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Novel Hydrogen-Bonded Three-Dimensional Networks Encapsulating One-Dimensional Covalent Chains: $[M(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot nH_2O$ (4,4′-bipy = 4,4′-Bipyridine; 4-abs = 4-Aminobenzenesulfonate) (M = Co, *n* = 1; M = Mn, *n* = 2)

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Two novel compounds, $[Co(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot H_2O$ (**1**) and $[Mn(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot 2H_2O$ (**2**) (4,4′-bipy = 4,4′-bipyridine; 4-abs = 4-aminobenzenesulfonate), have been synthesized in aqueous solution and characterized by single-crystal X-ray diffraction, elemental analyses, UV–vis and IR spectra, and TG analysis. X-ray structural analysis revealed that **1** and **2** both possess unusual hydrogen-bonded three-dimensional (3-D) networks encapsulating one-dimensional (1-D) covalently bonded infinite $[M(4,4'\text{-bipy})(H_2O)_4]^{2+}$ (M = Co, Mn) chains. The 4-abs anions in **1** form 1-D zigzag chains through hydrogen bonds. These chains are further extended through crystallization water molecules into 3-D hydrogen-bonded networks with 1-D channels, in which the $[Co(4,4'\text{-bipy})(H_2O)_4]^{2+}$ linear covalently bonded chains are located. Crystal data for **1**: $C_{22}H_{30}CoN_4O_{11}S_2$, monoclinic $P2_1$, $a = 11.380(2)$ Å, $b = 8.0274(16)$ Å, $c = 15.670(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 92.82(3)°$, $Z = 2$. Compound **2** contains interesting two-dimensional (2-D) honeycomb-like networks formed by 4-abs anions and lattice water molecules via hydrogen bonding, which are extended through other crystallization water molecules into three dimensions with 1-D hexagonal channels. The $[Mn(4,4'\text{-bipy})(H_2O)_4]^{2+}$ linear covalent chains exist in these channels. Crystal data for **2**: $C_{22}H_{32}MnN_4O_{12}S_2$, monoclinic $P2_1/c$, $a = 15.0833(14)$ Å, $b = 8.2887(4)$ Å, $c = 23.2228(15)$ Å, $\alpha = \gamma = 90°$, $\beta = 95.186(3)°$, $Z = 4$.

Introduction

The crystal engineering of supramolecular architectures based on metal and organic building blocks has been rapidly expanding in recent years owing to their novel and diverse topologies and potential applications in host−guest chemistry, catalysis, electrical conductivity, and magnetism.[1,2] These metal-containing supramolecular frameworks can be constructed through two different types of interactions: (i) coordinate covalent bonds linking metal centers and organic ligands,[3] and (ii) noncovalent intermolecular forces such as hydrogen bonding, $\pi-\pi$ stacking, and Coulombic interactions.[4] These weaker noncovalent interactions, especially hydrogen bonds, play a crucial role in fundamental biological processes, such as the expression and transfer of genetic information, and are essential for molecular recognition between receptors and substrates as well as construction of

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complicated supramolecular arrays through self-organization of molecules in the field of supramolecular chemistry.[4b,c] Currently, the rational design and synthesis of new extended supramolecular networks by means of both coordinative covalent and hydrogen-bonding interactions are of great interest and have brought forth a great variety of such frameworks with fascinating structural motifs.[5] In general, extended networks possessing higher dimensionalities can be obtained by the assembly of coordination polymers (or complexes) with lower dimensionalities via hydrogen-bonding interactions.[6] Typical examples include $[Zn(H_2O)_4(4,4'\text{-bipy})](NO_3)_2\cdot 2(4,4'\text{-bipy})$ (4,4′-bipy = 4,4′-bipyridine),[6a] $[Cu(4,4'\text{-bipy})(H_2O)_2(BF_4)_2]\cdot(4,4'\text{-bipy})$,[6b] $[Mn(4,4'\text{-bipy})(H_2O)_2(NCS)_2]\cdot(4,4'\text{-bipy})$,[6d] $[Co(H_2O)_4(4,4'\text{-bipy})][PF_6]\cdot 3(4,4'\text{-bipy})$,[6e] and $[M(H_2O)_4\,(4,4'\text{-dpdo})][ClO_4]_2\cdot 2(4,4'\text{-dpdo})$ (M = Co, Ni, Cu, or Zn; 4,4′-dpdo = 4,4′-bipyridine dioxide),[6f] which share a common feature that their extended 2-D or 3-D networks are fabricated from 1-D covalently bonded chains through hydrogen bonds between the coordinated water molecules and solvate pyridine-based organic ligands such as 4,4′-bipy. 4,4′-Bipyridine is an excellent rodlike bifunctional ligand and has been extensively employed as the rigid organic building block for the construction of infinite 1-D, 2-D, or 3-D coordination polymeric frameworks.[3a−d,6a−e,7]

