Three-Dimensional Organically Templated Open-Framework Transition Metal Selenites**

Amitava Choudhury, Udaya Kumar D, and
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A large variety of open-framework metal phosphates has been synthesized and characterized in the last few years.[1] Several open-framework metal carboxylates have also been reported.[2] Besides the phosphates and the carboxylates, open-framework phosphites,[3] arsenates,[4] and germanates[5] are also known. An organically templated layered zinc selenite was described recently by Harrison et al.,[6] but no three-dimensional (3D) open-framework structure with the oxo anions of sulfur or selenium has been isolated to date. We have synthesized for the first time a 3D open-framework iron fluoroselenite templated by various organic amines. Herein we report the synthesis and structure of $[A]^+[Fe_2F_3(SeO_3)_2]$ ($[A] = [C_4N_2H_{12}]_{0.5}$, $[C_4N_3H_{14}]_{0.5}$ or $[NH_4]$) possessing an 8-ring channel. This selenite is an interesting geometrically, frustrated magnetic material by virtue of possessing near-tetrahedral $Fe_4F_6O_{12}$ clusters, comprising equilateral triangles of Fe atoms. In addition to the Fe selenite, we have obtained a new 3D zinc selenite.

Synthesis of open-framework transition metal selenites by amine templating is difficult because of the low reduction potential of the Se^{IV}/Se^0 couple, which under hydrothermal conditions may cause reduction to metallic selenium. We have therefore employed the fluoride route (addition of HF to the reaction medium) of Guth et al.,[7] as elaborated by Férey and co-workers[8] in the case of metal phosphates. The fluoride ion stabilizes the higher oxidation states of the metal and acts as a good mineralizer besides getting incorporated into the framework. Reaction of a mixture of $FeCl_3 \cdot 6H_2O$, HF, SeO_2, and piperazine (PIP) in water under hydrothermal conditions yields pure **I** (see Experimental Section). This inorganic

$[C_4N_2H_{12}]_{0.5}[Fe_2F_3(SeO_3)_2]$ **I**

framework was obtained with diethylenetetramine (DETA), 1,3-diaminopropane (DAP), and ethylenediamine (en) as well. In the case of DAP and en, the amine decomposes to give the ammonium ion, but DETA remains intact with its two end nitrogen atoms being protonated. In the absence of fluorine in the reaction medium, only dense iron selenites were obtained.

The 3D inorganic framework of $[A]^+[Fe_2F_3(SeO_3)_2]$ is built up from the vertex-sharing FeF_3O_3 octahedra and SeO_3 pseudo-tetrahedra, and the structure can be described in terms of a unique tetrameric cluster, $Fe_4F_6O_{12}$ (Figure 1a). Since the 3D structure obtained with all the amines was the same, we shall only discuss **I** obtained with piperazine. The asymmetric unit of **I** contains 14 non-hydrogen atoms with two crystallographically distinct Fe and Se atoms. The Fe atoms are six-coordinate, surrounded by three oxygen atoms and three fluorine atoms. The average Fe–O bond lengths are 1.964 and 1.953 Å for Fe1 and Fe2, respectively; the corresponding Fe–F bond lengths of 1.987 and 1.982 Å are longer than in other oxyfluorinated Fe^{III} compounds.[9] The two Se atoms, each bound to three O atoms form a pyramid characteristic of the $Se^{III}O_3$ group, with the stereochemically active lone pair of electrons occupying the remaining tetrahedral site. The average Se–O bond lengths are 1.696 and 1.702 Å for Se1 and Se2 respectively, in agreement with

