

A thermally stable nanoporous nickel 5-sulfoisophthalate; crystal structure and adsorption properties†

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A 3D nanoporous nickel 5-sulfoisophthalate coordination polymer with a high surface area ($>700 \text{ m}^2 \text{ g}^{-1}$) has been synthesized hydrothermally and studied using single crystal and variable-temperature powder XRD, TGA, and BET porosimetry.

Hybrid coordination polymers with solvent accessible cavities show considerable promise for catalysis,¹ adsorption,² and chemical sensing.³ For the synthesis of new frameworks with open topologies, particular attention has been paid to rigid organic linking units with symmetrical geometries,⁴ such as trimesate.⁵ We have recently begun investigating metal 5-sulfoisophthalates (SIPA) in the expectation that this ligand may lead to new compounds structurally similar to trimesates. Nickel was selected based on our previous investigations that suggest high thermal stability in nickel hybrid materials.⁶ Here, we report $\text{NaNi}_3(\text{SIPA})_2(\text{OH})\cdot(\text{H}_2\text{O})_5\cdot\text{H}_2\text{O}$ (**1**), a novel 3D nanoporous material based on a unique hexameric cluster of Ni octahedra linked by SIPA anions. The compound, stable to 350 °C, shows surface areas in excess of $700 \text{ m}^2 \text{ g}^{-1}$ and dehydration–rehydration behavior. To our knowledge, only a few copper⁷ and cadmium⁸ hybrids containing the SIPA building unit are known.

1 was prepared hydrothermally‡ and the structure solved by single crystal XRD.§ The structure may be described as isolated clusters bridged into a three-dimensional coordination polymer through SIPA. S-shaped cavities running along the *c*-axis contain coordinated water molecules directed towards the cavity, which also contains uncoordinated water molecules (Fig. 1). The clusters consist of two Na and six Ni atoms octahedrally coordinated to carboxylate, sulfonate, μ_3 -hydroxide, and water oxygen atoms. While the Ni octahedra are regular, the Na octahedron is highly distorted, with O–Na–O angles ranging from 67.25(7) to 117.56(9)°, and bond lengths ranging from 2.326(2) to 2.754(4) Å.

An advantage of the SIPA ligand is the possibility that the sulfonate group may promote novel modes of coordination

compared to carboxylate groups, as observed in the case of copper.⁷ In the case of **1**, several differences in coordination between the sulfonate and carboxylate are evident. The carboxylate groups coordinate primarily to nickel centers, with the four crystallographically independent carboxylate groups coordinating Ni atoms through nine unique Ni–O bonds compared with only one Na–O bond. All but one of the eight unique carboxylate oxygen atoms coordinate to metal centers. By contrast, the two unique sulfonate groups coordinate primarily to the harder Na cations over Ni (3 Na–O bonds compared to 2 Ni–O bonds). Additionally, 1/3 of the sulfonate oxygen atoms do not coordinate to a metal center, but are instead involved in hydrogen-bonding interactions. Non-coordinating carboxylate oxygen atoms are less common for hydrothermally prepared transition metal carboxylates.⁹ This apparent tendency for sulfonate groups to preferentially coordinate with harder cations and to hydrogen bond with water molecules may aid in the design of more complicated hybrid systems than are possible with trimesate.

The three uncoordinated sulfonate and carboxylate oxygen atoms play an important structural role by participating in a number of hydrogen bonds. **1** contains three unique water molecules that coordinate to Ni(II) atoms (an average of 1 per nickel site), two distinct water molecules that coordinate with the Na(I) cation, and an uncoordinated water molecule. Of the two water molecules coordinating to the sodium cation, there is a dramatic difference in Na–O separation: 2.396(3) Å vs. 2.754(4) Å. The difference appears to result from the involvement of the closer water molecule in a moderately strong hydrogen bond (O–O distance 2.736 Å) while the second water molecule is not involved in a hydrogen bond. Presumably the hydrogen-bonding interaction results in a higher negative charge on the oxygen atom of the water molecule, leading to a much shorter bond.

