*Inorg. Chem.* **2007**, *46*, 4626–4631

Inorganic Chemistry
Article

# Hydrogen-Bonded Metal-Complex Sulfonate (MCS) Inclusion Compounds: Effect of the Guest Molecule on the Host Framework

**Xin-Yi Wang, Rachelle Justice, and Slavi C. Sevov***

*Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556*

Received February 19, 2007

Soft molecular host frameworks made of the hydrogen-bonded metal complex (MC) $Co(NH_3)_6^{3+}$ and 4,4′-biphenyldisulfonate (BPDS) include different guest molecules to form inclusion compounds of the type $(MC)_2(BPDS)_3 \cdot n$(guest). Structurally characterized were six compounds with guest molecules of DMSO, DMF, piperidine, acetone, acetonitrile, and THF. The metal-complex sulfonate frameworks in all of them are of the pillared layer type where the layers are constructed of extensively hydrogen-bonded metal-complex cations and sulfonate (S) anions (and some hydrogen-bonded water) while the organic residues of the 4,4′-biphenyldisulfonate serve as pillars. The hydrogen-bonded MCS layers and the orientations of the pillars adjust and rearrange in order to generate cavities that would accommodate different guest molecules. The steric, electronic, and hydrogen-bonding needs of the guest molecules mold the soft framework into different structures. These MCS host–guest frameworks are very close structural analogues of the well-studied guanidinium sulfonate (GS) networks and mimic their flexibility and overall durability.

## Introduction

Much research has been carried out on design and synthesis of inclusion compounds because of their potential for use in molecular recognition, separation, catalysis, optoelectronics, and magnetics.[1] The self-assembled soft molecular frameworks are a subgroup of these inclusion compounds.[2−4] They exhibit a number of unique features that are absent in the more rigid frameworks constructed by strong interactions such as covalent and coordination bonds. One such quality is their flexibility to adjust structures in order to encapsulate various guest molecules while preserving the overall topology and connectivity. The design strategy for generating soft frameworks is in the core of supramolecular chemistry and crystal engineering. The idea is to use molecular building blocks that can be organized in a rational manner through predictable intermolecular interactions such as hydrogen bonds and $\pi$-interactions.[5] A subclass of the hydrogen-bonded frameworks is made of compounds with charge-assisted hydrogen bonds between cationic and anionic molecular building blocks.[2,6] The electrostatic interactions in these compounds provide additional strength to the numerous hydrogen bonds and allow for maintaining the basic architecture of the framework upon chemical modifications such as treatment with different guest molecules. Most extensively studied among these are the pillared-layer guanidinium disulfonate (GS) frameworks where the guanidinium (G) cations and disulfonate (S) anions form robust layers via numerous charge-assisted hydrogen bonds between the amine protons of the guanidinium cations and the oxygen atoms of the sulfonate anions.[2,6−8] The organic residues of the disulfonates play the role of the pillars, while the cavities between the pillars are occupied by the guest inclusion. It has been shown by M. Ward et al. that these frameworks are amazingly durable and yet flexible in their ability to adjust to guest molecules with different sizes and shapes.[2,6−8] While the layers in all structures are virtually identical, the

* To whom correspondence should be addressed. E-mail: ssevov@nd.edu.

(1) (a) MacNicol, D. D.; Toda, F.; Bishop, R.; Eds. *Comprehensive Supramolecular Chemistry*, *Vol. 6: Solid-State Supramolecular Chemistry, Crystal Engineering*; Pergamon Press: Oxford, 1996. (b) Nassimbeni, L. R. *Acc. Chem. Res.* **2003**, *36*, 631−637.
(2) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107−108.
(3) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658.
(4) Dalrymple, S. A.; Shimizu, G. K. H. *Supramol. Chem.* **2003**, *15*, 591−606.
(5) (a) Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357−401. (b) Braga, D.; Maini, L.; Polito, M.; Tagliavini, E.; Grepioni, F. *Coord. Chem. Rev.* **2003**, *246*, 53−71. (c) Nishio, M. *CrystEngComm* **2004**, *6*, 130−158; d) Beatty, A. M. *Coord. Chem. Rev.* **2003**, *246*, 131−143.
(6) Ward, M. D. *Chem. Commun*. **2005**, 5838−5842.