Organosulfonate anions, RSO_3^-, where R is an aliphatic or aromatic group, have shown wide applications as surfactants and dyes in industry and have been recently explored as potential liquid crystalline and nonlinear optical materials.[8] Recent research on molecular layered materials consisting of guanidinium cations and organosulfonate anions has shown that the RSO_3^- anions are good hydrogen-bond acceptors and can form strong hydrogen bonds and even hydrogen-bonded networks with H-donors.[9] However, reports on metal-based RSO_3^--containing supramolecular compounds remain few.[10] Furthermore, metal-based supramolecular frameworks constructed by both nitrogen-containing ligands and organosulfonate anions have not been reported yet.

In view of the excellent coordination capability of 4,4′-bipy and the good H-acceptor nature of RSO_3^- anions, we employed 4,4′-bipy and 4-aminobenzenesulfonate anion (4-abs) as mixed organic building blocks to construct multidimensional supramolecular networks in the expectation that these two groups may generate covalent and/or hydrogen-bonding interactions with transition metal ions in the assembly process. Herein, we report the syntheses and structures of two novel compounds $[Co(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot H_2O$ (**1**) and $[Mn(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot 2H_2O$ (**2**) (4,4′-bipy = 4,4′-bipyridine; 4-abs = 4-aminobenzenesulfonate). Both **1** and **2** possess unusual hydrogen-bonded 3-D networks encapsulating 1-D covalently bonded infinite $[M(4,4'\text{-bipy})(H_2O)_4]^{2+}$ (M = Co, Mn) chains. To our knowledge, **1** and **2** represent the first metal-based supramolecular complexes constructed by mixed 4-abs and 4,4′-bipy ligands.

Experimental Section

General Considerations. All reagents were commercially available and used as received. The C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. UV−vis absorption spectra were recorded on a 756 CRT UV−vis spectrophotometer made in Shanghai, China. The FT-IR spectra were recorded as KBr pellets in the range 4000−400 cm^{-1} on an Alpha Centauri FT/IR spectrometer. The thermogravimetric analysis

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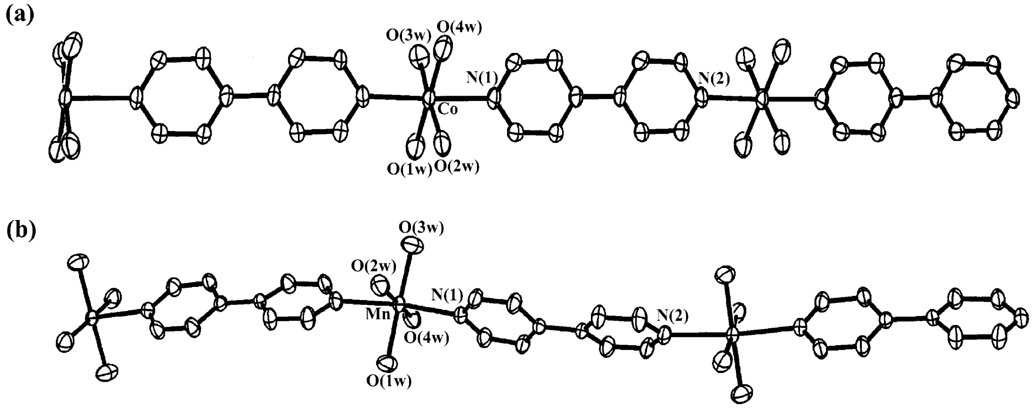

Figure 1. ORTEP drawings of the 1-D covalently bonded chains in **1** (a) and **2** (b) showing the coordination environment of the metal atom, respectively. Thermal ellipsoids are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

Table 1. Crystal Data and Refinement Summary for **1** and **2**

	1	**2**
empirical formula	$C_{22}H_{30}CoN_4O_{11}S_2$	$C_{22}H_{32}MnN_4O_{12}S_2$
fw	649.55	663.58
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$
a (Å)	11.380(2)	15.0833(14)
b (Å)	8.0274(16)	8.2887(4)
c (Å)	15.670(3)	23.2228(15)
α (deg)	90	90
β (deg)	92.82(3)	95.186(3)
γ (deg)	90	90
V (Å^3)	1429.7(5)	2891.5(4)
Z	2	4
D_{calcd} (g/cm^3)	1.509	1.524
T (K)	293(2)	293(2)
μ (Mo Kα) (cm^{-1})	8.09	6.68
λ (Mo Kα) (Å)	0.710 73	0.710 73
R1 ($I > 2\sigma(I)$)[a]	0.0814	0.0528
wR2 ($I > 2\sigma(I)$)[b]	0.1977	0.1689

