

# Hydrogen-Bonded Host Frameworks of Cationic Metal Complexes and Anionic Disulfonate Linkers: Effects of the Guest Molecules and the Charge of the Metal Complex

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Synthesized and structurally characterized is a new series of soft host frameworks assembled by charge-assisted hydrogen bonds between a cationic metal complex (MC) and an anionic disulfonate, in this case  $[\text{Co}(\text{en})_2(\text{ox})]^+$  and 4,4'-biphenyldisulfonate (BPDS), respectively. Four compounds with neutral guest molecules of DMF, *p*-nitrophenol (pnp), 4-acetylpyridine (acpy), and 4-dimethylaminopyridine (dmapy) have a general formula  $(\text{MC})_2(\text{BPDS}) \cdot n(\text{guest})$  and exhibit a "brick wall" topology of their neutral pillared-layer type frameworks. A fifth compound,  $(\text{H-dmapy})_2(\text{MC})_4(\text{BPDS})_3$ , forms at more acidic conditions that lead to protonation of dmapy and has a negatively charged pillared-layer framework. The layers in all five compounds are constructed of extensively hydrogen-bonded MC cations bonded both directly to each other and indirectly via the sulfonate groups and water while the organic residues of the latter serve as pillars. The structures of the layers and orientation of the pillars adjust to the specifics of the guest molecules, and as a result, the five compounds crystallize in different structures. Compared to the recently reported analogous compounds with the trication  $[\text{Co}(\text{NH}_3)_6]^{3+}$  these compounds have larger galleries between the pillars. The reason is the lower charge of  $[\text{Co}(\text{en})_2(\text{ox})]^+$  and the need for only 0.5 charge-balancing pillars per metal complex instead of 1.5 such pillars for the trication. These host-guest frameworks are analogs to the well-studied guanidinium sulfonate (GS) networks and mimic their flexibility and overall durability.

## Introduction

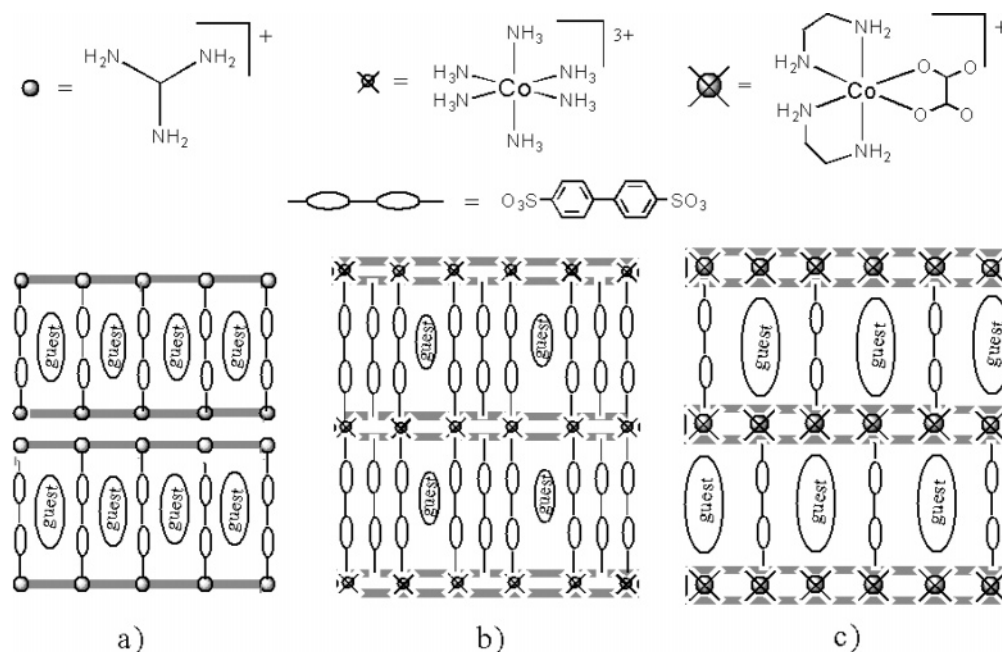
Inclusion compounds have attracted the attention of many synthetic chemists because of their capability to combine interesting structural features with compositional diversity as well as their potential for applications in a variety of technologically useful processes.<sup>1</sup> These compounds, also known as host-guest compounds, typically have three-dimensional frameworks made of building blocks held together by various interactions such as covalent, coordination, donor-acceptor, and hydrogen bonding while various guest molecules occupy cavities in the frameworks and are weakly bound to them by either van der Waals forces or a handful of hydrogen bonds.<sup>2</sup> In general, the weaker the bonding within the frameworks the more flexible and soft they are. Molecular frameworks assembled by hydrogen bonding are generally considered soft and differ greatly in flexibility from the much more rigid frameworks constructed by strong interactions such as covalent and coordination bonds.<sup>3–5</sup> Soft frameworks can readily adjust structure upon

formation in the presence of different guest molecules while preserving the overall topology and connectivity. Frameworks with hydrogen bonds between cationic and anionic building blocks, i.e., charge-assisted hydrogen bonds, are of special interest because of the additional strength provided by the electrostatic attractions to the overall bonding.<sup>3,6–7</sup> An example of such a system is the series of pillared-layer compounds with layers made of hydrogen-bonded guanidinium (G) cations and disulfonate (S) anions and pillars made of the organic residues of the disulfonates (Figure 1a).<sup>3,6,8,9</sup> The cavities between the pillars are occupied by various guest molecules which, in turn, define the specific structural details of the framework. It has been shown by

