

Selective guest inclusion in a non-porous H-bonded host

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A hydrogen-bonded host solid demonstrates reversible and selective guest inclusion, despite not having a porous interlayer.

Inclusion complexes based on components self-assembled by weak interactions possess features not found in more rigidly-bonded solids. Primary among these is the ability to shift structure such that what is formulaically the same host can adjust to accommodate a range of guest molecules. This is a phenomenon commonly observed for systems such as cholic acid,¹ Dianin's compound² and, as recently shown, *tert*-butylcalixarene.³ Two-component host systems have been developed and assembled by complementary H-bonding. Prime examples in this group would be guanidinium sulfonates⁴ and secondary ammonium carboxylates.⁵

We have reported two examples of layered hosts based on complementarity between the second coordination sphere of hexamine metal ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ and sulfonate anions.⁶ Two general structural types occur in this family; one where the Co octahedron adopts a local C3 orientation and H-bond complementarity with the RSO_3 groups is with the edges of a triangular face, and the other where the octahedron adopts a local C4 orientation and the RSO_3 groups are complementary to the triangular faces themselves. Both orientations are capable of including guests. For any inclusion system, a fundamental issue is the ability of the guest to percolate through the solid and the possibility of it being released or exchanged. This is intimately connected to the interactions binding the guest, but also the ability of the host to enable any required solid state dynamics. The present work concerns a member of the metal amine sulfonate host family which has a *non-porous* interlayer region but is also able to reorient and selectively absorb aniline and derivatives thereof.

$\{[\text{Co}(\text{NH}_3)_6](\alpha,\alpha'\text{-para-xylenedisulfonate})_{1.5}(\text{H}_2\text{O})_2\}$ (**1**) was formed by combining aqueous solutions of $[\text{Co}(\text{NH}_3)_6]\cdot 3\text{Cl}$ and disodium $\alpha,\alpha'\text{-para-xylenedisulfonate}$. The orange-colored precipitate that formed was dissolved with boiling in a minimal amount of H_2O and then slowly cooled to room temperature to yield orange single crystals. The structure of **1**† shows a pillared, layered solid where $\text{Co}(\text{NH}_3)_6$ octahedra, aligned along their C4 axes, hydrogen-bond with four neighboring sulfonate groups to form layers. The layers are pillared by the *para*-xylene linkers at a perpendicular distance of 12.74(1) Å. Fig. 1a shows the clear segregation of the solid into domains of hydrophilic (the H-bonded metal complex/sulfonate layer) and hydrophobic nature (the organic interlayer). Fig. 1b shows the composition of a single hydrophilic layer. The layers are stitched together by a myriad of H-bonds. There are two crystallographic types of Co complex,

