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Hydrogen-Bonded Inclusion Compounds with Reversed Polarity: Anionic Metal-Complexes and Cationic Organic Linkers

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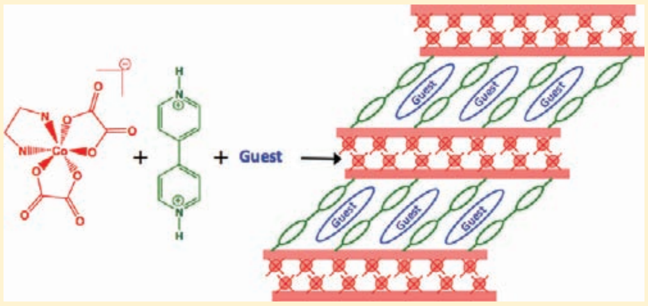
Supporting Information



ABSTRACT: Synthesized and structurally characterized is a new series of soft-host frameworks assembled by charge-assisted hydrogen bonds between an anionic metal complex (MC) and cationic organic linkers (OL), specifically $[Co(en)(ox)_2]^-$ and diprotonated 4,4′-bipyridinium (H_2bpy) or 1,2-bis(4-pyridinium)ethylene (H_2bpye). While frameworks built of cationic complexes and anionic organic linkers are already well-known, the seven new compounds described here represent the first series of frameworks with reversed polarity, that is, made of anionic complexes and cationic organic linkers. The compounds have a general formula $[OL][MC]_2 \cdot n(guest)$, where the guest molecules 4,4′-biphenol (*bp*), 4-methoxyphenol (*mp*), 1,4-dimethoxybenzene (*dmb*), 1,6-dimethoxynaphtalene (*dmn*), and 4-nitroanisole (*na*). Structurally the compounds can be described as pillared-layer frameworks with layers constructed of MC anions and linked together by hydrogen-bonded cationic OL pillars. The guest molecules occupy the galleries between the pillars while their steric, electronic, and $\pi-\pi$ and hydrogen-bonding capabilities influence the overall structure of the soft frameworks.

INTRODUCTION

Inclusion compounds, also known as host–guest compounds, are compounds where a framework host accommodates a variety of guest molecules by only adjusting its overall geometry and conformation. Such compounds are of particular interest for the diversity in hosting guests, and therefore, their potential for application in catalysis, separation, molecular recognition, etc.[1] Of special interest among them are the soft frameworks made of building units held together by weak but multiple intermolecular interactions, such as regular or charge-assisted hydrogen bonds.[2−9] Compared to the rigid frameworks with covalent and coordination bonds,[10] the weak interactions in the soft frameworks give them more flexibility and, thus, capability to host a greater variety of guest molecules by undertaking very small and virtually energy-free adjustments. Overall, the connectivity and the topology of the soft frameworks remain unchanged upon the encapsulation of different guests.[3]

Soft frameworks with charge-assisted hydrogen bonds between the building units have additional strength because of the additional electrostatic interactions.[3,6,7] Ward and coworkers have demonstrated this in numerous soft frameworks made of guanidinium cations and organic disulfonate anions.[3,8] The resulting pillared-layer type structures of guanidinium layers and disulfonate pillars are very stable frameworks with many different guest molecules. Typically, the latter interact with the framework via very weak forces such as van der Waals and $\pi-\pi$ interactions.

The guanidinium cations were later replaced with cationic transition-metal complexes in an attempt to further diversify the soft frameworks and add some of the benefits that come with transition metals. Effectively, an octahedral complex with six proton-donating ligands such as ammonia, amines, water, etc., can be viewed as replacing two parallel and staggered guanidinium cations to form “double layers” pillared again by hydrogen-bonded disulfonates.[11−16] It has been shown that these frameworks are also very flexible and can incorporate diverse guest molecules.[12,16] In addition, such frameworks have potential for various magnetic and redox properties because of the transition metal.

All these soft host–guest frameworks with charge-assisted hydrogen bonds, however, involve cationic layers linked with anionic pillars. To our knowledge pillared-layer frameworks made of anionic layers and cationic pillars and capable of encapsulating guest molecules have not been reported before. Here we present the synthesis and structures of the first such frameworks with reversed polarity made of the anionic metal complex $[Co(en)(ox)_2]^-$ and the cationic bis-protonated 4,4′-bipyridinium or 1,2-bis(4-pyridinium)ethylene pillars (Chart 1). The new compounds incorporate 4,4′-biphenol (bp), 4-methoxyphenol (mp), 1,4-dimethoxybenzene (dmb), 1,6-dimethoxynaphthalene (dmn), and 4-nitroanisole (na) as guest molecules (Chart 1).

