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Chemical Excision of Tetrahedral FeSe₂ Chains from the Superconductor FeSe: Synthesis, Crystal Structure, and Magnetism of Fe₃Se₄(en)₂

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Abstract

Fragments of the superconducting FeSe layer, FeSe₂ tetrahedral chains, were stabilized in the crystal structure of a new mixed-valent compound Fe₃Se₄(en)₂ (en = ethylenediamine) synthesized from elemental Fe and Se. The FeSe₂ chains are separated from each other by means of Fe(en)₂ linkers. Mössbauer spectroscopy and magnetometry reveal strong magnetic interactions within the FeSe₂ chains which result in antiferromagnetic ordering below 170 K. According to DFT calculations, anisotropic transport and magnetic properties are expected for Fe₃Se₄(en)₂. This compound offers a unique way to manipulate the properties of the Fe-Se infinite fragments by varying the topology and charge of the Fe-amino linkers.

The chemistry of the recently discovered Fe-based superconductors is far from being fully explored.¹ The main structural blocks of Fe-based superconductors are FeX square layers (X = pnictogen or chalcogen) with a PbO-like structure. Each layer is formed from linear FeX₂ tetrahedral chains sharing all vertices (Figure 1A). To understand the electronic and magnetic interactions in superconductors it is preferable to study a single building block, *i.e.* an isolated FeX layer or FeX₂ chain.² To compare the calculated results with experimental observations it is necessary to develop “chemical scissors” that are able to excise fragment of the superconducting phase. Additionally, it is desirable that the “chemical scissors” do not alter bonding within the cut fragment, *i.e.* the cutting reactant is only weakly coordinated to the FeX moiety. In this work we demonstrate how tetrahedral FeSe₂ chains (Figure 1B) can be isolated from each other by means of [Fe(en)₂]²⁺ inorganic complexes, en = ethylenediamine. We report the synthesis, crystal structure, and magnetic properties of the new compound Fe₃Se₄(en)₂.

Fe₃Se₄(en)₂ was synthesized through a solvothermal method. Elemental Fe and Se (both Sigma-Aldrich, 99.9%) were mixed together in a 3:4 molar ratio with a total weight of 50 mg. 100 mg of NH₄Cl (Sigma-Aldrich, 99.9%) was added to the reaction mixture as a mineralizer. Ethylenediamine (Sigma-Aldrich, 99%) was used as a solvent and the filling fraction of the autoclave was 70%. The reaction was performed at 473 K for 5 days. The product of the reaction was filtered and washed with water, ethanol, and acetone. The reaction product appeared as shiny black needle-like crystals up to 1 mm in length. The synthetic conditions were optimized by varying the amount of starting materials, reaction

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Supporting Information

Crystallographic files, additional X-ray and Mössbauer tables and figures are available free of charge via the Internet at <http://pubs.acs.org>.

temperature, and autoclave filling fraction. A small admixture of binary FeSe_2^3 was often present in the samples. To account for the contribution of this admixture a single phase sample of FeSe_2 was synthesized (See Supporting Information for synthetic details).

The samples were characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffractometer with CuK_α radiation (Figure SI 1). High resolution synchrotron XRD data were collected using beamline 11-BM at the Advanced Photon Source at Argonne National Laboratory using an average wavelength of 0.41 Å (Figure SI 2) at room temperature and at 100 K. Single crystal X-ray diffraction was performed using a Bruker Smart Apex II diffractometer with Mo-K_α radiation. The solution and refinement of the crystal structure were carried out using the SHELX suite of programs.^{4a} The final refinement (Table SI 1) was performed in the space group $C2/c$ (No. 15) with anisotropic atomic displacement parameters for all atoms except hydrogen. Further details may be obtained from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-962930. Elemental analysis of selected single crystals was carried out on a Hitachi S4100T scanning electron microscope (SEM) with energy-dispersive X-ray (EDX) microanalysis (Oxford INCA energy). Sample analysis confirmed the presence of Fe and Se as the only heavy elements (Figure SI 3). No traces of chlorine were detected. The observed Fe:Se ratio 42(2):58(2)% is in agreement with ratio of 43%:57% calculated from the crystal structure. Magnetic measurements were performed on powdered single crystalline samples with a Quantum Design SQUID magnetometer MPMS-XL. The sample was placed between two long strips of Kapton tape to ensure minimal contribution from the sample holder. Density functional theory calculations were performed using a full potential all-electron local orbital code FPLO 7.00–28 within the local density approximation.^{4b}