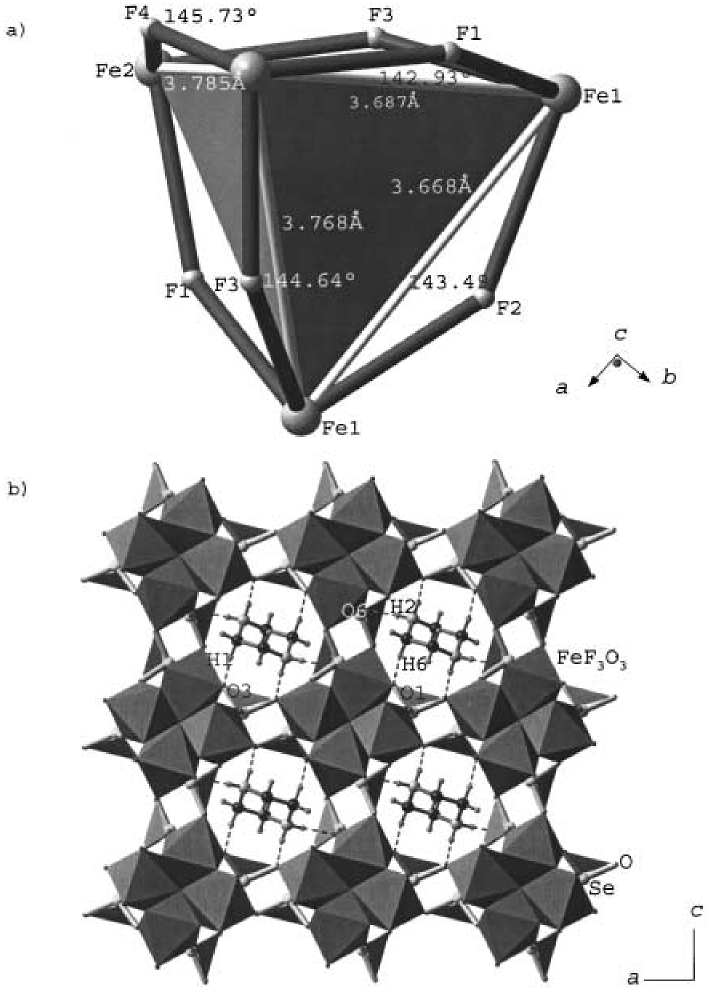

Figure 1. a) The tetrameric cluster of $Fe_4F_6O_{12}$ in **I** formed by the corner-sharing of FeO_3F_3 through six Fe-μF-Fe linkages. Note near perfect tetrahedron formed by connecting the Fe atoms. b) Polyhedral view of the inorganic framework of **I** along the *b* axis showing one-dimensional 8-ring channel. The amine molecules are located in the middle of the channel and interact with the framework through N–H⋯O hydrogen bonds (dotted lines).

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the literature values.[6] Both the Fe atoms form three Fe-F-Fe linkages and three Fe-O-Se linkages, the former being responsible for the $Fe_4F_6O_{12}$ cluster, wherein four FeF_3O_4 octahedra are corner-shared through six Fe-F-Fe linkages (Figure 1 a). This connectivity between the FeF_3O_3 octahedra creates four 3-rings in the cluster. The cluster, which can be considered to be the secondary building unit (SBU), is connected by Fe-O-Se linkages to form the 3D structure, possessing 4-, 5-, and 6-rings as well as an 8-ring 1D channel (with the dimensions 5.847 × 7.593 Å, the longest atom–atom distance, not including the van der Waal radii) along the *b* axis (Figure 1 b). A section of the intercluster connectivity along the *b* axis is shown in Figure 2. The protonated PIP molecules reside in the channel and interact with the framework through strong N–H$\cdots$O hydrogen bonding (d(H1$\cdots$O3) 1.913(8), d(N1$\cdots$O3) 2.764(8) Å, θ(N1-H1$\cdots$O3) 156.9(7)°; d(H2$\cdots$O6) 1.841(7), d(N1$\cdots$O6) 2.740(7) Å, θ(N1-H2$\cdots$O6) 175.2(7)°). There is evidence for C-H$\cdots$O (d(C$\cdots$O)$_{av}$ 3.320 Å) and C-H$\cdots$F (d(C$\cdots$F) 3.076 Å) interactions as well.

