Inorganic Chemistry Communication

Molecular Supertetrahedron Decorated with Exposed Sulfonate Groups Built from Mixed-Valence Tetranuclear $Fe_3^{3+}Fe^{2+}(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3$ Clusters

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We present the synthesis and characterization of a novel metal−organic molecular solid using the ligand 4,8-disulfonaphthalene-2,6-dicarboxylic acid. The solid features a sulfonated, isolated supertetrahedra, $[Fe_{16}O_4(SO_4)_{12}(L2)_6]$, built from mixed-valence $[Fe_3^{3+}Fe^{2+}(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3]$ clusters.

Complex molecular architectures with closed shape and large internal cavities, based on coordinating organic ligands and metal cations, have attracted considerable attention during the past decade primarily because they may serve as single-molecule magnets and as molecular capsules to trap and store reactive molecules and also mimic some biological systems.[1] A special class of this type of molecular system includes nanosized faceted polyhedra or metal−organic polyhedra (MOP), based on carboxylato secondary building units (SBUs).[2] In terms of design principles in these cases, the linking topology of both the organic linker and the inorganic SBUs plays a crucial role in obtaining a molecular system and not an extended network structure. For example, in the case of a planar (or nearly planar), paddlewheel-type SBU [e.g., $Cu_2(RCO_2)_4$], nonlinear carboxylate ligands need to be employed.[3] In the opposite case of using straight ligands, the formation of molecular structures is facilitated by SBUs of suitable connectivity. An example is the trinuclear $Fe_3(\mu_3\text{-}O)(\mu_2\text{-}SO_4)_3$ cluster used in the construction of a new family of porous MOPs (IRMOPs).[4,5]

As in the case of metal−organic frameworks (MOFs), the synthesis and characterization of functionalized MOPs are of particular importance if their full scientific and technological potential is to be achieved. We are interested in developing novel MOFs and MOPs with free Lewis base sites and, in particular, with sulfonate ($-SO_3^-$) groups. These groups are expected to enhance the sorption properties (e.g., CO_2, MeOH) of these materials[6] and, moreover, could be utilized to increase the storage capacity of important gases like H_2 and CH_4 by enhancing the binding strength through incorporation of small alkali-metal cations (e.g., Li^+, Na^+) as counterions.[6,7] To the best of our knowledge, functionalized MOPs with free sulfonate groups have not been reported.

We chose to functionalize the ligand 2,6-dicarboxylic acid (H_2L1; see Scheme 1) with sulfonic groups because the corresponding electrophilic substitution reaction preferentially orients these groups to the meta positions with respect to the carboxylic groups.[8] Therefore, the carboxylic and sulfonic groups could not bind simultaneously to the same metal centers. Moreover, because sulfonate groups have weaker coordination ability as compared to carboxylates, it is expected that first-row transition-metal cations would preferably bind to the carboxylate anions, leaving the sulfonate groups free.

We present here the synthesis (see the Supporting Information, SI) and characterization of a novel crystalline, sulfonated molecular solid (**1**) that features isolated supertetrahedra built from the ligand 4,8-disulfonaphthalene-2,6-dicarboxylic acid (H_4L2; Scheme 1) and $Fe_4(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3$ SBUs.

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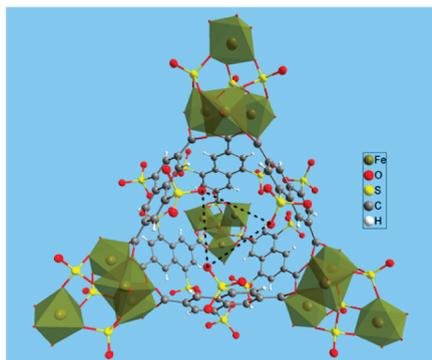(8) Qing, S. B.; Huang, W.; Yan, D. Y. *React. Funct. Polym.* **2006**, *66*, 219–227.