10.1021/ic070324p CCC: $37.00 
Published on Web 04/27/2007

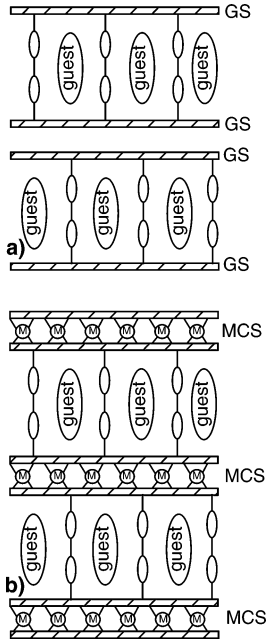


**Figure 1.** (a) Typical bilayer structure observed in the guanidinium disulfonate system with layers made of hydrogen-bonded guanidinium and sulfonate groups (labeled as GS) and pillars of the organic residue of the disulfonate (shown with 4,4′-biphenyl). The GS layers are paired by the pillars, but there is no bonding between the pairs (middle of the figure). The guest molecules occupy the galleries between the pillars. (b) A proposed structure of a metal-complex disulfonate with layers made of hydrogen-bonded metal complex and sulfonate groups (labeled MCS) and the same organic pillars as in (a).

pillars are "exchangeable", i.e., many different organic disulfonates can be used for this purpose and can be placed either at one or both sides of the layer. The available large number of inclusion compounds based on GS host frameworks has made possible further exploration of their potential for various applications as well as better understanding of the factors that control formation of such self-assembled frameworks.

While changing the disulfonate pillars and the guest molecules have been the main approaches for diversification of the GS frameworks, not much effort has been devoted to changing the layers themselves although some other building blocks for charge-assisted hydrogen bonds have been investigated.[6,9] One of the typical structures in the GS system is the bilayer structure (Figure 1a) where the pillars are positioned at only one side of a layer. Thus, while such a layer is well bonded by pillars to one neighboring layer, it is virtually nonbonded to its other neighbor. One idea, pioneered mainly by Shimizu and co-workers,[10,11] is to use layers that can coordinate to transition metals as shown in Figure 1b. Thus, the guanidinium cation with its three amino groups can be "substituted" by various transition-metal coordinated ligands with protons available for hydrogen bonding such as ammonia,[10−13] amines,[14−17] or water molecules.[14,18,19] The second coordination sphere of an octahedral hexaaqua or hexaammine metal complex, for example, can mimic two staggered guanidinium cations from neighboring layers when the complex is positioned with its $C_3$ axis perpendicular to the layers (Figure 2a, b). This arrangement, however, has been observed only in two compounds so far.[10,12] The preferred orientation of the metal complex seems to be rather with its $C_4$ axis normal to the layers and with hydrogen-bonded sulfonate groups that formally cap the faces (Figure 2c). Despite the different orientation, however, the octahedral metal complexes (MC) and the sulfonate groups (S) can form MCS layers that are then pillared by the organic residues of the disulfonate and can include guest molecules. One additional advantage of such frameworks is the presence of transition-metal centers which may bring some redox capabilities to the compounds, as well as possible magnetic and electronic properties that may designate the materials as multifunctional.

Despite all these attractive aspects, there are only a few known pillared layer MCS frameworks,[10−11,16] and none of them mimics the capability of the GS systems to host different guest molecules. Here we report the first such pillared framework with general formula $(MC)_2(BPDS)_3 \cdot n(\text{guest}) \cdot m(H_2O)$ constructed of cobalt hexaammine cations $Co(NH_3)_6^{3+}$ (MC) and 4,4′-biphenyldisulfonate anions (BPDS $= C_{12}H_8O_6S_2$) and with cavities that can be occupied by six different guests: DMSO (**1**, $n = 2$, $m = 5$), DMF (**2**, $n = 1$, $m = 2$), piperidine (**3**, $n = 1$, $m = 2$), acetone (**4**, $n = 2$, $m = 4$), acetonitrile (**5**, $n = 2$, $m = 4$), and THF (**6**, $n = 2$, $m = 4$). The framework adjusts to different guest molecules in order to accommodate their steric and hydrogen-bonding demands.

