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Rational Design of Molecular Sheets Composed of Interconnecting Eight- and Twenty-Four-Membered Rings: Use of Lithiated Aggregates To Control Network Assembly

Kenneth W. Henderson,*,† Alan R. Kennedy,‡ Lynn Macdonald,‡ and Dugald J. MacDougall†

Department of Chemistry and Biochemistry, University of Notre Dame,
Notre Dame, Indiana 46556-5670, and Department of Pure and Applied Chemistry,
University of Strathclyde, Glasgow, G1 1XL, U.K.

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The lithiated (organo)sulfonylacetonitrile complex [$MeSO_2CHCNLi\cdot THF$] (**3**) has been prepared and structurally characterized in order to demonstrate that well-known molecular aggregates of s-block metals may be used as building blocks in the controlled assembly of complex supramolecular architectures. The solid state structure of **3** can be described as a novel basket-weaved, 2-D network, composed of $(SO_2Li)_2$ “dimeric” rings joined via “interdimer” donation of nitrile units.

The synthesis and characterization of well-defined network assemblies continues to be an area of intense interest due to the potential of these materials in applications as diverse as catalysis,[1] chemical separation,[2] optics,[3] and electronics.[4] Although there have been remarkable advances in our understanding of the principles of self-assembly,[5] the development of rational routes to well-organized solid state materials remains a real challenge to the synthetic chemist. In this regard, two main strategies have been adopted in the formation of molecular networks, first through use of hydrogen-bonded organic solids[6] and second using inorganic coordination polymers containing transition elements and ligand spacer molecules.[7] A notable area of success in controlling the formation of solids has been the work of Yaghi by the use of metal carboxylate clusters as components of metal–organic frameworks (MOFs).[8] However, to our knowledge, the deliberate use of s-block metals,[9] and more precisely organolithium aggregates, to control the formation of complex 2-D network architectures has not previously been reported.[10] In contrast, the molecular coordination chemistry of organolithium compounds is well-developed, with a wealth of information known regarding their solid state and solution aggregation behavior.[11] Herein, we describe the synthesis and structural characterization of a weaved

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* Author to whom correspondence should be addressed. E-mail: khenders@nd.edu.

† University of Notre Dame.

‡ University of Strathclyde.

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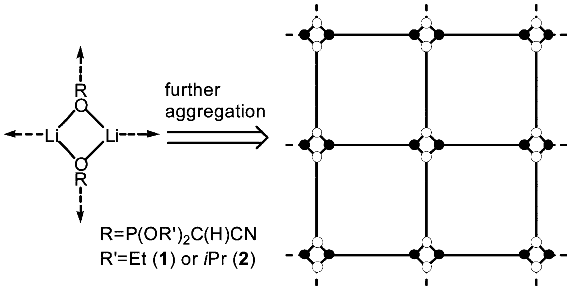
Scheme 1. Proposed Assembling Process of the Supramolecular Structures of **1** and **2**, Showing the Dimeric Li_2O_2 Fragments Acting as Square Planar Nodes[a]



[a] Only the atoms incorporated within the sheet structure are shown for clarity.

molecular sheet, which was rationally designed through the use of a lithiated (organosulfonyl)acetonitrile complex.[12]

Our interest in the possibility of using organolithium aggregates as supramolecular synthons was initiated after our serendipitous discovery that, in the solid state, the lithiated α-cyanophosphonates [$(RO)_2P(O)CHCNLi\cdot THF$], where R = Et (**1**) or *i*-Pr (**2**), form isostructural nets composed of interconnecting twenty-four-membered rings.[13] Furthermore, each ring has four (OPCCNLi) edges with Li_2O_2 rings at the corners of the square windows (Scheme 1).

Although the assembly of such large rings is unusual in organolithium chemistry, we previously did not speculate on the mechanism of their formation. However, we now believe that the solid state structures of **1** and **2** can be understood if the Li_2O_2 rings are considered to be supramolecular synthons.[14] More specifically, in the structures of **1** and **2** the dimeric Li_2O_2 ring aggregates commonly associated with metalated Wittig-type reagents remain intact and the extended structure results from "interdimer" ligation of the nitrile units.[15] The sheet structure formed can be considered to be topologically equivalent to a (4, 4) net, with the nodes at the center of the Li_2O_2 rings.[16] Hence, the formation of the stable Li_2O_2 rings arising from the metals bridging the P═O units results in an approximately square planar node, with the nitrile units of the phosphonates and an available coordination site on each lithium being approximately 90° to one another. Association of four dimers, by simply rotating each Li_2O_2 ring by 90° with respect to its neighbor, results in the formation of twenty-four-membered square windows (Scheme 1). The local geometry of the metals in **1** and **2** is distorted tetrahedral (as is most commonly found in lithium organometallics), with the fourth coordination site blocked for 3-D growth by a solvating THF ligand.