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**[a]

	1	**2**		**1**	**2**
M−OW1	2.119(5)	2.151(3)	OW1−M−OW2	89.7(2)	89.32(12)
M−OW2	2.073(5)	2.206(3)	OW1−M−OW3	88.2(2)	178.03(10)
M−OW3	2.095(5)	2.163(3)	OW1−M−OW4	179.3(3)	93.79(12)
M−OW4	2.111(6)	2.173(3)	OW2−M−OW3	176.0(2)	89.58(12)
M−N(1)	2.154(4)	2.281(3)	OW2−M−OW4	91.0(2)	173.70(11)
M−N(2)#1	2.134(4)	2.287(3)	OW3−M−OW4	91.2(2)	87.47(12)
S(1)−O(1)	1.448(6)	1.444(3)	OW1−M−N(1)	93.2(2)	86.34(10)
S(1)−O(2)	1.440(6)	1.447(3)	OW2−M−N(1)	88.3(2)	90.24(11)
S(1)−O(3)	1.451(7)	1.453(3)	OW3−M−N(1)	88.4(2)	92.03(11)
S(1)−C(11)	1.751(6)	1.758(4)	OW4−M−N(1)	86.7(2)	95.41(11)
S(2)−O(4)	1.434(6)	1.464(3)	OW1−M−N(2)#1	86.0(2)	85.71(11)
S(2)−O(5)	1.461(6)	1.453(3)	OW2−M−N(2)#1	95.4(2)	86.58(11)
S(2)−O(6)	1.461(6)	1.453(3)	OW3−M−N(2)#1	87.8(2)	95.86(11)
N(2)−M#2	2.134(4)	2.287(3)	OW4−M−N(2)#1	94.0(2)	88.19(11)
			N(2)#1−M−N(1)	176.2(2)	171.47(11)

[a] Symmetry codes: (1) $x + 1, y, z$ and (2) $x - 1, y, z$ for **1**; (1) $x, - y + {}^1/_2, z + {}^1/_2$ and (2) $x, -y + {}^1/_2, z - {}^1/_2$ for **2**.

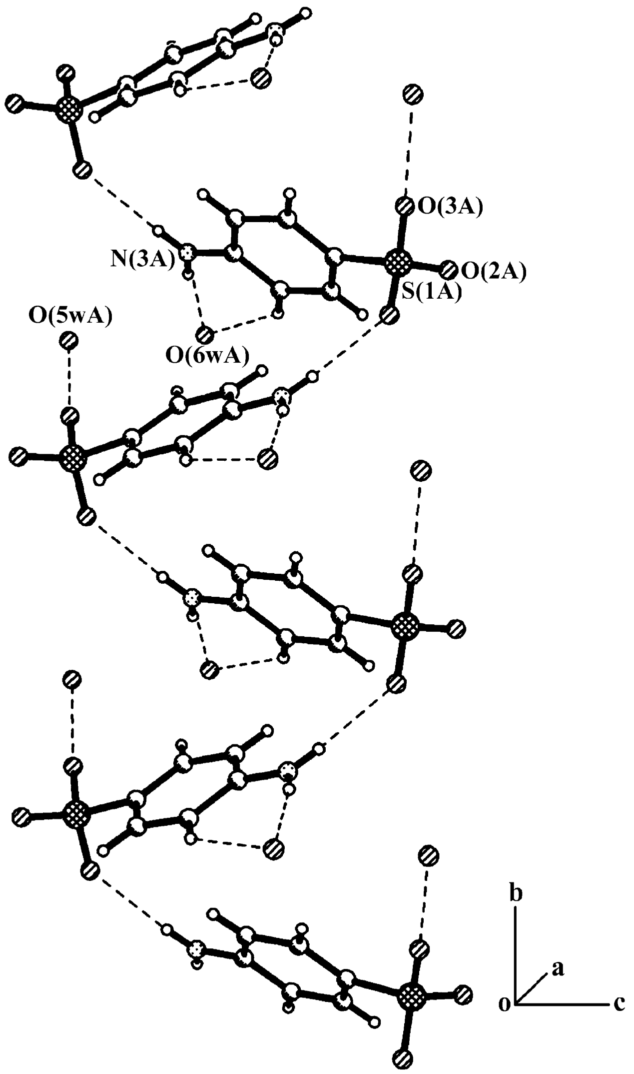

Figure 2. 1-D zigzag chain in **1** along the b axis, consisting of 4-abs anions.

(TGA) was performed from 30 to 600 °C in air using a Perkin-Elmer TGA-7 analyzer at a heating rate of 20 °C/min.