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**Figure 1.** (a) Typical guanidinium disulfonate bilayer structure with layers made of hydrogen-bonded guanidinium and sulfonate groups and pillars of the organic residue of the disulfonate. The ratio of the disulfonate to guanidinium is 0.5. (b) Proposed and later observed metal complex disulfonate structure with layers made of hydrogen-bonded  $[Co(NH_3)_6]^{3+}$  and sulfonate groups. The ratio of disulfonate to metal complex is 1.5. (c) Proposed framework made of  $[Co(en)_2(ox)]^+$  and disulfonate. The ratio of disulfonate to metal complex is 0.5.

M. Ward et al. that these frameworks are very durable yet flexible in their ability to adjust to very different guest molecules.<sup>3,6,8</sup> The large number of available GS-based inclusion compounds makes possible their further exploration for various applications and better understanding of the factors that control formation of such self-assembled frameworks.

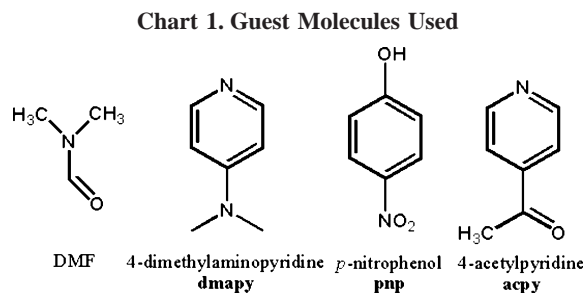
Another, yet still emerging, strategy toward soft inclusion frameworks with charge-assisted hydrogen bonding is to use cationic metal complexes (MC) instead of guanidinium cations.<sup>10–12</sup> The idea is to replace two guanidinium cations from two layers with a cationic octahedral metal complex with ligands that can provide protons for hydrogen bonding such as ammonia,<sup>10–14</sup> water,<sup>15–17</sup> and various amines.<sup>15,18–20</sup> As a result, two neighboring layers of guanidinium will be

replaced by one layer of the metal complex which provides a double layer of ligands capable of hydrogen bonding (Figure 1b,c). These double layers are then hydrogen bonded to the sulfonate terminals of the disulfonate linkers and thus pillared by the organic residues of the latter. One additional advantage of such frameworks is the presence of transition-metal centers and their potential for redox and magnetic properties.

In a previous publication we argued that the charge of the metal complex is most likely one of the most important parameters defining the size of the interpillar galleries available for guest molecules.<sup>10</sup> We proposed that reduction of this charge should lead to larger cavities and, therefore, improved capability to host larger guests. The reason for this is that, for example, a cation with a charge of 3+, as the previously reported compounds with  $[Co(NH_3)_6]^{3+}$ , needs 1.5 dianionic disulfonate pillars for charge balancing (Figure 1b) while a cation of approximately the same size but with a charge of 1+ needs only 0.5 such pillars (Figure 1c). The lower number of pillars per metal complex means fewer pillars between the layers and, therefore, more space between them. Even more spacious galleries can be achieved by increasing the size of the metal complex.

Here we report a series of inclusion compounds made of 4,4'-biphenyldisulfonate (BPDS) and  $[Co(en)_2(ox)]^+$  which, compared to  $[Co(NH_3)_6]^{3+}$ , has a lower charge and is larger. The general formula of the compounds with guest molecules of DMF, *p*-nitrophenol (pnp), 4-acetylpyridine (acpy), and 4-dimethylaminopyridine (dmapy) shown in Chart 1 is  $(MC)_2(BPDS) \cdot n(\text{guest})$ , and the topology of their pillared-layer structures is exactly as envisioned in Figure 1c. In order to test the possibility for constructing an anionic framework with cationic guest molecules we carried out an additional reaction at less basic conditions that resulted in protonation

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of dmapy. This led to a compound that does not conform to the same topology as the neutral frameworks but is nevertheless of pillared layer type and provides an interesting alternative. Contrasted to these open structures is the well-packed structure of a sixth compound made without a guest molecule.

### Experimental Section

The complex  $[\text{Co}(\text{en})_2(\text{ox})]\text{Br}\cdot\text{H}_2\text{O}$ , synthesized according to the literature,<sup>21</sup> was generously provided by Prof. A. G. Lappin. 4,4'-Biphenyldisulfonic acid ( $\text{H}_2\text{BPDS}$ , 98%, TCI America, IR:  $1189\text{ cm}^{-1}$  for  $\nu_{\text{S-O}}$ ), the solvents, and guest molecules (>98%, all from Acros Organics) were used as purchased without further purification. FT-IR spectra of the freshly prepared compounds (in KBr disks) were recorded on a Perkin-Elmer Paragon-1000 spectrophotometer in the  $4000\text{--}500\text{ cm}^{-1}$  region.