^{57}Fe Mössbauer spectra were collected using a conventional constant acceleration spectrometer. Additionally, the binary compound FeSe_2 was measured under the same conditions as $\text{Fe}_3\text{Se}_4(\text{en})_2$. The parameters from the fittings are summarized in Table SI 2. The $\text{Fe}_3\text{Se}_4(\text{en})_2$ sample used for Mössbauer spectroscopy contained 6 molar % of FeSe_2 . To ensure that the contribution from the impurity was correctly described an impurity-enriched sample (18% FeSe_2) and a sample of pure FeSe_2 were measured under identical conditions (Figure SI 5 and Table SI 3). FeSe_2 remains non-magnetic above 80 K. All subsequent discussions pertain to signals from $\text{Fe}_3\text{Se}_4(\text{en})_2$ after subtraction of the FeSe_2 signal.

Solvothermal syntheses of anisotropic selenides starting from soluble metal-containing precursors are well developed.⁵ Most of the reported syntheses require hazardous and air-/moisture-sensitive reducing reagents or starting materials (*e.g.* NaBH_4 or TiCl_4). We have developed a simple route, which utilizes elemental Fe and Se (Eq. 1):

This synthesis occurs at a low temperature (473 K) under aerobic conditions. Thus, no glovebox or Schlenk line is necessary. The addition of the mineralizer (NH_4Cl) is essential for increasing the solubility of Fe and the overall yield of the reaction. A similar increase in metal solubility was observed in our earlier studies of the synthesis of tin arsenide.⁶ NH_4Cl precipitates can be effectively washed out of the product with water or ethanol. $\text{Fe}_3\text{Se}_4(\text{en})_2$ appears to be stable against treatment with water and ethanol, however it decomposes in dilute acidic solutions. AFeSe_2 ($A = \text{K}, \text{Rb}, \text{Cs}$) containing structural fragments similar to $\text{Fe}_3\text{Se}_4(\text{en})_2$ were synthesized using a high temperature (1000 K) stream of highly toxic H_2Se gas.^{7a} Our reported synthetic method is much more attractive due to its simplicity and

the possibilities of fine tuning the metal-amino complex, which will result in new related materials.