Synthesis of [Co(4,4′-bipy)(H_2O)$_4$](4-abs)$_2$·H_2O (4-abs = 4-Aminobenzene Sulfonate) (1). To an aqueous solution of $CoCl_2$·6H_2O (0.2379 g, 1 mmol) was added 4-aminobenzene sulfonate (0.094 g, 0.67 mmol) with stirring, and the resulting solution was then adjusted to pH ∼ 5.5 by addition of a dilute NaOH solution. To this reaction mixture was slowly added 4,4′-bipy (0.078 g, 0.5 mmol), followed by further stirring for 30 min at 60 °C. After filtration, a clear solution was obtained and allowed to stand at room temperature. On evaporation, yellow block-shaped single crystals were obtained after two weeks. Yield: 63% based on Co. Calcd for $C_{22}H_{30}CoN_4O_{11}S_2$: C, 40.67; H, 4.65; N, 8.62; S, 9.87%. Found: C, 40. 82; H, 4.78; N, 8.90; S, 9.95%. IR data (ν/cm^{-1}): 3726 w, 3442 s, 3367 s, 2362 s, 1608 m, 1537 w, 1501 w, 1421 w, 1306 w, 1165 m, 1124 m, 1029 m, 1004w, 818 m, 699 m, 637 w.

Synthesis of [Mn(4,4′-bipy)(H_2O)$_4$](4-abs)$_2$·2H_2O (2). The reaction was carried out in the same way as for **1** except that Mn-