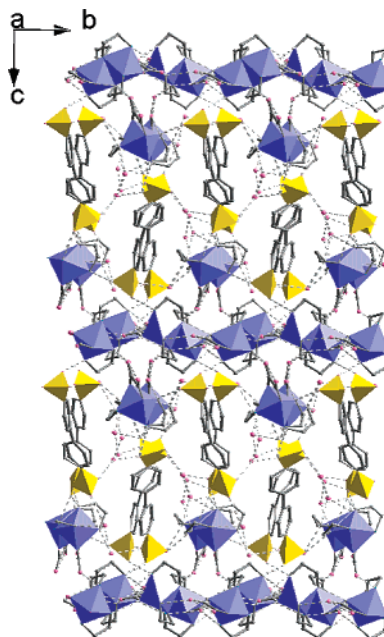
**Synthesis of  $[\text{Co}(\text{en})_2(\text{ox})]_2(\text{BPDS})\cdot 3.5\text{H}_2\text{O}$  (**1**).** A solution of  $[\text{Co}(\text{en})_2(\text{ox})]\text{Br}\cdot\text{H}_2\text{O}$  (0.3 mmol) in 8 mL of hot  $\text{H}_2\text{O}$  was mixed with 3 mL of acetonitrile solution of  $\text{H}_2\text{BPDS}$  (0.15 mmol) and NaOH (0.3 mmol). The resulting clear solution was stirred for 10 min, filtered, and left undisturbed at room temperature to allow for slow evaporation. Red-colored column-like crystals of **1** were obtained in 10 days as a single phase. IR ( $\text{cm}^{-1}$ ): 1670s, 1703s,  $\nu_{\text{C=O}}$ , oxalate; 1197s, 1219s,  $\nu_{\text{S-O}}$ , BPDS.

**Synthesis of  $[\text{Co}(\text{en})_2(\text{ox})]_2(\text{BPDS})\cdot 2(\text{DMF})$  (**2**).** A solution of  $[\text{Co}(\text{en})_2(\text{ox})]\text{Br}\cdot\text{H}_2\text{O}$  (0.3 mmol) in 8 mL of hot  $\text{H}_2\text{O}$  was mixed with 5 mL of DMF solution of  $\text{H}_2\text{BPDS}$  (0.15 mmol) and NaOH (0.3 mmol). The solution was stirred for 10 min, filtered, and left undisturbed at room temperature to allow for slow evaporation. Red-colored column-like crystals of **2** were obtained in 4 days as the only solid-state phase. IR ( $\text{cm}^{-1}$ ): 1678s, 1702 m,  $\nu_{\text{C=O}}$ , oxalate; 1650s,  $\nu_{\text{C=O}}$ , DMF; 1172 m, 1233 m,  $\nu_{\text{S-O}}$ , BPDS.

**Synthesis of  $[\text{Co}(\text{en})_2(\text{ox})]_2(\text{BPDS})\cdot 3(\text{pnp})\cdot 7\text{H}_2\text{O}$  (**3**).** A solution of  $[\text{Co}(\text{en})_2(\text{ox})]\text{Br}\cdot\text{H}_2\text{O}$  (0.3 mmol),  $\text{H}_2\text{BPDS}$  (0.15 mmol), and NaOH (0.3 mmol) in 12 mL of hot  $\text{H}_2\text{O}$  was mixed with 4 mL of methanol solution of 4-nitrophenol (1 mmol). The solution was stirred and heated for 5 min, filtered, and left undisturbed at room temperature to allow for slow evaporation. Red-colored plate-shaped crystals of **3** were obtained in 1 week (single phase). IR ( $\text{cm}^{-1}$ ): 1670s, 1701s,  $\nu_{\text{C=O}}$ , oxalate; 1334s, 1498s,  $\nu_{\text{N-O}}$ , pnp; 1169s, 1222 m,  $\nu_{\text{S-O}}$ , BPDS.

**Synthesis of  $[\text{Co}(\text{en})_2(\text{ox})]_2(\text{BPDS})\cdot 2(\text{acpy})\cdot 7\text{H}_2\text{O}$  (**4**).** A solution of  $[\text{Co}(\text{en})_2(\text{ox})]\text{Br}\cdot\text{H}_2\text{O}$  (0.3 mmol),  $\text{H}_2\text{BPDS}$  (0.15 mmol), and NaOH (0.3 mmol) in 12 mL of hot  $\text{H}_2\text{O}$  was mixed with 4 mL of methanol solution of 4-acetylpyridine (2 mmol). The solution was filtered and left undisturbed at room temperature. Red-colored plate-shaped crystals of **4** were obtained in 1 week (single phase). IR ( $\text{cm}^{-1}$ ): 1683s, 1703s,  $\nu_{\text{C=O}}$ , oxalate; 1662s,  $\nu_{\text{C=O}}$ , acpy; 1195s, 1220s,  $\nu_{\text{S-O}}$ , BPDS.

