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Three different pillared assemblies with abundant topological architectures based on 4-sulfobenzoic ligand

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HIGHLIGHTS

- Acetonitrile and propionitrile were obtained from the amination of glycerol.
- The parameters influencing the catalytic performance were studied thoroughly.
- The possible pathways for the generation of the products are given.
- The doping of potassium increases the BET surface of iron oxide based catalyst.
- The reasons for the deactivation of catalyst $Fe_{20}K_{0.2}/\gamma\text{-}Al_2O_3$ were revealed.

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ABSTRACT

One unprecedented three-dimensional 4-sbe complex $[K(4\text{-sbe})]_n$ (**1**) and two proton-transfer compounds of 4-Hsb with amines, named as $[(4\text{-Hsb})\cdot(NH_4)\cdot(H_2O)]_n$ (**2**) and $\{[(4\text{-Hsb})]_2\cdot(H_2bpe)\cdot 2(H_2O)\}_n$ (**3**) have been synthesized and characterized by single-crystal X-ray analyses, elemental analyses, IR spectra, TG analyses, and fluorescence studies, where 4-sbe is 4-sulfobenzoic ester, 4-Hsb is 4-sulfobenzoate monoanion and H_2bpe is protonated 1,2-bis(4-pyridyl)ethylene. All of the complexes share the common pillared architectures. Complex **1** is the first example of 4-sbe complexes with a 5-c bnn hexagonal BN net. In contrast, compounds **2** and **3** are two hydrogen-bonded 3D structures. In **2**, 4-Hsb ligands brace the adjacent layers constructed by NH_4^+ and water molecules through hydrogen bonds, generating a new 4, 5, 9-c 3-nodal net. In **3**, H_2bpe species further assemble the 2-D hydrogen-bonding network comprising of 4-Hsb and water molecules into a 3D InS net with channels. Basically, 4-sbe/4-Hsb either coordinates to metal centers or serves as hydrogen-bonding acceptors/donors giving 5, 9 and 4-connected nodes in the topological networks of compounds **1**–**3** respectively. Solid state properties such as luminescence and thermal stability of the complexes have been investigated.

1. Introduction

In recent two decades, network construction is an interesting topic in the pursuing of functional materials [1]. A large quantity of 1,4-benzenedicarboxylate (bdc) coordination polymers and organic compounds have been synthesized. A search of Cambridge Structural Database (Version 5.34; May, 2013 update; Allen, 2002) received 1719 hits concerning 1,4-bdc involved crystal structures, many of which displayed multiform layered networks for the bridging mode of the para-substituded carboxylate groups [2]. Actually, to some extent, the two carboxylate groups limit the construction of variable topologies which can be well compensated by the sulfonate group with very different coordination ability comparing to carboxylate. It bears a strong structural similarity with the phosphonate group $-PO_3$, which has been extensively studied owing to the regularity of assembling into layered networks with the M-PO_3 inorganic skeletons [3]. For example, the layered structures of guanidinium para-substituted benzenesulfonates $[C(NH_2)_3]^+(p\text{-}XC_6H_4SO_3)^-$ have been investigated. The hydrogen-bonding character stemming from the substituent X highly influences the planar guanidinium-sulfonate sheet. When X is –COOH, the network of guanidinium 4-Hsb is obtained, in which the sheet motif is completely disrupted due to competition of carboxylate and sulfonate [4].

Therefore a ligand containing sulfonate and carboxylate, 4-sulfobenzoate (4-sb), has been chosen for constructing novel diverse networks in our lab as well as other research groups [5–7].

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This ligand exhibits sorts of bonding modes (from $\eta^1\mu^1$ to $\eta^{10}\mu^9$), coordination sites and bonding directions [8]. The asymmetric structure contribute to the structural variation in the interlayer region. However, among the 74 4-sb compounds retrieved from the Cambridge Structural Database, most contain auxiliary ligands and transition metals [5–7,9]. So far, only 3 organic compounds were reported without 4-sbe structures. Such research status goes against to provide sufficient information for the supramolecular assembly interactions between ligands.

Herein, we report three unexpected pillared assemblies based on 4-sulfobenzoic ligands: one 4-sbe complex $[K(4\text{-sbe})]_n$ (**1**) and two 4-Hsb cation-anion compounds $[(4\text{-Hsb})\cdot(NH_4)\cdot(H_2O)]_n$ (**2**) and $\{[(4\text{-Hsb})]_2\cdot(H_2bpe)\cdot2(H_2O)\}_n$ (**3**), in which 4-sbe is 4-sulfobenzoic ester, 4-Hsb is 4-sulfobenzoate monoanion and H_2bpe is protonated 1,2-bis(4-pyridyl)ethylene.

2. Results and discussions

2.1. Synthesis

Compounds **1** and **3** are obtained by hydro (solvo)-thermal method. **1** was collected from the resulting solution of $AgNO_3$/4-Hsb/2-apy (apy = aminopyridine) methanol-thermal reactive system initially. However, it was proved that **1** can be prepared easily by the esterification between 4-sulfobenzoic acid monopotassium salt and methanol solvent in a higher yield. But good crystals were failed to be obtained in the later system, which indicates the reaction inhibition from 2-apy whereas $AgNO_3$ may be good for the growth of crystals. Compound **3** was obtained by slow evaporation of the mixed solution of 4-Hsb, $AgNO_3$ and bpe in water after 4-day hydrothermal reaction at 423 K. It is worthy of mentioning that the original reactive solution was baked to nearly dry during the experimental process. Some additional water was added ensuing hydrothermal reaction once more and the crystals of **3** were collected. Maybe the unique reaction process contributed to the 3-fold interpenetrated framework with protonated bpe ligand instead of complex $\{[Ag(bpe)]_2\cdot(4\text{-sb})\cdot5H_2O\}_n$ [9d]. Compound **2** was easy to be obtained in the ammonia solution of 4-Hsb with HNO_3 to adjust the pH of about 3. **2** is inclined to lose water molecules when storing, leading to opaque powders.