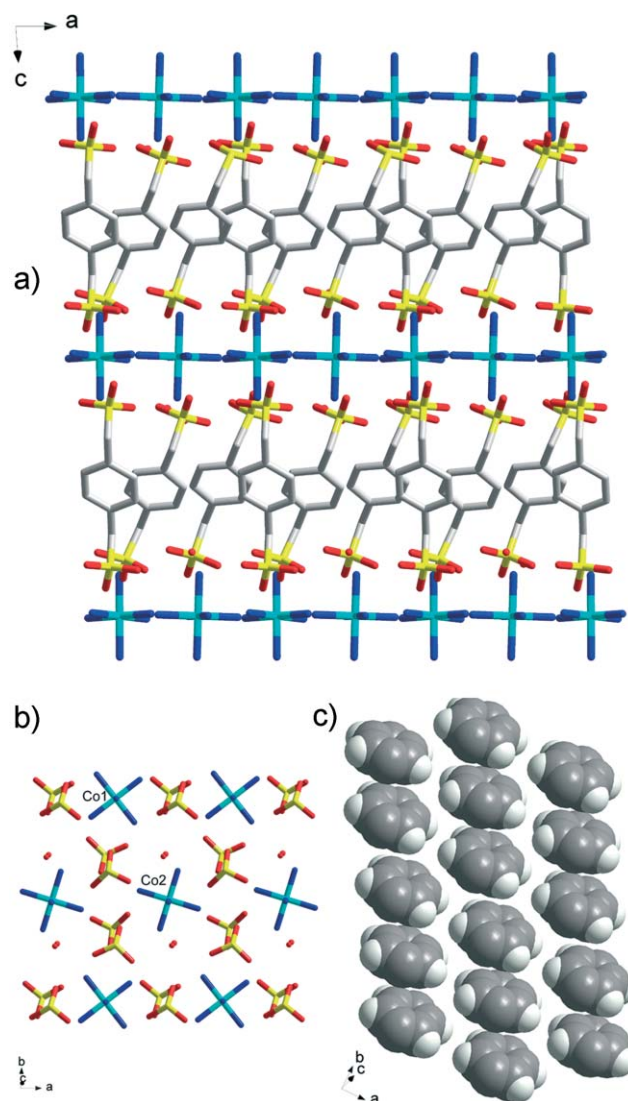


Fig. 1 X-Ray structure of the pillared, layered solid **1**. (a) View parallel to the layers. (b) View onto a single H-bonded layer with $\text{Co}(\text{NH}_3)_6$ centers aligned along their C4 axes. (c) Space-filling view showing the non-densely packed aryl rings of the disulfonate pillars in the interlayer. The middle column contains two repeating trimer 'ABA' motifs.

with half of each complex being unique. The Co1 complex forms a total of 26 H-bonds ($\text{N}-\text{O} = 2.884(5)\text{--}3.384(6)$ Å) exclusively to sulfonate oxygen atoms. Of these, four O atoms from four different SO_3 groups form H-bonds to the equatorial N1 and N3, and five from three different SO_3 groups to the axial N2. The Co2 complex forms 24 H-bonds ($\text{N}-\text{O} = 2.882\text{--}3.316$ Å) to both sulfonate groups and water molecules. The equatorial N5 forms

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four H-bonds to oxygen atoms from four different SO_3 groups, while the equatorial N4 and axial N6 both form two H-bonds to sulfonate oxygens from two different SO_3 groups and two H-bonds to the included water molecules. In the interlayer, two types of *para*-xylene unit exist and they are tilted from the vertical by 39.1° and 47.0° , respectively. The overall structure represents a compromise between the assembly of H-bonded layers and interactions between aryl groups of the *para*-xylene pillars. In this case, the H-bonded sheets dominate the structure as, despite the density of aryl rings in the interlayer, strong π -stacking interactions do not exist. Fig. 1c shows a space-filling representation of the benzene cores of the pillars. There are two unique rings which are arranged in a repeating 'ABA' fashion. Within each trimer, there is a slight overlap of single edges of adjacent rings at a mean distance of $3.52(1)$ Å. Between trimeric units, the shortest contact is between C6 vertices of 'A' rings at $3.780(7)$ Å. The pillaring rings are oriented such that no channels exist in the solid. While this is not an efficiently stacked interlayer, it would certainly not be deemed porous by any standards.

