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Metal-Organic Frameworks with Direct Transition Metal-Sulfonate Interactions and Charge-Assisted Hydrogen Bonds

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Seven compounds with framework structures made of divalent metal-imidazole (Im) complexes (M(II) = Co, Ni, and Mn) linked by 1,5-napthalenedisulfonate (1,5nds) were synthesized and structurally characterized. Five of these compounds, Mn(Im)$_4$(1,5nds) (two forms), Co(Im)$_4$(1,5nds) (two forms), and Ni(Im)$_4$(1,5nds), contain direct sulfonate-metal coordination and represent the first such compounds with open d-shell transition metals without Jahn−Teller distortion. The two disulfonate ligands in these octahedrally coordinated metal centers are found in both *trans*- and *cis*-geometries and link the centers into chains. The chains are held together by charge-assisted hydrogen bonds between sulfonate and imidazole ligands from different chains. The remaining two compounds, Co(Im)$_6$(1,5nds)·2H$_2$O and Ni(Im)$_6$(1,5nds)·2H$_2$O, exhibit only charge-assisted hydrogen bonds between the octahedral M(Im)$_6^{2+}$ cations and the disulfonate anions.

Introduction

The interest in self-assembled "soft" or "flexible" materials has been growing steadily in recent years. The molecular building blocks in such materials are interconnected by relatively weak bonds such as hydrogen bonds, π-interactions, electrostatic interactions, and so on.[1] The resulting host frameworks are capable of incorporating a range of guest molecules by bending, twisting, and changing conformation while maintaining the overall connectivity and topology. As such, these compounds have potential for application in chemical storage, catalysis, and separations to name a few.[2]

The more rigid frameworks, as can be expected, involve stronger interactions such as covalent and coordination or donor−acceptor bonds between the molecular building blocks. The coordination frameworks, typically referred to as metal-organic frameworks or MOFs, are constructed of transition-metal nodes that are linked by divergent organic ligands coordinated to them via oxygen or nitrogen atoms.[3] Most abundant among these are the transition-metal carboxylate and phosphonate frameworks where the metal nodes are interconnected by linkers that are coordinated directly to the metal atoms.[4−9]

To achieve some control over the structures of either the "soft" materials or the MOFs one needs to design strategies that use building blocks with specifically directed interactions between themselves and/or to introduce guest molecules (templates) that would define the structure of the host framework around them. A beautiful example of such designed soft frameworks is the diverse guanidinium disulfonate system explored extensively by Ward's group where a very large number of compounds were synthesized by utilizing different guest molecules and sulfonates with different organic residues.[10,11] Each sulfonate group with its three oxygen atoms and six lone pairs forms six charge-assisted and directional hydrogen bonds with the six protons of the flat guanidinium cation. The intrinsic C_3 symmetry of both sulfonate and guanidinium leads to a persistent pseudohexagonal hydrogen-bonded lameli. The organic residues of the disulfonate linkers form pillars between these lameli and can be systematically controlled by changing their lengths and geometries. Similarly, some level of design has been achieved in the more

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rigid MOFs by controlling the length and the number of functional groups at the linkers, the number of metal atoms at the nodes, that is, single-atom vertex versus a group of vertices, and so on.[4,12]

On the basis of analogies with the guanidinium cation in the guanidinium-sulfonate systems, the search for new frameworks has recently evolved into "replacing" the guanidinium cations with cationic metal complexes that can donate protons for hydrogen bonding, that is, complexes with ligands such as water, ammonium, and various amines. For example, two opposite triangular faces in an octahedral hexamine complex $[M(NH_3)_6]^{n+}$ can be viewed as replacing two staggered and parallel guanidinium cations $[C(NH_2)_3]^+$. Such a complex can hydrogen bond to disulfonate anions and eventually form pillared-layer or other porous type structures similar to those with guanidinium. In addition to their guest-inclusion capabilities, the resulting frameworks may have interesting redox, catalytic, and magnetic properties because of the transition metal they contain.

