Supramolecular Inclusion Compounds

A Family of Supramolecular Inclusion Solids Based Upon Second-Sphere Interactions**

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The ability to include and order molecules in the solid state is of fundamental importance in the design of new functional solids.[1] Layered solids with porous interlayer regions have long offered an attractive route to such compounds.[2] The focus of these studies has ranged from wholly inorganic solids, such as pillared clays,[3] to hybrid inorganic–organic solids, such as metal phosphonates (RPO_3^{2-})[4] and sulfonates (RSO_3^-).[5] For the metal phosphonates and sulfonates, in simple $[M^{n+}(XO_3^{m-})_{n/m}]$ ($X = P$, S) complexes, adjacent organic pendant groups are oriented in an efficiently packed manner by the metal ions and yield nonporous interlayer regions (Figure 1 a). For metal phosphonates, a typical approach to remedy this problem is to alternate a "pillaring" phosphonate group with either a methylphosphonate or with phosphate ion[6] (Figure 1 b). The evolution of layered solids continued to systems sustained by weaker interactions, such

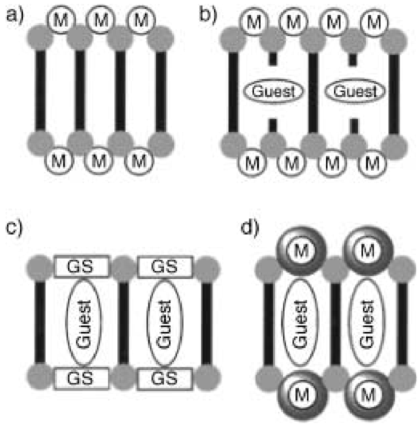

Figure 1. Representations of pillared layered solids: a) a simple metal diphosphonate with no space for guest inclusion, b) a mixed diphosphonate/phosphate with guests, c) a guanidinium disulfonate with guest inclusion, d) a second-sphere metal hexaamine disulfonate structure with guest inclusion.

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as charge-assisted hydrogen bonding. Notable examples in this domain include the complexes of secondary ammonium salts and polycarboxylate anions, studied by Zaworotko and co-workers,[7] and the layered networks formed between guanidinium (G) cations and organosulfonate (S) anions, extensively studied by Ward and co-workers and also by Masson and co-workers.[8,9] In contrast to $[\mathrm{M}^{n+}(\mathrm{XO}_3{}^{m-})_{n/m}]$ systems, the organic pillars in GS networks are oriented in a less densely packed manner, a result of the larger size of a guanidinium cation relative to a metal ion, which allows for guest inclusion in the interlayer region (Figure 1c). The vast array of inclusion phenomena observed for this family of compounds (> 350 structures) owe their existence to the ability of the GS framework to adjust to different guests by puckering of the layers and "turnstile-like" rotation of the pillars. The insights provided by this library have enabled the generation a framework containing highly ordered polar guest molecules for nonlinear optical applications.[8b] Our approach, shown in Figure 1d, extends our recent work on second-sphere aqua complexes of organosulfonate ligands[10] and represents an inorganic analogue of guanidinium sulfonates. In essence, an octahedral hexaamine metal complex should provide two triangular triamine faces with divergent N−H bonds to act as hydrogen-bond donors. Thus, each face would be similar to a guanidinium cation and could possibly form highly complementary hydrogen-bond pairs with sulfonate anions. Significantly, the larger radius of a second-sphere complex relative to a single metal ion would further distance the pendant organic groups on the sulfonates and facilitate guest inclusion. Herein, we present two complexes, formed from $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ and disulfonate anions, which form pillared layered structures and include guest molecules, $[\{[\mathrm{Co(NH_3)_6Cl}](\mathrm{PIPES})(\mathrm{H_2O})_6\}_\infty]$ (**1**, PIPES = 1,4-piperazinebis(ethanesulfonate) and $[\{[\mathrm{Co(NH_3)_6}](\mathrm{NDS})_{1.5}(\mathrm{H_2O})_2(\mathrm{dioxane})\}_\infty]$ (**2**, NDS = 2,6-naphthalenedisulfonate). The networks are sustained by charge-assisted hydrogen bonding and show two different assembly motifs, one based on the complementarity of the edges of the triangular triamine faces with sulfonate groups, this is the GS analogue, and the other on hydrogen-bond complementarity with the centroids of the triangular faces.