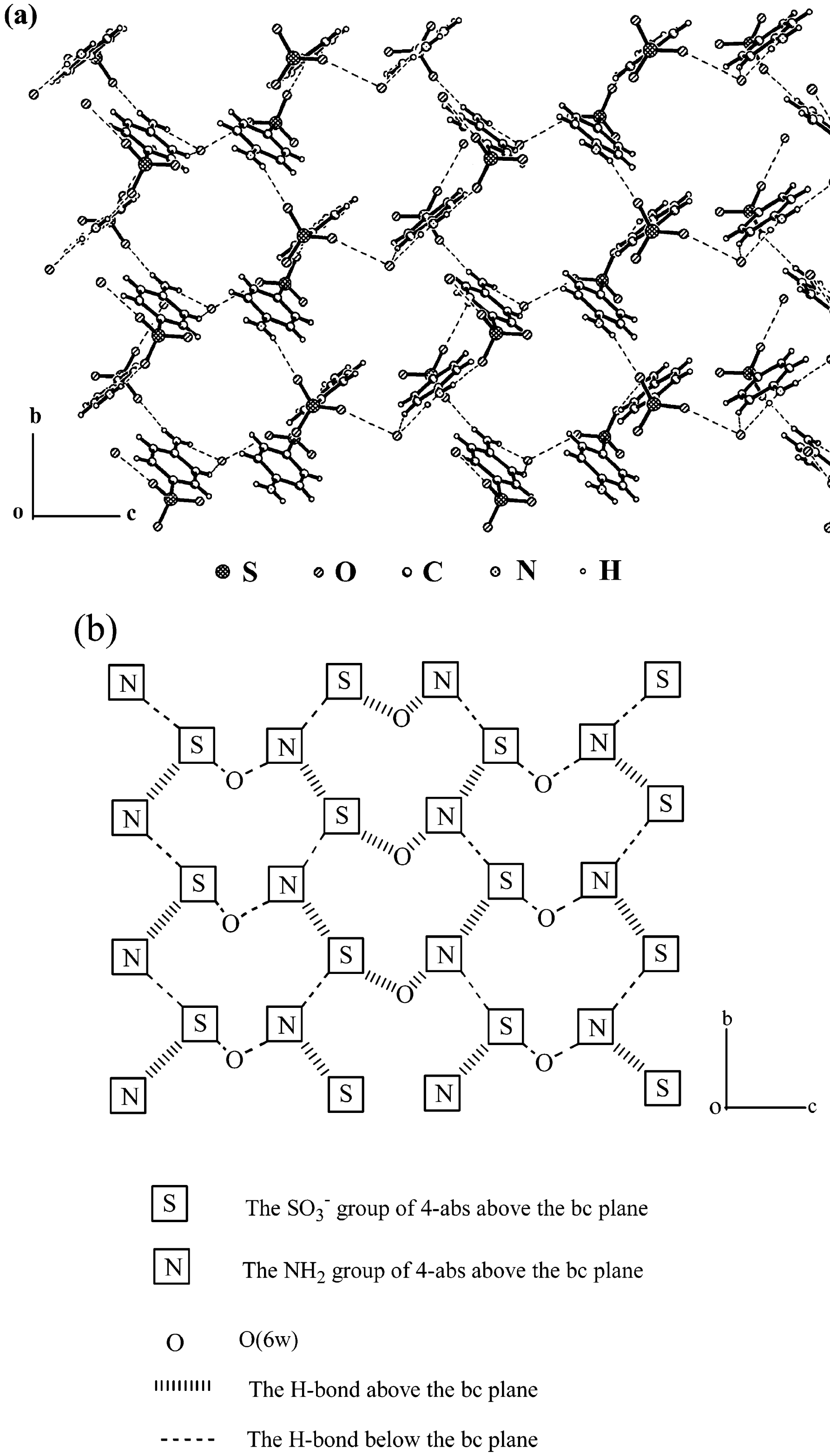

Figure 3. (a) 2-D layered network in **1** in the *bc* plane, formed by the 1-D zigzag chains through hydrogen-bonding interactions with the crystallization water molecule O(6w). (b) Schematic representation of this 2-D layered network in **1**.

$(CH_3COO)_2 \cdot 4H_2O$ was used instead of $CoCl_2 \cdot 6H_2O$. Yield: 58% based on Mn. Calcd for $C_{22}H_{38}MnN_4O_{12}S_2$: C, 39.82; H, 4.86; N, 8.44; S, 9.66%. Found: C, 40.16; H, 4.68; N, 8.91; S, 9.98%. IR data (ν/cm^{-1}): 3726 w, 3455 s, 2363 s, 2334 s, 1645 m, 1605 m, 1537 w, 1502 w, 1420 w, 1384 w, 1222 w, 1179 m, 1127 m, 1033 m, 835 w, 809 w, 700 w, 674 w, 568 m.

X-ray Crystallography. Crystals with dimensions 0.424 × 0.216 × 0.181 mm^3 for **1** and 0.493 × 0.311 × 0.299 mm^3 for **2** were selected for intensity data collections at 293 K on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα radiation. Empirical absorption corrections were applied. The structures were solved by direct methods and refined by a full-matrix least-squares technique based

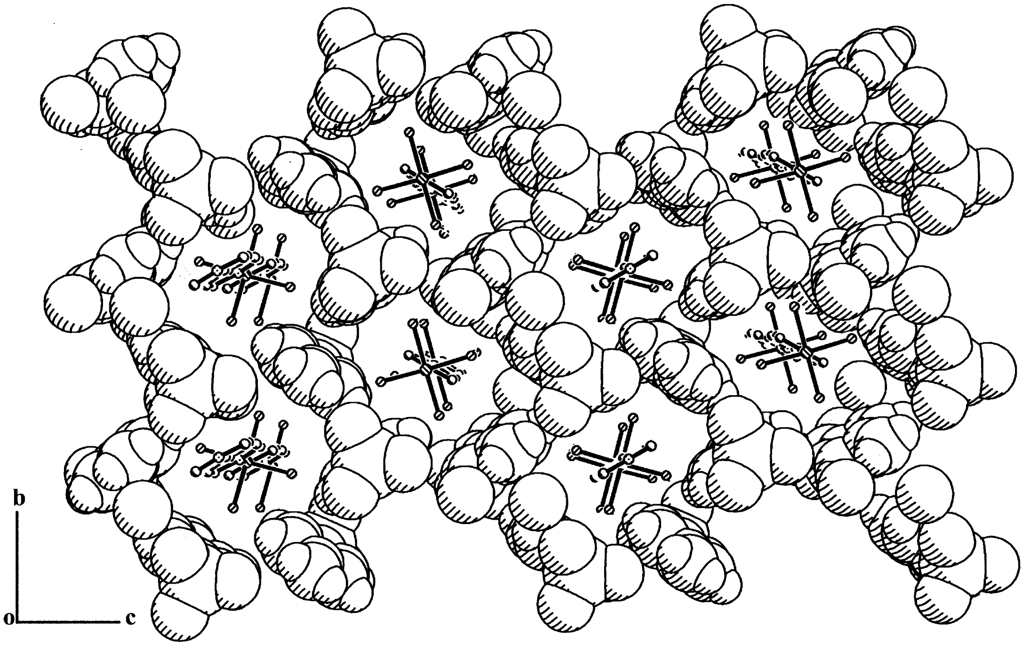

Figure 4. Space-filling diagram showing the hydrogen-bonded 3-D network of **1**, in which the $[Co(4,4'\text{-bipy})(H_2O)_4]^{2+}$ linear chains are located in the 1-D channels.

on F^2 using the SHELXL 97 program.[11] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in difference Fourier maps. Detailed data collection and refinement of the compounds are summarized in Table 1. Selected bond distances and angles are given in Table 2. CCDC reference number: 190490 for **1** and 190591 for **2**.

