A Reactive Intermediate in the Synthesis of Iron Arsenates: Synthesis of the First One-Dimensional Iron Arsenate Oxalate and Its Transformation into Two- and Three-Dimensional Iron Arsenates**

Sandip Chakrabarti and Srinivasan Natarajan*

Phosphate-based networks exhibiting open architectures have been prepared and studied with great intensity during the last two decades.[1] While it is desirable to synthesize large number of materials with new architectures, it is also important to understand the role of the building units and the reaction pathways involved in the formation of these solids.[2, 3] To this end, the principle of building up three-dimensional (3D) structures from structures of lower dimensionalities may be useful.[4] The transformation of a one-dimensional (1D) gallium phosphate into a 3D structure, under real time conditions, is a good example of this principle.[5, 6] The scope of the building up process has not been investigated in detail because of the lack of reactive lower (one-)dimensional solids. Recently, there has been growing interest in the study of arsenate-containing phases and the interplay of the chemical and geometric factors in determining their framework topology and composition.[7] We have been concerned with understanding the formation of framework solids and are investigating the transformation of lower-dimensional zinc phosphates, which has resulted in better understanding of the pathways involved in the formation of these phases.[4, 8, 9] During this study, we prepared an iron arsenate oxalate, $[C_4N_2H_{12}][Fe(OH)(HAsO_4)(C_2O_4)]\cdot H_2O$ (**I**), with a 1D edge-shared ladder structure and pendant oxalate groups on the iron centers, by use of hydrothermal methods. To our knowledge, this is the first iron arsenate oxalate material to be synthesized in the presence of an organic amine. Remarkably, **I** may be transformed into a two-dimensional (2D) iron arsenate, $[C_4N_2H_{12}]_{1.5}[Fe_3F_5(AsO_4)(HAsO_4)_2]$ (**II**), and a mixed-valent 3D iron arsenate, $[C_4N_2H_{12}][Fe^{III}_2Fe^{II}_1(AsO_4)_2(HAsO_4)_2]$ (**III**). This observation not only shows the importance of the building up process, but also establishes the reactive nature of lower-dimensional solids. It is of note that while **I** and **II** contain iron centers in +3 oxidation state, in **III**, the iron centers are in +2 and +3 oxidation states.

The structure of **I** comprises strictly alternating FeO_6 and AsO_4 polyhedral units, which form an edge-shared 1D ladder structure with the oxalate units pendant from the Fe centers (Figure 1 a). A doubly protonated piperazine molecule occupies the inter-ladder space and interacts with the framework through hydrogen bonds. The structure of **I** is isotypic with the recently described vanadyl phosphate oxalate, $[C_4N_2H_{12}][VO(HPO_4)(C_2O_4)]$.[10] The oxalate units in **I** occupy a similar position to that of the pendant phosphates in the 1D ladder structures.[4, 9] This observation prompted us to investigate the transformation of **I** under various conditions, as ladder zinc phosphates have been shown to undergo facile transformation into higher dimensional structures,[9a] though such studies have not been undertaken in any other system of compounds. Thus, **II** and **III** were obtained as good-quality single crystals by the prolonged reaction of **I**.

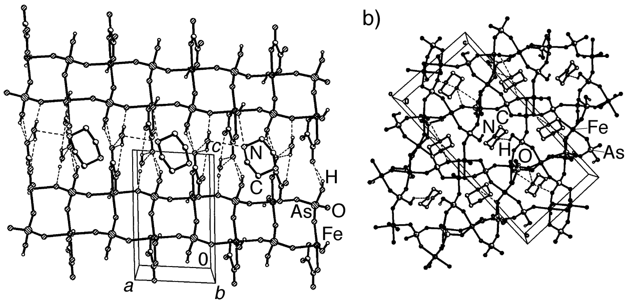

Figure 1. a) Structure of **I** in the *ac* plane, showing the ladder arrangement and the oxalate group pendant from the Fe center. Dotted lines represent hydrogen bonds. b) Structure of **II** in the *bc* plane, showing a single layer. The zigzag Fe-F-Fe chains are linked by SBU-4.

