. However, to our knowledge, the hydrogen bonding linkage described here has not been previously reported.

Thermogravimetric analysis

Compound **2** (6.44 mg) was heated in a helium atmosphere from 25 °C to 650 °C at a He flow rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) shows that the decomposition of compound **2** starts slowly at 112 °C, followed by a significant mass loss at 240 °C corresponding to the loss of one water molecule and two (presumably uncoordinated) bipy molecules per formula unit (observed 31.52%, calculated 31.58%). A further ill-defined weight loss was observed above 243 °C; the final residue was black and amorphous. Compound **1** was not subjected to TGA analysis.

Concluding remarks

Two new hydrogen-bonded coordination polymers were prepared using the transition metal nitrate hydrates $Cd(NO_3)_2\cdot 4H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ in combination with the organic bidentate ligand 4,4′-bipyridine. Single crystal X-ray diffraction was carried out to determine the structures of both compounds. Compound **1** contains a novel hydrogen bonded brick wall pattern assembled from an unprecedented dimeric $Cd_2(bipy)_5$-based "H-shaped" building block. Additionally, a new complementary binary hydrogen bonding model was observed in **1**. Compound **2** features a novel three-dimensional network based on $[Co(H_2O)_4(bipy)]_n$ linear polymer chains which are cross-linked to each other by a new type of $Co–H_2O(2)\cdots bipy\cdots H_2O(1)\cdots bipy\cdots H_2O(1)\cdots bipy\cdots H_2O(2)–Co$ hydrogen bonding linkage. In compound **1**, the only type of intermolecular connector is hydrogen bonding, while in **2** both hydrogen and extended coordination bonds serve as the connectors. We think that supramolecular interactions of mono- or poly-nuclear complexes and low-dimensional coordination polymers, like those described here, can play a significant role in the self-assembly of novel nanoporous materials, although structural control of systems involving hydrogen bonded water molecules and counterions is quite difficult.

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