Results and Discussion

Crystal Structures. X-ray crystallography shows that compounds **1** and **2** both contain one-dimensional covalently bonded chains formed by 4,4′-bipyridine ligands connecting metal Co or Mn atoms (see Figure 1), uncoordinated 4-aminobenzenesulfonate anions, and coordination and crystallization water molecules. The Co(II) or Mn(II) center exhibits slightly distorted octahedral coordination geometry, defined by four aqua ligands (Co−O(w) = 2.073(5)−2.119(5) Å, Mn−O(w) = 2.151(3)−2.206(3) Å) in the equatorial positions and two pyridyl nitrogen donors (average Co−N = 2.144 Å, average Mn−N = 2.284 Å) from two different 4,4′-bipy ligands in the apical positions. These M−O(w) and M−N distances for **1** and **2** are comparable to those observed for $[Co(H_2O)_4(bipy)][PF_6]\cdot 3bipy$,[6c] $Co(H_2O)_3(4,4'\text{-bipy})SO_4\cdot H_2O$,[7a] and $[Mn(4,4'\text{-bipy})(H_2O)_2(NCS)_2]\cdot(4,4'\text{-bipy})$.[6d] The N−M−N bond angle is 171.47(11)° for **1** and 176.2(2)° for **2**, respectively.

The 4,4′-bipy groups serve as bis-monodentate ligands and bridge adjacent Co or Mn centers (Co···Co = 11.380 Å, Mn···Mn = 11.635 Å) into 1-D infinite chains. The two pyridyl rings in a 4,4′-bipy group are not coplanar (the dihedral angles are 5.3° and 12.5° for **1** and **2**, respectively). The linear chains of **1** run parallel to the crystallographic *a* axis with an interchain separation of 9.481 Å, while those of **2** run parallel to the *c* axis with an interchain separation of 8.289 Å.

The significant structural difference between **1** and **2** originates from their dissimilar hydrogen-bonded 3-D networks constructed by 4-abs anions and crystallization water molecules. In compound **1**, the uncoordinated 4-abs anions form a 1-D zigzag chain through hydrogen bonding in a head-to-tail way as shown in Figure 2. That is, the NH_2 group of one 4-abs anion serves as a H-donor and interacts with the SO_3^- group (H-acceptor) of another 4-abs anion (N−H···O(S) 2.777 Å). These 1-D chains along the *b* axis are connected by the crystallization water molecule O(6w) via hydrogen-bonding interactions (O(6w)···O(6) 2.847 Å, O(6w)···N(3) 2.871 Å) into a 2-D layered network with large cavities in the *bc* plane (see Figure 3). In addition, the 2-D layers are further linked by the lattice water molecule O(5w) through hydrogen bonds (O(5w)···O(3A) 3.296 Å, O(5w)···O(3B) 2.800 Å) into a 3-D network with 1-D channels along the *a* axis. The covalent linear $[Co(4,4'\text{-bipy})(H_2O)_4]^{2+}$ chains are located in these channels (see Figure 4) and are stabilized by hydrogen bonding to the SO_3^- groups of the 4-abs anions (O(w)···O(S) 2.695−3.024 Å) and to the crystallization water molecule O(5w) (O(3w)···O(5w) 2.640 Å).

Compared with the hydrogen-bonded network of **1**, **2** displays a different, yet interesting, structural motif. That is, in the *ab* plane, the 4-abs anions together with the crystallization water molecule O(6w) are connected into a 2-D honeycomb-like framework via hydrogen bonding. The basic building block of this network is made up of two abs anions and one crystallization water molecule O(6w), as shown in Figure 5. The two abs anions are linked to each other through one NH_2 group and one SO_3^- group also in a head-to-tail fashion (vide supra) with N−H···O(S) 2.491 Å, while the remaining NH_2 group and SO_3^- group are connected via O(6w) with O(6w)···O(4A) 2.805 Å and O(6w)···H−N(3B) 2.168 Å. These building blocks are

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[11] Sheldrick, G. M. *SHELXL-97, Program for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