The structure of **II** is similar to the iron–arsenate structure reported recently by Luo et al.,[11] which consists of infinite chains of corner-sharing FeX_6 (X = O, F) octahedra and dimers of edge-sharing FeO_3F_3 octahedra, linked into 2D sheets through arsenate tetrahedra (Figure 1 b). The piperazinium cations occupy interlamellar space and interact with the framework through N–H⋯O hydrogen bonds. Strong interlayer hydrogen bonds between the terminal OH groups of $HAsO_4$ lead to the formation of pseudo-1D channels. The edge-shared dimer with the arsenate group has been classified as an SBU-4 (secondary building unit) and has been observed in many ULM-*n* phases.[2]

Unlike **II**, compound **III** does not have any fluorine atoms in its framework. The fluorine atoms are replaced by three-coordinate oxygen atoms. The structure consists of a network of FeO_6 octahedra and AsO_4 tetrahedra, linked through their vertices to form a unique 3D structure. The framework structure can be understood in terms of secondary building units. Thus, four three-coordinate oxygen atoms connect three iron atoms, which form an Fe_3O_{14} core consisting of two Fe^{III} atoms and an Fe^{II} atom, all of which are perfectly ordered, as shown in Figure 2 a. This is the first time, to our knowledge, that this trimer unit has been observed in an iron–arsenate system. The Fe_3O_{14} trimeric core is connected to $HAsO_4$ tetrahedra in an out-of-plane mode, through the three-coordinated oxygen atoms (Figure 2 b), which forms four interconnected SBU-4 units. These SBU-4 units are further linked by AsO_4 tetrahedra, to form an unusual $[Fe_6As_8O_{36}(OH)_4]$ cluster, which is connected through the oxygen atoms, which results in large 1D tunnels surrounded by 12 T atoms (T = As) along the [001] direction as shown in Figure 3. The AsO_4 units cover all the tunnel walls. This may be contrasted with the open-framework nickel phosphate

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[*] Prof. Dr. S. Natarajan, S. Chakrabarti
Framework Solids Laboratory
Chemistry and Physics of Materials Unit
Jawaharlal Nehru Centre for Advanced Scientific Research
Jakkur P.O., Bangalore 560 064 (India)
Fax: (+91) 80-846-2766
E-mail: raj@jncasr.ac.in

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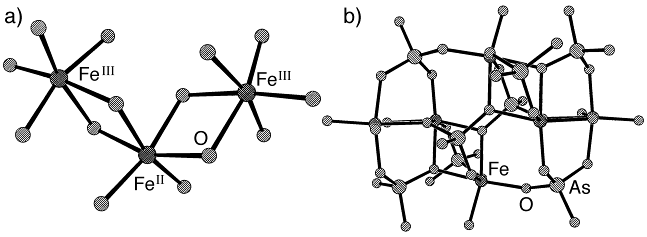

Figure 2. a) The unusual building unit observed in **III**, the Fe–O trimer, $[Fe_3O_{14}]$. Note the ordering of the Fe^{III} and Fe^{II} centers. b) The $[Fe_6As_8O_{36}(OH)_4]$ cluster in **III**. Note the presence of SBU-4 units and their connectivity.

structure described recently, in which the tunnel walls consist only of NiO_6 octahedra.[12] The structure of **III**, constructed entirely of SBU-4 units, can be considered as the upper homologue of ULM-4.[2] The various structural features in **III** have been observed for the first time.

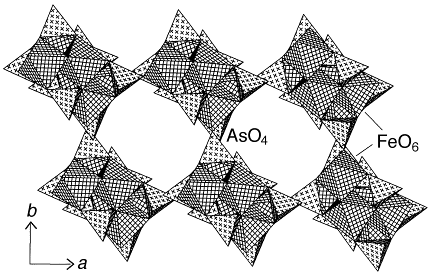

Figure 3. Structure of **III** in the *bc* plane showing the large 1D tunnels. The tunnel walls consist only of the arsenate tetrahedra. The amine molecules are not shown.

The bond distances and angles in **I**–**III** are in the ranges expected for this type of bonding. The observed average As–O distance is 1.6954 Å, the O-As-O bond angle is 109.5°, the Fe-O/F distance is 2.0051 Å, and the O/F-Fe-O/F angle is 106°, all of which are in agreement with those values reported in the literature.