What makes possible such hydrogen-bonding interactions between the cationic metal complex and the anionic sulfonates instead of ligand replacement is the relatively weak coordination of the sulfonate functionality to transition-metal centers, so weak that it cannot replace ligands such as water and amines.[13,14] Unlike other anionic functionalities such as organic phosphonates and carboxylates that readily replace weak ligands, the sulfonates tend to hydrogen-bond to the available proton-donating ligands instead. Several series of pillared-layer type frameworks with cobalt-based complexes and various disulfonate anions have been already reported by us and others.[15−18] Also, we have demonstrated that the charge of the metal complex is directly related to the size of the open space available for inclusion of guest molecules between the pillars. Thus, a low-charged complex requires fewer disulfonate counteranions than a high-charged one and, therefore, has fewer pillars with more interpillar free space. For example, a framework with the monocationic $[Co(en)_2(ox)]^+$ has three times fewer pillars than a framework with tricationic $[Co(NH_3)_6]^{3+}$ and allows for the inclusion of much larger guests.[19,20]

Frameworks with direct sulfonate-to-metal coordination are very rare, and the few known examples involve either main-group elements or closed-shell d^{10} cations such as Ag(I) and Cd(II) or mixed-ligand complexes with large Jahn−Teller elongation with the two sulfonate oxygen atoms taking the farthest positions and barely coordinated. Many of these have been included in two recent reviews by Shimizu and Cai.[14,21] Here we present several frameworks made of divalent metal imidazole (Im) complexes (M(II) = Co, Ni, and Mn) and 1,5 naphtalenedisulfonate (1,5nds). Five of these compounds contain direct sulfonate-metal linkages and represent the first such compounds with open d-shell transition metals with normal octahedral coordination, that is, without Jahn−Teller distortion.

Experimental Section

The starting hexaimidazole metal complexes $Co(Im)_6(H_2O)_4$ and $Ni(Im)_6(H_2O)_4$ were synthesized according to the literature.[22,23] The 1,5-napthanlenedisulfonic acid tetrahydrate $HO_3S-C_{10}H_6-SO_3H\cdot 4H_2O$, $MnCl_2\cdot 4H_2O$, and solvents were used as received. Thermogravimetric analyses of the compounds were carried out on a Netzsch TG-209 analyzer under flowing nitrogen from 22 to 800 °C at a rate of 5 °C/min.

Synthesis of [Co(Im)$_6$(1,5nds)](H$_2$O)$_2$ (1) and [Ni(Im)$_6$(1,5nds)](H$_2$O)$_2$ (2). A solution of the hexaimidazole complex (0.15 mmol) in 3 mL of H_2O was mixed with 3 mL of an aqueous solution containing 1,5nds (0.15 mmol) and NaOH (0.030 mmol). Dark purple and light blue precipitates formed for the cobalt and nickel complexes, respectively. These precipitates were redissolved with the addition of 2 mL of ethanol or acetone for **1** and **2**, respectively, and the solution was filtered. Large blocky crystals of approximately 0.5 mm sizes formed upon evaporation of the solution for 2 days (single phase, moderate yields).

Synthesis of *trans*-[Mn(Im)$_4$(1,5nds)] (3). $MnCl_2(H_2O)$ (0.15 mmol) and imidazole (1.8 mmol) were dissolved in 2 mL of methanol. In a separate beaker 1,5nds (0.30 mmol) was dissolved in 2 mL of methanol, and the two solutions were combined. Clear crystals of approximately 0.3 mm in length formed upon evaporation of the solution after 24 h (single phase, moderate yields).

Synthesis of [Co(Im)$_4$(1,5nds)] (*trans*-, 4 and *cis*-, 5) and *cis*[Ni(Im)$_4$(1,5nds)] (6). A solution of $Co(Im)_6(H_2O)_4$ or $Ni(Im)_6(H_2O)_4$ (0.10 mmol) in 2 mL of methanol was mixed with 1,5nds complex (0.10 mmol in 2 mL of methanol). The solution was allowed to evaporate for 24 h and resulted in the formation of several crystal morphologies. Compounds **4** and **5** were found in the same synthesis with approximate yields of 40% and 60%, respectively. The Ni complex **6** was found intermixed with traces of compound **2**.