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Chart 1. Pillars and Guest Molecules

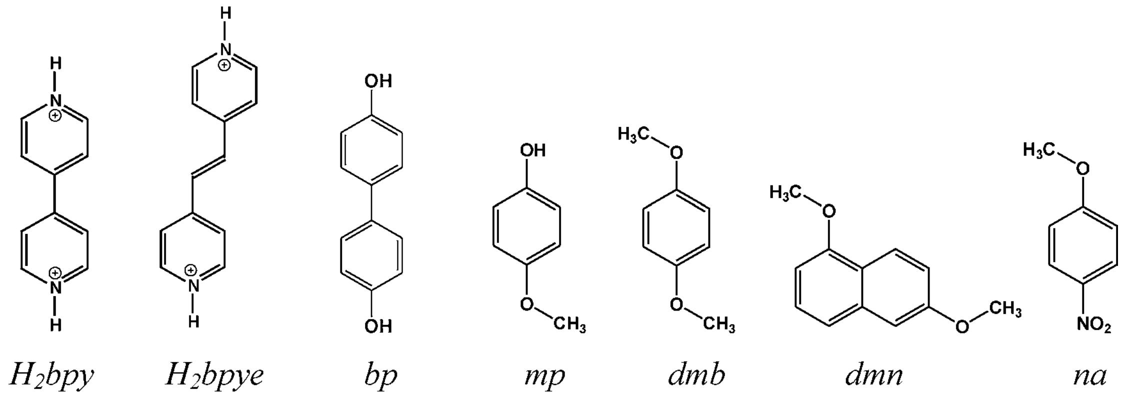


Table 1. Selected Data Collection and Refinement Parameters for Compounds 1−7

	(1) Co(en)(ox)$_2$-BPY	(2) Co(en)(ox)$_2$-BPY-BP	(3) Co(en)(ox)$_2$-BPY-MP	(4) Co(en)(ox)$_2$-BPY-DMB
formula	$C_{22}H_{28}N_6O_{17}Co_2$	$C_{34}H_{46}N_6O_{23}Co_2$	$C_{18}H_{23}N_3O_{11}Co$	$C_{17.5}H_{13}N_3O_9Co$
mw [g·mol^{-1}]	766.36	1024.63	516.32	468.24
space group, *Z*	*P*2$_1$/*c*, 4	*P*2$_1$/*c*, 4	$P\bar{1}$, 2	$P\bar{1}$, 2
a (Å)	18.804(2)	24.49(3)	6.9527(5)	7.6147(7)
b (Å)	10.1968(12)	7.1666(9)	11.1455(8)	9.5563(9)
c (Å)	14.8753(17)	23.967(3)	13.9779(9)	14.0275(13)
α (deg)	90	90	94.164(1)	83.879(20
β (deg)	92.448(3)	109.581(3)	103.116(1)	82.156(2)
γ (deg)	90	90	96.828(1)	74.29(2)
V (Å^3)	2849.6(6)	3963.2(9)	1041.86(13)	970.83(16)
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
ρ_{calcd} (g·cm^{-3})	1.786	1.717	1.646	1.602
μ (mm^{-1})	1.258	0.939	0.892	0.942
R1/wR2,^{a} $I \geq 2\sigma I$	0.0315, 0.0789	0.0426, 0.0938	0.0236, 0.0591	0.0606, 0.1647
R1/wR2,^{a} all data	0.0417, 0.0851	0.0876, 0.1110	0.0257, 0.0605	0.0800, 0.1802

	(5) Co(en)(ox)$_2$-BPY-DMN	(6) Co(en)(ox)$_2$-BPYE	(7) Co(en)(ox)$_2$-BPYE-NA
formula	$C_{17}H_{12}CoN_3O_{10}$	$C_{12}H_{14}N_3O_{11}Co$	$C_{19}H_{21}N_4O_{14}Co$
mw [g·mol^{-1}]	477.23	435.19	588.33
space group, *Z*	$P\bar{1}$, 2	$P\bar{1}$, 2	$P\bar{1}$, 2
a (Å)	7.6517(17)	6.7369(6)	6.9094(6)
b (Å)	9.726(2)	11.7201(1)	13.4452(12)
c (Å)	13.855(3)	12.3229(11)	13.4974(13)
α (deg)	84.740(4)	63.138(1)	96.748(2)
β (deg)	83.334(4)	77.106(2)	92.489(2)
γ (deg)	73.420(4)	80.187(2)	101.009(2)
V (Å^3)	979.7(4)	843.39(13)	1219.49(19)
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
ρ_{calcd} (g·cm^{-3})	1.618	1.714	1.602
μ (mm^{-1})	0.938	1.084	0.783
R1/wR2,^{a} $I \geq 2\sigma I$	0.0677, 0.1870	0.0392, 0.0982	0.0452, 0.1088
R1/wR2,^{a} all data	0.0773, 0.1963	0.0414, 0.0996	0.0708, 0.1195

^{a}R1 = $[\Sigma||F_o| - |F_o||]/\Sigma|F_o|$; wR2 $=\{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o{}^2)^2)]\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$. Mo K$\alpha$, 0.71073