Of the many noteworthy features in the structure of **I**, the tetrameric SBU is rather unusual. The cluster in $[A][Fe_2F_3(SeO_3)_2]$ has a near-tetrahedral geometry with four nearly equilateral triangles, which do not share a common vertex; they are linked by Fe-μ_2-F-Fe and not capped by SeO_3 pyramids (Figure 1 a). The literature examples of SBUs formed by Fe-X-Fe (X = O, F, OH) linkages in open-framework phosphates or oxyfluorinated phosphates are generally constructed from a dimer, trimer, or a tetramer of edge- or corner-shared Fe-F_xO_{6-x} ($x = 0-3$) octahedra and capped by PO_4 units; the few known iron–oxo tetranuclear clusters are also different.[10] A somewhat related tetranuclear cluster is that formed by joining of four trigonal-bipyramidal iron centers in $[enH_2]_2[Fe_4O(PO_4)_4]\cdot H_2O$.[11]

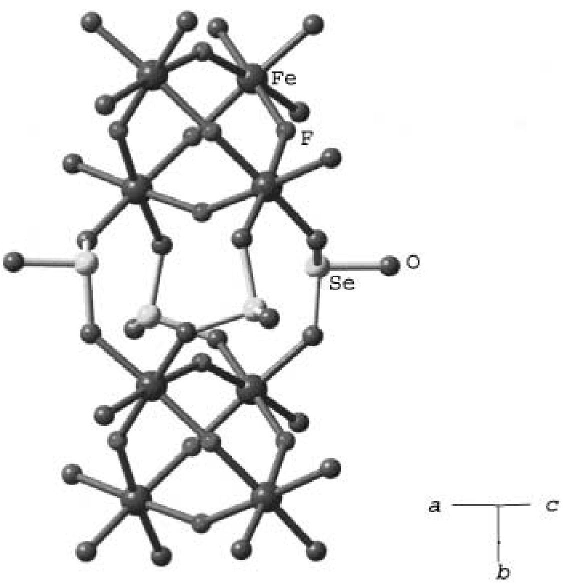

Figure 2. Section of the intercluster connectivity along the *b* axis showing the presence of 5- and 6-rings.

Variable-temperature magnetic susceptibility χ measurements on **I** in the 2–300 K range show a continuous increase in the susceptibility with the decrease in temperature, with a sharp jump occurring around 20 K (T_t) (Figure 3). The plot of $1/\chi$ versus T ($T > 150$ K) is linear with a μ_{eff} value of 6.1 characteristic of the high-spin Fe^{III} center and a θ_P of -366 K showing predominantly antiferromagnetic interaction. We have measured the isothermal magnetization (M versus H) and the zero-field cooled (ZFC) susceptibility. Careful measurements showed that a small remnant field (~1 Oe) was sufficient to force the orientation of the moments below