The crystal structure of $\text{Fe}_3\text{Se}_4(\text{en})_2$ consists of two main structural units, one-dimensional FeSe_2 infinite chains and $\text{Fe}(\text{en})_2$ fragments (Figures 2A and 2B). The FeSe_2 chains are formed by FeSe_4 tetrahedra, which share opposite edges. A similar structural fragment is present in the superconducting tetragonal FeSe (Figure 1) where FeSe_2 chains are condensed together by sharing two additional edges, forming square layers with the overall composition FeSe .^{1c} In the crystal structure of $\text{Fe}_3\text{Se}_4(\text{en})_2$ half of the Se atoms from different FeSe_2 chains are connected via additional iron atoms, labeled Fe2. The Fe2-Se bond (2.70 Å) is significantly longer than the Fe1-Se bond within the tetrahedral chains (2.37 Å). The atomic coordination of Fe2 atoms is completed by four coplanar nitrogen atoms from two ethylenediamine molecules (Figure 2B). Tetrahedral Fe1Se_2 chains run along the [001] direction (Figures 2C and 2D). Se atoms that are not bound to Fe2 atoms are additionally coordinated by one hydrogen atom from the ethylenediamine moiety at a distance of 2.56 Å. Thus, every Se atom has a 2+1 coordination. The average Fe2-N distance of 2.18 Å is typical for the high spin state of Fe^{2+} .⁸ Isolated FeSe_2 chains were stabilized only by the presence of high concentrations of alkali metals cations in AFeSe_2 (A = K, Rb, Cs) compounds.^{7a} In AFeSe_2 the tetrahedral chains are slightly distorted from ideal $p4_2/mmc$ rod group symmetry. For example, in RbFeSe_2 the Fe-Se distances are 2.383 Å and 2.386 Å and the angles $\angle\text{Se-Fe-Se}$ (107.1-111.5°) are close to the ideal tetrahedral angle of 109.5°. ^{7a} Theoretical investigations of the sulfur analogs by *Silvestre and Hoffmann* predict little distortion of the $[\text{FeS}_2]^{1-}$ tetrahedral chains based solely on electronic factors.^{7b} Strong Peierls distortion was predicted for the $[\text{FeS}_2]^{1-}$ reduced chains, which was indeed observed in $\text{A}_3\text{Fe}_2\text{X}_4$ (X = S, Se).^{7c,7d} In $\text{Fe}_3\text{Se}_4(\text{en})_2$ the tetrahedral chains bear a -1 formal negative charge (see the Mössbauer section below). However, they exhibit much stronger deviation from the ideal $p4_2/mmc$ rod group symmetry with Fe-Se distances varying from 2.352 Å to 2.397 Å and angles $\angle\text{Se-Fe-Se}$ from 103.8° to 117.1°. These distortions are caused by chain-cation interactions. In AFeSe_2 each Se atom is additionally coordinated by four A^+ cations at distances greater than 3.5 Å.^{7a} In $\text{Fe}_3\text{Se}_4(\text{en})_2$ the FeSe_2 chains are further apart from each other compared to AFeSe_2 . Nevertheless, in $\text{Fe}_3\text{Se}_4(\text{en})_2$ each Se atom has one short neighbor outside the chain: either Fe2 atoms at distance of 2.70 Å or a H atom at a distance of 2.56 Å. Such secondary Se-cation interactions introduce significant distortions to the tetrahedral chain, which are unexpected from a solely electronic point of view.

High-resolution XRD confirmed the structure established by single-crystal diffraction (Figure SI 2 and Table SI 1). Comparison of the structural data obtained from single crystal and powder XRD experiments performed at 90 K, 100 K, and 295 K reveals the absence of any structural transition. Fe2-N and Fe1-Se distances remain almost unchanged and the structural shrinkage upon cooling occurs mainly due to shortening of the long Fe2-Se bonds (Tables SI 1 and SI 4).

The role of the ethylenediamine ligand in $\text{Fe}_3\text{Se}_4(\text{en})_2$ is to coordinate Fe2 atoms connecting the FeSe_2 chains. This differentiates the title compound from Metal-Organic-Frameworks where coordinating ligands provide connectivity between metal centers and dictate the topology of the framework.⁹ $\text{Fe}_3\text{Se}_4(\text{en})_2$ also stands alone the majority of solvothermally synthesized metal chalcogenides. For most of them amine molecule either connects two inorganic fragments (*e.g.* MnSe slabs connected by *en*)^{5d} or coordinates to the inorganic fragments (*en* coordinated to TiX_2 chains, X = S, Se).^{5a,5b} In the crystal structure of $\text{Fe}_3\text{Se}_4(\text{en})_2$ two independent subsystems can be identified: FeSe_2 chains and $\text{Fe}(\text{en})_2$ complexes. Each subsystem has different contributions to the magnetism and electronic structure as shown below.

