

As-Se pentagonal linkers to induce chirality and polarity in mixed-valent Fe-Se tetrahedral chains resulting in hidden magnetic ordering

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Abstract

A novel mixed-valent hybrid chiral and polar compound, $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$, has been synthesized by a single-step solvothermal method. The crystal structure consists of 1D $[\text{Fe}_5\text{Se}_9]$ chains connected via $[\text{As}_3\text{Se}_2]$ -Se pentagonal linkers and charge-balancing interstitial $[\text{Fe}(\text{en})_3]^{2+}$ complexes (*en* = ethylenediamine). Neutron powder diffraction verified that interstitial water molecules participate in the crystal packing. Magnetic polarizability of the produced compound was confirmed by X-ray magnetic circular dichroism (XMCD) spectroscopy. X-ray absorption spectroscopy (XAS) and ^{57}Fe Mössbauer spectroscopy showed the presence of mixed-valent $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the Fe-Se chains. Magnetic susceptibility measurements reveal strong AFM nearest neighbor interactions within the chains with no apparent magnetic ordering down to 2 K. Hidden short-range magnetic ordering below 70 K was found by ^{57}Fe Mössbauer spectroscopy showing that a fraction of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ atoms in the chains are magnetically ordered. Nevertheless, the magnetic ordering is incomplete even at 6 K. Analysis of XAS spectra demonstrates that the fraction of Fe^{3+} in the chain increases with decreasing temperature. Computational analysis points out several competing ferrimagnetic ordered models within a single chain. This competition, together with variation of the Fe oxidation state and additional weak *intrachain* interactions, are hypothesized to prevent full 3D magnetic ordering.

Introduction

Transition metal based pnictides and arsenides are an interesting class of compounds with exciting magnetic and superconducting properties that have been extensively studied and categorized. The family of 1111 compounds is characterized by negatively charged FePn (Pn : pnictogen, P and As) and positively charged LnO (Ln : lanthanide) layers with high superconducting transition temperatures (T_c).^{1,2} In 2008, doping of BaFe_2As_2 ^{3–5} with alkali metals was shown to induce superconductivity in $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$ with $T_c \sim 38$ K, introducing a new family of 122 superconductors.^{6–8} In the same year, *Jin et al.* synthesized LiFeAs compound belonging to a new family termed 111 superconductors with $T_c = 18$ K.⁹ A simplest 11 family consists of binary iron chalcogenides such as tetragonal FeCh ($\text{Ch} = \text{Se}$, $T_c = 8$ K;¹⁰ $\text{Ch} = \text{S}$, $T_c = 5$ K),¹¹ and Te-doped Fe sulfides and selenides, $\text{FeCh}_{1-x}\text{Te}_x$.¹² The majority of aforementioned compounds have been synthesized by traditional solid state methods. Only a few attempts have been made to synthesize Fe-based superconductors in solution.¹³ A new small bandgap iron sulfide hybrid semiconductor composed of $[\text{Fe}_8\text{S}_{10}]^{2-}$ puckered layers was synthesized by solvothermal methods using ethylenediamine (*en*) as solvent.^{14,15} Variation of the synthetic conditions allowed the excision of 1D FeSe_2 chains from FeSe layers due to separation of these chains by positively charged Fe-amine complexes.^{16–18} Using a combination of $[\text{Fe}(\text{en})_3]^{2+}$ and Cl^- ions to stabilize 1D FeSe_2 chains led to the tuning of magnetic properties into spin-glass state.¹⁹ Although the octahedral complexes such as *tris*- $[\text{Fe}(\text{en})_3]^{2+}$ are chiral, presence of both Δ - and Λ -isomers in solution makes most of the compounds crystallize in centrosymmetric space groups. An exception to this rule was recently reported for a Co-Se layered hybrid compound.²⁰ In the current work we hypothesize that chiral low-dimensional Fe-Se fragments can be stabilized using chiral inorganic covalent linkers, such as As-Se rings.

Chiral magnetic materials may show short-range hidden ordering and frustrated moments because of the breaking of the inversion symmetry in the crystal field.^{21,22} While extensive research has been conducted to synthesize magnetic pnictide and chalcogenide materials in solution, experimental studies on such chiral compounds are rare. Some of the mostly studied chiral compounds include magnetic silicides such as MnSi ²³ and $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ ²⁴ that exhibit spin helix chirality and skyrmion excitations due to Dzyaloshinskii-Moriya (DM) interactions.^{25,26} Ferromagnetic $\text{Nd}_2\text{Mo}_2\text{O}_7$ ²⁷ and antiferromagnetic $\text{LiZn}_2\text{Mo}_3\text{O}_8$ ^{28–31} have been widely analyzed for their intriguing magnetic frustration driven by spin chirality. Reports on chiral transition metal chalcogenides are quite uncommon, except for $\text{Cr}_{1/3}\text{NbS}_2$, which exhibits a helical spin structure due to DM exchange interaction.^{32–34} Solution synthesis of magnetic and chiral organic-inorganic hybrids mainly relies on the use of chiral ligands, which, due to weak non-covalent host-framework interactions, may have little impact on the framework structure and properties. Although many compounds with anionic As-Se fragments have been studied, no compound with 1D or 2D Fe-As-Se covalent framework has been reported to the best of our knowledge.