(7) (a) Holman, K. T.; Ward, M. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1653−1656. (b) Custelcean, R.; Ward, M. D. *Cryst. Growth Des.* **2005**, *5*, 2277−2287. (c) Russell, V. A.; Etter, M. C.; Ward, M. D. *Chem. Mater.* **1994**, *6*, 1206−1217. (d) Swift, J. A.; Reynolds, A. M.; Ward, M. D. *Chem. Mater*. **1998**, *10*, 4159−4186. (e) Pivovar, A. M.; Holman, K. T. Ward, M. D. *Chem. Mater.* **2001**, *13*, 3018−3031. (f) Pivovar, A. M.; Ward, M. D.; Brown, C. M.; Neumann, D. A. *J. Phys. Chem. B* **2002**, *106*, 4916−4924. (g) Holman, K. T.; Martin, S. M.; Parker, D. P.; Ward, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 4421−4431. (h) Holman, K. T.; Pivovar, A. M.; Ward, M. D. *Science* **2001**, *294*, 1907−1911. (i) Russell, V. A.; Evans, C. C.; Li, W. J.; Ward, M. D. *Science* **1997**, *276*, 575−579.
(8) Mathevet, F.; Masson, P.; Nicoud, J. -F.; Skoulios, A. *Chem. Eur. J.* **2002**, *8*, 2248−2254.
(9) (a) Melendez, R. E.; Sharma, C. V. K.; Zaworotko, M. J.; Bauer, C.; Rogers, R. D. *Angew. Chem., Int. Ed.* **1996**, *35*, 2213−2215. (b) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, K. C. V.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894−11903.
(10) Reddy, D. S.; Duncan, S.; Shimizu, G. K. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1360−1363.
(11) Dalrymple, S. A.; Shimizu, G. K. H. *Chem. Commun*. **2006**, 956−958.
(12) Sharma, R. P.; Bala, R.; Sharma, R.; Venugopalan, P. *J. Mol. Struct.* **2004**, *694*, 229−234.
(13) Sharma, R. P.; Bala, R.; Sharma, R.; Bond, A. D. *Acta Crystallogr.* **2006**, *E62*, m2113−m2115.
(14) Dalrymple, S. A.; Shimizu, G. K. H. *J. Mol. Struct*. **2006**, *796*, 95−106.
(15) (a) Cai, J. W.; Hu, X. P.; Yao, J. H.; Ji, L. N. *Inorg. Chem. Commun.* **2001**, *4*, 478−482. (b) Cai, J. W.; Feng, X. L.; Hu, X. P. *Acta Crystallogr.* **2001**, *C57*, 1168−1170. (c) Chen, C. H.; Cai, J. W.; Chen. X. M. *Acta Crystallogr.* **2002**, *C58*, m59−m60.
(16) Chen, C. H.; Cai, J. W.; Feng, X. L.; Chen. X. M. *J. Chem. Cryst.* **2002**, *31* (5), 271−280.
(17) Huo, L. H.; Gao, S.; Lu, Z. Z.; Xu, S. X.; Zhao, H. *Acta Crystallogr.* **2004**, *E60*, m1205−m1207.
(18) (a) Dalrymple, S. A.; Parvez, M.; Shimizu, G. K. H. *Chem. Commun*. **2001**, 2672−2673. (b) Dalrymple, S. A.; Parvez, M.; Shimizu, G. K. H. *Inorg. Chem.* **2002**, *41*, 6986−6996. (c) Côté, A. P.; Shimizu, G. K. H. *Chem. Eur. J.* **2003**, *9*, 5361−5370.
(19) Zhou, J. S.; Cai, J. W.; Ng, S. W. *Acta Crystallogr.* **2003**, *E59*, o1185−o1186.

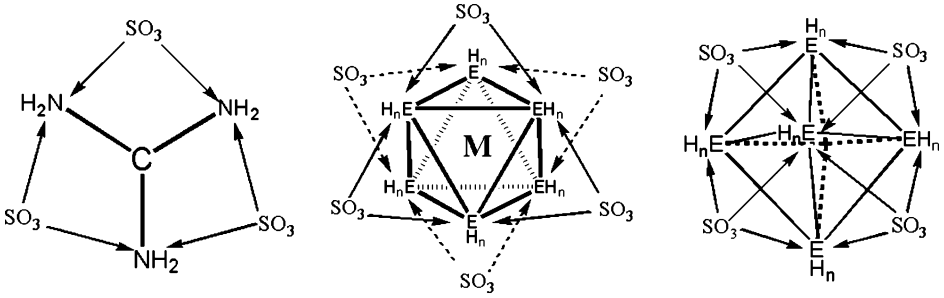


**Figure 2.** Shown are the building blocks for layers made of hydrogen-bonded (arrows) sulfonate groups and (a) guanidinium cations $C(NH_2)_3^+$, (b) octahedra of $M(EH_n)_6^{m+}$ (E = N, O) with a 3-fold axis perpendicular to the layer, and (c) the same octahedron as in (b) but with a 4-fold axis perpendicular to the layer (four more $SO_3$ groups that should be on the back side of the octahedron are not shown).