$\text{Fe}_3\text{Se}_4(\text{en})_2$ is paramagnetic at 300 K (Figure 3). No satisfactory Curie-Weiss fitting can be achieved involving a temperature independent contribution, χ_{TIP} (Table SI 5). Fixing $\chi_{\text{TIP}} = 0$ results in a reasonable fit with the asymptotic Curie temperature, $\theta = -105(8)$ K, which indicates antiferromagnetic (AFM) nearest-neighbor interactions (Table SI 5, Figure SI 6). The χ^T value at 300 K is only $4.2 \text{ emu}\cdot\text{K}\cdot\text{mole}^{-1}$, while from Curie-Weiss fitting it is $5.6(2) \text{ emu}\cdot\text{K}\cdot\text{mole}^{-1}$. Such low χ^T values indicates that the Fe states may differ from high spin Fe^{2+} ($S = 2$) and Fe^{3+} ($S = 5/2$). To further clarify the oxidation and spin states of Fe atoms, Mössbauer spectroscopy was applied. The room temperature spectrum for $\text{Fe}_3\text{Se}_4(\text{en})_2$ was fitted with two doublets, Q_1 and Q_2 , with a 2:1 intensity ratio (Figure 4A, Table SI 2). Q_1 , with a low chemical shift (0.27 mm/s) and quadrupole splitting (0.39 mm/s), corresponds to tetrahedral Fe^{3+} . The chemical shift of the Fe^{3+} is slightly smaller than the reported chemical shift for Fe^{3+} atoms in AFeSe_2 .^{7e} Q_2 , with a high chemical shift (0.88 mm/s) and high quadrupole splitting (0.86 mm/s), corresponds to a high-spin Fe^{2+} . The high value of the chemical shift unambiguously indicates an $S = 2$ spin state, despite the $4/mmm$ distortion of the Fe^{2+} environment.¹⁰ Thus, $\text{Fe}_3\text{Se}_4(\text{en})_2$ is a mixed valent compound containing well separated Fe^{3+} and Fe^{2+} sublattices. In the crystal structure the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is 2:1. Assuming that *en* is a neutral ligand, the formula of the compound can be written as $(\text{Fe}^{2+})_2(\text{en}^0)_2(\text{Fe}^{3+})_2(\text{Se}^{2-})_4$. Therefore, iron atoms in the tetrahedral chains are Fe^{3+} , while iron atoms coordinated to *en* are Fe^{2+} , differentiating the title compound from the binary FeSe superconducting phase in which all iron atoms are Fe^{2+} .^{1c,11} The bond-valence sum calculations support the Mössbauer assignments giving +3.1 and +1.9 oxidation states for tetrahedral and octahedral Fe atoms, respectively.¹²

Fe^{3+} in a strongly distorted tetrahedral environment with +0.27 mm/s Mössbauer chemical shift may have three spin states with $S = 1/2, 3/2$, and $5/2$.^{7e,10} According to neutron diffraction data, local crystal field and extended band structure calculations, Fe^{3+} in AFeSe_2 exhibit an intermediate spin state between $S = 3/2$ and $1/2$.⁷ For $\text{Fe}_3\text{Se}_4(\text{en})_2$ χ^T values in the range of 3.75 to $6.75 \text{ emu}\cdot\text{K}\cdot\text{mole}^{-1}$ are expected assuming $S = 2$ for Fe^{2+} and $S =$ either $1/2$ or $3/2$ for Fe^{3+} . The observed χ^T values are in this range indicating mixed spin states for Fe^{3+} . Gradual decrease of the χ^T with temperature indicates the presence of AFM coupling between Fe atoms, which is supported by the investigation of the isothermal field dependence of magnetization indicate (Figure 3 inset). The magnetic moment at room temperature at the highest applied field of 5 T was only $0.1 \mu_B\cdot\text{f.u.}^{-1}$.