**Synthesis of  $[\text{Co}(\text{en})_2(\text{ox})]_2(\text{BPDS})\cdot 2(\text{dmapy})\cdot 10\text{H}_2\text{O}$  (**5**).** A solution of  $[\text{Co}(\text{en})_2(\text{ox})]\text{Br}\cdot\text{H}_2\text{O}$  (0.2 mmol),  $\text{H}_2\text{BPDS}$  (0.10 mmol),



**Figure 2.** Three-dimensional well-packed structure of **1** without guest molecules.

and NaOH (0.2 mmol) in 8 mL of hot  $\text{H}_2\text{O}$  was mixed with 3 mL of methanol solution of 4-dimethylaminopyridine (1 mmol). The solution was filtered and left undisturbed at room temperature. Red-colored column-shaped crystals of **5** were obtained in 1 week (single phase). IR ( $\text{cm}^{-1}$ ): 1676s, 1698s,  $\nu_{\text{C=O}}$ , oxalate; 1197s, 1217s,  $\nu_{\text{S-O}}$ , BPDS.

**Synthesis of  $(\text{H-dmapy})_2[\text{Co}(\text{en})_2(\text{ox})]_4(\text{BPDS})_3\cdot 16\text{H}_2\text{O}$  (**6**).** The synthetic procedure was the same as for compound **5** except that the amount of NaOH was reduced by one-half. Red-colored plate-shaped crystals of **6** were obtained in 2 weeks (single phase). IR ( $\text{cm}^{-1}$ ): 1684s, 1702s,  $\nu_{\text{C=O}}$ , oxalate; 1193s, 1218s for  $\nu_{\text{S-O}}$ , BPDS.

**Structure Determination.** Single-crystal X-ray diffraction data sets were collected on a Bruker APEX-II diffractometer with a CCD area detector at 100 K ( $\text{Mo K}\alpha$ ,  $\lambda = 0.71073\text{ \AA}$ ). The crystals were taken from the mother liquid and immediately covered with Paratone-N oil in order to prevent eventual loss of guest molecules. The crystals of compounds **1**, **2**, **5**, and **6** were of very good quality, while those of **3** and **4** were always naturally twinned with the two components related by a rotation of  $180^\circ$  (at least three different crystals were checked for each compound). The program CELL\_NOW was used to identify the matrices of the twin components which were then used for integration of the data frames,<sup>22</sup> and the program TWINABS was then applied to scale the data.<sup>23</sup> The twin structures were solved by using data from one of the components but refined using the data from both of them. All structures were solved by direct methods and refined by full-matrix least squares based on  $F^2$  using the SHELXL97 program.<sup>24</sup> (The multiple components of compounds **3** and **4** cause false data completeness of higher than 100%.) It should be pointed out that although some of the angles in compounds **3** and **4** are very close to  $90^\circ$ , their structures can be solved and refined only in the triclinic crystal system. The  $R_{\text{int}}$  values were very high in higher symmetry systems, and in addition, the PLATON software with the "ADDSYMM" command did not suggest any additional sym-

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Table 1. Crystallographic Data for Compounds 1–6

compound	1	2	3	4	5	6
formula	C <sub>48</sub> H <sub>94</sub> N <sub>16</sub> O <sub>35</sub> S <sub>4</sub> Co <sub>4</sub>	C <sub>15</sub> H <sub>27</sub> N <sub>5</sub> O <sub>8</sub> SCo	C <sub>42</sub> H <sub>69</sub> N <sub>11</sub> O <sub>30</sub> S <sub>2</sub> Co <sub>2</sub>	C <sub>38</sub> H <sub>68</sub> N <sub>10</sub> O <sub>23</sub> S <sub>2</sub> Co <sub>2</sub>	C <sub>38</sub> H <sub>80</sub> N <sub>12</sub> O <sub>24</sub> S <sub>2</sub> Co <sub>2</sub>	C <sub>74</sub> H <sub>144</sub> N <sub>20</sub> O <sub>50</sub> S <sub>6</sub> Co <sub>4</sub>
<i>M<sub>r</sub></i> [g·mol <sup>-1</sup> ]	1819.35	496.41	1390.06	1215.00	1271.11	2542.15
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>P</i> 1
<i>a</i> [Å]	13.0907(2)	6.3228(1)	7.7782(16)	11.781(2)	38.284(7)	11.7217(8)
<i>b</i> [Å]	11.9219(2)	11.9946(2)	10.310(2)	12.915(3)	10.195(2)	18.1519(13)
<i>c</i> [Å]	22.7569(3)	26.4024(4)	18.272(4)	17.417(4)	15.276(3)	26.4208(19)
α [deg]			99.69(3)	89.52(4)		70.693(3)
β [deg]	96.0620(10)	91.4020(10)	94.23(4)	73.11(3)	110.18(1)	89.401(3)
γ [deg]			90.10(3)	89.75(3)		87.117(3)
<i>V</i> [Å <sup>3</sup> ]	3531.72(9)	2001.74(6)	1440.4(5)	2535.6(10)	5596.3(17)	5298.6(6)
<i>Z</i>	2	4	1	2	4	2
ρ <sub>calcd</sub> [gcm <sup>-3</sup> ]	1.711	1.647	1.603	1.591	1.509	1.601
μ(Mo Kα) [mm <sup>-1</sup> ]	1.146	1.017	0.750	0.829	0.757	0.838
R1/wR2 <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0384/0.0935	0.0279/0.0692	0.0402/0.1117	0.0451/0.1242	0.0730/0.1889	0.0369/0.1023
R1/wR2 <sup>a</sup> (all data)	0.0429/0.0985	0.0305/0.0707	0.0433/0.1186	0.0553/0.1323	0.0804/0.1984	0.0427/0.1090