$\{[\text{Co}(\text{NH}_3)_6](\alpha,\alpha'\text{-para-xylenedisulfonate})_{1.5}(\text{aniline})(\text{H}_2\text{O})_3\}$, (**2**) differs from **1** by solvation only. Aniline is included in the solid both by π -stacking and H-bonding, and **2** is also more hydrated than **1**. Bulk quantities of **2** were prepared by dissolving **1** in boiling H_2O and adding an excess of aniline. Upon slow cooling of this orange-brown solution, single crystals formed.† As will be shown, **2** can also form from crystals of **1**. Fig. 2a shows that **2** is also a pillared, layered solid but with aniline molecules incorporated between the *para*-xylene units at a stoichiometry of one aniline molecule for every three *para*-xylyl pillars. The pillars have adopted a more vertical alignment, and this is reflected in an increase in the perpendicular layer spacing to $13.55(1)$ Å (*cf.* 12.74 Å for **1**). There is also increased hydration in the hydrophilic layers (Fig. 2b) as three molecules of water are incorporated for each Co center. Within each layer there are four types of Co center. Similarly to **1**, each metal complex forms a multitude of H-bonds. The hexaamine complexes of Co1 and Co3 exist in fully sulfonated domains, the complexes forming 28 (N–O = $2.914(7)$ – $3.364(8)$ Å) and 26 (N–O = $2.892(8)$ – $3.267(8)$ Å) H-bonds, respectively, exclusively to sulfonate O atoms. The hexaamine complexes of Co2 and Co4 exist in more hydrated domains. The complex of Co2 forms eight H-bonds to sulfonate O atoms and 16 H-bonds to water molecules. Similarly, the Co4 complex forms 10 H-bonds to sulfonate O atoms and 12 H-bonds to water molecules. The interlayer region is more densely packed in **2** than **1**, as would be expected with the incorporation of aniline guests (Fig. 2c). All aryl units in the interlayer region align in rows along the plane of the aryl rings (left to right in Fig. 2c). These rows are staggered and tilted, such that half of each face overlaps with the adjacent row of aryl rings (vertically in Fig. 2c). The tilt angle of the aniline relative to the Co layers is 52.9° , whereas the xylyl groups range from 57.0 – 61.2° . For each aniline guest, this results in four π -interactions with neighboring xylyl groups (C–C = $3.371(9)$ – $3.436(9)$ Å). For the two types of xylyl pillars, one has partial overlap with four other xylyl rings (C–C = $3.431(8)$ and $3.489(8)$ Å) and the other forms four partial overlaps with two xylyl rings and two aniline molecules (C–C = $3.371(9)$ – $3.498(8)$ Å). The aniline amino group also forms two H-bonds with sulfonate O atoms (N–O = $2.958(6)$ and $3.284(7)$ Å) that further augment the π -stacking interactions.

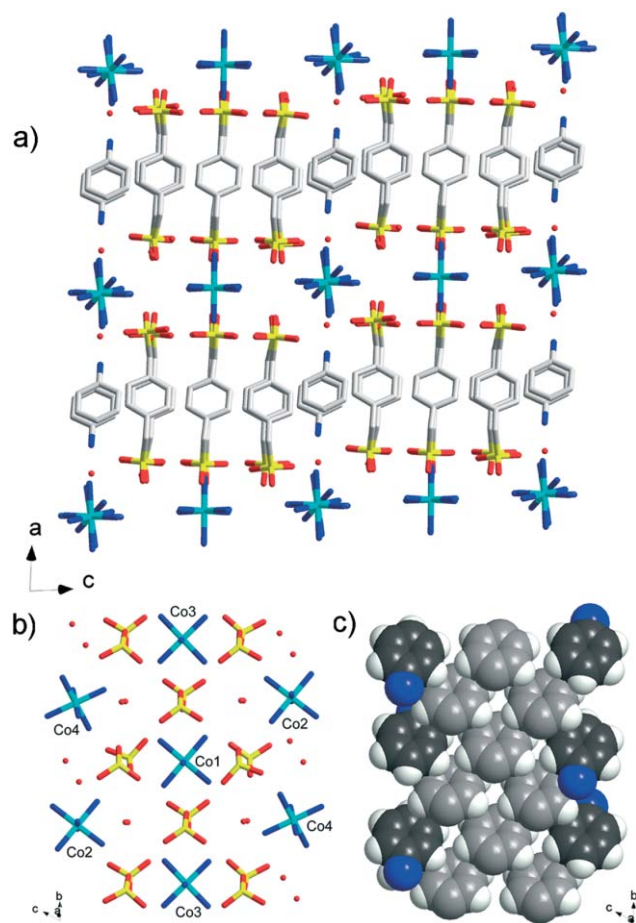


Fig. 2 X-Ray structure of compound **2**. (a) View parallel to the layers. The aniline guests appear above and below some Co centers and alternate in their orientation. Red dots are water molecules. (b) View onto a single H-bonded layer with $\text{Co}(\text{NH}_3)_6$ centers aligned along their C4 axes. Aniline molecules sit above the Co2 and Co4 centers. (c) Space-filling view of the interlayer showing the pillars packing with aniline guests (darker grey).