Synthesis of *cis*[Mn(Im)$_4$(1,5nds)] (7). $MnCl_2(H_2O)$ (0.15 mmol) and imidazole (1.8 mmol) were dissolved in 2 mL of H_2O. Two milliliters of an aqueous solution containing 1,5nds (0.15 mmol) were added to the manganese solution. The solution color changed from clear to light yellow upon addition of the disulfonate complex. Large blocky crystals of approximately 0.6 mm in length formed upon evaporation of the solution after 24 h (single phase, moderate yields).

Crystal Structure Determination. Single crystals were isolated from all compounds, and X-ray diffraction data sets were collected on a Bruker single crystal X-ray diffractometer equipped with an APEX II CCD detector. The data were collected using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K using a frame width of 0.5° in omega and a count time per frame of 5, 20, 10, 30, 40, and 10 s for compounds (**1**−**7**), respectively. The unit cell parameters were refined by least-squares, and the data sets were integrated using the Bruker APEX II suite of software. Semiempirical absorption corrections were applied using the program SADABS. Selected data collection parameters and crystallographic information are provided in Table 1.

The structures were solved by direct methods and refined on F^2 by least-squares using the Bruker SHELXL Version

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Table 1. Selected Crystallographic Data for Compounds **1**−**7**

	$[\mathrm{Co(Im)_6(1,5nds)}]$-$\mathrm{H_2O}$ (**1**)	$[\mathrm{Ni(Im)_6(1,5nds)}]$-$\mathrm{H_2O}$ (**2**)	$[\mathrm{Mn(Im)_4(1,5nds)}]$ (**3**)	$[\mathrm{Co(Im)_4(1,5nds)}]$ (**4**)	$[\mathrm{Co(Im)_4(1,5nds)}]$ (**5**)	$[\mathrm{Ni(Im)_4(1,5nds)}]$ (**6**)	$[\mathrm{Mn(Im)_4(1,5nds)}]$ (**7**)
formula	$C_{28}H_{34}O_8N_{12}S_2Co$	$C_{28}H_{34}O_8N_{12}S_2Ni$	$C_{22}H_{22}O_6N_8S_2Mn$	$C_{22}H_{22}O_6N_8S_2Co$	$C_{22}H_{22}O_6N_8S_2Co$	$C_{22}H_{22}O_6N_8S_2Ni$	$C_{22}H_{22}O_6N_8S_2Mn$
formula weight	789.74	773.50	613.56	617.55	617.55	617.43	613.56
space group, Z	$P\bar{1}$, 1	$P\bar{1}$, 1	$P\bar{1}$, 1	$P\bar{1}$, 1	Cc, 1	Cc, 1	Cc, 1
a (Å)	8.3402(7)	8.3058(4)	8.211(2)	8.2318(4)	9.7292(3)	9.6229(3)	9.762(1)
b (Å)	9.8944(9)	9.8443(5)	9.802(2)	9.7087(5)	16.9366(5)	16.7604(5)	17.091(1)
c (Å)	10.8515(9)	10.7517(5)	9.862(2)	9.7569(5)	15.4101(5)	15.8224(5)	15.460(1)
α (deg)	70.150(2)	70.188(2)	60.31(3)	60.601(2)			
β (deg)	85.002(2)	85.193(3)	86.79(3)	86.866(2)	100.521(2)	101.639(1)	100.386(8)
γ (deg)	79.917(2)	80.093(3)	74.06(3)	73.920(2)			
V (Å^3)	828.9(1)	814.43(7)	660.0(2)	649.69(6)	2496.58(13)	2499.4(1)	2537.2(4)
density (g/cm^3)	1.582	1.577	1.544	1.578	1.643	1.640	1.606
μ (mm^{-1})	0.713	0.791	0.713	0.876	0.912	1.001	0.741
F(000)	409	402	315	317	1268	1272	1260
reflections collected/unique	42385/19886	31117/10446	20805/5998	38533/8785	10817/4265	16080/4807	57423/12276
data/restraints/parameters	19886/5/247	10446/17/283	5998/11/211	8785/11/213	4265/24/418	4807/24/419	12276/6/346
R_1/wR_2 [$I > 2\sigma(I)$]	0.0393/0.0773	0.0364/0.0976	0.0389/0.1096	0.0354/0.1023	0.0231/0.0567	0.0353/0.0897	0.0264/0.0643
R_1/wR_2 (all data)	0.0663/0.0836	0.0505/0.1038	0.0530/0.1143	0.0437/0.1057	0.0237/0.0569	0.0374/0.0907	0.0292/0.0656