Two of the water molecules coordinate to single nickel atoms and are involved in typical hydrogen-bonding interactions with free sulfonate oxygen atoms and a water molecule. The third water molecule bridges two nickel centers and has an unusually short hydrogen bond (O–O distance 2.498(6) Å). Given the high acidity of protons on a μ_2 water molecule and the relative basicity of terminal carboxylate oxygen atoms, it is reasonable to expect a very strong hydrogen bond, explaining the short O–O distance. Similar hydrogen bonding between terminal carboxylate oxygen atom and bridging water molecules has been noted in an open-framework cobalt 1,3,5-cyclohexanecarboxylate¹⁰ and an open-framework nickel cyclopropanate.¹¹ A more complete description of the structure is available as electronic supplementary materials.†

Based on the presence of hydrated channels in **1**, we studied the dehydration–rehydration properties. Thermogravimetric analysis under N_2 reveals four distinct weight losses. The first two losses correspond to the loss of all water molecules from the structure by 350 °C (calculated 13.3%, observed 12.3%), and the second two, beginning at 390 °C, correspond to incomplete pyrolysis of the organic ligand (calculated 55.2%, observed 39.3%). Although **1** is stable to 350 °C, TGA experiments show a very slow decomposition for samples held at this temperature (~5% weight loss per 12 h).

Since thermogravimetric analysis indicated that all of the water of hydration could be removed without decomposition of the

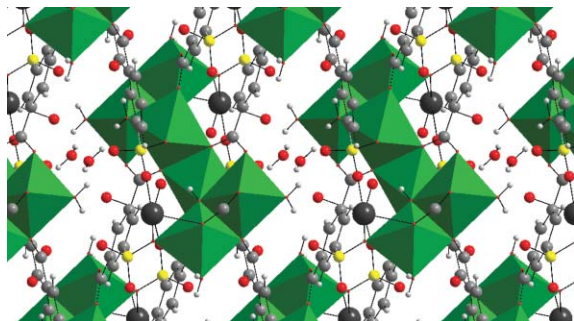


Fig. 1 The crystal structure of **1**, displaying pores with crystallographic water molecules along the *c*-axis. NiO_6 octahedra are represented in green, Na, O, S, and H atoms as dark grey, red, yellow, and grey balls.

† Electronic supplementary information (ESI) available: crystallographic description of **1**, additional figures, single crystal X-ray refinement experimental details and tables. See <http://www.rsc.org/suppdata/cc/b4/b408535c/>

organic ligand, we studied the re-adsorption of water and the adsorption of several organic solvents on samples dehydrated at 300 °C. **1** re-adsorbs water from the air and produces identical TGA traces to the as-synthesized material after at least two cycles. X-ray powder diffraction shows no obvious changes in the material aside from significant broadening of the peaks following rehydration. Methanol, 2-propanol, and acetonitrile are also adsorbed by the material, as verified by different weight loss percentages and temperatures according to TGA (Fig. 2). Following desolvation, these samples show similar water adsorption capacity.

The loss of coordinated water molecules causes **1** to change color from green to tan. Exposure of a dehydrated sample to air for a few minutes restores the original color, implying that the sample rehydrates very quickly. Although the crystal structure did not lead us to expect large pores, the very rapid rehydration prompted us to investigate the thermal behavior of **1** more carefully. Variable-temperature XRD, conducted under vacuum, indicates significant changes to the unit cell at low temperatures (electronic supplementary materials†). The appearance of a very large, low angle peak at higher temperatures suggests that significant structural changes occur, although they are not so drastic that the structure cannot be regenerated by rehydration. Nitrogen adsorption indicates no porosity following heating to 200 °C under vacuum, but high surface areas following heat treatments of 300 or 350 °C (743 and 640 m² g⁻¹, respectively).