Compound **1** forms a hexagonal hydrogen-bonding motif with complementarity between the periphery of the triangular $\{\mathrm{Co(NH_3)_3}\}$ faces and two sulfonate oxygen atoms as shown in Figure 2a and b.[11] The N···O hydrogen bonds between the amine groups and sulfonate ions are in the range 2.94–3.17 Å with N−H···O angles between 128–167°. The $[\mathrm{Co(NH_3)_6}]^{3+}$ ions align in a plane with their C_3 axes perpendicular to the layer. The layers in **1** are pillared by the bis(ethyl)piperazine moieties at a distance of 14.12(1) Å. The distances between neighboring S atoms, which anchor the pillars, in a given layer are between 7.376(3)–7.975(3) Å. Thus, this structural motif is well organized for guest inclusion. The greater separation between pillars allows for the inclusion of approximately 7.5 molecules of water in the interlayer region for each disulfonate unit. With the substitution of guanidinium cations for the pyramidalized $\{\mathrm{Co(NH_3)_3}\}$ units, this hydrogen-bonding motif is identical to that observed in GS networks. For an octahedral hexaamine metal complex to function as two (monovalent) guanidinium cations and form a similar hydrogen-bonding motif with sulfonate anions, the metal ion would be expected to be divalent. Interestingly, with respect to its hydrogen-bonding pattern, the Co^{3+} center in structure **1** behaves effectively as a divalent center by the incorporation of a chloride ion which "nests" atop one triamine face of each metal complex (Figure 2c). The N···Cl hydrogen bonds between the amine groups and chloride ions are between 3.32–3.35 Å.

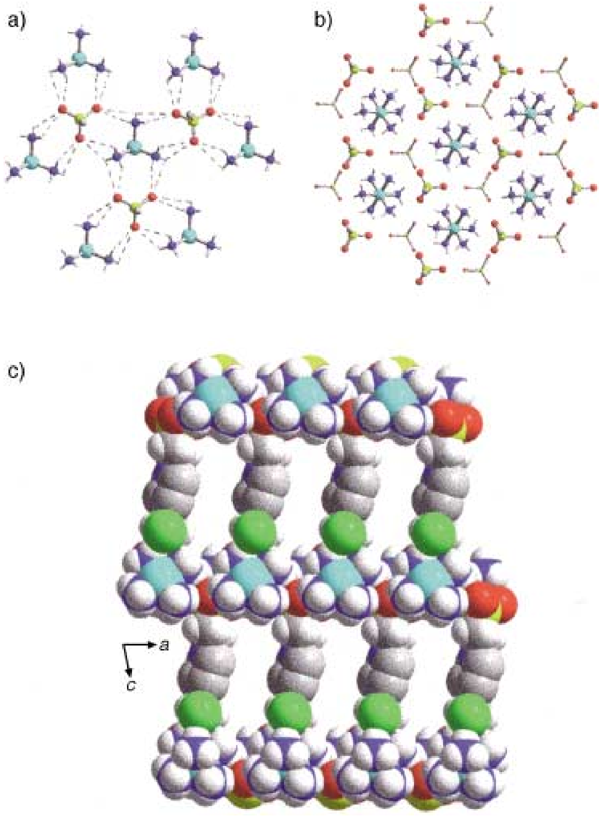

Figure 2. Structure of **1** showing: a) the hydrogen-bonding pattern about each triangular $\{\mathrm{Co(NH_3)_3}\}$ face, b) the hexagonal assembly of a single layer, and c) space-filling representation, perpendicular to the layers, showing the spatial arrangement of the pillars and the "nesting" of the Cl^- ions (green). One $\mathrm{NH_3}$ molecule in the top layer (to show the Co centers) and guest water molecules have been deleted. Co light blue, N dark blue, S yellow, O red, H gray.

Compound **2** also forms a perfectly flat layered structure based upon hydrogen bonding between $[\mathrm{Co(NH_3)_6}]^{3+}$ units and pillaring sulfonate anions.[12] In this case, with a 2,6-naphthyl unit as the pillar, no chloride ion is incorporated and the hydrogen-bonding complementarity is shifted. In **2**, the metal octahedra align with their C_4 axes perpendicular to the layers (Figure 3a and 3b). The predominant hydrogen-bonding interaction of each $[\mathrm{Co(NH_3)_6}]^{3+}$ unit with neighboring sulfonate groups is then between the centroids of each triangular triamine face and single sulfonate oxygen atoms (N···O distances from 2.90–3.33 Å with N−H···O angles from 112–163°). The layers in **2** are separated at a distance of 13.987(6) Å by the naphthyl spacers, which is half the length of the *a* axis. As in **1**, the second-sphere approach results in the orientation of the organic pillars in a less densely packed