5.1 programs.[24] Compounds (**1**−**4**) were originally solved in the triclinic space group $P1$, but a center of symmetry was later located using the program PLATON, and the final structure model was refined in $P\bar{1}$. Compounds (**5**−**7**) were solved in the monoclinic space group Cc, and no additional symmetry elements were found. The transition metals and sulfur atoms were located by the direct methods for all compounds, while the O, N, and C atoms were identified from difference Fourier maps following the refinements of the partial-structure models. The final refinements include anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen positions were located from difference Fourier maps and were refined with soft constraints (fixed thermal parameter and a range of distances). Mode details for the data collection and structure refinements are listed in Table 1.

Results and Discussion

The structures of the isostructural $[\mathrm{Co(Im)_6(1,5nds)}](\mathrm{H_2O})_2$ (**1**) and $[\mathrm{Ni(Im)_6(1,5nds)}](\mathrm{H_2O})_2$ (**2**) are made of octahedral cationic complexes $[\mathrm{M(Im)_6}]^{2+}$ that are linked by 1,5nds disulfonate anions via charge-assisted hydrogen-bonds. The M−N distances in the metal complexes range from 2.1470(4)−2.1778(4) Å for **1** and from 2.0994(8)−2.1268(8) Å for **2** while the N−M−N angles are very close to 90° giving an almost ideal octahedral coordination (Figure 1a). The charge-assisted hydrogen bonds between the complex and the disulfonate involve the amine proton of the imidazole (Figure 1b) and the six disulfonate oxygen atoms with very short N−O distances of 2.825−2.894 Å. Each of the amine nitrogen atoms is hydrogen-bonded to one sulfonate oxygen atom and vice versa, and this results in a ratio of imidazole to disulfonate of 6: 1 in the formulas, that is, $\mathrm{M(Im)_6(1,5nds)}$. The resulting framework is made of discrete layers of metal complexes and disulfonate anions along the *ac* plane. The complexes are positioned with a 4-fold axis perpendicular to the layers, an orientation often observed before in similar frameworks.[19,20] The void spaces between the metal complexes are filled with water molecules that are hydrogen-bonded between themselves and to disulfonate anions. Since the positive charge of the complex equals the negative charge of the disulfonate the two species are in 1:1 ratio in the structure.

The majority of known soft frameworks with charge-assisted hydrogen bonds between metal complexes and disulfonates are Co(III)-based. Nonetheless, the charge of the complex can be manipulated by changing the ligands, for example, replacing neutral ethylenediamine (*en*) with anionic oxalate (*ox*) ligand reduces the charge from 3+ in $[\mathrm{Co^{III}(en)_3}]^{3+}$ to only 1+ in $[\mathrm{Co^{III}(en)_2(ox)}]^{+}$, and this, in turn, changes the complex-to-disulfonate ratio.[19,20] There is only one reported nickel-based compound, $[\mathrm{Ni^{II}(tame)_2}]$[bseb] where *tame* = 1,1,1-tris(aminomethyl)ethane and *bseb* = 4,4′-bis(sulfethynyl)biphenyl, although its structure has not been determined by single-crystal X-ray diffraction.[25] Thus, compounds **1** and **2** add two more compounds to the very limited collection of disulfonate-linked metal complexes of Co(II) and Ni(II).

The metal centers in the two isostructural compounds $[\mathrm{Mn^{II}(Im)_4(1,5nds)}]$ (**3**) and $[\mathrm{Co^{II}(Im)_4(1,5nds)}]$ (**4**) are also octahedrally coordinated but, unlike all known open-shell transition-metal sulfonates, two of the ligands are sulfonate groups directly coordinated to the metal center via one of their three oxygen atoms (Figure 2a). The metal centers are at inversion centers and, therefore, the two oxygen atoms are in *trans*-geometry with the remaining four imidazole ligands occupying the equatorial plane. The M−O distances, 2.1806(6) Å for the d^7 Co(II) and 2.195(2) Å for the d^5 Mn(II), and the M−N pairs of distances, 2.1128(7)/2.1207(7) Å in **3** and 2.235(1)/2.237(1) Å in **4**, are within the expected ranges although the Co−O distance is slightly longer than the typical 2.09 Å while the Co−N distances are slightly shorter than the observed 2.17 Å in $[\mathrm{Co(Im)_6}]^{2+}$.