Synthesis of transition metal arsenides in solution is challenging due to difficulties in solubilizing elemental arsenic.³⁵ However, synthesis of transition metal chalcogenidoarsenates has been achieved by solution-based approaches.^{36–38} A majority of such organic-inorganic hybrid compounds contain arsenic not as a part of the transition metal-chalcogenide framework but as

charge-balancing selenoarsenate anions.^{39–42} *Sheldrick* and co-workers synthesized a series of manganese selenoarsenate compounds with terpyridine ligands.^{43–45} Non-centrosymmetric molecular arsenic selenides such as As_4Se_4 (D_{2d}) and As_4Se_3 (C_{3v}) are more soluble than elemental arsenic. Consequently, they have been used as precursors to synthesize hybrid selenoarsenates.^{46–48} *Ansari et al.* reported that dissolution of As_4Se_4 in amine solvents cleaves As-As bonds to form $\text{As}_4\text{Se}_6^{2-}$ (D_{2d}) and, in the presence of excess polyselenide anions, this ion further fragments resulting in the formation of $\text{As}_2\text{Se}_6^{2-}$ (C_i) with exocyclic As-Se bonds.^{48,49} Reports by *Ibers et al.* showed how $[\text{As}_x\text{Se}_y]^{z-}$ anions can be extracted from metal arsenic selenides using ammonia and ethylenediamine.^{50,51} These anionic motifs can combine with transition metals in solution to form extended structures. Here we report the structure and properties of a unique mixed-valent, antiferromagnetic, chiral and polar compound, $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O}) = [\text{Fe}(\text{en})_3]_2[\text{Fe}_5\text{Se}_9][\text{As}_3\text{Se}_2]\text{-Se}(\text{H}_2\text{O})$, with pentagonal $[\text{As}_3\text{Se}_2]\text{-Se}$ linkers connecting 1D quintotetrahedral Fe-Se chains in a 2D layered network. This compound was synthesized using molecular As_4Se_4 precursor in a low temperature solvothermal reaction free of chiral ligands.

Experimental section

Warning

In the solid state reactions performed in sealed silica ampoules at elevated temperatures, arsenic can generate high vapor pressures that can compromise the silica ampoules. Minimum amounts of arsenic (mM scale) should be used in a single ampoule, and the ampoules should be covered with silica wool to contain the shattered glass in case of an explosion. Thermal annealing and opening of ampoules should be performed in a well-ventilated space, preferably in a fume hood.

Synthesis of As_4Se_4

Stoichiometric amounts of arsenic powder (Sigma Aldrich, 99.99%) and selenium powder (-100 mesh, Sigma Aldrich, 99.5%) were weighed in a 1:1 ratio (total weight 300 mg) and loaded into a silica ampoule in an argon-filled glovebox. The ampoule was subsequently evacuated and flame-sealed. Then it was wrapped with a cocoon of silica wool, placed in a muffle furnace, heated to 500 °C over 10 h, maintained at this temperature for another 10 h, and cooled to room temperature. This procedure yielded shiny brittle gray chunks of As_4Se_4 (Figure S1) which were finely ground using mortar and pestle. The product was not crystalline, with broad amorphous humps observed in the powder X-ray diffraction (PXRD) pattern at the positions expected for the diffraction peaks of the target phase.

Warning

Solvothermal vessels (autoclaves) may develop high autogenic pressures which may result in the release of hot pressurized hazardous ethylenediamine vapors during the reaction. Splashing of the solvent may occur upon opening the autoclaves, causing severe burns. It is highly recommended to wear proper personal protective equipment, such as face-shields, long-sleeve gloves, and tight-cuff lab coats, to place the autoclaves in secondary containment before opening, and to keep furnaces in well-ventilated spaces such as fume hoods.