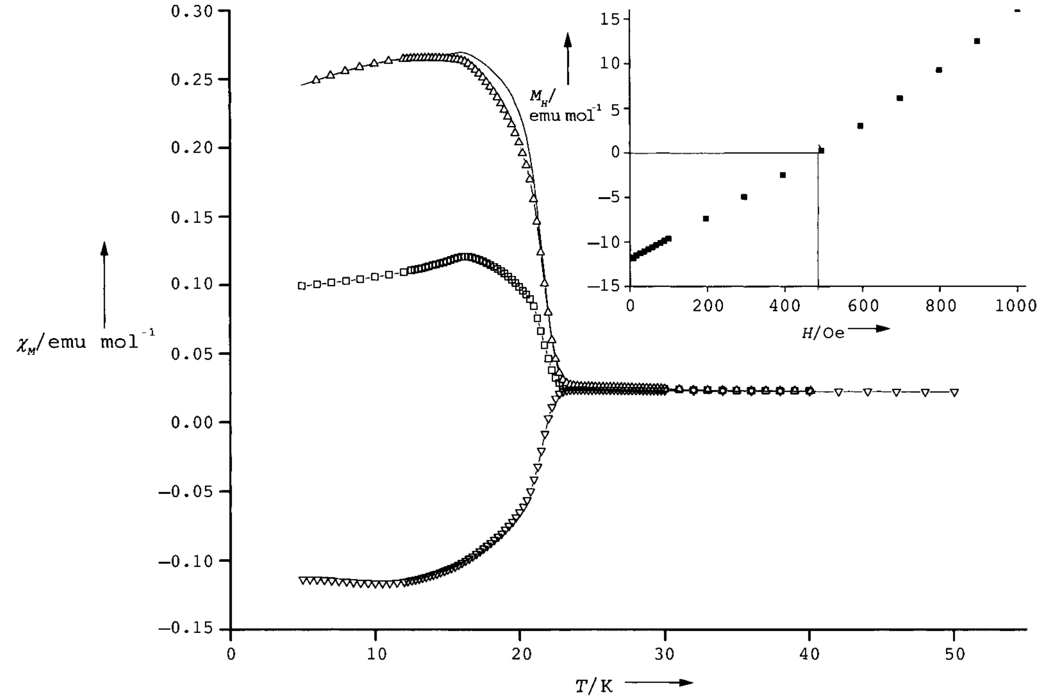

Figure 3. Temperature dependence of the magnetic susceptibility for **I** measured in the presence of a magnetic field of 100 Oe under ZFC and FC conditions. Inset: Section of the *M* versus *H* curve at 5 K with a –1 Oe field-cooled state that demonstrates that a field as high as 500 Oe is required to make *M* positive; (—— FC while decreasing *T*, △ FC while warming, □ ZFC, ▽ ZFC (in the presence of a remnant field of ~ –1 Oe)).

T_t. The ZFC data, recorded after making sure that the remnant field was much smaller than 1 Oe but on the positive side of zero, reveal the divergence shown in Figure 3. We have measured the M versus H curve as well as the ZFC curve after cooling at a small remnant field of -1 Oe. The ZFC curve becomes negative under these conditions as shown in Figure 3, a behavior reported earlier for Ca_3LiRuO_6[12] and for low-dimensional $AFe^{II}Fe^{III}(C_2O_4)_3$.[13] A field of about 500 Oe is required to make M positive in the M versus H plot (Figure 3). The M versus H curve at 5 K is practically linear and does not exhibit any spontaneous magnetization. While the magnetic behavior of **I** is clearly due to magnetic frustration, it is not due to a spin glass as corroborated by AC susceptibility measurements. The frustrated behavior may arise from the tetrahedral geometry[14] of the Fe^{3+} subnetwork of the cluster (Figure 1 a) involving four near-equilateral triangles. Such tetrahedral frustrating topology has been observed earlier in the pyrochlore form of FeF_3 (Pyr-FeF_3).[15, 16] The transition temperature in Pyr-FeF_3 is about 18 K compared to $T_t = 23$ K in **I**. The higher T_t value in **I** indicates a relaxation of the frustrated character compared to FeF_3, due to the absence of a long-range frustration by super exchange via the SeO_3 group.

We have, however, obtained an unusual open-framework 3D zinc selenite **II** by hydrothermal synthesis in the presence

$[C_2N_2H_8]_{0.5}ZnSeO_3$ **II**

of en. The polyhedral network of this selenite is built up from ZnO_3N tetrahedra and SeO_3 pyramids connected to form a layer in the *ac* plane. The nitrogen atom in ZnO_3N tetrahedra comes from the amine (en), the other nitrogen atom of the amine coordinates to the Zn atom of the next nearest layer along the *b* axis to form a 3D structure. The en molecules thus act as pillars through end-to-end (Zn-N-C-C-N-Zn) connectivity and create channels along the *a* and *c* axis (Figure 4). The structure of **II** is similar to a recently reported zinc phosphite, $[C_2N_2H_8]_{0.5}Zn(HPO_3)$, in which there are two such completely independent interpenetrating networks.[3b]