**Table 1.** Crystallographic Data for Compounds **1**−**6**

| compound | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| formula | $C_{40}H_{82}N_{12}O_{25}S_8Co_2$ | $C_{39}H_{71}N_{13}O_{21}S_6Co_2$ | $C_{41}H_{75}N_{13}O_{20}S_6Co_2$ | $C_{42}H_{80}N_{12}O_{24}S_6Co_2$ | $C_{40}H_{74}N_{14}O_{22}S_6Co_2$ | $C_{44}H_{84}N_{12}O_{24}S_6Co_2$ |
| $M_r$ [g·mol$^{-1}$] | 1505.52 | 1368.29 | 1380.36 | 1447.40 | 1413.36 | 1475.44 |
| crystal system | monoclinic | monoclinic | monoclinic | triclinic | triclinic | triclinic |
| space group | *Pn* | *C*2/*c* | *C*2 | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| *a* (Å) | 18.4773(6) | 30.0959(8) | 30.2942(11) | 7.81110(10) | 7.7896(3) | 7.8222(4) |
| *b* (Å) | 7.9410(3) | 15.3393(5) | 15.0722(6) | 13.1879(2) | 13.1339(5) | 13.1884(6) |
| *c* (Å) | 22.4534(7) | 12.8545(4) | 13.1166(5) | 15.6203(3) | 15.6698(5) | 15.5464(7) |
| α (deg) | | | | 101.1350(10) | 100.318(2) | 101.091(2) |
| *β* (deg) | 98.494(2) | 101.280(2) | 97.896(2) | 93.1870(10) | 93.647(2) | 93.105(2) |
| *γ* (deg) | | | | 96.4740(10) | 96.525(2) | 96.714(2) |
| *V* (Å$^3$) | 3258.41(19) | 5819.6(3) | 5932.3(4) | 1563.77(4) | 1561.21(10) | 1558.21(13) |
| *Z* | 2 | 4 | 4 | 1 | 1 | 1 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.534 | 1.550 | 1.546 | 1.537 | 1.503 | 1.577 |
| $\mu$(Mo, Kα) (mm$^{-1}$) | 0.849 | 0.868 | 0.852 | 0.816 | 0.814 | 0.821 |
| R1/wR2[a] ($I > 2\sigma(I)$) | 0.0460/0.1365 | 0.0522/0.1430 | 0.0420/0.1133 | 0.0371/0.01008 | 0.0715/0.1862 | 0.0639/0.1581 |
| R1/wR2[a] (all data) | 0.0480/0.1415 | 0.0686/0.1524 | 0.0499/0.1205 | 0.0440/0.1044 | 0.0851/0.1902 | 0.0835/0.1636 |

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

## Experimental Section

The starting materials of hexaamminecobalt(III) chloride (99%, Aldrich), 4,4′-biphenyldisulfonic acid ($H_2$BPDS, 98%, TCI America, IR: 1189 cm$^{-1}$ for $\nu_{S-O}$), and the solvents (reagent grade) 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 4000−500 cm$^{-1}$ region. When kept in air, all six new compounds readily lose their transparence and crystallinity by losing the guest molecules.

**Synthesis of $[Co(NH_3)_6]_2(C_{12}H_8O_6S_2)_3\cdot 2(DMSO)\cdot 5(H_2O)$ (1).** A solution of $Co(NH_3)_6Cl_3$ (0.1 mmol) in 6 mL of $H_2O$ was mixed with 6 mL of a DMSO solution of $H_2$BPDS (0.15 mmol). The resulting clear solution was filtered immediately and left undisturbed at room temperature. Orange-colored blocklike crystals of **1** were obtained in 2 days. IR(cm$^{-1}$): 1433w for $\nu_{C-S}$ in DMSO, 1186s and 1208s for $\nu_{S-O}$.

**Synthesis of $[Co(NH_3)_6]_2(C_{12}H_8O_6S_2)_3\cdot(DMF)\cdot 2(H_2O)$ (2).** A solution of $Co(NH_3)_6Cl_3$ (0.1 mmol) in 15 mL of $H_2O$ was mixed with 8 mL of a DMF solution of $H_2$BPDS (0.15 mmol). Orange-colored precipitate appeared immediately. Upon heating and vigorous stirring, most of the precipitate dissolved. The solution was hot-filtered and left undisturbed at room temperature. Orange-colored blocklike crystals of **2** were obtained in 1 day. IR(cm$^{-1}$): 1662m for $\nu_{C=O}$ in DMF, 1195s and 1200s for $\nu_{S-O}$.

**Synthesis of $[Co(NH_3)_6]_2(C_{12}H_8O_6S_2)_3\cdot(piperidine)\cdot 2(H_2O)$ (3).** A solution of $Co(NH_3)_6Cl_3$ (0.1 mmol) in 5 mL of $H_2O$ was added to a 6 mL of a piperidine/$H_2O$ solution (piperidine/water = 5:1) of $H_2$BPDS (0.15 mmol). (Piperidine alone does not dissolve $H_2$BPDS.) The solution was filtered and left undisturbed at room temperature. Orange-colored blocklike crystals of **3** were obtained in 2 days. IR(cm$^{-1}$): 1439w for $\nu_{-CH_2-}$ (scissor vibration) and 2928w for $\nu_{-CH_2-}$ (asym vibration) in piperidine, 1199s for $\nu_{S-O}$.

