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Molecular Tectonics: Self-Complementary Supramolecular Se···N Synthons Directing Assembly of 1D Silver Chains into 3D Porous Molecular Architectures

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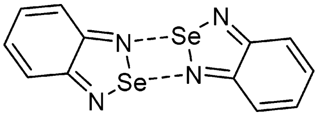
Reaction of 2,1,3-benzoselenadiazole (bsd) with $AgNO_3$ results in the formation of a novel model example of a Se···N synthon directed molecular network of different polymorphs at different temperatures. α-[Ag(bsd)$_2$(NO$_3$)]·0.5bsd formed at ambient temperature, has a 3D porous molecular network constructed with monomeric [Ag(bsd)$_2$(NO$_3$)] motif, and has 1D channels that are encapsulated with 1D arrays of two-fold-disordered dimeric (bsd)$_2$ guests aggregated by the self-complementary nonbonded Se···N interactions. This is the first molecular net directed by supramolecular Se···N synthons. The second polymorph, β-[Ag(bsd)$_2$(NO$_3$)]·0.5bsd, formed from an analogous reaction at 50 °C, contains a similar 3D molecular network constructed with tetrameric [Ag$_4$(bsd)$_8$(NO$_3$)$_4$] motif and 1D arrays of well-ordered dimeric (bsd)$_2$ guests are encapsulated in the channels. Such ordered (bsd)$_2$ dimers provide an excellent simplified dimeric model for MO calculations of *intermolecular* nonbonded Se···N interactions.

Molecular architectures can be generated in the crystalline phase through self-assembly processes engaging self-complementary tectons.[1] So far, molecular tectonics is still in its developing stage, and many more systematic investigations are needed before a claim can be made to understand well the formation of molecular networks, although some intriguing tectons have been designed to predict their interconnections into molecular networks in the crystalline phase.[2] On the other hand, the chemistry of organoselenium derivates stabilized by nonbonded Se···N interactions has attracted considerable interest in recent years because of their vital role in many chemical phenomena, such as molecular recognition and molecular packing in crystal phases as well as their biological role.[3] To date, great effort has been focused on those cases with weak *intramolecular* and *intermolecular* nonbonded Se···N interactions;[4] however, no real example has been reported of the construction of periodic supramolecular architectures using the promising Se···N synthons (Chart 1). Herein, we present a novel model example of this construction, in which Se···N interactions direct the assembly of one-dimensional (1D) silver chains into a three-dimensional (3D) periodic porous molecular architecture of [Ag(bsd)$_2$(NO$_3$)]·0.5bsd with two polymorphs (bsd = 2,1,3-benzoselenadiazole).

Chart 1. Self-Complementary Supramolecular Se···N Synthon



Reaction of $AgNO_3$ (0.085 g, 0.5 mmol) with bsd (0.183 g, 1.0 mmol) in acetonitrile/water (v/v 2:1, 10 mL) at room temperature yields pale yellow prismatic crystals of α-[Ag(bsd)$_2$(NO$_3$)]·0.5bsd (**1**) in ca. 90% yield based on bsd.

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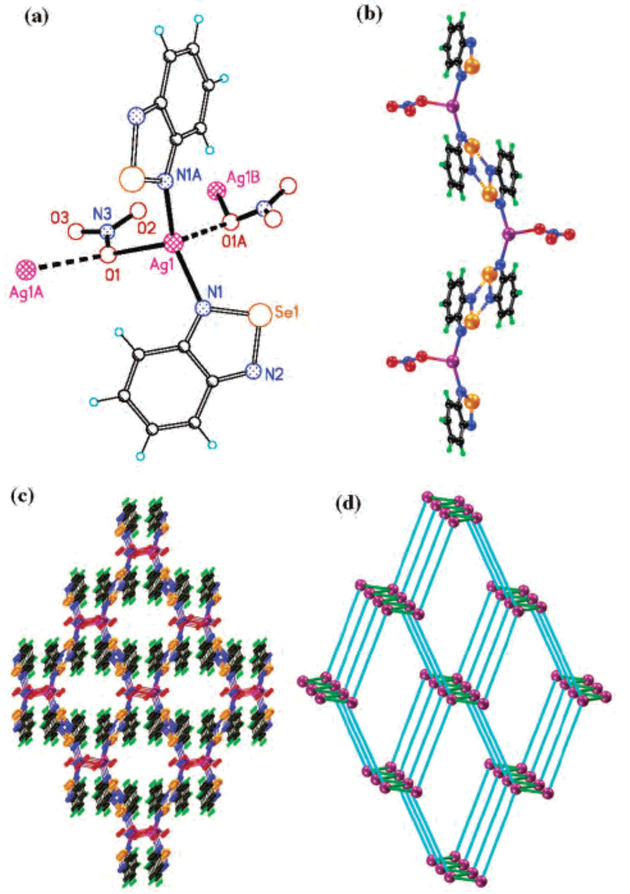

Figure 1. Views of the (a) coordination geometry, (b) S-shaped Se$\cdots$N chain, (c) 3D porous molecular network, and (d) topological net in the structure of **1**. The bridging NO_3^- and dimeric $(bsd)_2$ connections between the Ag nodes are represented by green bold lines and cyan bold lines, respectively.