The ability of structures **1** and **2** to interconvert was examined through the powder X-ray diffraction experiments summarized in Fig. 3. The low angle peaks, relating to interlayer distances, are particularly diagnostic. Fig. 3a and Fig. 3b show powder patterns for **1** and **2**, respectively. Compound **1**, even if immersed in aniline (A), excludes it and remains as **1** (Fig. 3c). Desolvation of **1** and **2** by heating at 150°C for 12 h brings about a conversion to the same dehydrated phase, compound **0** (Fig. 3d). If exposed to water vapor (W), compound **0** readily converts to the hydrate **1** (Fig. 3e). If immersed in aniline, compound **0** excludes it (Fig. 3f), as did the pre-formed hydrate. However, interestingly, if the fully dehydrated network **0** is immersed in aniline with an atmosphere of moist air, conversion to compound **2** occurs readily (Fig. 3g). This transformation can also be brought about by both aniline and water as vapors.

The most unusual observations concern aniline uptake. Desolvated network **0**, with a powder pattern very similar to the hydrate **1**, does not absorb aniline, even upon immersion. More surprising is the fact that the hydrated network **1** does not also take up aniline to form the aniline/hydrate complex **2**. However, if both aniline and water vapor are present, compound **2** forms readily. The implication of this data is that there is some

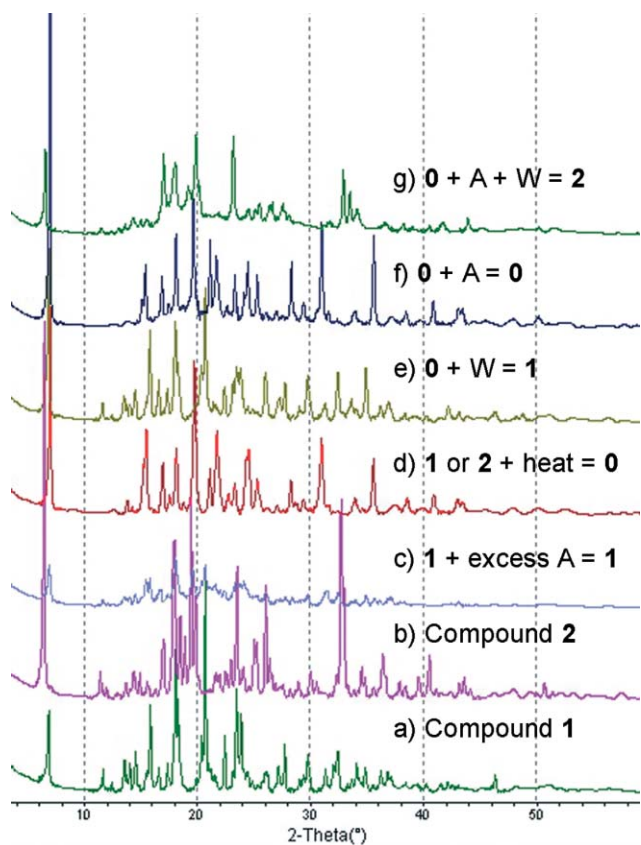


Fig. 3 Powder X-ray diffraction patterns of the relations between compounds **1**, **2** and the desolvated phase **0** with aniline (A) and water vapor (W).

cooperative mechanism, involving both water and aniline, that allows the network to take up aniline. Evidence corroborating this observation can be seen upon closer examination of the single crystal structure of **2**. As mentioned, there are two Co centers in **2** that H-bond exclusively to SO₃ groups and two others which are more hydrated. The hydrated [Co(NH₃)₆]³⁺ centers, Co2 and Co4, in the hydrophilic layers are found exactly above and below the aniline molecules (Fig. 2a), and one molecule of water H-bonds to the aniline amino group. Given that there is no obvious porosity in **1**, and that the desolvated form **0** would be expected to be more dense, guest uptake by this system requires rearrangement of the components. In the conversion of **0** to **2**, this can be viewed as arising from multiple factors operating cooperatively. Strong H-bond interactions in the host are compromised when aniline is included. These interactions are then compensated-for by a combination of a more efficient π -stacking in the interlayer as well as the H-bonds formed between the host and aniline amino group. The inclusion of aniline results in a more diffuse layer structure, since in **1**, a positive charge is accommodated for every 16.50 Å², whereas this value becomes 19.95 Å² in **2**. This additional area is then compensated-for by the inclusion of the extra molecule of water. While an open framework structure is key to the functional porosity of strongly bonded network solids (e.g. zeolites), inclusion in non-porous solids has been observed in more weakly bonded network solids. Atwood *et al.*^{3a} and Ripmeester *et al.*^{3b} have independently examined the structural transformations that take place as dense *para-tert*-butylcalix[4]arene rearranges to

accommodate guests. In that case, van der Waals interactions were the contacts being compromised and formed.