Upon cooling an antiferromagnetic transition due to the interaction between the chains is observed starting at ~ 150 K (Figure 3). The AFM nature of the transition is emphasized by a significant decrease of χ^T with decreasing temperature and supported by the low temperature field dependences of magnetization (Figure 3 inset). Mössbauer spectroscopy was used to trace the AFM ordering. The spectrum collected at 170 K is similar to room temperature one taking into account second order Doppler effect, which is reflected in the increase in chemical shifts with decreasing temperature (Figure 4B). At 150 K, the Fe^{3+} component, Q_1 , is completely transformed to a magnetic sextet with a hyperfine field of 13.5 T (blue line in Figure 4C). This is comparable with the hyperfine field found in AFeSe_2 .^{7e} The Fe^{2+} component consists of two signals: a non-magnetic doublet (green line in Figure 4C) and a magnetically split sextet (red line in Figure 4C). The latter component exhibits a significantly smaller hyperfine field of 5.9 T. Similar behavior was observed for BaFe_2Se_3 , where double-tetrahedral chains are present.¹³ Further cooling to 80 K decreased the intensity of the non-magnetic part of Fe^{2+} and increased the intensity of the Fe^{2+} sextet (Figure 4D and Table SI 2). Additionally, the hyperfine field for both observed sextets increased. Mössbauer signals from $\text{Fe}_3\text{Se}_4(\text{en})_2$ collected at 10 K are similar to those observed at 80 K with a small increase of hyperfine field to 6.6 T for the magnetic Fe^{2+} component (Figure SI 4 and Table SI 2). At 10 K the hyperfine field for Fe^{3+} is 25.7 T which is expected for $S = 3/2$ state^{7e} and lower than typical values of ~ 50 T for $S = 5/2$.¹⁰

Simple molecular orbitals calculations based on local structure may explain the low spin state of Fe^{3+} , but will also predict the lower spin state of $S = 1$ for Fe^{2+} in $\text{Fe}(\text{en})_2\text{Se}_2$. This contradicts the Mössbauer data, since for Fe^{2+} with $S = 1$ a significantly smaller chemical shift (below 0.6 mm/s) is expected.¹⁰ *Silvestre and Hoffmann* have performed a detailed analysis of local and extended bonding in $[\text{FeS}_2]^{1-}$ tetrahedral chains and have shown that simple local MO analysis is not sufficient to explain the magnetic and electronic properties. We performed non-magnetic quantum mechanical calculations to qualitatively estimate the electronic structure of $\text{Fe}_3\text{Se}_4(\text{en})_2$ (Figure 5). The title compound exhibits a high peak in the electronic density of states (DOS) in the vicinity of the Fermi level. Contrary to the simple valence description $(\text{Fe}^{2+})(\text{en}^0)_2(\text{Fe}^{3+})_2(\text{Se}^{2-})_4$, orbital overlap leads to the closing of the bandgap.¹⁴ As expected from the crystal structure, the electronic structure of $\text{Fe}_3\text{Se}_4(\text{en})_2$ is strongly anisotropic. In the band diagram there are no bands crossing the Fermi level in the Γ -X and Z-L directions (Figure SI 7) of the Brillouin zone. As expected, ethylenediamine and selenium have minor contributions to the states near the Fermi level. Our calculations indicate that magnetic ordering is expected for Fe^{3+} atoms but not for Fe^{2+} . The strongest contribution to the states in the vicinity of the Fermi level is from the 3d orbitals of Fe^{3+} atoms, while the 3d orbitals of Fe^{2+} are located below the Fermi level (Figure 5B). In itinerant magnets, the presence of a high DOS peak in the vicinity of the Fermi level is a prerequisite for magnetic ordering.¹⁵ This explains the results of Mössbauer spectroscopy. Fe^{3+} atoms indeed exhibit magnetic ordering inside the tetrahedral chains resulting in a strong internal magnetic field and high hyperfine splitting of the Mössbauer spectra. In turn, Fe^{2+} atoms do not exhibit magnetic ordering. The small hyperfine splitting is induced by the magnetic field of FeSe_2 chains. The absence of the sharp AFM peak in the magnetic susceptibility temperature dependence indicates that three-dimensional ordering of the magnetic moments of the chains is not perfect. Thus two situations are possible: $\text{Fe}^{3+}(\uparrow)\text{Se}-\text{Fe}^{2+}-\text{SeFe}^{3+}(\downarrow)$ and $\text{Fe}^{3+}(\uparrow)\text{Se}-\text{Fe}^{2+}-\text{SeFe}^{3+}(\uparrow)$. The former results in the cancelation of the induced magnetic field on Fe^{2+} and the appearance of the non-magnetic doublet for Fe^{2+} , while the latter leads to the emergence of the magnetically induced sextet with a small hyperfine field.