Figure 1. Molecular supertetrahedron $[Fe_{16}O_4(SO_4)_{12}(L2)_6(DMF)_{24}]$ in **1**. The size of the supertetrahedron, measured between terminal Fe atoms, is ~21 Å. The window aperture, defined by the three cofacial $-SO_3^-$ groups, is indicated by the dashed regular triangle having an edge length of ~2 Å (excluding the van der Waals radius).
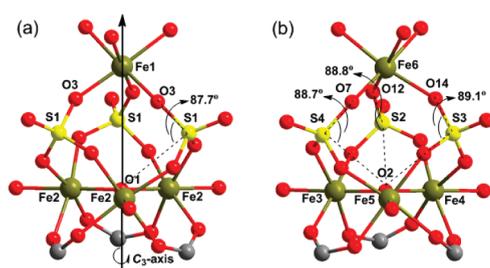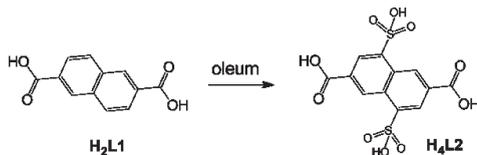

Figure 2. Two crystallographically independent tetranuclear $[Fe_4(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3(DMF)_6]$ SBUs found in **1** with (a) and without (b) 3-fold symmetry. The characteristic angles shown are compared to those in the related trinuclear $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}SO_4)_3(-CO_2)_3]^-$ SBU found in IRMOPs (see the text).

Scheme 1. Preparation of the Sulfonated Ligand H_4L2 from H_2L1 Using H_2SO_4 and 20% SO_3 (oleum)

To the best of our knowledge, the ligand H_4L2 has never been reported in the entire family of MOFs and MOPs, and also the tetranuclear $Fe_4(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3$ SBU, in contrast to the known trinuclear $Fe_3(\mu_3\text{-}O)(\mu_2\text{-}SO_4)_3$-$(-CO_2)_3$ cluster,[4,5] is observed for the first time.

Compound **1** crystallizes in the trigonal system (space group $R\bar{3}c$) with a very large unit cell size (see the SI) and features isolated anionic supertetrahedra with an overall chemical composition of $[Fe_{16}O_4(SO_4)_{12}(L2)_6(DMF)_{24}]$ (where DMF = *N*,*N*-dimethylformamide; see Figure 1). The SBU of these supertetrahedra is a new tetranuclear $[Fe_4(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3(DMF)_6]$ cluster with a triangular connectivity (see Figure 2). Accordingly, each SBU is connected to three others by three bridging **L2** ligands through the terminal carboxylate groups. The resulting supertetrahedron features a relatively large cavity of

(9) The volume of the cavity was calculated as the volume of a regular tetrahedron having as vertexes the μ_3-O atoms of the SBUs. The distance between μ_3-O atoms, excluding the van der Waals radius, is ~11.8 Å.

(10) IR spectroscopy (see Figure S5 in the SI), CHN analysis, and charge-balance considerations indicate that $-SO_3-$ groups are not protonated.
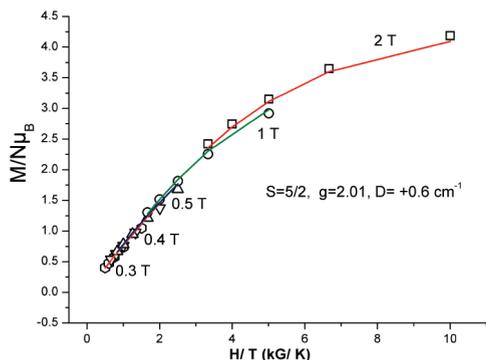
volume,[9] ~195 $Å^3$. The sulfonate groups[10] $(-SO_3^-)$ are found to be noncoordinated and decorate all four faces of each supertetrahedron (see Figure 1).

