

Review

Coordination and supramolecular network entanglements
of organodisulfonates

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Abstract

The infinite solid state architectures of variable organodisulfonate coordination complexes, retrieved from CSD v. 5.27, have been analyzed. The extended metal-organic frameworks (MOF) of 90 compounds are discussed with respect to binding preferences and repeating structural and linking motifs, leading to coordination polymerization and/or supramolecular self-assembly. A disentanglement method is applied in order to gain insight into the ordered periodic arrangement and understand the structure-controlling factors, amenable for that organization. Such factors as coordination predisposition and geometrical preferences of the metal ion are particularly addressed. The functionality of the disulfonate ligands is considered with respect to the topology and binding abilities of the coordinating sites, from one side, and the nature, symmetry and the additional substituent(s) of the organic spacer, from the other side. A graph-set notation, similar to that used in hydrogen bonded systems, is proposed for identification of the structural and linking motifs, observed in the extended solids of the studied compounds.

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1. Introduction

Organization on both the molecular and supramolecular level is governed by the same fundamental physical force (the electromagnetic repulsion and attraction), which dominates on the whole scale of 10^{-10} to 10^{-6} m. Roughly 100 elements,

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with unique electronic system of their atoms, account for the wealthy molecular world, and therefore, account for the steadily growing realm of sophisticated supramolecular systems and novel materials. However, the ordered information for structural organization on each level is decoded on its sublevel. The chemical properties of the molecule result from the combination of atoms and covalent bonds between them and the information for bond formation is carried by the individual atoms, that share their electrons. On the other hand the ordered information for molecular recognition and organization is deciphered in the structure of molecules themselves. According to the supramolecular conception the intermolecular interactions are considered as (bonding) connections between molecules [1]. So, it is reasonable that the synthetic and research efforts during the last two decades have moved from the traditional organic, inorganic and organometallic chemistry to supramolecular chemistry and focus on problems of (high level) molecular organization. The collective properties of well defined molecular assemblies have been compared with those of the individual components and addressed with respect to the structural relationships [2]. Nowadays the supramolecular paradigm is particularly shifting towards controlling the periodical distribution of non-covalent bonding and constructing ordered networks. In this context the crystal is reasonably considered as a “supermolecule par excellence” [3]. Variable approaches, targeted into reliable high-dimensional arrangement of molecular/ionic building blocks with predictable final architecture, are pursued by different research groups. Despite the none-questionable progress made in this direction [4,5], there are still white areas and black points. Managing the collective interplay and the periodical distribution of weak (non-specific) interactions is indispensable for directing the network entanglement. Such problems as understanding the nuclei formation and predicting the final outcome of the crystallization process, control over the supramolecular isomorphs and crystalline polymorphs continue to be challenging.

An useful way for gaining insight into the principles governing the ordered molecular organization, is to analyse a large number of representative crystal structures using disentanglement methods [6–9]. The present paper studies the coordination and supramolecular chemistry of disulfonic acids, with respect to their solid state arrangement. There is no systematic study of the extended metal-organic frameworks (MOF) of organodisulfonates with respect to the binding preferences of the sulfonic group, and especially, of the repeated structural and linking motifs used for coordination polymerization and interweavement. This review is purposely directed to analyze the infinite disulfonate architectures with respect to their coordination entanglement and to reveal the role of, and the mutual interrelation, between variable structure controlling factors. In particular, the preferred structural motifs, used for formation and multidimensional extension of the crystal chemical units are addressed. For this reason the metal organic frameworks (MOF) are compared and systemized using a modified topological approach. Originally the principles for delineation of MOF were developed by Batten and Robson [6] and successfully used for a topological classification of variable interpenetrating nets [7]. However, for comparison reasons we have adopted a

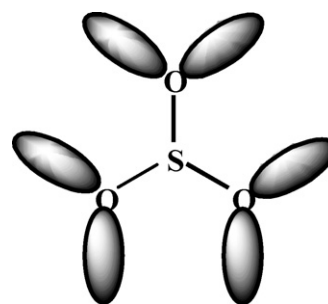
somewhat different approach which allows for specifying the individual coordination units and the motifs linking them into extended coordination framework [9].

2. General properties of sulfonic acids

Sulfonic acids are a class of compounds in which an R-group is attached to the sulfonic group. Usually they appear in zwitterionic forms, whenever there is a lone pair in the auxiliary R-group. Unlike the carbon atom, the central atoms of the sulfonic and phosphonic groups are able to accommodate more than eight electrons in the outer electron shell, which accounts for a greater bonding flexibility in these groups compared to the carboxylic group. However, the proton of the sulfonic group is more easily dissociable than the proton of the carboxylic group or the first proton of the phosphonic group and in this respect the sulfonic acids are stronger than their phosphonic and carboxylic analogues. On the other side, the disulfonic acids with a general formula $\text{SO}_3\text{H}-\text{R}-\text{SO}_3\text{H}$ are bifunctional compounds, analogous to the diphosphonic and dicarboxylic acids. They fully deprotonate at very low $\text{p}K_{\text{a}}$, which causes serious problem with their stability. Usually, they are commercially available as sodium salts. Modification of the R spacer between the two sulfonic groups can lead to broad structural differentiations.

3. Hydrogen bond and coordination abilities of the sulfonate group

The sulfonic group very readily releases its proton in order to transform into a highly symmetric sulfonate group possessing a three-fold symmetry axis. Additionally, three symmetry planes (C_{3v}) should be taken into account considering the six electron pairs on the sulfonate oxygen atoms (Scheme 1). Therefore, the supramolecular chemistry of sulfonic acids is extremely exciting with respect to the ability of the sulfonate group to accept up to six hydrogen bonds along these lone pairs. The equal number of hydrogen bond donors and acceptors, located on two separated sites with matched geometry and stereoavailability, allows for a formation of persistent, six-member guanidinium sulfonate module. The (pseudo)hexagonal module GS, resembling a rosette, is predisposed for further hydrogen bond recognition in order to form periodically extended, two-dimensional networks GS2 (see Scheme 2). All three hydrogen bonded motifs R2,2(8), used for generation of the network, represent



Scheme 1.

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