Lastly, the metal coordination in the remaining three compounds, the isostructural $[\mathrm{Co^{II}(Im)_4(1,5nds)}]$ (**5**), $[\mathrm{Ni^{II}(Im)_4(1,5nds)}]$ (**6**), and $[\mathrm{Mn^{II}(Im)_4(1,5nds)}]$ (**7**), similarly involves four imidazole and two disulfonate ligands but the latter are in *cis* geometry instead (Figure 2b). As a result, the whole structure is acentric and crystallizes in the Cc space group. The lack of inversion center allows for two different M−O

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(24) *SHELXTL, version 5.1*, Burker Analytical Systems: Madison, WI, 1997.

(25) Dairymple, S. A.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2007**, *129*, 12114.

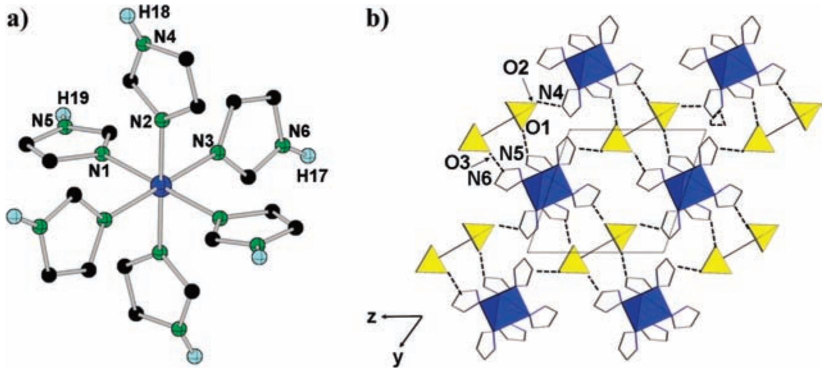

Figure 1. (a) Octahedral $[M(Im)_6]^{2+}$ cationic complex in **1** and **2**. (b) The three-dimensional framework created by charge-assisted hydrogen bonding between the $[M(Im)_6]^{2+}$ cations and the 1,5nds anions in **1** and **2**.

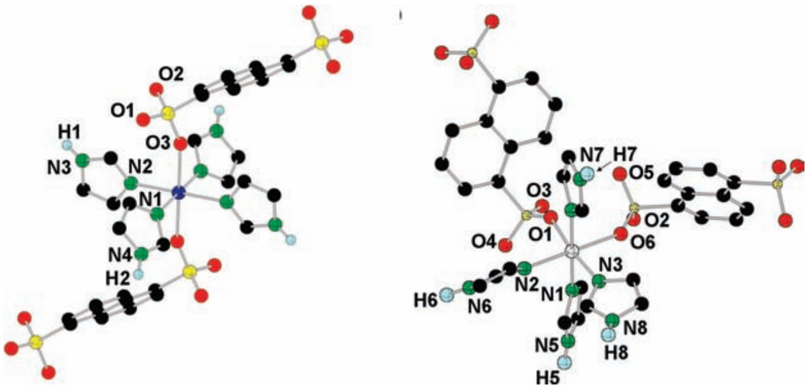

Figure 2. Metal centers in compounds **3**−**7** are octahedrally coordinated by four imidazole and two disulfonate ligands. The latter are *trans*- to each other in **3** and **4** (left) but are *cis*- in **5**, **6**, and **7** (right).

distances in each compound, and these are quite different for **5**, 2.145(2) and 2.217(2) Å, and **7**, 2.1789(8) and 2.2791(7) Å, but very similar in **6**, 2.123(2) and 2.140(3) Å. The M−N distances, on the other hand are in relatively narrow ranges for all three compounds, 2.101(3)−2.151(3), 2.064(3)−2.082(3), and 2.2137(9)−2.2535(9) Å for **5**, **6**, and **7**, respectively.