$$^a R1 = [\sum||F_o| - |F_c||]/\sum|F_o|; wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F_o)^2]\}^{1/2}; w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1} \text{ where } P = [(F_o)^2 + 2(F_c)^2]/3.$$

metry.<sup>25</sup> The latter also confirmed the acentric space groups for **1** and **3**. More details for the data collections and structure refinements are given in Table 1.

## Results and Discussion

The six new compounds are all with pillared-layer-type frameworks assembled by a multitude of charge-assisted hydrogen bonds between the metal complex [Co(en)<sub>2</sub>(ox)]<sup>+</sup> and the 4,4'-biphenyldisulfonate [O<sub>3</sub>S–C<sub>6</sub>H<sub>4</sub>–C<sub>6</sub>H<sub>4</sub>–SO<sub>3</sub>]<sup>2-</sup>, often involving water molecules near the metal complexes. Since this specific metal complex has both hydrogen-donating and -accepting groups, the amine –NH<sub>2</sub> and oxalate –C<sub>2</sub>O<sub>4</sub>, respectively, the layers in these structures exhibit the commonly observed hydrogen bonds not only between the metal complex and the sulfonate groups but also between the metal complexes themselves. The layers are pillared by the 4,4'-biphenyl residues of the disulfonates, and the various guest molecules occupy the galleries available between the pillars.

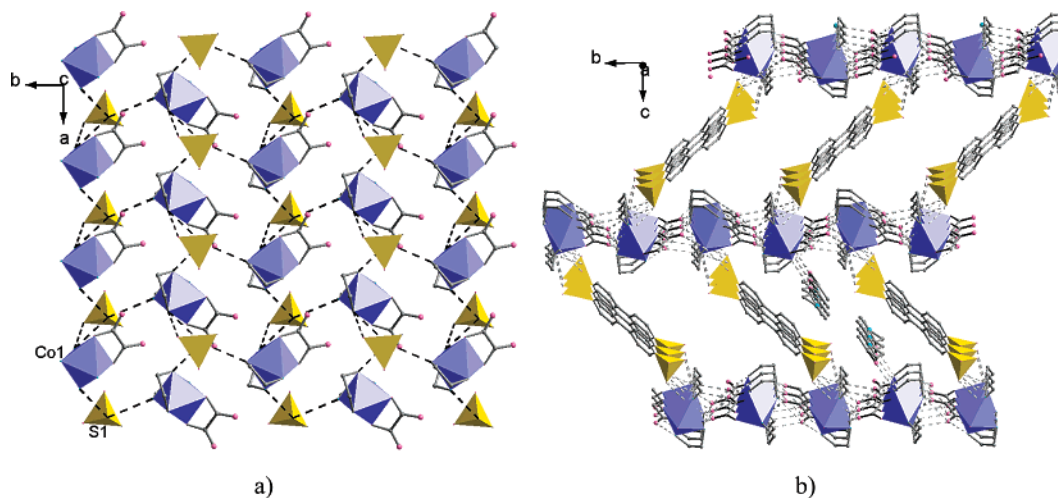
**Structure of 1.** This compound, [Co(en)<sub>2</sub>(ox)]<sub>2</sub>(BPDS)·3.5H<sub>2</sub>O, forms when no organic guest molecules are available. Its structure resembles a pillared-layer-type structure (Figure 2), but additional metal complex cations are inserted between the layers, resulting in a well-packed structure without noticeable cavities. The layers are made of metal complexes centered by two different atoms, Co1 and Co2, that are hydrogen bonded to each other both by direct hydrogen bonds involving the oxalate and ethylenediamine ligands and by indirect hydrogen bonding via –SO<sub>3</sub> groups above and below the layers. Another two cobalt complexes, centered by Co3 and Co4, are attached as pendants on both sides of the layers, also by hydrogen bonds. Each pillar hydrogen bonds to the layer with one of its sulfonate groups and to a pendant metal complex with the other sulfonate group. The pendant metal complexes effectively increase the overall charge of the layer which, in turn, requires more charge-balancing disulfonate groups per layer unit and results in the observed packed structure. The underlying reason for all this is, of course, the absence of large and less polar than water guest molecules that can occupy eventual galleries

between the hydrophobic pillars. The water molecules in the structure, as in many other similar compounds, gravitate around the hydrophilic parts of the structure, i.e., the charged metal complexes and sulfonate groups, and form hydrogen bonds with them.