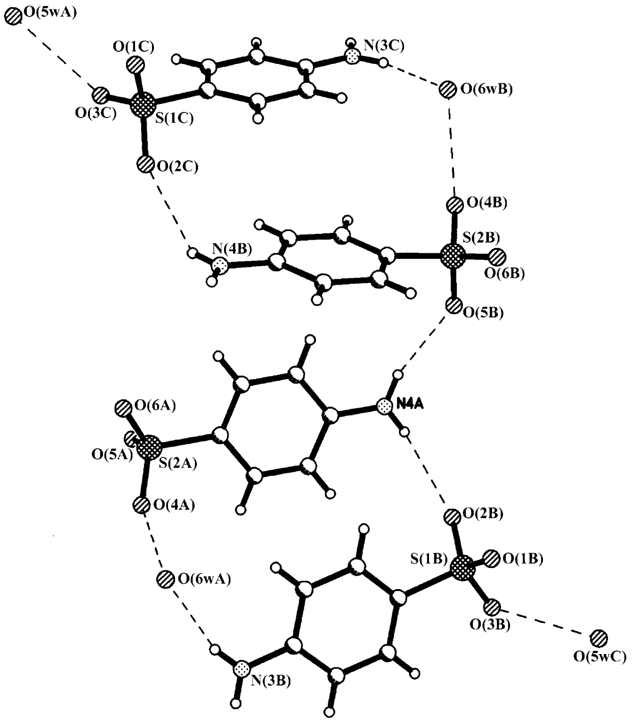

Figure 5. Basic building block of the hydrogen-bonded 2-D honeycomb-like network in **2**, made up of two 4-abs anions and one crystallization water molecule O(6w).

connected into a 2-D network via strong hydrogen bonds between the NH_2 group and the SO_3^- group from two different building blocks (N(4A)−H···O(5B) 2.293 Å) (Figure 6). The 2-D frameworks are further extended into a 3-D network with 1-D hexagonal channels along the *c* axis through hydrogen-bonding interactions involving the SO_3^- group and the lattice water molecule O(5w) (O(5w)···O(3A) 2.831 Å, O(5w)···O(1A) 3.343 Å). The covalent linear $[Mn(4,4'\text{-bipy})(H_2O)_4]^{2+}$ chains exist in the channels and are further stabilized by hydrogen-bonding interactions associated with the coordinated water molecules and the SO_3^- groups of the 4-abs anions (O(w)···O(S) 2.713−2.831 Å).

The extended 3-D hydrogen-bonded networks of **1** and **2** are obviously different from those mentioned in the first part of this paper (vide ante), which can be explained from two points of view. In the first place, the reported networks contain only one kind of organic ligand (4,4′-bipy or 4,4′-dpdo), which not only coordinates to the metal ions to generate 1-D covalently bonded chains but also interacts with metal-coordinated water molecules to connect the 1-D chains.[6] In our case, compounds **1** and **2** both contain two organic ligands, namely 4,4′-bipy and 4-abs. Each of them plays only one role in the networks; that is, 4,4′-bipy participates in the coordination with metal centers, while 4-abs acts as both H-donor through its NH_2 group and H-acceptor through its SO_3^- group. Also, for the reported systems, the solvate organic ligands are often located between the linear chains and link these chains into higher dimensional networks through hydrogen-bonding interactions, whereas for **1** and **2** in the present work the linear $[M(4,4'\text{-bipy})(H_2O)_4]^{2+}$ chains exist in the 1-D channels of the 3-D networks consisting of 4-abs anions and crystallization water molecules. Considering the point of view of host−guest chemistry, the flexible 3-D hydrogen-bonded networks constructed by 4-abs anions and crystallization water molecules may be deemed the host, while the robust 1-D $[M(4,4'\text{-bipy})(H_2O)_4]^{2+}$ chains may be deemed the guest, which is somewhat an interesting phenomenon in this field.