The structures of all five compounds **3**− **7** exhibit one-dimensional chains of metal centers coordinated by four imidazole molecules and interconnected by disulfonate linkers. For compounds **3** and **4** the *trans* configuration of the linkers creates a stepwise chain that extends along the [111] direction (Figure 3a). The *cis* conformation in **5**−**7**, on the other hand, results in zigzag chains that propagate along [001] (Figure 3b). Since each sulfonate group uses only one of its three oxygen atoms to coordinate to the metal centers, the remaining two atoms per $-SO_3$ group (four per disulfonate) are available as proton acceptors for charge-assisted hydrogen bonding. The donors are the nitrogen-bonded hydrogen atoms of the imidazole groups with each imidazole forming one hydrogen-bond to a terminal disulfonate oxygen atom and vice versa. This leads to a ratio of imidazole/disulfonate = 4:1 in the formulas of the five compounds, that is, $M(Im)_4(1,5nds)$. Thus, the strong-bonded chains by direct disulfonate-metal bonds are interconnected by secondary weaker interactions to each other to form three-dimensional soft frameworks. The interatomic distances between the hydrogen donor and acceptor range from 2.776−2.880 Å.

Direct coordination of sulfonate groups to transition metals is very rare and, until now, was unknown for "true" transition metals, that is, metals with open d-shell. They are very weak ligands that, depending on the conditions, may not be able to replace even the water molecules in solvated transition-metal cations typically produced upon dissolving metal salts in water. However, manipulation of the synthetic conditions by varying different parameters has proven successful in achieving a few examples with direct metal-sulfonate interactions.[21] As already discussed, all of them are either with closed-shell d^{10} metals or involve greatly elongated octahedra because of Jahn−Teller distortion. The latter are almost squares, and the sulfonate groups occupy the two remote axial positions with very long distances the metal. This, in turn, makes it very questionable whether they interact with the metal centers at all (besides electrostatic attraction). The d^{10} examples are limited to a few Cd(II) and Ag(I) compounds: $Cd(N,N''\text{-meen})_2(1,5nds)$, $Cd(N,N''\text{-meen})_2(2,6nds)$, $Cd(N\text{-meen})_2(2,6\text{-}nds)$, $Cd(inia)_4(H_2O)_2(peds)_2$, $Cd(H_2O)_2(meds)$, $Cd_2(H_2O)_4(meds)_2$, $Cd(H_2O)_2(1,5nds)$, $Ag_2(meds)_2$, $Ag_2(etds)$, $Ag_2(buds)$, and $Ag_2(1,5nds)$ where *N*,*N''*-meen = *N*,*N''*-methethylenediamine, *N*-meen = *N*-methethylenediamine, inia = isonicotinamide, 2,6nds = 2,6 napthalenedisulfonate, peds = 4,4′-phenyletherdisulfonate, meds = methanedisulfonate, etds = ethane-1,2-disulfonate, and buds = butane-1,4-disulfonate.[14,21,26] Similar to compounds **3** and **4**, the sulfonate groups in the first four are in *trans* geometry, and the structures contain similar one-dimensional chains. Also similarly, the chains are held together by hydrogen bonds to form framework structures. The last three cadmium disulfonates in the list above contain

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(26) Videnova-Adrabinska, V. *Coord. Chem. Rev.* **2007**, *251*, 1987.