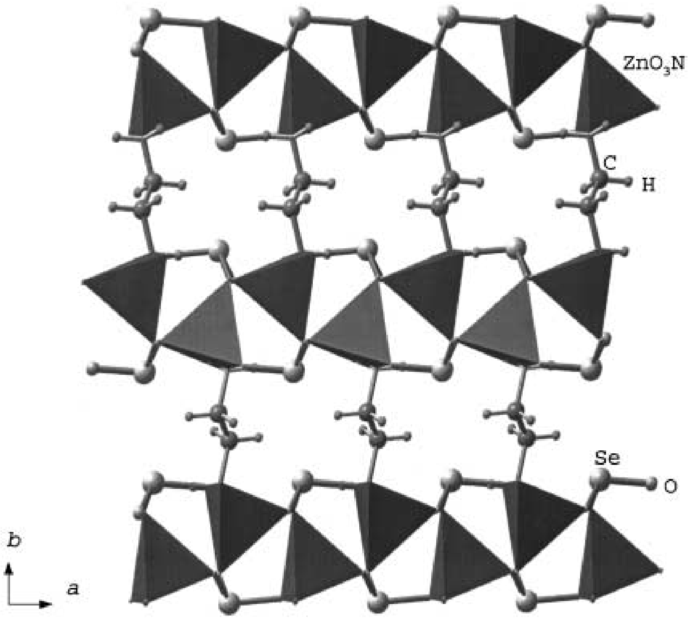

Figure 4. Structure of $[H_2N(CH_2)_2NH_2]_{0.5} \cdot ZnSeO_3$ along the *c* axis, showing the zinc selenite layers pillared by the en molecule through coordinate bonds.

Experimental Section

I: $FeCl_3 \cdot 6H_2O$ (0.8153 g) was dissolved in water (5.4 mL) in a teflon beaker. To this solution HF (0.43 mL) was added with stirring followed by SeO_2 (0.6692 g). Finally, PIP (0.2598 g) was added to this mixture and stirring continued for another 30 min to obtain a homogeneous gel. The resulting gel with a molar ratio $FeCl_3 \cdot 6H_2O$:4HF:2SeO_2:PIP:100H_2O was transferred into a 23 mL PTFE-lined stainless steel autoclave and heated at 150 °C for 5 days. The pH of the starting reaction mixture was 2, and there was little change in pH after completion of the reaction. Rod-shaped faint brown crystals (yield 70 %) of **I** were collected, washed with deionized water, and dried under ambient conditions. Similar reactions were carried out with the amines DETA, DAP, and en.

II: Compound **II** was synthesized starting with the following mixture: ZnO (0.0814 g), H_2SeO_4 (0.515 mL), en (0.067 mL), 36 % HCl (0.062 mL), and H_2O (3.6 mL) at 100 °C for three days.

Structure determination: Single-crystal data were collected on a Siemens SMART-CCD diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å($T = 298$ K)). An absorption correction based on symmetry-equivalent reflections was applied using SADABS.[17] The structures were solved by direct methods using SHELXS-86[18] and difference fourier synthesis. The hydrogen atoms associated with piperazine molecules in **I** were placed geometrically and refined in the riding mode. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[19] package of programs. The non-hydrogen atoms were refined anisotropically.

Characterization: The X-ray powder data for all the compounds were in excellent agreement with their simulated patterns based on single-crystal data, indicating the phase purity. The thermogravimetric analysis of **I** reveals that the selenites are thermally stable up to 300 °C, above which there is a sharp one-step weight loss corresponding to the loss of amine molecules, SeO_2, and HF. The calcined products diffracted poorly and showed a few reflections of Fe_2O_3.

Crystal data: $[C_4N_2H_{12}]_{0.5}[Fe_2F_3(SeO_3)_2]$, **I**, $M_r = 466.70$, monoclinic, space group = $C2/c$ (no. 15), $a = 16.1683(14)$, $b = 7.3973(6)$, $c = 16.1275(14)$ Å, $\beta = 90.044(2)°$, $V = 1928.9(3)$ Å^3, $Z = 8$, $\mu = 10.616$ mm^{-1}, $\rho_{calcd} = 3.14$ g cm^{-3}. $[C_2N_2H_8]_{0.5}ZnSeO_3$, **II**: $M_r = 222.38$, monoclinic, space group = $P2_1/n$ (no. 14), $a = 4.8180(7)$, $b = 15.197(2)$, $c = 6.4863(9)$ Å, $\beta = 91.724(2)°$, $V = 474.71(12)$ Å^3, $Z = 4$, $\mu = 12.724$ mm^{-1}, $\rho_{calcd} = 3.112$ g cm^{-3}. Unique reflections: **I**, 1391($R_{int} = 0.0352$); **II**, 686($R_{int} = 0.0432$). Final R, R_w: **I**, 0.03, 0.07; **II**, 0.04, 0.09. GOF: **I**, 1.07; **II**, 1.05.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-170619 (**I**) and CCDC-170620 (**II**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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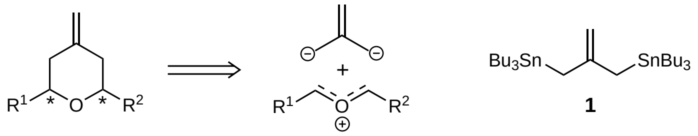
Sequential Catalytic Asymmetric Allylic Transfer Reaction: Enantioselective and Diastereoselective Construction of Tetrahydropyran Units[**]