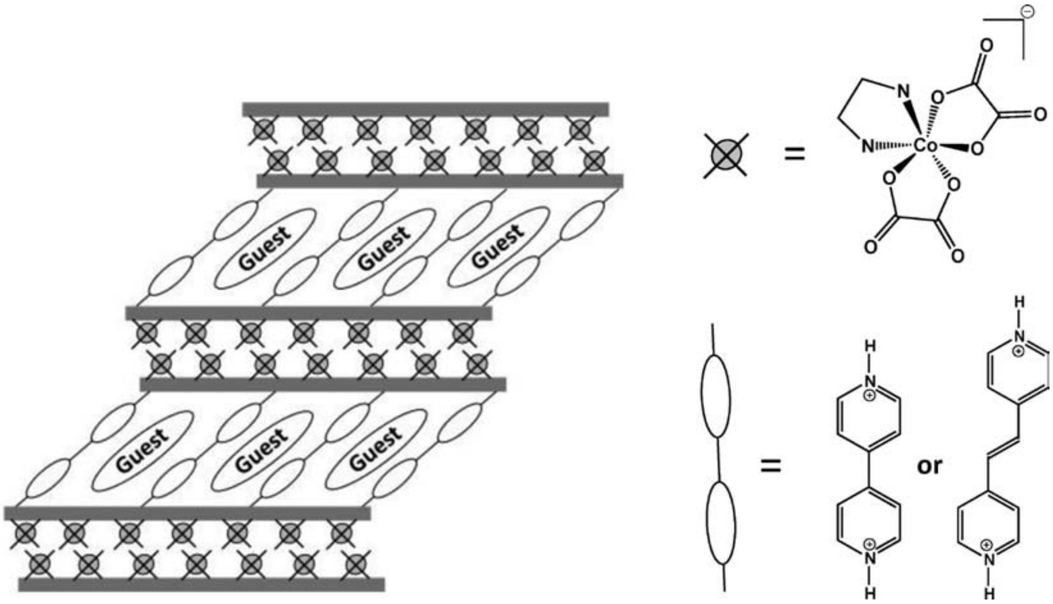
EXPERIMENTAL SECTION

The metal complex Ca[Co(en)(ox)$_2$]$_2$·4H$_2$O was synthesized according to the literature.[17] 4,4′-Bipyridine (Sigma Aldrich), 1,2-di(4-pyridyl)-ethylene (Sigma Aldrich), 4-methoxyphenol (Alfa-Aesar), 1,6-dimethoxynaphthalene (Alfa-Aesar), 1,4-dimethoxybenzene (TCI America), 4-nitroanisole (TCI America), 4,4′-biphenol (Across), and methanol (Fischer Scientific) were used as received without further purification. FT-IR spectra of the freshly prepared compounds in crystalline form were recorded on a Bruker TENSOR-27 FT-IR spectrophotometer in ATR mode in the 4000−400 cm^{-1} region.

Synthesis of [H$_2$bpy][Co(en)(ox)$_2$]$_2$·H$_2$O (1). A suspension of Ca[Co(en)(ox)$_2$]$_2$·4H$_2$O (0.82 mmol) in 30 mL of hot water (80 °C) was mixed with 20 mL of aqueous solution of 4,4′-bipyridinium oxalate (0.4 mmol), and the mixture was heated for 15 min. The white precipitate of Ca(ox) was filtered off and the solution was left undisturbed at room temperature to allow for slow evaporation. Pink-colored block-shaped crystals of **1** were obtained in 10 days as a single phase. IR (cm^{-1}): 1645s, 1701m, $\nu_{C=O}$, *oxalate*; 1591m, 1425m, $\nu_{C=C}$, 1490s, $\nu_{C=N}$, 3490m, ν_{N-H}, *bpy*.

Synthesis of [H$_2$bpy][Co(en)(ox)$_2$]$_2$·(bp)·5H$_2$O (2). A solution of **1** (0.2 mmol) in 10 mL of water was mixed with 5 mL of methanol

Scheme 1. Schematic Representation of the Typical Pillared-Layer Framework Structures Formed of the Anionic Metal Complex $[Co(en)(ox)_2]^-$ and the Cationic Bipyridinium Pillars $(H_2bpy)^{2+}$ and $(H_2bpye)^{2+a}$



^{a}The general formulas of the compounds are $[Co(en)(ox)_2]_2(H_2bpy)\cdot n(guest)$ and $[Co(en)(ox)_2]_2(H_2bpye)\cdot n(guest)$, where n is one or two molecules per interpillar cavity

solution of 4,4′-biphenol (0.6 mmol) and left undisturbed at room temperature to allow for slow evaporation. Reddish-pink block-shaped crystals of **2** were obtained in 5 days as a single phase. IR (cm^{-1}): 1645, 1701, $\nu_{C=O}$, *oxalate*; 1261, ν_{C-O}, *bp*; 1492, 1394, $\nu_{C=C}$, 3496, ν_{N-H}, *bpy*.

Synthesis of $[H_2bpy][Co(en)(ox)_2]_2\cdot 2(mp)\cdot H_2O$ (3). A solution of **1** (0.2 mmol) in 10 mL of H_2O was mixed with 5 mL of methanol solution of 4-methxyphenol (0.6 mmol) and left undisturbed at room temperature to allow for slow evaporation. Reddish-pink block-shaped crystals of **3** were obtained in 5 days as a single phase. IR (cm^{-1}): 1697, 1662, $\nu_{C=O}$, *oxalate*; 1220, ν_{C-O}, *mp*; 3342, ν_{N-H}, *bpy*.

Synthesis of $[H_2bpy][Co(en)(ox)_2]_2\cdot(dmb)\cdot H_2O$ (4). A solution of **1** (0.2 mmol) in 10 mL of H_2O was mixed with 5 mL of methanol solution of 1,4-dimethoxybenzene (0.6 mmol) and left undisturbed at room temperature to allow for slow evaporation. Reddish-pink block-shaped crystals of **4** were obtained in 5 days as a single phase. IR (cm^{-1}): 1650, 1701, $\nu_{C=O}$, *oxalate*; 1243, ν_{C-O}, *dmb*; 3261, ν_{N-H}, *bpy*.