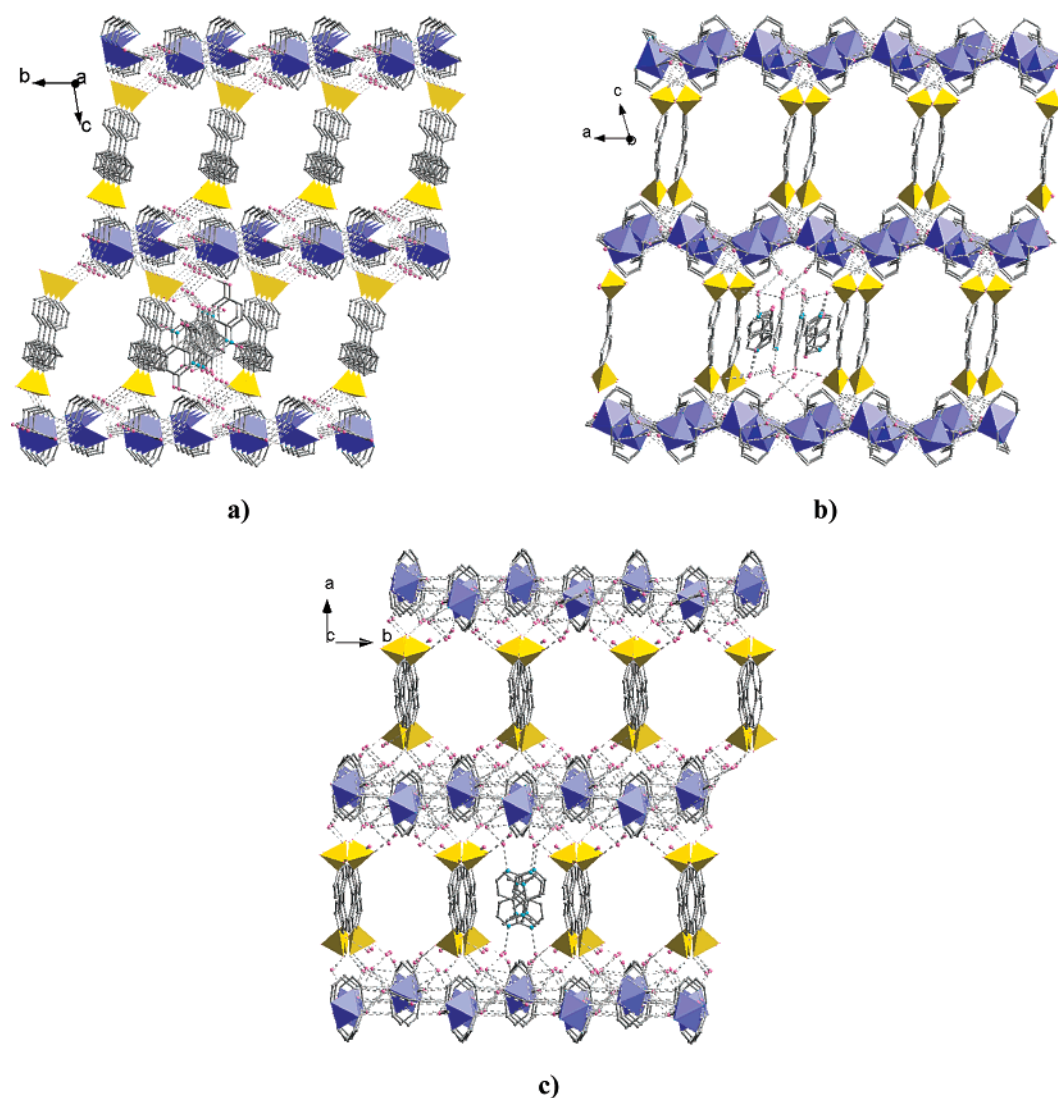
**Structure of 2.** The structure of [Co(en)<sub>2</sub>(ox)]<sub>2</sub>(BPDS)·2(DMF) is dramatically different from **1** although the building blocks and their ratio are the same. Clearly, the presence of DMF influences the assembly of these building blocks by its shape and electronic structure. The framework of **2** exhibits large cavities occupied by DMF guest molecules, almost exactly as envisioned in Figure 1c. The layers in the structure are built of one unique cobalt complex in two different orientations (Figure 3a). The complexes are bonded to each other by numerous hydrogen bonds between the amino and carboxylic groups of their ligands. In addition, the anionic sulfonate groups of the pillars, found on both sides of the layers, hydrogen bond to the amino groups of the complexes and reinforce further the intralayer bonding. The arrangement of the complexes in the layer differs significantly from the very densely packed [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> complexes in the previously reported series of compounds with a general formula [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>(BPDS)<sub>3</sub>·*n*(guest).<sup>10</sup> The sulfonate groups alternate on the sides of the layer (Figure 3a) which means that the pillars also alternate, and this results in a “brick wall” pattern (Figure 3b). This arrangement places the pillars relatively far from each other at a distance of ca. 8.5 Å (perpendicular to the pillars). The pillars are tilted along *c* at about 45° with respect to the layers, and their tilting directions alternate upon going from one layer to another as shown in Figure 3b. Residing in the infinite galleries along *a* are the DMF guest molecules (Figure 3b). They are hydrogen bonded to the amino groups of [Co(en)<sub>2</sub>(ox)]<sup>+</sup>. The calculated void space available for guest molecules is 25.8%, and this is much higher than the maximum of 18% for the series of analogous compounds with [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>.