**Synthesis of $[Co(NH_3)_6]_2(C_{12}H_8O_6S_2)_3\cdot 2(guest)\cdot 4(H_2O)$ with Guest = Acetone (4), Acetonitrile (5), THF (6).** The three compounds were synthesized by the diffusion method following similar procedures. A water solution (2 mL) of $Co(NH_3)_6Cl_3$ (0.1 mmol) was carefully layered with distilled water (4 mL) in a test tube. The guest compound (2 mL) was mixed with 0.5 mL of $H_2O$ in a separate container, and $H_2$BPDS (0.15 mmol) was added to this mixture. The resulting solution was carefully layered on top of the water in the first test tube. The test tube was then left undisturbed at room temperature, and orange-colored crystals were obtained in 2−3 days. IR(cm$^{-1}$): 1712w for $\nu_{C=O}$ in acetone, 1178s and 1216s for $\nu_{S-O}$ in **4**; 2254w for $\nu_{C-N}$ in acetonitrile, 1188s and 1209s for $\nu_{S-O}$ in **5**; 1437w for $\nu_{-CH_2-}$ (scissor vibration) in THF, 1180s and 1208s for $\nu_{S-O}$ in **6**.

**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 (Mo Kα radiation, $\lambda = 0.71073$ Å). The crystals were taken from the mother liquid and were immediately covered with Paratone-N oil in order to prevent any loss of guest molecules. The structures were solved by direct methods and refined by full-matrix least-squares based on $F^2$ using the SHELXL97 program.[20] All hydrogen atoms of the framework were refined as riding on the corresponding non-hydrogen atoms, while they were

(20) *SHELXTL*, version 5.1; Bruker Analytical Systems: Madison, WI, 1997.

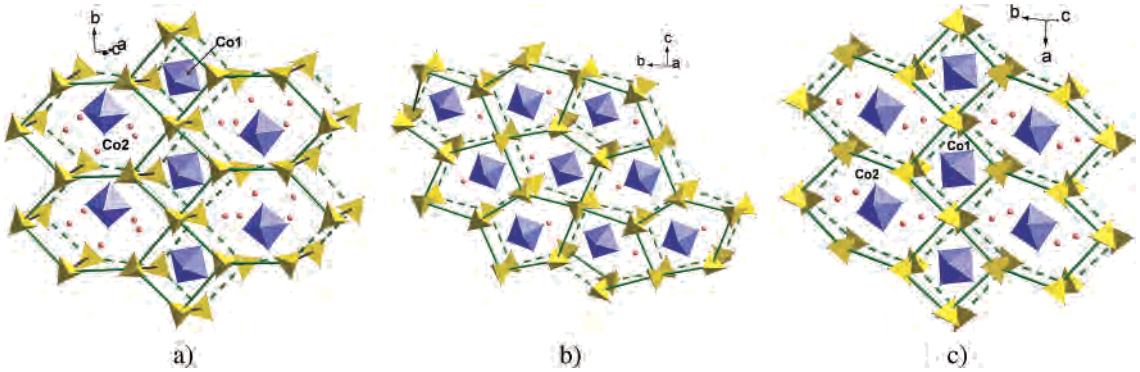


**Figure 3.** Hydrogen-bonded layers of $Co(NH_3)_6^{3+}$ (blue octahedra) and sulfonate groups (yellow tetrahedra) in (a) structure **I** represented by compound **1**, (b) structure **II** represented by compounds **2** and **3**, and (c) structure **III** represented by compounds **4**−**6**. The lines between the sulfonate groups are added to highlight the environments around the cobalt complexes.