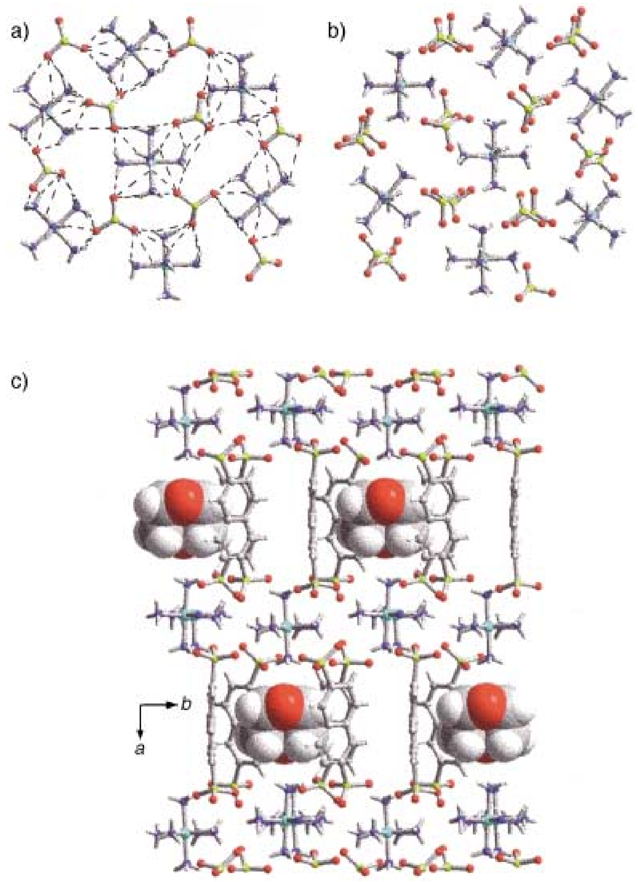

Figure 3. Structure of **2** showing: a) the hydrogen-bonding pattern about the fourfold axis of each $[Co(NH_3)_6]$ octahedron, b) the view down onto a single layer, c) the view perpendicular to the layers showing the 2,6-naphthyl pillars and, in space-filling representation, the included dioxane molecules. Colors as in Figure 2.

manner to enable guest inclusion. In **2**, two molecules of water and one dioxane molecule are included for each 2,6-naphthyl unit (Figure 3c).

Thermogravimetric analyses (TGA) and powder X-ray diffraction (PXRD) data of the two structures show very different features. The PXRD studies confirmed that bulk powders of both compounds **1** and **2** were indeed the same phases as those observed in the respective single-crystal structures. In the TGA, **1** shows a fairly rapid mass loss from 25–60 °C, which corresponds to the loss of the guest water molecules from the interlayer region. A steadier decline in mass is then observed from 60–200 °C. The PXRD of **1** revealed changes in intensities but not in peak positions upon drying for 44 h at room temperature (or for 30 min at 50 °C). In both these cases, exposure to water vapor generated a solid with the same PXRD as the original solid. Heating **1** to 140 °C for 30 min gave a PXRD pattern with weak signal relative to the background albeit with small peaks which did correlate with the original sample. At this temperature, as supported by the TGA data, NH_3 is being lost from the primary coordination sphere, which results in the disruption of the hydrogen-bonded framework. In this case, resolvation did not regenerate the original PXRD pattern. In light of the behavior of **1**, the results for 2,6-naphthyl analogue are quite striking (see below).

PXRD studies of a bulk aqueous precipitate from sodium 2,6-naphthalenedisulfonate and $[Co(NH_3)_6]Cl_3$ in the absence of dioxane showed this sample to possess the same framework as that of structure **2**. Figure 4a and b show the simulated PXRD pattern from **2** and the pattern for the dioxane-free bulk precipitate **2a**, respectively. Compound **2a** is formulated as $[\{[Co(NH_3)_6](NDS)_{1.5}(H_2O)_x\}_\infty]$ (**2a**). As a sufficient quantity of **2** in single-crystal form was not obtainable for all required TGA and PXRD experiments, further characterization was performed on the bulk aqueous precipitate, **2a**.[13] TGA measurements reveal that **2a** loses included water molecules up to roughly 100 °C. From this temperature, the compound is completely stable until loss of the coordinated NH_3 molecules at about 270 °C. As shown in Figure 4c, a PXRD pattern of **2a** acquired after heating to 140 °C for 90 min is virtually identical to the original solid, not only with respect to the positions of the peaks, but also the sharpness of the lines. Remarkably, the differential scanning calorimetry