2.2. IR spectroscopy

Comparing the IR spectra of 4-Hsb and compounds **1**–**3**, the characteristic vibration peak of –COOH at about 1725 cm^{-1} is present in **1**, indicating of esterification not influencing on carbonyl absorption. In IR spectra of compounds **2** and **3**, the broad band around 3200 cm^{-1} reveals the presence of the ν(O–H) stretching frequency for lattice water molecules. In contrast, the broad peaks around 3000 cm^{-1} is ascribed to the ν(N–H) stretching frequency. The strong broad peak at about 1406–1441 cm^{-1} shows the existence of NH_4^+ in **2**. The characteristic vibrations of SO_3^- are at 1224 and 1199 cm^{-1} in **1**, at 1266, 1245 and 1171 cm^{-1} in **2** and at 1210 and 1201 cm^{-1} in **3** for $\nu_{as}(SO_3^-)$ respectively, whereas they are at 1040 and 1013 cm^{-1} in **1**, 1033 and 1009 cm^{-1} in **2** and 1032 and 1006 cm^{-1} in **3** for $\nu_s(SO_3)$. In **3**, the stretching frequency of 837 cm^{-1} indicates the presence of H_2bpe ligand.

2.3. Crystal structures

2.3.1. Crystal structure and packing of complex $[K(4\text{-sbe})]_n$ (1)

Complex **1** is the first example of 4-sbe complex. The structure, as shown in Figs. 1a–c, is a three-dimensional framework built from potassium cations and the layers stacked by 4-sbe anions along the *c* axis. Each potassium cation adopts a distorted octahedral geometry surrounded by six oxygen atoms contributing from carboxylate and sulfonate groups, with K–O distances ranging from 2.664(2) to 2.859(2) Å. The bonding between the potassium cations and 4-sbe anions is primarily ionic in nature. Indeed, the absence of regular coordination geometries suggests potassium cations being positioned by electrostatic attraction and packing effects rather than orbital interactions [10]. As shown in Fig. 1a, there are two intramolecular C–H···O hydrogen bonds, with O2 and O3 involved.

The 4-sbe anion in **1** adopts a similar μ_5-coordination mode as 4-sb in potassium 4-sulfonatobenzoic acid [11]. The anions within a layer are co-planar arranged in a repeated *head-to-tail* bridging pattern with 29.16° angle, resulting in slabs with nonpolar organic interiors and anionic surfaces (Fig. S1a). The sulfonate group binds to four potassium ions in two manners, two chelated κ^2-O and one κ^1-O as shown in Chart 1. Obviously, the para-substituted 4-sbe ligands act as bridging spacer to link metal atoms resulting in the

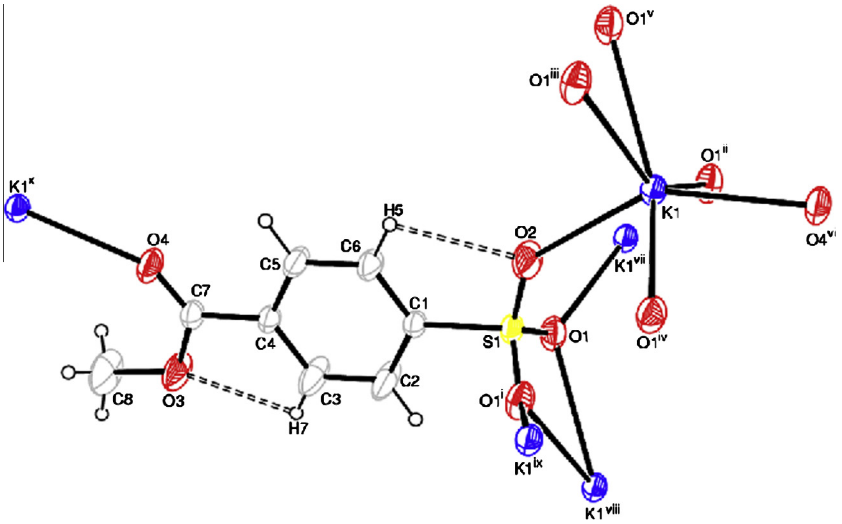

Fig. 1a. ORTEP view of the asymmetric unit of complex **1**. The thermal ellipsoids are drawn at 30% probability. Symmetry codes: i = *x*, 1/2 − *y*, *z*; ii = *x* − 1/2, −*y*, 1/2 − *z*; iii = *x* − 1, 1/2 − *y*, *z*; iv = *x* − 1/2, 1/2 + *y*, 1/2 − *z*; v = *x* − 1, *y*, *z*; vi = 1/2 − *x*, *y*, −1/2 + *z*; vii = 1/2 + *x*, −*y*, 1/2 − *z*; viii = 1 + *x*, *y*, *z*; ix = 1/2 + *x*, 1 − *y*, 1/2 − *z*; x = 1/2 − *x*, *y*, 1/2 + *z*. Two intramolecular C–H···O hydrogen bonds are also labeled with 2.50 and 2.37 Å at O2 and O3 for the H···O distances respectively.