**Structures of 3, 4, and 5.** These three compounds, [Co(en)<sub>2</sub>(ox)]<sub>2</sub>(BPDS)·3(pnp)·7H<sub>2</sub>O, [Co(en)<sub>2</sub>(ox)]<sub>2</sub>(BPDS)·2(acpy)·7H<sub>2</sub>O, and [Co(en)<sub>2</sub>(ox)]<sub>2</sub>(BPDS)·2(dmapi)·10H<sub>2</sub>O, form when three similar guest molecules, *p*-nitrophenol, 4-acetylpyridine, and 4-dimethylaminopyridine, respectively, are present during the synthesis. The three structures have different unit cells and somewhat different stoichiometries

(25) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2007.



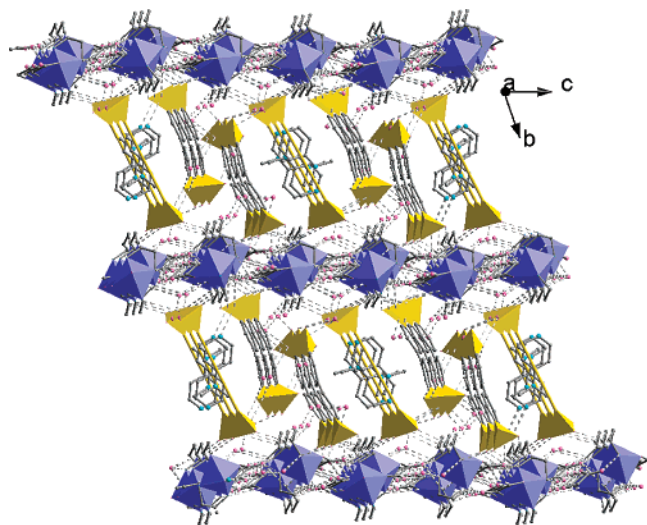
**Figure 3.** (a) Hydrogen-bonded layers of  $[\text{Co}(\text{en})_2(\text{ox})]^+$  (blue octahedra) in **2** with the sulfonate groups of the pillars (yellow tetrahedra) alternating above and below the layers. (b) Pillared-layer "brick wall" type framework of **2** viewed along *a* with DMF molecules shown in only one of the infinite galleries.



**Figure 4.** Pillared-layer frameworks of (a) **3** with *p*-nitrophenol, (b) **4** with 4-acetylpyridine, and (c) **5** with 4-dimethylaminopyridine guests. Shown are the guest molecules in only one gallery for each compound. They are hydrogen bonded (broken lines) to water molecules which, in turn, are hydrogen bonded to the metal complexes and sulfonate groups.

but are overall very similar in construction and volume and are described together (Figure 4). They are also very similar to compound **2** and exhibit all expected features for a di-sulfonate structure with a monocationic metal complex. The

layers of hydrogen-bonded metal complexes are parallel to the *ab* plane in **3** and **4** and to the *bc* plane in **5**. The hydrogen bonding within the layers involves both direct interactions between the complexes as well as indirect interactions via



**Figure 5.** Pillared-layer framework of **6** with protonated 4-dimethylaminopyridine cations in the isolated cavities of the anionic framework. Parts of the organic residues of the BPDS are omitted for clarity.

water and sulfonate groups. The sulfonate groups are positioned in straight lines along *a* in **3** (Figure 4a), while they zigzag along *b* in **4** (Figure 4b) and along *c* in **5** (Figure 4c). The BPDS pillars separate the layers at interlayer distances of 18.0, 16.7, and 18.0 Å for **3**, **4**, and **5**, respectively. Large infinite galleries are formed between the pillars in all of them. These galleries are efficiently occupied by three different pnp guest molecules in **3** and two acpy or dmapy molecules in **4** and **5**. All compounds also contain water molecules which, as in **1**, are found near the hydrophilic parts of the framework, i.e., the metal complexes and sulfonate groups, and form numerous hydrogen bonds with them. They form such bonds also with the polar parts of the guest molecules and serve as bridges between the framework and the guests. Eventual  $\pi$  interactions between the guest molecules as well as guests-to-pillars were expected, but none was found. The calculated space available for guest molecules in these three hosts is 35.3% for **3**, 28.2% for **4**, and 30.8% for **5**, and these numbers are even larger than that for **2**.