Synthesis of $[H_2bpy][Co(en)(ox)_2]_2\cdot(dmn)\cdot H_2O$ (5). A solution of **1** (0.2 mmol) in 10 mL of H_2O was mixed with 5 mL of methanol solution of 1,6-dimethoxynaphthalene (0.6 mmol) and left undisturbed at room temperature to allow for slow evaporation. Reddish-pink block-shaped crystals of **5** were obtained in 5 days as a single phase. IR (cm^{-1}): 1650, 1701, $\nu_{C=O}$, *oxalate*; 1220, ν_{C-O}, *dmn*; 3494, ν_{N-H}, *bpy*.

Synthesis of $[H_2bpye][Co(en)(ox)_2]_2\cdot 3H_2O$ (6). A suspension of $Ca[Co(en)(ox)_2]_2$ (0.82 mmol) in 30 mL of hot H_2O was mixed with 15 mL of aqueous solution of 1,2-(4-pyridinium)ethylene oxalate (0.4 mmol), and the mixture was heated for 15 min. The white precipitate of Ca(ox) was filtered off and the solution was left undisturbed at room temperature to allow for slow evaporation. Pink-colored needle-shaped crystals of **6** were obtained in 10 days as a single phase. IR (cm^{-1}): 1680, 1716, $\nu_{C=O}$, *oxalate*; 3396, ν_{N-H}, 1492, 1269, $\nu_{C=C}$, *bpye*.

Synthesis of $[H_2bpye][Co(en)(ox)_2]_2\cdot 2(na)\cdot 3H_2O$ (7). A solution of **6** (0.2 mmol) in 10 mL of H_2O was mixed with 5 mL of methanol solution of 4-nitroanisole (0.6 mmol) and left undisturbed at room temperature to allow for slow evaporation. Reddish-pink block-shaped crystals of **7** were obtained in 5 days as a single phase. IR (cm^{-1}): 1680, 1714, $\nu_{C=O}$, *oxalate*; 1265, 1496, $\nu_{C=C}$, 1589, ν_{N-O}, *na*; 3135, 3396, ν_{N-H}, *bpye*.

Structure Determination. Single crystal X-ray diffraction data sets were collected on a Bruker APEX-II diffractometer with a CCD area detector at 120 K (Mo Kα, λ = 0.71073 Å). The crystals were taken from the mother liquid, dried in the air, and covered with Paratone-N oil. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXL 97 program.[18] All hydrogen atoms of the framework were refined as riding on the corresponding non-hydrogen atoms, while they were omitted for all disordered guest molecules and lattice water. The guest molecules 1,6-dimethoxynaphthalene in **5** and 1,4-dimethoxybenzene in **4** were found disordered, and their thermal parameters were refined only as isotropic. Although a *c*-glide symmetry was suggested for compound **2** (by *checkcif*),[19] this was not the case since such a symmetry would have superimposed the *bpy* and *bp* molecules. More details for the data collections and structure refinements are given in Table 1.

■ RESULTS AND DISCUSSION

The structures of the seven new compounds are topologically quite similar. They can be described as made of anionic layers of metal complexes that are then pillared by the bipyridinium cations (Scheme 1). Guest molecules, if any, occupy the interpillar galleries. Extensive charge-assisted hydrogen bonding is found between layers and the pillars, while additional hydrogen bonds occur between the metal complexes within the layers involving their different ligands of ethylenediamine and oxalate. All these features make the compounds isotopological but of reversed polarity with the already well studied host−guest frameworks made of cationic metal complexes and anionic disulfonate pillars.[11,12,16]

The host framework in a host−guest system typically takes different guest molecules to form series of inclusion compounds but it also can exist on its own, i.e. without any guest. In order to check the latter we carried out reactions between $Ca[Co(en)(ox)_2]_2\cdot 4H_2O$ and H_2bpy or H_2bpye without guest molecules. Both reactions produced crystalline compounds, $[H_2bpy][Co(en)(ox)_2]_2\cdot H_2O$ (**1**) and $[H_2bpye]$-$[Co(en)(ox)_2]_2\cdot 3H_2O$ (**6**). The metal complexes in **1** form