Our magnetic, Mössbauer, and theoretical investigations of $\text{Fe}_3\text{Se}_4(\text{en})_2$ indicate that within the FeSe_2 chains there is a strong antiferromagnetic interaction, while the interactions between the FeSe_2 chains are weaker. Upon cooling, the interactions between the chains strengthen resulting in the attenuation of the non-magnetic Fe^{2+} component in the Mössbauer spectra. However, one quarter of the Fe^{2+} atoms remains non-magnetic at 10 K, indicating that complete three-dimensional antiferromagnetic ordering of the Fe^{3+} magnetic moments has not been achieved even at temperatures as low as 10 K.

A new crystal structure with tetrahedral FeSe_2 chains was synthesized from the simplest starting materials, elemental Fe and Se. $\text{Fe}_3\text{Se}_4(\text{en})_2$ exhibits antiferromagnetic ordering within the tetrahedral chains. This compound offers a unique way to study magnetic and electronic interactions in an isolated fragment of the superconductor FeSe . In condensed matter physics, the application of hydrostatic pressure is a common way to modify magnetic and superconducting properties of a material.¹⁶ $\text{Fe}_3\text{Se}_4(\text{en})_2$ compound offer an alternative chemical method to introduce internal pressure. The “chemical pressure” can be achieved by varying the nature of the amine ligand, *i.e.* the length of the carbon chain or number of chelating amino groups. A variety of interesting magnetic and superconducting properties may arise from compounds with tunable, antiferromagnetically-coupled tetrahedral FeSe_2 chains. Investigations of the synthesis, structure, and properties of new compounds with similar FeSe chains and different amino ligands are currently underway.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

A) Superconducting FeSe layer. Fe: black; Se: white/yellow. The FeSe₂ chain is emphasized in color. B) Tetrahedral FeSe₂ chain in the crystal structure of Fe₃Se₄(en)₂.

Figure 2. Crystal structure of $\text{Fe}_3\text{Se}_4(\text{en})_2$: A) tetrahedral Fe1Se_2 chain; B) $\text{Fe2(en)}_2\text{Se}_2$ fragment connecting two tetrahedral chains; C) and D) general views along the $[010]$ and $[001]$ directions. Long Se–Fe and Se–H bonds are shown using dashed lines. The unit cell is shown in green. Fe: black; Se: yellow; N: blue; C: red; H: grey, FeSe_4 tetrahedra: red.

Figure 3. Temperature dependence of magnetic susceptibility χ (red triangles) and χT (blue circles) for $\text{Fe}_3\text{Se}_4(\text{en})_2$ in the applied field of 3 mT. Inset: isothermal field dependence of the magnetization.

Figure 4. Mössbauer spectra for $\text{Fe}_3\text{Se}_4(\text{en})_2$ collected at different temperatures. Experimental data: black circles; calculated spectrum: black line; Fe^{3+} : blue; Fe^{2+} : red and green.

Figure 5. Non spin-polarized DOS for $\text{Fe}_3\text{Se}_4(\text{en})_2$. In (A) the contributions from $\text{Fe}^{3+}\text{Se}_2$ chains, *en*, and Fe^{2+} are shown. In (B) the contributions of Fe^{3+} (blue) and Fe^{2+} (red line) atoms are compared.