**Structure of 6.** Although this compound,  $(\text{H-dmapy})_2[\text{Co}(\text{en})_2(\text{ox})]_4(\text{BPDS})_3 \cdot 16\text{H}_2\text{O}$ , has a framework made of the same metal complex and disulfonate (Figure 5) as compounds **2–5**, it differs significantly from them both structurally and stoichiometrically. The origin for these differences is the basicity of the 4-dimethylaminopyridine which exists as a protonated cation at less basic conditions. This, in turn, results in a negatively charged framework achieved by changing the ratio between the metal complex monocation  $[\text{Co}(\text{en})_2(\text{ox})]^+$  and the disulfonate dianion in favor of the latter. From a charge-balancing perspective, there is an infinite number of possible combinations of cationic metal complex,  $\text{H-dmapy}^+$ , and anionic disulfonate, but the one observed in **6** of four metal complexes, two  $\text{H-dmapy}^+$  cations, and three disulfonates is apparently the most structurally sound at these conditions. Despite these differences, however, the structure of **6** exhibits many features that are typical for the pillared-layer structures of **2–5**. Thus, likewise it has layers made of hydrogen-bonded metal complexes, both directly and via sulfonate groups, and the

layers are similarly covered with the sulfonate groups on both sides. Unlike the other compounds, however, it has three disulfonate groups per four metal complexes, a ratio of 0.75:1, which is one more than in **2–5** with a ratio of 0.5:1. The larger number of pillars per unit of layer results in less available space between the pillars which, in turn, translates into fewer cavities for the cationic molecules. Thus, instead of infinite galleries as in compounds **2–5**, compound **6** has only isolated cavities between the pillars available for the cationic molecules (Figure 5). This results in a very reduced guest-uptake capacity for this framework with only 0.5  $\text{H-dmapy}^+$  molecules per metal complex. This number is 2–3 times lower than the corresponding numbers of 1.0, 1.5, 1.0, and 1.0 guest molecules per metal complex for compounds **2**, **3**, **4**, and **5**, respectively. Despite these shortcomings of compound **6**, its existence shows that not only neutral frameworks made of hydrogen-bonded metal complexes and disulfonates are possible but so are negatively charged constructions of the same building blocks.

The two building blocks in all six compounds, the monocationic metal complex  $[\text{Co}(\text{en})_2(\text{ox})]^+$  and the dianionic 4,4'-biphenyldisulfonate, produce topologically similar but otherwise different structures. The differences are clearly the result of the presence or absence of guest molecules during synthesis. The specifics of the guests, such as the size, shape, electronic structure, charge, polarity, etc., define the exact arrangement of the building blocks in the final construction. The absence of less hydrophilic and less polar than water guest molecules in the reaction mixture results in a well-packed structure as seen in **1**. Water in such compounds naturally avoids the hydrophobic interpillar space near the biphenyl residues and is found typically within or near the layers of hydrogen-bonded metal complexes, often participating in this bonding. Compounds **2–6** are made in the presence of molecules that have hydrophobic parts and prefer the space between the pillars. The role of these molecules during synthesis seems to be primarily the fine tuning of the structures by “guiding” the orientation and connectivity of the pillars in order to fit snugly around the molecules. All this is possible because of the “softness” of the host frameworks which, in turn, is due to the weaker hydrogen bonding when compared to the more rigid frameworks assembled by the much stronger covalent and/or coordination bonds. The soft hosts can easily change the connectivity and overall configuration of the framework in order to adapt to the steric, electronic, hydrogen-bonding, hydrophilicity, and polarity needs of the guest molecules. In a previous publication this capability was demonstrated by the synthesis of six compounds with a general formula  $[\text{Co}(\text{NH}_3)_6]_2(\text{BPDS})_3 \cdot n(\text{guest})$  and with relatively small guests of DMSO, DMF, piperidine, acetone, acetonitrile, and THF.<sup>10</sup> Here this is reinforced further with the analogous series of compounds with a general formula  $[\text{Co}(\text{en})_2(\text{ox})]_2(\text{BPDS}) \cdot n(\text{guest})$  which have larger galleries and can accommodate both the small DMF and the much larger *p*-nitrophenol, 4-acetylpyridine, and 4-dimethylaminopyridine. One interesting side observation is that the cavities in compounds **3**, **4**, and **5** are so large that each contains more than one large guest molecule, 4-nitrophenol, 4-acetylpyridine,

and 4-dimethylaminopyridine, respectively, positioned quite close to each other. This could be potentially exploited further by eventual encapsulation of photoreactive molecules as guests and performing photosynthesis in the solid state.

In conclusion, the presented series of host–guest compounds of hydrogen-bonded metal complex and disulfonate were semi-rationally designed after realizing the effect of the charge of the metal complex on the interpillar space for guest molecules. Since this charge and overall geometry of the complex can be readily varied by the choice of metal and ligands it is clear that it should be possible to tune the resulting frameworks to various desired specifications. The existence of the two series of compounds with two different metal complexes and variety of guest molecules analogous to the rich guanidinium system shows that much richer structural chemistry should be expected for metal complex disulfonate inclusion compounds. The presence of the metal

in these compounds may also bring some additional physical properties such as spin-crossover behavior, redox capabilities, etc. It is clear that many more such soft host frameworks are to be built by careful design, meticulous experimental work, and using the above ideas as guiding principles.

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**Supporting Information Available:** X-ray crystallographic CIF files for the six compounds and additional figures of the structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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