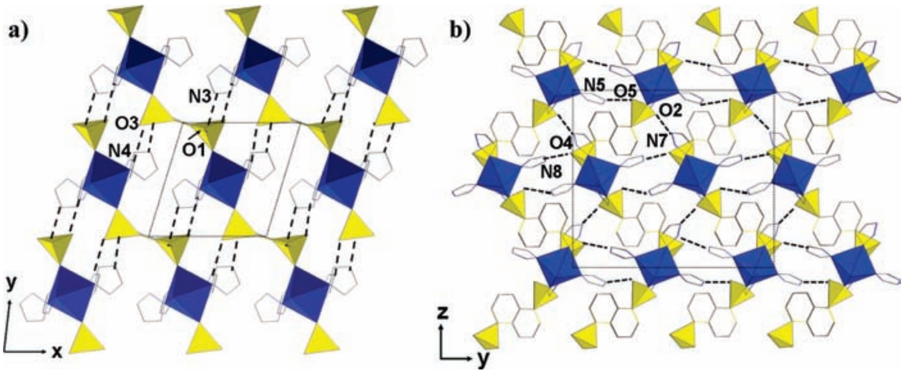

Figure 3. Structures of compounds **3**−**7**: (a) The direct metal-disulfonate linkages in **3** and **4** create a stepwise chain along [111]. (b) The *cis* conformation in **5**−**7** results in zigzag chains along [001]. The chains are held together by hydrogen bonding.

two-dimensional sheet structures with H-bonding linking the sheets into a framework, while the silver compounds have complex three-dimensional structures connected entirely through direct metal-sulfonate linkages. The examples with Jahn−Teller distortion are also very few and involve the d^9 and d^8 metal centers Cu(II) and Ni(II), respectively: [Cu(en)$_2$(1,5nds)](H$_2$O)$_2$, [Cu(N-meen)$_2$(1,5nds)](H$_2$O)$_2$, Cu(dpn)$_2$(bpds), Cu(cyclam)(1,5nds), and Ni(cyclam)(1,5nds) where dpn = 2,3-diaminopropane, bpds = biphenyldisulfonate, and cyclam = 1,4,8,11-tetrazacyclotetradecane.[26] For example, the equatorial Ni−N distances in Ni(cyclam)(1,5nds) range from 1.963(2)−2.102(2) Å whereas the axial Ni−O bonds are 2.451(2) Å.[27] For comparison, all metal−ligand distances in compounds **3**−**7** are within the narrow range 2.1−2.3 Å. It should be mentioned that Cu(II) and Ni(II) form also disulfonate compounds without direct coordination of the sulfonate group, for example, Cu(dpn)$_2$(H$_2$O)$_2$(1,5nds), [Cu(*N*,*N*′-meen)$_2$(H$_2$O)$_2$](1,5nds)H$_2$O, and [Ni(*N*,*N*′-meen)$_2$(H$_2$O)$_2$](2,6nds).[21] This illustrates clearly how small changes in the ligand and/or the synthetic conditions can impact greatly the metal coordination and the overall structure of the resulting compound.

The Co(II) *cis*- and *trans*-isomers (**4** and **5**) crystallized from the same reaction, indicating that there is little steric influence of the disulfonate ligands on the overall coordination geometry. Both isomers were also observed for the Mn(II) compounds, however, small changes (methanol vs water) in the synthetic conditions resulted in their separate crystallization. On the other hand, only the *cis* isomer for the Ni(II) compound has been found so far. However, this observation is based solely on crystallization results which can not rule out the presence of the other isomer in solution. Indeed, although a series of solutions of tetraimidazole Ni(II) histidine complexes repeatedly produced crystals of the *trans* isomers, quantitative potentiometric studies suggested that the crystalline product actually represented less than one-fifth of the complexes in solution with the *cis*-isomer dominating.[28]

According to TGA analysis, the compounds are structurally stable up to at least 200 °C (Figures 4 and 5). The purely hydrogen-bonded frameworks seem to show slightly lower stability compared to those with direct metal-sulfonate coordination. Thus, compound **1** loses two imidazole ligands at 200 °C (after dehydration above 110 °C) in a step that is then followed by more imidazole loss at 275 and 335 °C and a final disulfonate loss above 570 °C (Figure 4). According to X-day diffractions of the heated sample at different stages, structural disintegration occurs after the removal of the first imidazole molecule. The breakdown of the frameworks, also according to X-day diffraction, in compounds **4** and **5** begins at somewhat higher temperature, at approximately 250 °C, again with the loss of two imidazole ligands. The weight loss curves of the two compounds are nearly identical and indicate that the coordination geometry of the sulfonate linkers, *trans*-in **4** and *cis*- in **5**, does not affect the stability of the structure. The nature of the metal centers does not seem to affect the stability either as can be seen from the virtually identical curves for **5**− **7** (Figure 5). Similar TGA curves have been observed before for Cd(H$_2$O)$_2$(1,5nds) with sulfonate ligands that chelate and bridge the cadmium centers into two-dimensional layers.[21] The two water molecules coordinated to each cadmium atom provide protons for interlayer hydrogen bonding with the sulfonate group and formation of a framework structure. Upon heating, these two water molecules are the first to leave at around 250 °C, just like the imidazole ligands in compounds **1**−**7**.