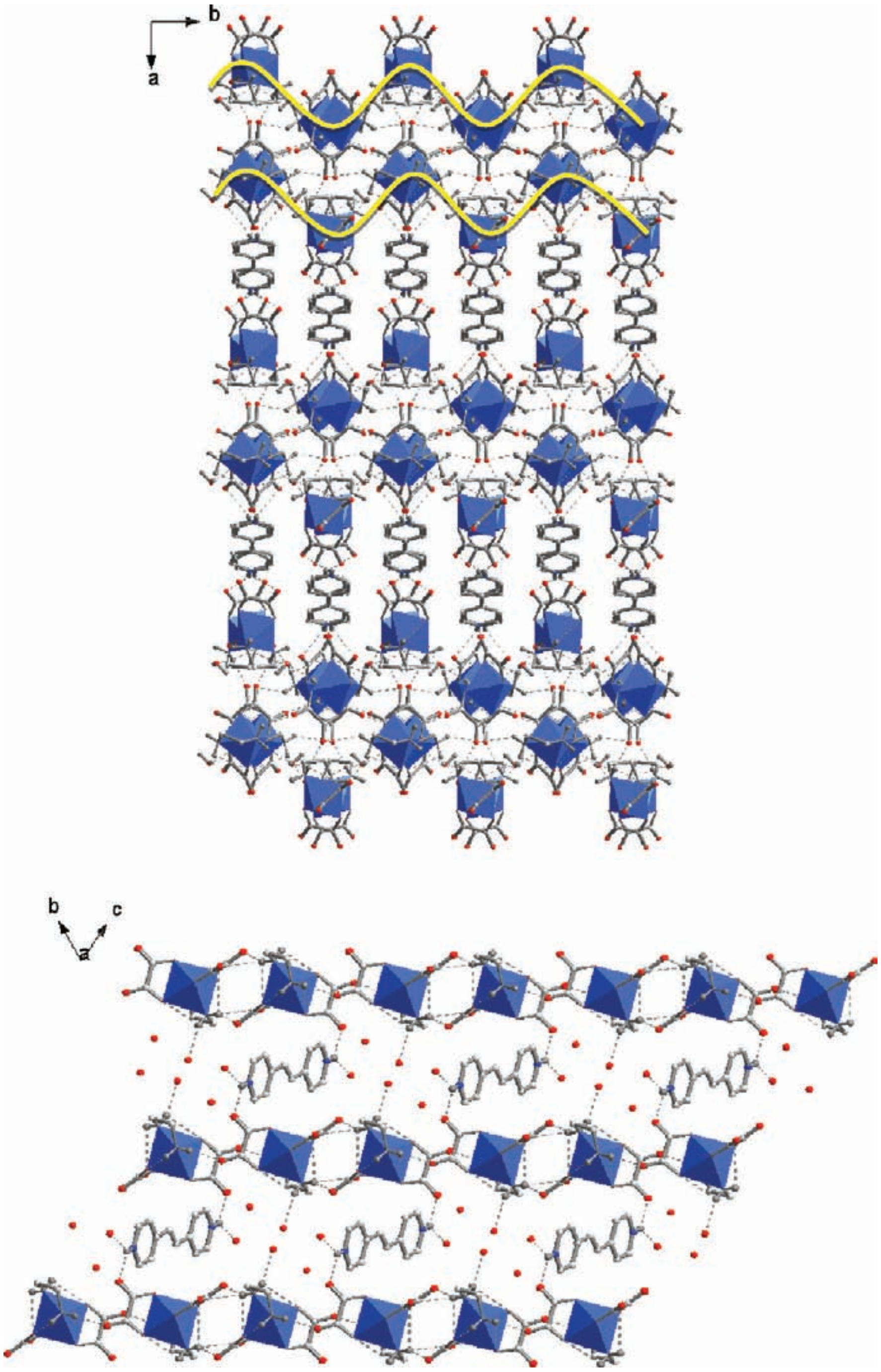


Figure 1. Structures of the guest-free compounds $[H_2bpy][Co(en)(ox)_2]_2 \cdot H_2O$ (**1**, top) and $[H_2bpye][Co(en)(ox)_2]_2 \cdot 3H_2O$ (**6**, bottom). Both are fairly well packed although the extra water in the latter can be viewed as a guest that makes the structure more open. While the metal complexes form flat single layers in **6**, the layers are double and wavy in **1** (outlined in yellow). Hydrogen bonds (broken lines) are found between the complex and the pillars, as well as between the different ligands within the layers.

wavy double layers (Figure 1, top) in which the metal complexes are extensively hydrogen-bonded to each other (Supporting Information Figure S1). The hydrogen bonds, in the range of 2.929(3)−3.129(3) Å, occur between the amino groups of the ethylenediamine ligand of one complex and the oxalate oxygen atoms from another one. Exactly the same type of intralayer hydrogen bonding is observed in the previously reported disulfonate systems with $[Co(en)_2(ox)]^+$ countercations. The layers are separated by the H_2bpy cations which bond to the oxalate ligands of the metal complexes by charge-assisted hydrogen bonds. Each pyridyl nitrogen atom interacts with two oxalate oxygen atoms at relatively short distances in the range 2.716(3)−2.935(3) Å (Supporting Information Table S1). These distances are significantly shorter than the observed hydrogen bonds in the already mentioned $[Co(en)_2(ox)]^+$/disulfonate frameworks which are in the range 2.854(3)−3.064(4) Å.[12,16] The reason for this difference could be the capability of the sulfonate group to form more hydrogen bonds via its three oxygen atoms compared to only one nitrogen atom per pyridyl group.

The second guest-free framework, compound **6**, is somewhat more open (Figure 1, bottom) most likely because of the additional two water molecules in its formula compared to **1**. Here the metal complexes form a single flat layer with intralayer hydrogen bonds that are very similar to **1** in both numbers and distances. The pillars of the longer H_2bpye are greatly tilted and almost parallel to the layers. Each bipyridinium nitrogen atom forms only one hydrogen bond to an oxalate oxygen at 2.886(3) Å and a second bond to a water molecule at 2.933(4) Å. All water molecules in the compound are confined within infinite galleries between the pillars in the structure. This is the space typically occupied by the guest molecules in guest-filled compounds and, therefore, these water molecules can be viewed as playing such a role in this case. The volume that they occupy is calculated at 18.1%.