The SBUs found in **1** can be viewed as iron-capped trinuclear $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}SO_4)_3(-CO_2)_3]$ clusters. The latter have been observed in the crystal structures of IRMOP-50, -51, -52, and -53.[4] In marked contrast to these IRMOPs, the three cofacial sulfate groups of the tetranuclear SBU found in **1** are highly bended and coordinate to an additional Fe atom (μ_3-SO$_4$ groups). For comparison, the characteristic angles in the tetranuclear clusters, shown in Figure 2, were found in the range 87.7−89.1°, while in the trinuclear analogue in IRMOPs, they were between 114.1° and 133.7°.[4] It is important to emphasize here that this is a remarkable bonding flexibility of the capping sulfate groups in these types of clusters, and their ability to coordinate an additional metal center could be utilized to synthesize more complex heteronuclear tetrameric SBUs.

The octahedral coordination sphere of the three coplanar oxo-bridged Fe atoms in the tetranuclear SBUs is completed by a terminal DMF ligand, while the fourth capping Fe atom accommodates three cofacial DMF ligands (see Figure S15 in the SI). We note here that the synthetic protocol in the IRMOP family of solids[4] strictly requires a pyridine/DMF mixture, and in contrast to **1**, pyridine was found to be the terminal ligand that completes the octahedral coordination sphere of all Fe atoms.

Interestingly, the supertetrahedra in **1** are made of two crystallographically nonequivalent tetranuclear SBUs, denoted here as SBU-1 and SBU-2 (see Figure 2). Moreover, each supertetrahedron consists of one SBU-1 and three SBU-2. In SBU-1, the Fe_3O unit has a 3-fold symmetry (three indistinguishable Fe2 atoms) and the μ_3-O1 atom lies in the same plane as the three Fe2 atoms. The Fe2−O1 bond length is 1.9305(10) Å. The fourth capping Fe1 atom is placed on the C_3 axis of SBU-1. Bond valence sum (BVS) calculations[11] revealed mean oxidation states of 3.08+ and 3.14+ for Fe2 and Fe1, respectively. In contrast, SBU-2 does not present 3-fold symmetry, and all Fe atoms are crystallographically independent. The mean oxidation states of Fe3, Fe4, Fe5, and Fe6, revealed from BVS calculations, are 3.05+, 3.11+, 2.93+, and 2.89+, respectively. However, as we present below, detailed magnetic measurements, ^{57}Fe Mössbauer spectroscopy, and elemental analysis data strongly suggest that SBU-1 and SBU-2 are neutral with the chemical formula $[Fe_3^{3+}Fe^{2+}(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3]$. We note here that mixed-valence states, Fe^{3+}/Fe^{2+}, have also been observed in some oxo-centered trinuclear iron complexes.[12,13]

Direct current (dc) magnetic susceptibility measurements were performed in the temperature range 5−300 K at a constant magnetic field of 500 G. At 300 K, the $\chi_M T$ value

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Figure 3. Plot of reduced magnetization ($M/N\mu_B$) versus H/T for **1** in the field and temperature ranges of 0.3−2 T and 2−7 K. The solid lines correspond to the fit of the data (see the SI).

per SBU was 11.4 cm^3 mol^{-1} K (four Fe atoms; see Figure S8 in the SI), which is considerably smaller that the calculated spin-only value of 16.12 cm^3 mol^{-1} K for three uncoupled $S = {}^5/_2$ Fe^{3+} and one $S = 2$ Fe^{2+} centers. With decreasing temperature, $\chi_M T$ decreased gradually, reaching the value of 4.5 cm^3 mol^{-1} K at 5 K and suggesting an antiferromagnetic interaction between the Fe centers within each tetranuclear SBU and an $S = {}^5/_2$ ground state. These results are also confirmed by alternating current magnetic susceptibility measurements (see the SI for details). We have successfully simulated the dc magnetic susceptibility data, and the results show a low-spin ground state of $S = {}^1/_2$, with the first and second excited states of $S = {}^3/_2$ and ${}^5/_2$ located within 1 cm^{-1} above the ground state (see the SI). Conclusive results regarding the spin ground state were obtained from reduced magnetization measurements; see Figure 3 and the SI. Accordingly, a ground state of $S = {}^5/_2$ was confirmed, indicating that the tetranuclear SBUs are made of three Fe^{3+} ($S = {}^5/_2$) and one Fe^{2+} ($S = 2$). The origin of Fe^{2+} is attributed to a partial reduction of Fe^{3+} by CO, which, as we explain below, is released from a partial decomposition of DMF.