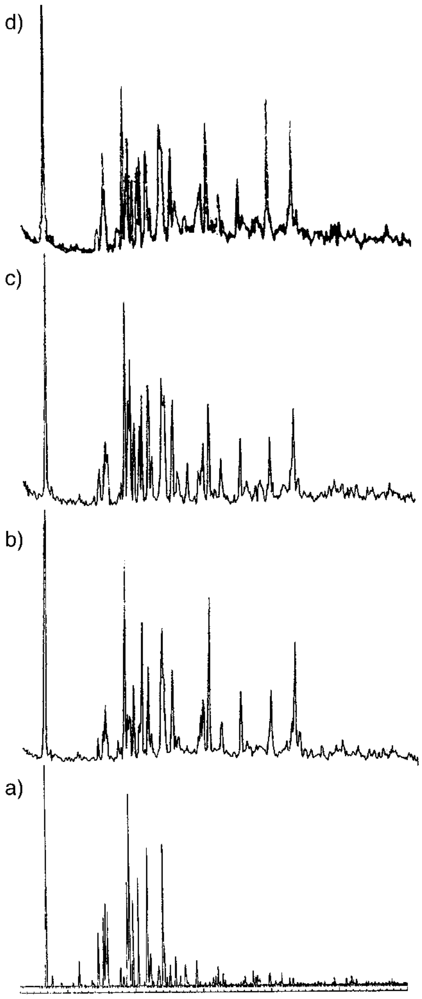

Figure 4. a) PXRD simulation from the single-crystal data of **2**. PXRD data of compound **2a**, b) run at room temperature without drying, c) run after heating at 140 °C for 90 min, DSC/TGA indicate this phase persists until ≈270 °C, and d) after resolvation of the sample in (c) with water.

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(DSC)/TGA data indicate that this phase is stable until around 270 °C. For a sample sustained by charge-assisted hydrogen bonding, this is a surprising degree of stability. Upon resolvation of the heated sample with water, there is again little change in the observed PXRD pattern (Figure 4 d).

The difference in stability of compounds **1** and **2a** can be rationalized by two factors. The first is the nature of the pillaring group. In compound **2a**, the 2,6-naphthyl unit is much more rigid as it has a fused aromatic skeleton and is locked into a plane with the sulfonate groups perfectly antiparallel. Thus, one sulfonate group in a highly favorable hydrogen-bonding orientation with a layer would necessarily orient the other sulfonate group in a similar manner with the next layer resulting in a mutual stabilizing effect. We have documented these effects for the stabilization of a primary hexaaqua coordination sphere.[10] In comparison, the bis(ethyl)piperazine unit in **1** is a not-at-all rigid pillar and the enhanced stabilization effects through cooperative bonding by the disulfonates are not optimized. Second, in **1**, in addition to the sulfonate anions, there is incorporation of a chloride ion which also hydrogen bonds to the amine groups of the Co^{3+} center. This interaction would serve to neutralize some of the positive charge on the metal amine unit. Thus, effectively, the hydrogen bonds to the sulfonate groups in **1** are not as charge-assisted as those in **2**.

The compounds presented here, beyond being two examples of supramolecular inclusion compounds, are members of an entire new family of hosts.[14] Significantly, these compounds can be considered as inorganic analogues of guanidinium sulfonates, the single most structurally characterized supramolecular host family.[1,8] The breadth of structures possible with the second-sphere approach should, in principle, be even greater than with the GS structures. This statement is based on the fact that all the pillaring options with the GS structures are equally available to be employed with the second-sphere approach, however, both the identity and charge of the metal center can also be varied. As may be discerned from the structure of compound **1**, the GS motif should also occur for divalent hexaamine metal centers.