Compounds **2**–**5** and **7** are the corresponding guest-filled versions of **1** and **6**, respectively. It is not clear why the different hosts are compatible with different sets of guests, but it can be speculated that pillar-guest size ratios and $\pi-\pi$ interactions availability are among the reasons. The overall formula remains the same except that one or more guest molecules are added, that is, $[H_2bpy$ or $H_2bpye][Co(en)(ox)_2]_2 \cdot n(guest)$. The structures of all these compounds are of the pillared-layer type, just like the metal-complex disulfonates,[11,12,16] with guest molecules in the interpillar galleries. Since the two pillar molecules, H_2bpy and H_2bpye, are flat and aromatic, all guests used in the studies were also aromatic molecules functionalized with different groups. It is expected that $\pi-\pi$ interactions between pillars and guests bring additional driving force for the insertion of the guests in the galleries. On the basis of the observed parallel but displaced positioning of the pillars and the guest molecules in all the compounds reported here, such interactions indeed occur to some degree in all of them. The observed change of color from pink for the empty frameworks to red for the corresponding inclusion compounds clearly illustrates the effect of these interactions.

Taking a closer look at each of the filled compounds, we see that the metal complexes in compound **2** form single layers and the pillars of H_2bpy are significantly tilted with respect to the planes of the layers at about 41° (Figure 2). Furthermore, the tilt direction alternates to left and right on going along the galleries, the *c* axis in this case. The galleries are occupied by the guest molecules of 4,4′-biphenol (*bp*). The benzene rings of the latter are parallel to the pillars at a distance of 3.24 Å (plane-to-plane), and this indicates $\pi-\pi$ interactions. It is generally assumed that such interactions occur between parallel aromatic molecules at distances below 3.5 Å.[20] This parallel positioning, in turn, makes the *bp*-molecules also tilted at the same angle as the pillars and, furthermore, their tilt direction also alternates in the same manner as the pillars (Figure 2). The metal complexes are held together in the layers by numerous hydrogen bonds in the range 2.875(3)–3.024(3) Å. Each H_2bpy molecule forms two very short charge-assisted hydrogen bonds to oxalate oxygens of the metal complexes, 2.759(4) and 2.723(4) Å. In addition, the *bp* guest in this particular case is also very strongly hydrogen bonded to oxalate oxygens with two even shorter bonds of 2.712(4) and 2.661(4) Å. Such guest-to-framework interactions that are comparable in strength with the interactions within the framework itself raises the question whether the *bp* molecules should be considered as true guests. Clearly the two hydroxy groups of the *bp* guest are the problem in this case, that is, they are hydrogen donors in forming hydrogen bonds, and they were subsequently replaced with methoxy groups in the remaining guest molecules (see below). The calculated space for the guest and water molecules in this structure is 34.7%,[21] and this compares well with the space calculated for the previously reported $[Co(en)_2(ox)]^+$/disulfonate compounds with various guests.[12,16]

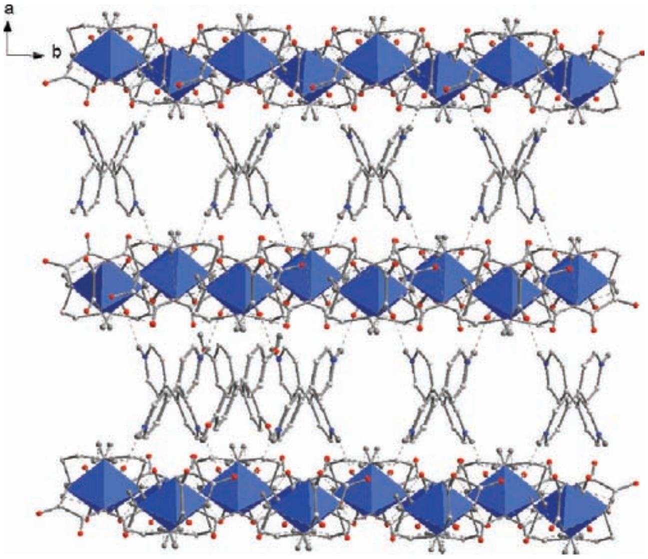


Figure 2. Structure of $[H_2bpy][Co(en)(ox)_2]_2 \cdot (bp) \cdot 5H_2O$ with 4,4′-biphenol guest molecules (shown in only one gallery). The tilt direction of both the pillars and the guests alternates left and right on going along the galleries (the viewing direction).

The remaining four compounds **3**, **4**, **5**, and **7** are structurally very similar (Figures 3–6). They all exhibit densely packed double layers of metal complexes with pillars that are parallel to each other and are tilted in one direction only. Furthermore, the tilt direction in all of them is within the planes of the flat molecules. In other words, the planes of the pillar molecules are nearly perpendicular to the planes of the metal complex layers as can be seen in the views shown in Figures 3–6. The guest molecules in all four compounds are parallel to the pillars.