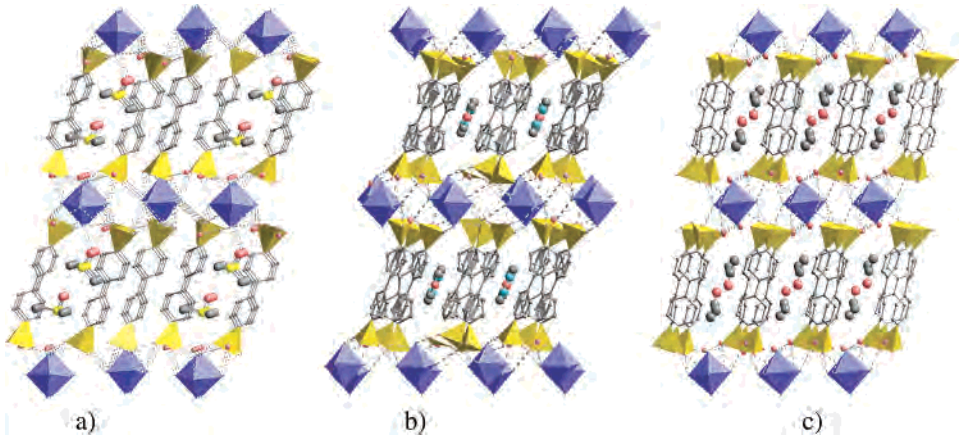


**Figure 4.** Pillared-layer frameworks of (a) structure **I** with DMSO guest molecules, (b) structure **II** shown with DMF in the cavities, and (c) structure **III** shown with acetone in the cavities.

omitted for all disordered guest molecules and lattice water. More details for the data collections and structure refinements are given in Table 1.

## Results

All six new compounds are pillared-layer frameworks assembled by a multitude of charge-assisted hydrogen bonds between the metal complexes $Co(NH_3)_6^{3+}$ and the disulfonate groups $[O_3S-C_6H_4-C_6H_4-SO_3]^{2-}$. The layers are made of the metal complex cations, all with their $C_4$ axis normal to the layers, interconnected by hydrogen bonds to the $[-SO_3]$ groups of the disulfonates positioned at both sides of the layer. The 4,4′-biphenyl residues are the pillars between the layers and create galleries that are occupied by the guest molecules. The latter affect the shape and size of the galleries and define the overall structure. Thus, the six compounds crystallize in three structure types: type I represented by compound **1**, type II includes compounds **2** and **3**, and type III is represented by compounds **4**, **5**, and **6**.

**Structure Type I.** This structure (monoclinic, *Pn*) forms when the guest molecules are DMSO. It has layers parallel to the (101) plane that contain the octahedral $Co(NH_3)_6^{3+}$ cations ordered in a pseudo-close-packed array (Figure 3a). The metal complexes are bonded by charge-assisted hydrogen bonds to the anionic sulfonate groups that cover the layers on both sides ($NH_3\cdots SO_3\cdots NH_3$), as well as to water molecules dispersed within the layers ($NH_3\cdots H_2O\cdots SO_3\cdots NH_3$). The octahedral cations, centered by Co1 and by Co2, are all positioned with their $C_4$ axes approximately normal to the layers (Figure 3a). All eight triangular faces of the Co1 octahedron are capped by $SO_3$ groups (bonded by 32 hydrogen bonds) that form a distorted cube around the octahedron. The Co2 octahedron, on the other hand, has only four faces capped by $SO_3$ groups (12 hydrogen bonds) while the rest of the coordination sphere is occupied by five water molecules (11 hydrogen bonds). The latter provide protons for a number of O−H···O hydrogen bonds to eight more sulfonate groups. This essentially places the Co2 octahedron inside a hexagonal prism of $SO_3$ groups (Figure 3a).

The layers of $Co(NH_3)_6^{3+}$ octahedra and sulfonate groups are pillared and interconnected by the 4,4′-biphenyl residues of the disulfonates (Figure 4a; interlayer distance of 15.3 Å; dihedral angles between the phenyl rings in the range 29.9−32.4°). Although there are many aryl rings in the interlayer space, there are no obvious $\pi$-interactions between them. This suggests that the assembly is dominated by the hydrogen bonds within the layers. All pillars are parallel to each other and also parallel to the $[10\bar{1}]$ direction, which makes them tilted by about 23° from the normal to the layers. The shapes and the sizes of the galleries between the pillars are defined by the positions of the sulfonate groups that enclose the metal-complex layers (Figure 3a). This results in square- and hexagonal-prismatic voids with bases capped by Co1- and