X-ray structural analysis[5] shows that **1** crystallizes in monoclinic $C2/c$ space group with an asymmetric unit consisting of one-half of a formula unit. Each Ag lies on a special position and is coordinated in a Y-shaped geometry to two bsd units [Ag$-$N = 2.214(4) Å] and one nitrate oxygen atom [Ag$-$O = 2.495(7) Å], as shown in Figure 1. The nitrate is in two-fold disorder. The adjacent monomeric $Ag(bsd)_2(NO_3)$ motifs are weakly linked by sharing μ_2:η^2-nitrate bridges into 1D chains running along c-axis direction [Ag$\cdots$O = 2.673(1) Å]. Of particular interest in the structure of **1** is that adjacent monomeric $Ag(bsd)_2(NO_3)$ motifs are precisely arranged into 1D S-shaped arrays along the a-axis direction (Figure 1b). What interests us is that the intermotif interaction of the nitrogen with the selenium. The atomic Se$\cdots$N separation of 2.847(1) Å is longer than the sum of their covalent radii (1.80 Å) but significantly shorter than the sum of the corresponding van der Waals radii (3.5 Å),[6] showing significant intermolecular nonbonded Se$\cdots$N interactions, which play an important role in directing the molecular network topology. As a result, mononuclear $Ag(bsd)_2(NO_3)$ motifs are connected by pairs of self-complementary Se$\cdots$N synthons as well as weak Ag$-$O(NO_3) interactions into a three-dimensional porous molecular network (Figure 1c). To our knowledge, **1** is the first molecular network directed by Se$\cdots$N synthons. This result is expected to afford important information for molecular tectonics.

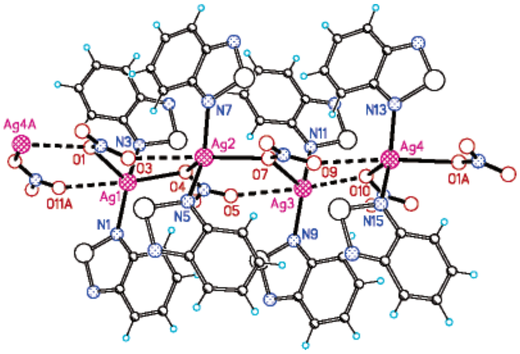

Figure 2. Perspective view of the coordination geometries in **2**.

In analyzing the network topology of **1**, the Ag atoms act as 4-connecting centers. The network can thus be represented topologically simply by the Ag nodes and the two types of connections between them: bridging NO_3^- and dimeric $(bsd)_2$ ligands (Figure S1). This analysis reveals a tetrahedral network with a Schäfli symbol[7] of $6^4{\cdot}8^2$ (Figure 1d). An interesting feature of this net is the presence of 1D channels running along c-axis direction, which have effective dimensions[8] of ca. 5.5 × 6.6 Å. The channels are occupied by the bsd guests, which are in two-fold disorder. Pairs of bsd guest molecules are aggregated into dimers through the nonbonded Se$\cdots$N interactions [Se$\cdots$N = 2.937(1) Å]. However, such a dimer, $[bsd]_2$, is not a good candidate for a simplified dimeric model for MO calculations because of its disorder. This fact moved us to conduct further experiment.

Interestingly, when the above-mentioned reaction was carried out at 50 °C, nearly colorless needle crystals of a second polymorph, β-$[Ag(bsd)_2(NO_3)]{\cdot}0.5bsd$ (**2**) as a single phase were isolated (yield > 80% based on bsd).

The structure of **2**[5] crystallizes in the monoclinic $P2_1/n$ space group with an asymmetric unit consisting of four formula units, and therefore there are four crystallographically unique (but chemically similar) Ag atoms, eight unique bsd ligands, four nitrate ions, and two bsd guest molecules. Each Ag lies on a general position and is coordinated in a distorted square-pyramidal geometry to two trans bsd ligands [Ag$-$N = 2.199(4)$-$2.237(4) Å] and three nitrate oxygen atoms [Ag$-$O = 2.464(3)$-$2.714(3) Å], as shown in Figure 2. Similarly to **1**, the adjacent tetrameric $Ag_4(bsd)_8(NO_3)_4$ motifs are linked by sharing the μ_3: η^1:η^2-nitrate bridges into 1D chains running along the a-axis direction [Ag$-$O =

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[5] Crystal data for **1**: $C_{15}H_{10}AgN_6O_3Se_{2.5}$, M = 627.56, monoclinic, space group $C2/c$ (No. 15), a = 18.038(1) Å, b = 13.511(1) Å, c = 7.438(1) Å, β = 95.502(1)°, V = 1804.3(2) Å^3, Z = 4, D_c = 2.310 g/cm^3, T = 123 K. R1 = 0.0251, wR2 = 0.0812. Crystal data for **2**: $C_{60}H_{40}Ag_4N_{24}O_{12}Se_{10}$, M = 2510.24, monoclinic, space group $P2_1/n$ (No. 14), a = 14.880(1) Å, b = 26.989(2) Å, c = 18.855(1) Å, β = 107.687(1)°, V = 7214.2(9) Å^3, Z = 4, D_c = 2.311 g/cm^3, T = 123 K. R1 = 0.0435, wR2 = 0.0798.