Experimental Section

1: The Na salt of piperazinebis(ethanedisulfonate) (292 mg, 0.843 mmol) and hexaamminecobalt(III) chloride (150 mg, 0.561 mmol) were dissolved separately in a minimum amount of water. The dissolved components were added to 10-mL round-bottom flask and stirred at room temperature for 12 h. The pale yellow solid which precipitated was collected by filtration and dried. Yield: 0.246 g, 0.320 mmol (77 % with respect to Co). Crystals suitable for an X-ray analysis were grown by slow evaporation of an aqueous solution. Elemental analysis calcd (%) for $C_8H_{34}ClCoN_8O_6S_2$ (dehydrated) C 18.17, H 6.46, N 21.19; found C 18.46, H 7.01, N 20.54. IR (KBr): $\tilde{\nu} = 3448, 3261, 1356, 1326, 1250, 1211, 836, 587\ cm^{-1}$.

2: The Na salt of naphthalene-2,6-disulfonate (200 mg, 0.602 mmol) and hexaamminecobalt(III) chloride (107 mg, 0.401 mmol) were dissolved separately in water (25 mL). The dissolved components were placed in a H-tube and pure water added to fill the linking bridge. A small amount of p-dioxane was added to the H-tube and the tube allowed to stand at room temperature. A small sampling (≈10) of light brown crystals of **2** suitable for an X-ray analysis were observed after 10 days. Elemental analysis calcd (%) for $CoS_3O_{11}N_6C_{19}H_{35}$: C 32.16, H 4.92, N 13.24; found C 32.61, H 4.97, N, 13.26. IR (KBr): $\tilde{\nu} = 3295, 1330, 1306, 1224, 1179, 1087, 1032, 869, 662, 544\ cm^{-1}$.

The differences in O and H stoichiometries between samples employed for elemental analyses and the crystal data reflect loss of water and that the H atoms on the free water molecules in the channels were not included in the single-crystal refinement.

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[11] Crystal data for **1**, $[\{[Co(NH_3)_6Cl](PIPES)(H_2O)_6\}_\infty]$: $C_8H_{38}ClCoN_8O_{12}S_2$: M_r596.96, triclinic, space group $P\bar{1}$ (No. 1), $a = 7.247(1)$, $b = 7.281(1)$, $c = 14.493(3)$ Å, $\alpha = 78.62(3)$, $\beta = 83.60(3)$, $\gamma = 69.40(3)°$, $V = 701.0(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.414\ Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 0.915\ mm^{-1}$, crystal size $0.01 \times 0.01 \times 0.02$ mm. Data were collected on a Nonius Kappa CCD diffractometer using $Mo_{K\alpha}$ radiation. A total of 4939 reflections ($1.43° < \theta < 26.03°$) were processed and considered significant with $I_{net} > 2\sigma(I_{net})$. Structure solution, refinement and molecular graphics were carried out with the SHELXTL software package, release 5.1.[15] Final residuals for $I_{net} > 2\sigma(I_{net})$ were $R1 = 0.0606$

and $wR_2 = 0.1545$ (GoF = 1.088) for 258 parameters. CCDC-194474 (**1**) CCDC-194475 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[12] Crystal data for **2**, $[\{[Co(NH_3)_6](NDS)(H_2O)_2(dioxane)\}_\infty]$: $C_{19}H_{35}CoN_6O_{12.25}S_3$, $M_r = 698.64$, monoclinic, space group $C2/c$ (No. 15), $a = 27.973(6)$, $b = 12.701(3)$, $c = 15.338(3)$ Å, $\alpha = \gamma = 90$, $\beta = 113.14(3)°$, $V = 5011(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.852$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.016$ mm^{-1}, crystal size $0.01 \times 0.015 \times 0.02$ mm. Data were collected on a Nonius Kappa CCD diffractometer using $Mo_{K\alpha}$ radiation. A total of 20678 reflections ($3.12° < \theta < 27.72°$) were processed of which 5775 were considered significant with $I_{net} > 2\sigma(I_{net})$. Structure solution, refinement and molecular graphics were carried out with the SHELXTL software package, release 5.1.[15] Final residuals for $I_{net} > 2\sigma(I_{net})$ were $R1 = 0.0428$ and $wR_2 = 0.0875$ (GoF = 1.004) for 340 parameters.[12]

[13] This is because crops of single crystals of **2** were grown by diffusion in H-shaped tubes. Each preparation yielded no more than 8–10 small crystals.

[14] To date, we have characterized some 20 members of this family. Whereas the hydrogen-bonding patterns observed are not as regular as with the GS networks (some incorporate Cl^- ions and adopt C_3-symmetric structures and others adopt the C_4 orientation) the structures are all 2D. A more extensive study will be reported as a full paper in due course.

[15] SHEXTL Version 5.1, Bruker AXS Inc., Madison, Wisconsin, **1997**.