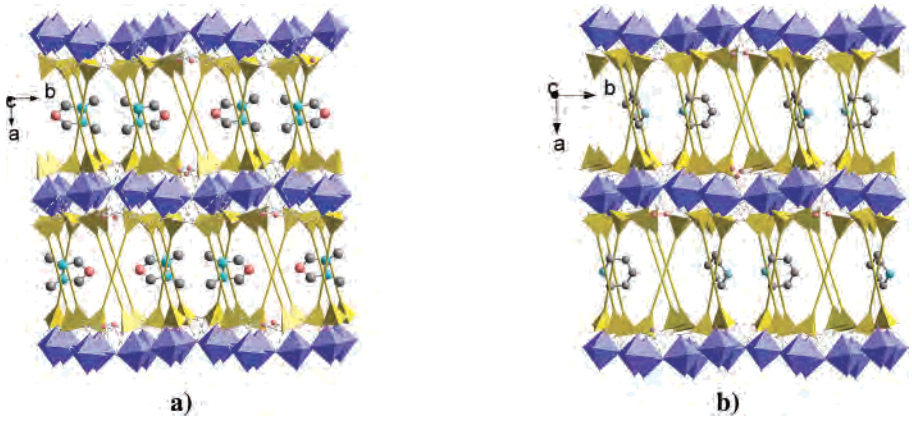


**Figure 5.** Identical frameworks of compounds **2** (a) and **3** (b) with criss-crossing pillars of 4,4′-biphenyl (shown as lines for clarity) are stuffed differently with guest molecules. The DMF molecules in **2** (a) are disordered among two positions related by the 2-fold axis, but the planes of all molecules are parallel to the *ab* plane. The piperidine molecules in **3**, on the other hand, have two different orientations, half of them are parallel to *ab* while the other half are parallel to *ac*.

Co2-centered octahedra, respectively. The square prisms are too small for guest molecules and stay empty. The hexagonal prisms, on the other hand, are large enough to accommodate two DMSO molecules each. One of the guest molecules forms a hydrogen bond via its oxygen atom to the ammonia vertex of one of the two Co2 octahedra positioned above and below the hexagonal bases of the prism. The second molecule does not seem to interact with the framework by anything stronger than van der Waals forces. Viewed along *b*, the hexagonal prisms form infinite galleries, as shown in Figure 4a. The calculated packing coefficient of the framework is 0.61, while the void space available for guest molecules is 16.5%.

**Structure Type II.** Compounds **2** and **3** with DMF and piperidine as guest molecules, respectively, belong to this structure type (Figures 3b and 4b). However, although the frameworks in the two compounds are topologically identical, the overall structures were refined in two different space groups: centrosymmetric *C*2/*c* for **2** and acentric *C*2 for **3**. All attempts to refine **3** in *C*2/*c* were unsuccessful. The *R*-factors stayed high and, more importantly, 693 reflections with $I \geq 3\sigma_I$ violated an eventual *c* glide (average $I/\sigma_I = 5.7$).

The framework of the structure is again made of hydrogen-bonded layers of $Co(NH_3)_6^{3+}$ (only one type cobalt atoms in **2** but two types in **3** because of the absence of an inversion center) and sulfonate groups (Figure 3b). The layers in this structure type are parallel to the *bc* plane with interlayer distances of 14.8 and 15.0 Å in **2** and **3**, respectively. The octahedra are again with their $C_4$ axes normal to the layers. Each octahedron (and a nearby water molecule) is surrounded by 10 sulfonate groups ordered in roughly a pentagonal prism. Eight of the sulfonate groups cap the faces of the octahedron while the remaining two groups are hydrogen bonded to a water molecule which, in turn, is hydrogen bonded to the octahedron.

The 4,4′-biphenyl pillars in this structure type are aligned along two different directions, as shown in Figures 4b and 5. This may suggest flexibility in the positioning of the pillars in order to accommodate particular guest molecules. Despite of the two different orientations of the pillars, this structure also exhibits infinite galleries along *b*. However, because of the two different orientations of the pillars, each cavity can host only one guest molecule and not two as in **1**. This is also reflected in the calculated void space of 9.5% available for guest molecules which is approximately half of that for **1**.

The reasons for the different space groups for **2** and **3** are the different guest molecules and their different positioning within the galleries of the framework. Thus, while the planes of all DMF molecules in **2** are parallel to the *ab* plane (Figure 5a), half of the piperidine rings in **3** are parallel to the *ab* plane and the other half are parallel to the *ac* plane (Figure 5b). It should be noted that the lattice parameters and particularly the $\beta$ angles of the two compounds are somewhat different (Table 1), and this is yet another sign of the flexibility of the framework.

**Structure Type III.** This structure is represented by compounds **4**, **5**, and **6** with guest molecules of acetone, acetonitile, and THF, respectively. The structure is very similiar to compound **1** despite the different space groups and lattice parameters. The layers are made of two crystallographically different $Co(NH_3)_6^{3+}$ octahedra of which one is surrounded by a square prism of sulfonate groups capping all eight faces of the octahedron while the second one has a few hydrogen-bonded water molecules nearby and is positiond within a hexagonal prism of 12 sulfonate groups (Figure 3c). The layers are parallel to the *ab* planes in this case (interlayer distance of 15.3 Å) and all octahedra are with their 4-fold axes perpendicular to the layers.