Given the exactness of the fit of the guest aniline molecules in **2**, the selectivity of uptake of other guests was examined using direct treatment of **0** with various guests in the presence and absence of water vapor. Simple aromatic guests such as benzene and toluene were not included. The derivatized aromatics chlorobenzene, benzonitrile, nitrobenzene and benzyl chloride were also not included. In fact, based on PXRD experiments, only amines are absorbed by the host. The PXRD pattern of the complex of 1,4-phenylenediamine closely matched that of **2**. Varying the breadth of the aryl group did affect the uptake of guest since 3-methylaniline was absorbed, again giving a PXRD pattern similar to that of **2**, while the broader 3,5-dimethylaniline was excluded.

We have reported a host network which can selectively uptake guest molecules, despite not having a porous structure. This inclusion is enabled by a rearrangement mediated by cooperative H-bond interactions between metal hexaamine complexes and organosulfonate ions. Work on the tunability and inclusion properties of second sphere networks is continuing in our group.

Notes and references

† Data for **1** and **2** were collected on a Nonius Kappa CCD diffractometer using Mo-K_α radiation. Structures were solved by direct methods and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.⁷ For **1**, {[Co(NH₃)₆](α,α' -*para*-xylenedisulfonate)_{1.5}(H₂O)₂]_∞: C₁₂H₂₅CoN₆O₁₁S₃, $M = 584.49$, triclinic, space group P-1 (no. 2), $a = 7.5100(2)$, $b = 13.2100(3)$, $c = 13.8450(4)$ Å, $\alpha = 63.9100(11)$, $\beta = 84.7360(11)$, $\gamma = 86.8150(18)^\circ$, $V = 1228.19(6)$ Å³, $Z = 2$, $D_c = 1.580$ mg m⁻³, $\mu(\text{Mo-K}\alpha) = 0.508$ mm⁻¹, crystal size $0.4 \times 0.4 \times 0.2$ mm. A total of 5586 reflections ($1.22^\circ < \theta < 26.42^\circ$) were processed, of which 4021 were unique and considered significant with $I_{\text{net}} > 2\sigma(I_{\text{net}})$. Final residuals for $I_{\text{net}} > 2\sigma(I_{\text{net}})$ were $R = 0.0429$ and $R_w = 0.1188$ (GoF = 1.058) for 301 parameters. For **2**, {[Co(NH₃)₆](α,α' -*para*-xylenedisulfonate)_{1.5}(aniline)(H₂O)₃]_∞: C₃₈H₈₄Co₂N₁₂O₁₈S₆, $M = 1302.17$, triclinic, space group P-1 (no. 2), $a = 14.567(5)$, $b = 15.427(5)$, $c = 15.552(5)$ Å, $\alpha = 60.837(5)$, $\beta = 74.578(5)$, $\gamma = 66.910(5)^\circ$, $V = 2795.2(16)$ Å³, $Z = 2$, $D_c = 1.553$ mg m⁻³, $\mu(\text{Mo-K}\alpha) = 0.896$ mm⁻¹, crystal size $0.45 \times 0.15 \times 0.2$ mm. A total of 12781 reflections ($1.22^\circ < \theta < 26.42^\circ$) were processed, of which 5800 were unique and considered significant with $I_{\text{net}} > 2\sigma(I_{\text{net}})$. Final residuals for $I_{\text{net}} > 2\sigma(I_{\text{net}})$ were $R = 0.0592$ and $R_w = 0.1385$ (GoF = 1.054) for 694 parameters. CCDC 289134 (**1**) and 289135 (**2**). For final atomic coordinates, thermal parameters and complete listings of bond lengths and angles in CIF or other electronic format see DOI: 10.1039/b515735h

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