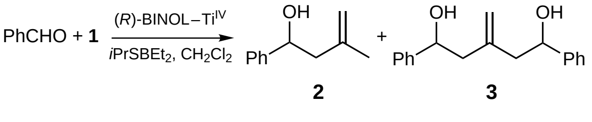
Chan-Mo Yu,* Jae-Young Lee, Byungran So, and Junghyun Hong

There is considerable interest in the enhancement of catalysts for Lewis acid promoted reactions so that practical and useful levels of asymmetric synthesis can be achieved.[1] Other research groups have used a ligand-accelerated strategy[2] to activate the chiral Lewis acid through the internal regulation of the chiral catalyst by a modification of the ligand, thus leading to impressive advances in carbonyl addition reactions.[3] In previous studies we demonstrated that the use of molecular synergistic reagents in catalytic asymmetric allylic transfer reactions resulted in a significant increased catalytic ability as the chiral catalyst could be regenerated expediently. Our strategy involves the use of BINOL–Ti^{IV} complex (BINOL = 2,2'-binaphthol) as a chiral promoter along with *i*PrSBEt$_2$ or *i*PrSSiMe$_3$ as an accelerating synergistic reagent. Recently, this approach provided highly catalytic versions of enantioselective allylic transfer reactions of achiral aldehydes, for example, allylation,[4] propargylation,[5] allenylation,[6] and dienylation.[7] The efficiency of this protocol in terms of enantioselectivity and catalytic ability has encouraged us to apply the extension of this method to more versatile systems, which would expand the scope and utility of allylic transfer reactions. Described herein is an extension of our strategy aimed at finding new reagents and realizing practical ways to advance new levels of asymmetric synthesis. In this study we focus on the sequential addition of a bifunctional reagent to two aldehydes to form an asymmetric tetrahydropyran system (Scheme 1). An efficient method for this reaction would be useful in the synthesis of biologically active substances that contain a tetrahydropyran unit.[8] Several crucial points emerged from this investigation, including the development of a new catalyst and reagents for the sequential allylic transfer reaction, the introduction of highly efficient promoters for the formation of the tetrahydropyran ring, and the highly stereoselective synthesis of four different tetrahydropyran systems that contain an exocyclic double bond.



Scheme 1. General protocol for the synthesis of a tetrahydropyran by means of sequential allylic transfer reactions.

Our initial studies began with bis-stannane **1** as a dianion equivalent which was prepared from Bu$_3$SnLi (two equivalents) and methallyl dichloride at −78 °C in THF. Initial attempts to add **1** to benzaldehyde in the presence of BINOL–Ti^{IV} [a 2:1 mixture of BINOL and Ti(O*i*Pr)$_4$][9] were not successful. The reactivity was improved by introducing a synergistic reagent.[4–7] Treatment of **1** with benzaldehyde in the presence of the catalyst (10 mol %), followed by the dropwise addition of *i*PrSBEt$_2$ at −20 °C for 20 h in CH$_2$Cl$_2$ afforded undesired **3** and **2** in a combined yield of 44 % (2:1) [Eq. (1)]. The formation of alcohol **2** was attributed to a proton source in the reaction mixture (*i*PrOH with Ti^{IV} species). We speculated that the limited scope and side reaction with **1** could be solved by introducing a relatively less bulky and more stable silyl substituent instead of the stannyl



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