We reasoned that if this assembling process is valid, we should be able to rationally build similar architectures using other organolithium aggregates. We chose lithiated (organosulfonyl)acetonitriles as candidates since, in theory, these should form supramolecular assemblies similar to **1** and **2** but with the replacement of the four-membered Li_2O_2 rings with the larger eight-membered $(SO_2Li)_2$ rings that are a common feature of simple lithiated sulfones.[17] Accordingly, the monolithiated salt [$MeSO_2CHCNLi\cdot THF$] (**3**) was prepared by the direct deprotonation of the parent ligand $MeSO_2CH_2CN$ with 1 molar equiv of *n*-BuLi in neat THF.[18] X-ray crystallographic analysis of **3** revealed an extended sheet structure composed of eight-membered $(SO_2Li)_2$ rings fused with twenty-four-membered, $(OSCCNLi)_4$, rings, in agreement with our proposal and similar to the structures of **1** and **2** (Figure 1).[19]

Although the detailed connectivity within the sheets is consistent with our predictions, the topology of **3** differs somewhat from that of **1** and **2**. The closest approximation for the supramolecular structure of **3** is that of large rectangular windows joined through smaller square windows. Each rectangular window consists of two long nine-atom edges and two short five-atom edges, which share alternate S and Li atoms at the corners (nodes), i.e., the nodes are

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(18) Synthesis of **3**: (Methyl)sulfonylacetonitrile (0.24 g, 2 mmol) was dissolved in a solution of THF (5 mL). *n*-Butyllithium (2 mmol of a 1.6 M solution in hexanes) was added dropwise to the mixture while gentle heating was maintained. The solution was diluted with 5 mL of THF and gently heated. The reaction mixture was stirred at ambient temperature for 1 h, after which the Schlenk flask was placed in a freezer at −28 °C for 4 days. A batch of clear, colorless crystals were deposited. Exposure of **3** to air resulted in hydrolysis, as evidenced from the IR spectrum of the sample, which displayed a sharp signal at 1679 cm^{-1} and a broad signal centered at 3400 cm^{-1} due to the presence of LiOH and H_2O, respectively. Once precipitated, complex **3** displays negligible solubility in common organic solvents (hydrocarbons, arenes, and ethers) but was completely soluble in the highly polar solvent DMSO. Yield: 240 mg, 67%. Mp: decomposes at >70 °C. Elemental analyses are based on the formula [$MeSO_2CHCNLi\cdot THF_{0.75}$] since this was the integrated ratio of ligand to THF determined by ^1H NMR spectroscopy on isolation of **3**, presumably due to partial removal of solvent in vacuo. Found: C, 40.61; H, 5.86; N, 7.49. $C_7H_{12}LiNO_3S$ requires C, 40.66; H, 5.67; N, 7.70. IR: ν_{max}/cm^{-1} (C≡N) 2161s (Nujol). ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): $\delta = 3.60$ (m, 3H; O−CH_2, THF), 2.67 (s, 3H; CH_3, Me), 2.36 (s, 1H; SO_2−CH), 1.75 (m, 3H; CH_2, THF). ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): $\delta = 127.33$ (C≡N), 67.43 (O−CH_2, THF), 47.91 (SO_2−CH), 37.49 (CH_3), 25.53 (CH_2, THF).

(19) Crystal data for **3**: $C_7H_{12}LiNO_3S$. A colorless plate of approximate dimensions 0.30 × 0.25 × 0.08 mm gave a monoclinic space group $P2_1/c$, $a = 9.172(3)$ Å, $b = 9.787(3)$ Å, $c = 10.899(4)$ Å, $\beta = 98.833(15)°$, $V = 976.2(6)$ Å^3, $T = 123$ K, $Z = 4$, $\rho_{calc} = 1.342$ Mg m^{-3}, $2\theta_{max} = 47$ °, Mo Kα $\lambda = 0.71073$ Å. The fragile crystals diffracted weakly, and the diffraction spots were badly split. The structure was solved, and refined on F^2, using programs of the Shelx family to convergence at R1 = 0.0739 (for 1023 reflections with $I > 2\sigma(I)$), wR2 = 0.1644 and $S = 1.105$ for 123 parameters and 1423 unique reflections. Highest residual electron density: 0.423 e Å^{-3}. H1, the hydrogen atom on the carbanion, was refined isotropically, but all other H atoms were placed in calculated positions and in riding modes.