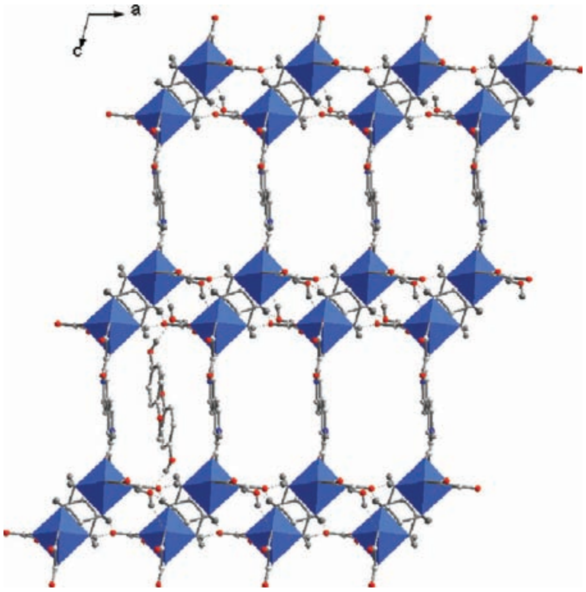


Figure 3. Structure of $[H_2bpy][Co(en)(ox)_2]_2 \cdot 2(mp) \cdot H_2O$ (**3**) with 4-methoxyphenol guest molecules (shown in only one gallery).

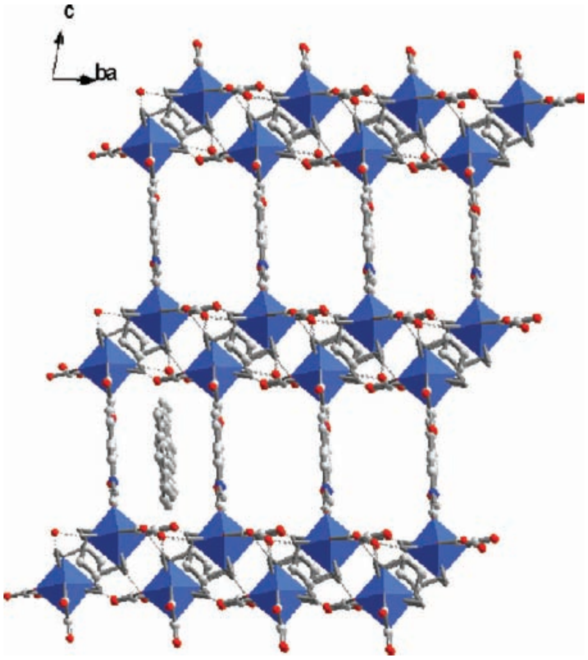


Figure 4. Structure of $[H_2bpy][Co(en)(ox)_2]_2\cdot(dmb)\cdot H_2O$ (**4**) with 1,4-dimethoxybenzene guest molecules (shown in only one gallery).

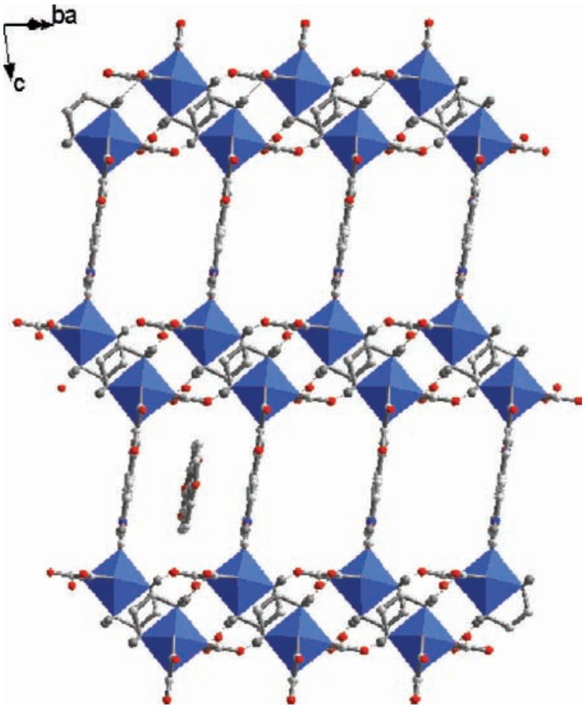


Figure 5. Structure of $[H_2bpy][Co(en)(ox)_2]_2\cdot(dmn)\cdot H_2O$ (**5**) with 1,6-dimethoxynaphthalene guest molecules (shown in only one gallery).

Starting with the guest in compound **3**, instead of a molecule with two benzene rings and two hydroxy groups as in *bp* of compound **2** used here was a smaller molecule with a single benzene ring and with one hydroxy and one methoxy groups, namely 4-methoxyphenol (*mp*, Chart 1). These modifications eliminated all guest–host hydrogen bonds (Figure 3). The smaller size of the guest resulted in twice more *mp* molecules per formula compared to **2**. This, in turn, leads to higher guest space in the structure which is calculated at 39.4%. All guest molecules are parallel to the H_2bpy pillars and at a distance of 3.40 Å. Each pyridyl ring of the pillars interacts with two guest molecules, one on each side. In this particular structure the intralayer hydrogen bonds are very few and relatively long, at 2.9702(17) Å and longer. This means that the structure is held together predominantly by the charge assisted hydrogen bonds between pillars and layers where each pillar forms three such bonds in the range 2.7618(17)–2.9140(16) Å.