Compounds **3** and **7** represent the first Mn-disulfonates while all five compounds **3**−**7** represent the first examples of direct disulfonate coordination to “true” transition metals, that is, metals with open d-shell and without Jahn−Teller distortions. Replacing water with methanol as the solvent was instrumental for the synthesis of the Co(II) and Ni(II) compounds **4**−**6** with direct metal-sulfonate interactions. The same syntheses, but carried out in water, results in compounds **1** and **2** with only hydrogen-bonded sulfonate groups. One possible reason for the different outcome of the same reaction in different solvents is the different solvation energy of the metal ions by the two solvents, that is, the strength of coordination of the solvent molecules. Replacing water with the more weakly coordinating methanol may facilitate replacement of solvating molecules with sulfonate anions. Another possible reason might be related to the different degree of dissociation of the disulfonic acid in the two solvents and, subsequently, eventual protonation of imidazole to imidazolium cations. The Mn(II) compound **7**, on the other hand, was synthesized from aqueous solution and yet has direct Mn-sulfonate interactions. The reason for this might be the fact that Mn(II) with d^5 configuration has one of the lowest hydration energies among the first-row transition metals, substantially lower than those of Co(II) and Ni(II).

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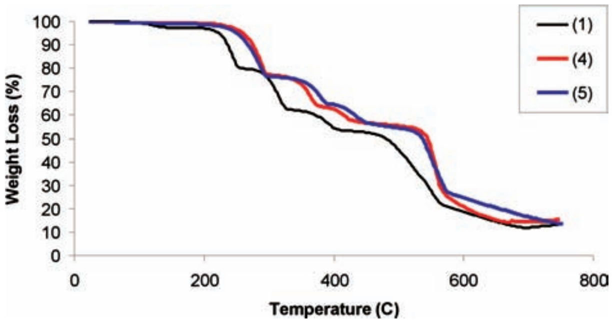

Figure 4. TGA analysis of the Co(II)-based compounds **1**, **4**, and **5**. The purely hydrogen-bonded framework **1** seems to be slightly less stable than **4** and **5** with direct metal-sulfonate bonds.

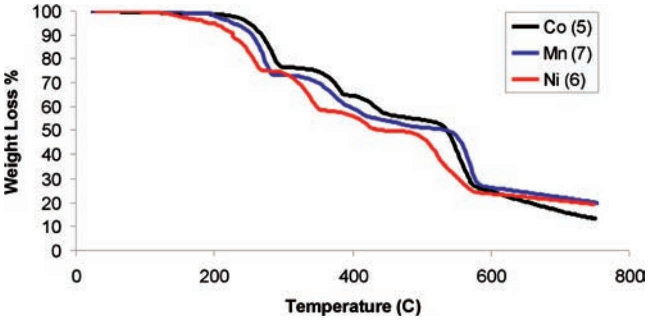

Figure 5. TGA analysis of compounds **5**−**7**. Clearly, the thermal stability is not influenced by the different metal centers.

So far, all of the compounds with direct metal-sulfonate interactions have metal centers with only two disulfonate ligands. These ligands are found in *trans* geometry in all previously reported metal disulfonate compounds with octahedrally coordinated metal centers, including the d^{10} group.[26] In this respect, therefore, compounds **5**−**7** represent the first structures with sulfonate linkers in *cis* geometry.

The discovery that direct linkages between transition metals and disulfonates are possible may have important implications for the future development of the field of hybrid inorganic−organic soft framework materials. The sulfonate group with its three oxygen atoms can provide variable coordination modes that could result in various frameworks, even some that contain solely direct metal-sulfonate interactions. Such frameworks may need additional cations for charge balancing the additional anionic disulfonate linkers that would be needed in these cases.

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Supporting Information Available: Tables with selected interatomic distances, angles, and hydrogen-bonding information for compounds **1**−**7** and a combined CIF file for the structures of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.