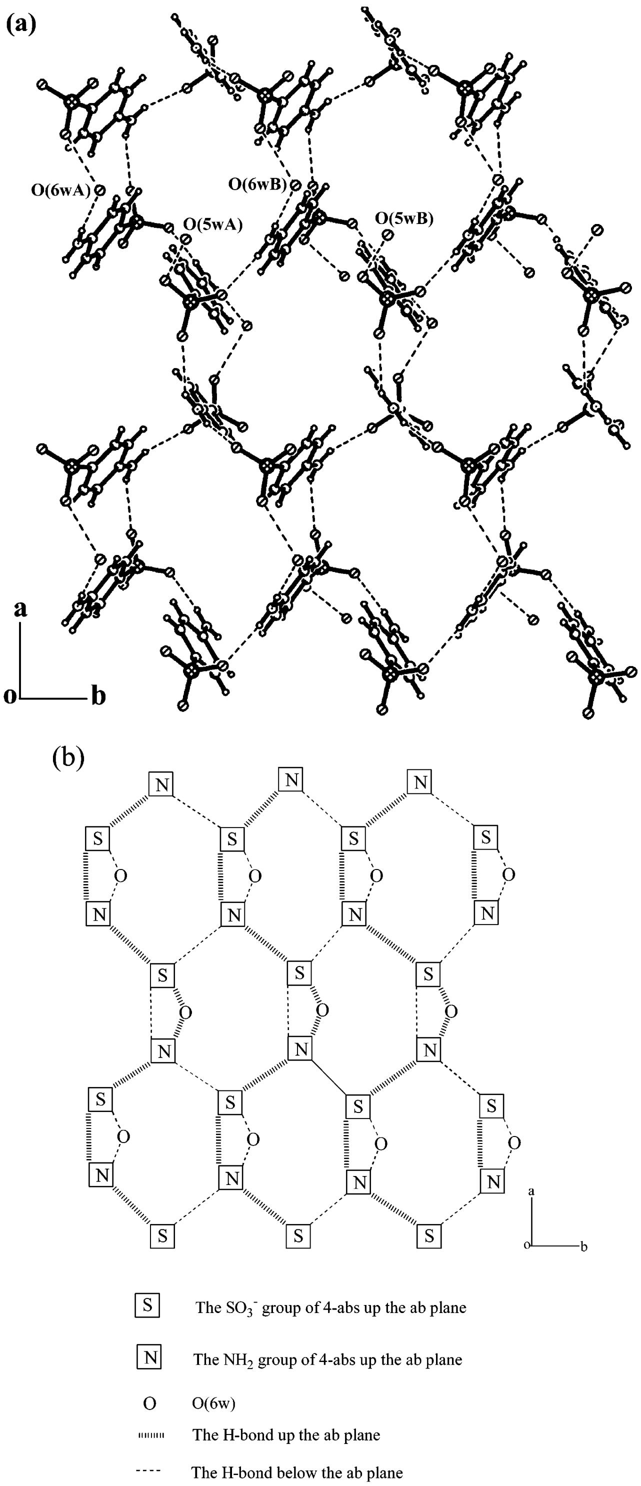

Figure 6. (a) 2-D honeycomb-like network in **2** generated from the basic building blocks through hydrogen-bonding interactions. (b) Schematic representation of this 2-D honeycomb-like network in **2**.

Spectroscopic Properties. Compounds **1** and **2** both exhibit two UV absorption bands at ca. 205 and 247 nm, which can be ascribed to the $\pi-\pi^*$ transitions of the phenyl groups from 4,4′-bipy ligands and 4-abs anions. The IR spectra of **1** and **2** both show the characteristic vibration peaks of 4,4′-bipy and 4-abs. Compound **1** shows a broad OH stretching band at 3442 cm^{-1} (3454 cm^{-1} for **2**), showing the presence of water molecules in the compound. The strong peak at ca. 3367 cm^{-1} for **1** (3364 cm^{-1} for **2**) is due to the N−H stretching band. The well resolved peaks of aromatic rings span over the regions 637−818 and 1306−1637 cm^{-1} for **1** (614−835 and 1284−1644 cm^{-1} for **2**). Bands in the range 1004−1187 cm^{-1} for **1** (1016−1222 cm^{-1} for **2**) are characteristic of the fundamental and split ν_3 S−O stretching modes.[10b,c]

Thermal Analyses. Thermogravimetric analyses have been performed in air for **1** and **2** between 30 and 600 °C. Both compounds show a three-step weight-loss process. For **1**, the initial weight loss of ca. 13.67% from 80 to 150 °C corresponds to the loss of five water molecules (calcd 13.87%). A second weight loss of ca. 24.11% in the range 220−330 °C corresponds to the removal of one 4,4′-bipyridine molecule (calcd 24.05%). Thus, it can be seen that the first two weight losses are consistent with the calculated values. However,because the percentage of the two 4-aminobenzenesulfonate anions in compound **1** is calculated to be 53.02%, the third weight loss of ca. 44.96% from 350 to 500 °C cannot be unambiguously assigned, perhaps corresponding to the decomposition of 4-abs anions and the oxidation of the cobalt atom.

The thermal decomposition behavior of **2** is much like that observed for **1**. The compound loses water molecules in the range 75−145 °C [weight loss found (calcd): 16.32 (16.29)%]. The release of the 4,4′-bipy ligand in **2** occurs between 240 and 310 °C [weight loss found (calcd): 23.61 (23.54)%]. From 355 to 510 °C, the compound loses an additional 39.65% weight (calcd for 4-abs: 51.89%), the explanation for which is analogous to that of **1**. The residues in both cases could not be clearly identified.

Conclusions

In the present work, two novel hydrogen-bonded 3-D supramolecular networks $[Co(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot H_2O$ (**1**) and $[Mn(4,4'\text{-bipy})(H_2O)_4](4\text{-abs})_2\cdot 2H_2O$ (**2**) have been synthesized and structurally characterized. The successful syntheses of **1** and **2** demonstrate that the introduction of mixed ligands may provide multiple binding forces such as coordinate covalent and hydrogen-bonding interactions, which may endow enormous potential for assembling multidimensional supramolecular architectures. Furthermore, the use of the 4-abs group, which acts as both H-donor and H-acceptor, contributes new features to the rapidly expanding area of supramolecular chemistry.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2**. Additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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