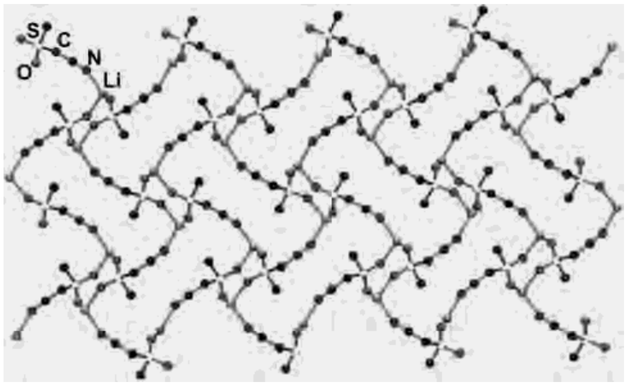
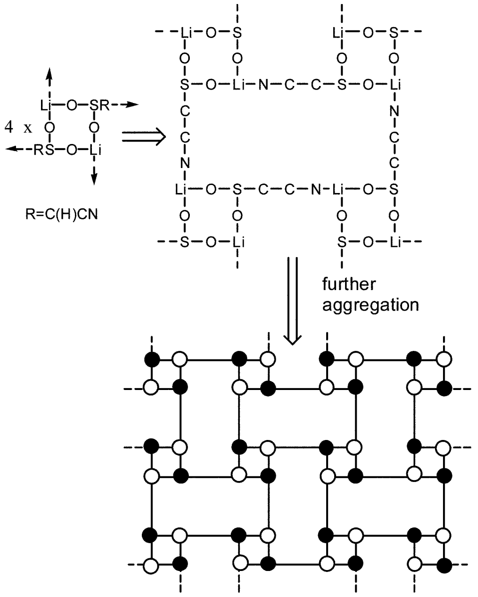


Figure 1. Section of the supramolecular structure of **3**, with hydrogens and THF molecules removed for clarity.

Scheme 2. Proposed Assembling Process of the Supramolecular Structure of **3**, a Basket-Weaved Network Constructed from Offset Pseudo Square Planar $(SO_2Li)_2$ Synthons[a]



[a] Only the atoms incorporated within the sheet structure are shown for clarity.

now associated with either a Li or S center rather than at the center of the dimer as found for **1** and **2**. The lithium nodes are rendered pyramidal by THF molecules blocking one coordination site, and similarly the sulfur nodes are pyramidal with each carrying a terminal methyl group. The end of each long edge of these rectangles is fused to two eight-membered $(SO_2Li)_2$ rings, and this unit is repeated to give the overall framework shown in Scheme 2.

In fact, the overall structure of **3** can be described as a basket weave, a network that has not previously been prepared, as recently highlighted in a review by Zaworotko.[20] This network is closely related to the well-known brick wall, herringbone, and bilayer nets (Figure 2).

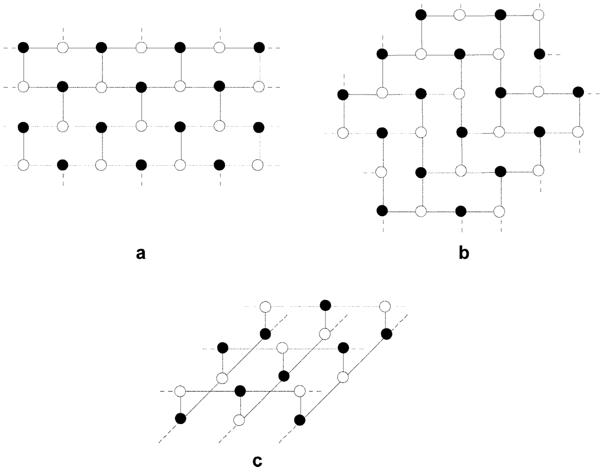


Figure 2. Known three-connected (T-shaped) nets: (a) brick wall; (b) herringbone (parquet floor); (c) bilayer.

In **3** the lithium and sulfur atoms act as distorted T-shaped nodes, and overall the $(SO_2Li)_2$ rings can be regarded as offset *pseudo* square planar supramolecular synthons, i.e., the pair of rods associated with the Li and S centers in each ring are not coincident but rather they are parallel with one another, being offset by a single atom linkage (either Li−O or S−O). Nevertheless, a repeating (4, 4) net similar to **1** and **2** can be delineated for **3** by placing a square planar node at the center of each $(SO_2Li)_2$ ring. However, this representation of **3** is less appealing than for **1** and **2** since the atom linkages do not coincide with the edges of the squares (rods). It should be noted that the rings within the network of **3** are highly puckered, and most likely contort to fill space efficiently.[21]

Overall, our predictions of forming a network consisting of interconnecting eight- and twenty-four-membered rings has been realized; however, the detailed topology of the net created is somewhat different from our initial expectations. It is intriguing to speculate on the role that aggregated s-block and, in particular, lithium complexes may play in the future of supramolecular chemistry. Since the molecular coordination chemistry of many classes of organolithium complexes is well established, there are numerous sizes, shapes, and compositions of aggregates (dimers, trimers, ring tetramers, cubic tetramers, prismatic hexamers, etc.) already at hand that merit investigation as supramolecular synthons.[11]

Supporting Information Available: Crystallographic data for **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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