An examination of the structures of **I**, **II**, and **III** reveals the similarities between them. Compounds **II** and **III** possess the same building unit (SBU-4) formed with fluorine and oxygen atoms, respectively, but linked differently. In contrast, **I** contains only four-membered rings. The formation of SBUs from **I**, however, can be easily visualized, as it possesses a terminal oxalate group. Metal oxalates have traditionally been employed as the initial reactive source of metal ions, in the synthesis of open-framework materials. It is possible that, during the hydrothermal reaction, the oxalate group leaves the framework, and the F^- ion attacks the bare iron atom and links two iron atoms within the ladder, which forms Fe-F-Fe 1D chains, such as those observed in **II** (Figure 1 b). The continuous reaction of F^- ions at the Fe center may also lead to a breakdown of the ladder, thereby causing formation of four-membered rings and the linking of pairs of iron centers by two F^- ions. This breakdown of the ladder would result in SBU-4. These building units are connected through the arsenate units forming the structure of **II**. In the case of **III**, we find that two four-membered rings form the SBU-4 units, and are joined through three-coordinate oxygen to form a $[Fe_3O_{14}]$ trimer, which is then connected through arsenate tetrahedra to form the framework. The formation of four-membered rings appears in both cases to be crucial, as such four-membered-ring monomers have been isolated and shown to be highly reactive in the formation of 1D, 2D, and 3D structures.[8, 9a] This hypothesis suggests that the transformation of the ladder material to the 3D structure is a solution-mediated process, which involves dissolution of the first phase, rather than a solid-state transformation. A schematic of the formation, from **I**, of the various building units observed in **II** and **III** is shown in Figure 4. A key feature in this evolution is the existence of the same tetramers (SBU-4) which act as building blocks in the solids. It is likely that the reaction pathway (Figure 4) can be followed by in situ synchrotron radiation experiments, as such studies have been used to elucidate similar building processes.[5, 6, 13, 14] Within this hypothesis, the identification by Taulelle et al. of various oligomeric building blocks, under hydrothermal reaction conditions and by using NMR spectroscopy, is also important.[15]

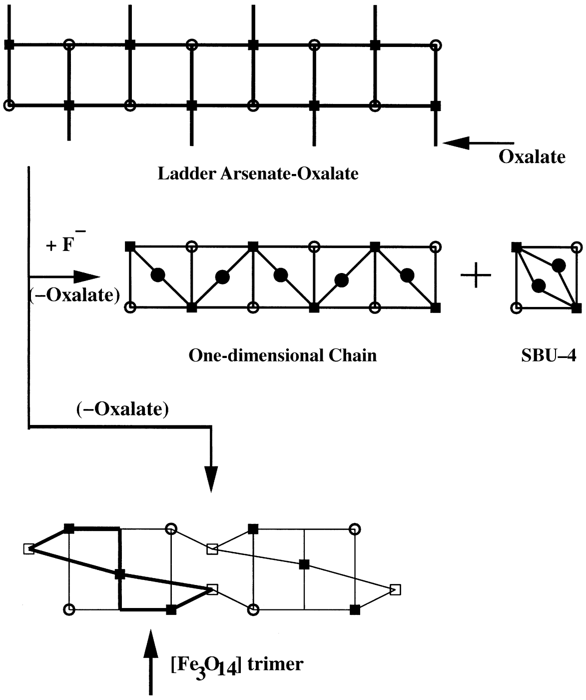

Figure 4. A schematic of the formation of the secondary-building units (SBU) observed in **II** and **III**. ■ Fe, ○ As, ● F, □ O (three coordinate).

In summary, a 1D ladder iron arsenate oxalate has been prepared for the first time, and shown to be reactive. This is the first time that the transformation of a low-dimensional solid has been observed in a family of transition metal arsenates and arsenate oxalates. It is likely that crystalline materials with unknown structures might also be formed during the hydrothermal reactions. The sequential crystallization of 2D (**II**) and 3D (**III**) structures from **I** shows the evolution of a chemical system.

Experimental Section

Colorless rodlike crystals of **I** were obtained in $\sim$40% yield, by the hydrothermal reaction in the presence of piperazine (PIP). Typically, a mixture of $Fe(C_2O_4)\cdot 2H_2O$:H_3AsO_4:PIP:HF:water (1:8:4:6:200) was heated at 150°C for 72 h in a PTFE-lined acid digestion bomb (7 mL). The initial pH of the reaction mixture was 2; this did not change significantly after the heat treatment. Mildly pink colored platelike crystals of **II** (50% yield) were obtained by reacting the above mixture at 150°C for 168 h or at 180°C for 24 h, and deep green colored rodlike crystals of **III** (35% yield) resulted when the mixture was heated at 180°C for 60 h. **II** and **III** can also be obtained by heating a mixture of $Fe(acac)_3$:$6H_3AsO_4$:4-PIP:4HF:$200H_2O$ at 180°C for 48 h, or $Fe(C_2O_4)\cdot 2H_2O$:$8.6H_3AsO_4$:1.4-PIP:$285H_2O$ at 150°C for 48 h. When the crystals of **I** (0.5 g) were heated with water (2 mL) at 150°C in an acid digestion bomb, **III** was formed, along with a mixture of condensed iron arsenates. The compounds **I**, **II**, and **III** have been obtained as pure single-phase materials, and were characterized using energy dispersive X-ray analysis (EDAX), IR, and thermogravimetric analysis (TGA). An X-ray photoemission spectroscopy (XPS) investigation clearly indicated the presence of both Fe^{II} and Fe^{III} species in **III**.