These high surface areas, together with the very fast re-adsorption of water from the atmosphere, suggest that a structural rearrangement creates moderately sized pores upon the second step of dehydration. We note that the material obtained following the first dehydration step will readily re-adsorb water, but does not develop channels large enough for N₂ adsorption until the structure expands following the loss of coordinated water. The color change, loss of considerable amounts of coordinated water molecules, and two-step desorption mechanisms for coordinated solvents (particularly acetonitrile) strongly suggest the presence of unsaturated metal sites in the dehydrated phase. Given that the color returns to green on rehydration and that TGA curves for rehydrated samples have identical weight loss percentages and temperatures, it is clear that water recoordinates to Na and Ni sites during rehydration.

The powder diffraction pattern for the high temperature phase shows considerable broadening, but our attempts to index the data yielded a triclinic cell that is very similar to the hydrated cell. The lattice parameters indicate that the dehydrated phase is expanded 7.5% relative to the hydrated phase.§ A volume increase following dehydration is not at all unprecedented; for example, the “breathing” chromium terephthalate shows a 3.2% volume increase following the loss of water.¹²

To date, the major obstacle to the application of hybrid materials

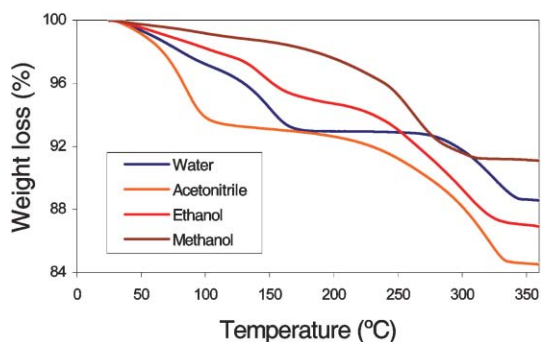


Fig. 2 TGA curves for different solvents adsorbed in **1**.

in catalysis has been their poor thermal stability.¹ **1** remains crystalline and porous up to at least 350 °C and may adsorb a variety of solvents with no loss in porosity. Furthermore, the presence of unsaturated nickel sites suggests that **1** is an interesting candidate for hydrogen storage.¹³ Finally, despite no suggestion of channels large enough to support porosity in the crystal structure, **1** shows remarkably high surface areas, suggesting that other apparently dense hybrid systems may be rendered porous on dehydration. We are currently assessing the catalytic and gas sorption properties of this compound and are actively working to prepare new SIPA-based hybrid materials.

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Notes and references

‡ Green crystals of **1** were prepared by reaction of 0.50 g Ni(OH)₂ (Alfa Aesar) and 0.729 g of the monosodium salt of 5-sulfoisophthalic acid (NaO₃SC₆H₃-1,3-(CO₂H)₂, Aldrich) in 1.0 g deionized water. Dropwise addition of 0.25 ml of a concentrated (37%) HCl solution was performed with manual agitation. This mixture was sealed in a Teflon-lined autoclave and heated at 180 °C for 2 days under autogenous pressure. The resulting product (yield: 62.7%, final pH of the solution ca. 3.5) was recovered by filtration, rinsed with water, and dried in air. X-Ray powder diffraction data collected from **1** indicate that the material is a single phase by comparison with a simulated powder diffraction pattern.

§ Crystallographic data of NaNi₃(SIPA)₂(OH)(H₂O)₅·H₂O: P $\bar{1}$, *a* = 9.833(2) Å, *b* = 11.107(2) Å, *c* = 12.615(3) Å, α = 74.884(3)°, β = 89.323(4)°, γ = 69.755(3)°, *V* = 1243.2(5) Å³, *Z* = 2, *D*_{calc} = 2.154 g cm⁻³, *T* = 293 K, *R* = 0.0299 [*I* > 2σ(*I*)], and 5513 independent reflections. Lattice parameters for the dehydrated cell: *a* = 10.76 Å, *b* = 10.98 Å, *c* = 12.21 Å, α = 83.10°, β = 81.95°, γ = 70.73°, *V* = 1331.05 Å³. Further information is available as electronic supplementary materials.† CCDC 241102. See <http://www.rsc.org/suppdata/cc/b4/b408535c/> for crystallographic data (excluding structure factors) in .cif or other electronic format.

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