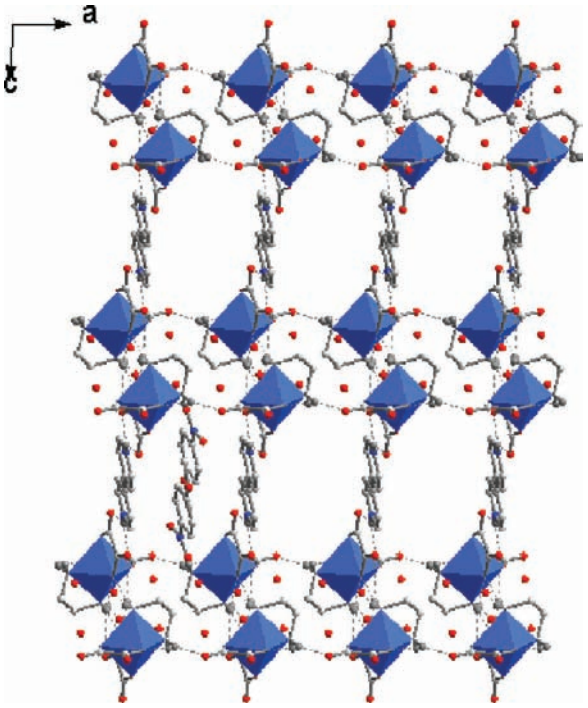


Figure 6. Structure of $[H_2bpye][Co(en)(ox)_2]_2\cdot 2(na)\cdot 3H_2O$ (**7**) with 4-nitroanisol guest molecules (shown in only one gallery).

The *mp* guest molecule from compound **3** was further modified by replacing the remaining hydroxy group with another methoxy group resulting in 1,4-dimethoxybenze (*dmb*) in **4** (Chart 1 and Figure 4). Again, the guest molecules lack hydrogen bonds and their benzene rings interact with the bipyridinium pillars (parallel and at 3.35 Å). The second methoxy group makes the molecule bulky enough that only one guest per formula is taken by the framework. This results in relatively small volume of 32.7% for the guest in this structure. The hydrogen bonding within the layers (2.879(5) and 2.956(5) Å) and between layers and pillars (2.707(5) and 2.953(5) Å) is very similar to that seen in compound **3**.

The last member of this series, compound **5**, accommodates the largest guest molecule, namely, 1,6-dimethoxynaphthalene (*dmn*), which, in turn, generates the greatest gallery volume of 35.8% (Figure 5). The guest molecule can be viewed as yet another modification of the guest from the previous compound, the 1,4-dimethoxybenzene (*dmb*) in **4**. Changed this time, however, is the core of the molecule which is expanded from a single benzene ring in *dmb* to a naphthalene double ring in *dmn*. The two methoxy groups are retained and are at positions 1 and 6 of the naphthalene (Chart 1). Again, the guest molecule does not form hydrogen bonds with the framework and only exhibits possible $\pi-\pi$ interactions with the pillars at a relatively short distance of 3.20 Å. The intralayer and layer-pillar hydrogen bonding, 2.871(5)–2.948(5) and 2.690(5)–

3.019(5) Å, respectively, is again very similar to that in compounds **3** and **4**.

While the framework host made of metal complex and H_2bpy pillars have been very "hospitable" to a number of various guests, the one involving the longer H_2bpye pillars has accommodated only one guest so far. That guest is 4-nitroanisole (*na* in Chart 1) and is found in the galleries of compound 7 (Figure 6). As in compound **3**, the guest molecule is quite shorter than the pillar and this results in taking two guest molecules per formula unit, that is, $[H_2bpye][Co(en)(ox)_2]_2\cdot 2(na)\cdot 3H_2O$. Again, this produces very large gallery volume of 45.3% in this case, a number which is quite larger than in previously reported systems.[12,16] Also as in compound **3** each of the two pyridyl rings of the H_2bpye pillars interacts with the benzene rings of two *na* guests, one on each side, at a distance of 3.30 Å. The guest does not form any hydrogen bonds with the host. The hydrogen bonds occur within the layers (3.005(4) and 3.007(4) Å) and between them and the pillars (2.733(3) and 2.888(3) Å).

The reported here seven new framework compounds, five of them with guest molecules, illustrate once again how relatively weak interactions, such as hydrogen bonding, are used for building soft frameworks that are flexible enough to accommodate different guests by relatively small conformational adjustments within the building blocks and small changes in the interactions between them. They also show that such soft hosts can be constructed not only from cationic complexes and anionic linkers but also from similar building blocks with reversed polarity. In both cases the frameworks are of the pillared-layer type where the layers are made of the metal complexes and the linkers play the role of the pillars. In both cases, the hydrogen bonding within the layers occurs between the oxalate and ethylenediamine ligands in either $[Co(en)_2(ox)]^+$ or $[Co(en)(ox)_2]^-$. What is slightly different is that each sulfonate group has three oxygen atoms capable of hydrogen bonding while pyridyl ring has only a single nitrogen atom for hydrogen bonding. This results in more extensive hydrogen-bonding in the disulfonate compounds. However, the fewer hydrogen bonds in the bipyridinium systems seems to be compensated by shorter distances. While the average layer-disulfonate hydrogen bond is 3.01 Å that number for the layer-bipyridinium system is 2.80 Å. Thus, both framework types exhibit good stability and crystallinity combined with excellent flexibility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format and a distances table and figures for the hydrogen bonding. This material is available free of charge via the Internet at http://pubs.acs.org.

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