The 4,4′-biphenyl pillars are parallel to each other and point along the direction of the *c* axis. Therefore, as in **1**, the pillars define smaller square prismatic and larger hexagonal prismatic cavities between the layers. The large cavities form infinite galleries along $[1\bar{1}0]$, as shown in Figure 4c. These cavities are apparently large enough and of the right shape in order to accommodate two acetone, two acetonitrile, or two THF guest molecules each. Unlike **1**, however, none of the guest molecules is hydrogen-bonded to the metal complex. The packing coefficient of the framework is 0.62, and the void space is 15.7%.

## Discussion

Using common cobalt hexaammine complex, 4,4′-biphenyldisulfonic acid, and guest molecules, we have synthesized a series of MCS soft host frameworks with cavities occupied by six different guests. All six compounds exhibit three-dimensional structures made of hydrophilic layers of hydrogen-bonded metal complex and sulfonate groups, and the layers are pillared and interconnected in the third dimension by the hydrophobic 4,4′-biphenyl organic residues. This soft host is capable of changing connectivity and overall configuration in order to adjust to the steric and hydrogen-bonding needs of the guest molecules. These capabilities are demonstrated by the existence of three different structure types for the six compounds with chemically identical framework.

The hydrogen-bonded layers in the three structure types are very similar, aside of some minor differences. They are all made of similarly oriented octahedral complexes aligned with their $C_4$ axes perpendicular to the layers. This orientation is not accidental but is rather defined by the nature of the metal complex and the pillars, as well as the ratio between them, i.e., the average number of pillars per metal complex. The ratio is directly defined by the charge of the metal complex, and for $Co(NH_3)_6^{3+}$, this number is 1.5 dianionic disulfonate pillars per complex. Compared to the guanidinium disulfonate frameworks, for which the ratio is 0.5 pillars per monocation of guanidinium, this number is quite high. This high number of pillars per metal complex most likely forces the specific orientation of the metal complexes so that more ligands are exposed and available for hydrogen bonding with pillars. This, in turn, leads to more packed pillars, smaller galleries, and limitted guest sizes. It is very likely that in order to achieve layers of octahedra alligned with their $C_3$ axes perpendicular to the layers, the metal complex needs to be of lower charge. This is corroborated by the fact that the only example of a pillared-layer structure with such orientation is found in $[Co(NH_3)_6Cl](PIPES)(H_2O)_6$ where PIPES =1,4-piperazinebis(ethanesulfonate).[10] The effective charge of the metal complex in this case is reduced to 2+ by the chloride anion which is positioned within the layers and is not involved in the framework bonding. The number of pillars per metal complex of $[Co(NH_3)_6Cl]^{2+}$ in this compound is 1, and this may be the reason for the specific orientation.

All three structure types described here can be viewed as made of alternating hydrophilic and hydrophobic slabs. The cavities are in the hydrophobic regions and are expected to accommodate guest molecules that are not extremely hydrophilic. Water molecules and ionic species, on the other hand, would understandably reside within or very close to the hydrophilic layers, as is the case of the present six compounds. As observed here, the presence of the water molecules in the layers and their number can influence the overall structure of the layers which, in turn, affects the positioning of the pillars and the size and shapes of the galleries between the layers. This provides even more flexibility to the host, i.e., the host can adjust to different guest molecules by incorporating different numbers of water molecules inside the hydrophilic layers and develop appropriate cavities.

Finally, the metal-complex sulfonate host in the six compounds behaves very similarly to the well-studied guanidinium sulfonates.[2,6,7] Both systems show extraordinary flexibility in assembling in different ways in order to fit their guest molecules. This close similarity may allow for further development of design strategies for new MCS compounds based on analogy with the numerous available GS compounds. Considering the great success with the GS system, there are many reasons to expect similar performance from the MCS systems. Furthermore, the MCS systems have an additional advantage of one more variable, the transition-metal complex. There are a number of parameters that can be varied for the complex such as the metal itself, the ligands, the charge, and its overal geometry. The presence of the metal in these compounds may also bring some additional physical properties and result in multifunctionality. For example, eventual replacement of $Co(NH_3)_6^{3+}$ with $Cr(NH_3)_6^{3+}$ will add some magnetic properties.

In conclusion, the six new hydrogen-bonded pillared-layer architectures with different guest molecules demonstrate the feasibility of the idea to utilize the MCS system for generating functional porous frameworks. It is very likely that careful design and meticulous experimental work would lead to a wide array of flexible host frameworks with a number of functionalities that can be tailored to the need of specific applications.

**Acknowledgment.** We thank the National Science Foundation for the financial support of this research (DMR-0600320) and for the purchase of a Bruker APEX II diffractometer (CHE-0443233).

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

IC070324P