The presence of Fe^{2+} in **1** was confirmed by ^{57}Fe Mössbauer spectroscopy. The corresponding spectrum recorded at 77 K (see Figure S6 in the SI) is well fitted with two doublets, one for Fe^{3+} (88% area) and one for Fe^{2+} (12% area) with isomer shifts δ of 0.530 and 1.340 mm s^{-1} and quadrupole splittings ΔE_q of 0.55 and 1.23 mm s^{-1}, respectively. The corresponding spectrum recorded at room temperature consists of three doublets, two for Fe^{III} and one assignable to a fractional oxidation state between Fe^{3+} and Fe^{2+} (see Figure S7 in the SI). These results indicate a change from a more localized to a delocalized state. A very similar behavior in which quadrupole split doublets of Fe^{2+} and Fe^{3+} converge onto each other with increasing temperature has been observed in some mixed-valence oxotrinuclear iron complexes.[12] The observed delocalized character that causes the mixing of Fe^{3+} and Fe^{2+} sites in Mössbauer spectra of **1** with increasing temperature may account for the fact that the ratio of Fe^{3+} and Fe^{2+} areas (7.3) in the spectrum at 77 K is higher than the expected value of 3 revealed from the magnetic measurements (three Fe^{3+} and one Fe^{2+}) and also the observed BVS results.

A common problem in MOF/MOP chemistry in the case of large unit cells such as in **1** is the extraction of a charge-balancing chemical formula from single-crystal X-ray diffraction data.[4,14] However, taking into account that dimethylammonium cations, $(CH_3)_2NH_2^+$, are formed in situ upon heating of DMF in the presence of bases[15] via a decarbonylation reaction (release of CO), it is natural to consider these as charge-balancing cations. Accordingly, the proposed chemical formula of **1** is $[(CH_3)_2NH_2]_{12}[Fe_{12}{}^{III}Fe_4{}^{II}(\mu_3\text{-}O)_4(\mu_3\text{-}SO_4)_{12}(L2)_6(DMF)_{24}]$. This formula is in good agreement with CHN analysis[16] and thermogravimetric (TGA) measurements (see the SI).

The relatively large number of coordinated DMF molecules in **1** prompts us to investigate the possibility of removing these and accessing the available space. Because of its limited stability in air, we performed solvent-exchange reactions, using CHCl$_3$, inside a moisture-free, nitrogen-filled glovebox (see the SI). However, TGA analysis (see the SI) revealed only a partial removal of DMF, and gas (N$_2$, H$_2$, and CO$_2$) sorption measurements show no accessible space. These results suggest that, as in the case of some IRMOPs,[4] the presence of $(CH_3)_2NH_2^+$ counterions has a negative impact in accessing any available space.

In conclusion, the successful synthesis of **1** demonstrates that the ligand H_4L2 is capable of directing the formation of a new metal−organic molecular solid functionalized with exposed sulfonate groups. In an effort to elucidate the mixed-valence state and the delocalized charge character found in **1**, we are currently performing detailed electron paramagnetic resonance and ^{57}Fe Mössbauer spectroscopy measurements. We are also investigating the possibility of exchanging the dimethylammonium counterions in **1** with small alkali-metal cations such as Li$^+$ and Na$^+$ in an effort to establish porosity. Finally, the novel tetranuclear $[Fe_4(\mu_3\text{-}O)(\mu_3\text{-}SO_4)_3(-CO_2)_3]$ cluster found in **1** may serve as a new SBU for the construction of extended, framework solids, utilizing the possibility of bridging different clusters through the terminal Fe atom.

Supporting Information Available: Instrumentation, experimental procedure, X-ray crystallographic file for **1** in CIF format, and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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