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[8] The van der Waals radius of C (1.70 Å), H (1.20 Å), N (1.55 Å), O (1.52 Å), and Se (1.90 Å) were employed in the determination of the distance parameters.

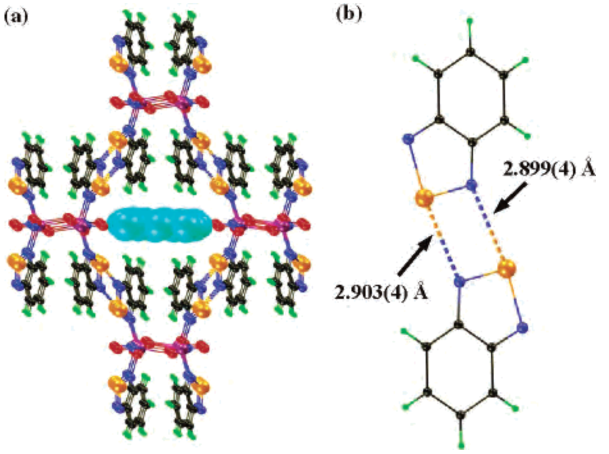

Figure 3. (a) Cavity and (b) dimeric guests in the structure of **2**.

2.492(3) Å], and adjacent tetrameric $Ag_4(bsd)_8(NO_3)_4$ motifs are also arranged into 1D S-shaped arrays along the *c*-axis direction through the Se···N synthons [Se···N = 2.771(4)−2.900(4) Å]. Both intermotif self-complementary Se···N synthons and Ag−O interactions result in a 3D molecular network with 1D channels of effective dimensions of ca. 5.8 × 6.8 Å and constitute 19.8% of the crystal volume (Figure S2). Of most interest to us is that the ordered guest bsd molecules line up in these 1D channels and are aggregated in pairs into $(bsd)_2$ dimers (Figure 3) through the self-complementary Se···N interactions [Se···N = 2.899(4) and 2.903(4) Å]. It is worth noting that the discrete $(bsd)_2$ dimer provides a good candidate of a simplified dimeric model for MO calculations. This method of a trapped dimeric model in a porous molecular network[9] provides a new pathway for the investigation of other weak interactions because such a dimeric model could hardly be obtained directly from the solution or crystalline phase because of solvation or stacking effects, which will undoubtedly influence or modify the calculation results.[10]

On the basis of the geometry of the dimeric $(bsd)_2$ model in **2**, MO calculations[11] at the MP2/6-31++G** level with correction for basis set superposition error (BSSE) shows that the well depth is -40.9 KJ mol^{-1} at $r_{Se-N} = 2.9$ Å (Figure 4), which is very similar to the value from the structural data. This fact also indicates that the strength of the Se···N interactions is analogous to that (15−40 kJ mol^{-1}) of common hydrogen bonding.[12]

In summary, we have prepared and characterized the first molecular network directed by supramolecular Se···N synthons. We have also, for the first time, experimentally obtained the dimeric $(bsd)_2$ structural model and theoretically demonstrated the strength of *intermolecular* Se···N interactions. We are extending research to other silver salt cases and other chalcogen···N/O synthon systems, and further systematic investigation will focus on the influence of reaction conditions and guests on a diversity of Ag−bsd networks.

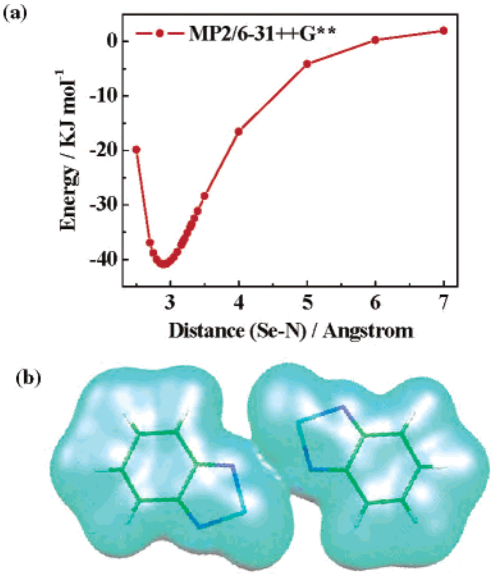

Figure 4. Variation with the Se···N distance of (a) the total interaction energy of the $(bsd)_2$ dimers and (b) the electrostatic potential mapped on the 0.02 au density isosurface in the $(bsd)_2$ dimer.

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Supporting Information Available: Figures illustrating topological networks for **1**, **2**, and bsd. X-ray crystallographic file in CIF format for the structure determination of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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