Suitable single crystals of **I**, **II**, and **III** were subjected to X-ray diffraction studies on a Siemens SMART-CCD diffractometer at 298 K. Crystal data for **I**: triclinic, space group $P\bar{1}$ (no. 2), $a = 6.5668(3)$, $b = 9.1040(3)$, $c = 10.4715(4)$ Å, $\alpha = 86.35(1)$, $\beta = 85.34(1)$, $\gamma = 83.32(4)°$; $V = 618.8(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.184$ g cm^{-3}, and $\mu(Mo_{K\alpha}) = 3.928$ mm^{-1}. Crystal data for **II**: monoclinic, space group $P2_1/c$ (no. 14), $a = 8.4048(1)$, $b = 22.000(5)$, $c = 10.848(2)$ Å, $\beta = 95.97(1)°$; $V = 1995.0(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.709$ g cm^{-3}, and $\mu(Mo_{K\alpha}) = 7.201$ mm^{-1}. Crystal data for **III**: monoclinic, space group $C2/c$ (no. 15), $a = 14.6850(3)$, $b = 10.6696(3)$, $c = 10.1699(3)$ Å, $\beta = 90.12(1)°$; $V = 1593.4(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 3.067$ g cm^{-3}, and $\mu(Mo_{K\alpha}) = 9.993$ mm^{-1}. For **I**, a total of 2632 reflections were collected and merged to give 1754 unique reflections ($R_{int} = 0.02$) of which 1488 with $I > 2\sigma(I)$ were observed. For **II**, a total of 8348 reflections were collected and merged to give 2867 unique reflections ($R_{int} = 0.06$) of which 2393 with $I > 2\sigma(I)$ were observed. For **III**, a total of 3255 reflections were collected and merged to give 1145 unique reflections ($R_{int} = 0.04$) of which 993 with $I > 2\sigma(I)$ were observed. The structures were solved and refined using the SHELXTL-PLUS programs to obtain $R_1 = 0.04$, $wR_2 = 0.1$, and $S = 1.06$ for 190 parameters for **I**, $R_1 = 0.04$, $wR_2 = 0.09$, and $S = 1.07$ for 289 parameters for **II**, $R_1 = 0.03$, $wR_2 = 0.08$, and $S = 1.03$ for 121 parameters for **III**. The piperazine molecules within the channels in **III** were difficult to locate, and only a fragment of the molecule was observed. It is likely that the piperazine molecule decomposed during the preparation of the crystal. CCDC-172356 (**I**), -172357 (**II**), and -172358 (**III**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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$[Zn_4(thf)_4(MeZn)_4(O_3SiR)_4]$ ($R = 2,6\text{-}i\mathrm{Pr}_2C_6H_3N(SiMe_3)$), A Compound Containing Trigonal-Planar, Tetrahedral, and Trigonal-Bipyramidal Metal Atoms: A New Route to Larger Aggregates[**]

Ganapathi Anantharaman, Herbert W. Roesky,* and Jörg Magull

Dedicated to Professor Dieter Fenske
on the occasion of his 60th birthday

Metallasiloxanes derived from Si–OH species have received considerable attention in recent years. A number of such compounds obtained starting from monosilanol, silanediol, silanetriol, disilanol, and trisilanol have been discussed in recent reviews.[1] These compounds can be used as precursors for metal silicates and mixed-metal oxide systems[2] as well as for models for heterogeneous silica-supported catalytic systems.[3] Recently, a zinc-containing zeolite (H-ZSM5) system has been reported that catalyzes aromatization reactions, dehydrochlorination and dehydrofluorination, and conversion of methyl iodide to hydrocarbons.[4] Metallasiloxanes are also important because of their ability to act as model compounds for complex zeolite systems.[5] In recent years we have synthesized a variety of metallasiloxane compounds starting from kinetically stable silanetriol ($2,6\text{-}i\mathrm{Pr}_2C_6H_3N(SiMe_3)Si(OH)_3$) that exhibits novel structural features.[6] We[7] and others[8] have also reported that the framework of aluminosiloxane and gallasiloxane compounds has similar structural features to naturally occurring mineral and zeolite systems.

A polyhedral zinc siloxane compound which was obtained by using dimethylzinc and trimethylsilanol has been reported by Schmidbaur et al.[9] More recently, dimeric, trimeric, and

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[*] H. W. Roesky, G. Anantharaman, J. Magull
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-393373
E-mail: hroesky@gwdg.de

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