Synthesis of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$

$\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ was synthesized by the solvothermal approach under atmospheric conditions. Iron powder (0.4 mmol, <10 microns, Alfa Aesar, 99.5%), selenium powder (0.4 mmol, -100 mesh, Sigma Aldrich, $\geq 99.5\%$), and the pre-synthesized As_4Se_4 (0.2 mmol) were weighed (total weight ~ 175 mg) with addition of 100 mg of ammonium chloride (Fisher Scientific, 99%). The starting materials were placed in a 23 mL Teflon liner filled with 10 mL of ethylenediamine (filling fraction 43%) which was tightly closed in a stainless-steel autoclave and dwelled at 200 °C in a furnace. After 4 days, the autoclave was taken out of the furnace and naturally cooled to room temperature. The products were filtered and washed with 100% ethanol to obtain a mixture of shiny black needles and shiny orange particles. The latter were washed away by stirring the mixture in ethylenediamine to give a sample composed of black needles only (Figure S2). The orange admixture phase was identified as $[\text{Fe}(\text{en})_3]\text{As}_2\text{Se}_5$ based on the resemblance of its unit cell, found by single crystal X-ray diffraction, to that of $[\text{Mn}(\text{en})_3]\text{As}_2\text{Se}_5$.³⁷ Formation of this impurity can be prevented by using a higher filling fraction of ethylenediamine (65%) for the reaction, but such reactions resulted in the formation of fine powders of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ rather than needle-like crystals.

EDS performed on individual needles gave a composition of heavier elements to be $\text{Fe}_{7.2(2)}\text{As}_{3.2(1)}\text{Se}_{12}$ when normalized to the expected Se content. SEM images showed leftover arsenic that recrystallized into globules (Figure S3). The PXRD pattern of the product washed with en resembled the calculated pattern of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ phase but had a significant elemental arsenic peak at $2\theta = 33.4^\circ$ (Figure S4). The As admixture can be minimized by the addition of elemental Se powder into the starting reaction medium. $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ sample showed good air- and moisture-stability to be stored under ambient conditions for months without oxidation or degradation, as revealed by PXRD. Hand-picked needles from purified samples were used for physical property measurements.

Characterization

$\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ was characterized by powder X-ray diffraction (PXRD), single crystal X-ray diffraction, neutron powder diffraction (POWGEN at SNS ORNL), SQUID magnetometry, ^{57}Fe Mössbauer spectroscopy, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) (ALS ANL), SEM/EDS, and TGA/DSC coupled with IR/MS detection techniques. Heat capacity and resistivity measurements were conducted on a physical property measurement system (PPMS). Density functional theory (DFT) calculations were conducted using Vienna *ab initio* simulation package (VASP). Further details about the experimental and theoretical methods are provided in the Supporting Information.

Results and Discussion

FT-IR spectroscopy and TGA/DSC

Single crystal X-ray diffraction pointed out the presence of neutral water molecules co-crystallized in the structure. Since it is hard to distinguish H_2O from $\text{NH}_3/\text{NH}_4^+$ molecules with X-ray diffraction data, additional characterization measurements were performed to confirm the presence of H_2O molecules in the lattice. FTIR spectrum of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ contains a broad signal $\sim 3435\text{ cm}^{-1}$ corresponding to O-H stretching mode and another band $\sim 1630\text{ cm}^{-1}$ corresponding to H-O-H bending modes that indicate the presence of lattice water (Figure S5).^{52,53} Absence of a sharp peak at $\sim 1450\text{ cm}^{-1}$ pertaining to N-H stretching vibrations⁵⁴ also suggests that the low molecular weight ion/molecule present in the crystal structure is not $\text{NH}_4^+/\text{NH}_3$. To confirm this outcome, TGA/DSC coupled with QMS-FTIR was conducted on $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$, revealing the decomposition of the bulk material above $200\text{ }^\circ\text{C}$ with the loss of lattice water molecules (Figure S6). QMS also detected evolution of NH_3 produced by decomposition of carbamate derivatives of ethylenediamine.⁵⁵ Gradual degradation of the bulk structure is indicated by the significant FTIR bands corresponding to the ligand ethylenediamine released in $250\text{--}275\text{ }^\circ\text{C}$ temperature range. With the loss of ethylenediamine, heavy elements combine to form the selenium counterpart of arsenopyrite, FeAsSe , as confirmed by PXRD. Decomposition of the sample placed in an alumina crucible under a constant N_2 flow inside a flow furnace yielded binary FeSe_2 , ternary FeAsSe , and elemental arsenic around $300\text{ }^\circ\text{C}$. Treatment of the decomposition products in 10 mL ethylenediamine under the same solvothermal conditions does not result in reformation of the parent compound.

Crystal structure

The chiral and polar compound $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ crystalizes in a monoclinic non-centrosymmetric space group $P2_1$ (No. 4) with the lattice parameters $a = 8.7648(6)\text{ \AA}$, $b = 21.6607(1)\text{ \AA}$, $c = 12.2894(8)\text{ \AA}$, and $\beta = 91.726(2)^\circ$ (Table S1). The final refined Flack parameter was $0.032(8)$ for the $P2_1$ space group, confirming the crystal structure to be non-centrosymmetric. In order to further confirm the crystal structure, neutron powder diffraction data were obtained at 100 K and 20 K, which resulted in identical patterns, suggesting the compound does not undergo any structural transition at low temperatures (Figure S7a).

Being neighbors in the Periodic Table, As and Se are hard to distinguish by X-ray diffraction due to similar scattering factors, but they have relatively good contrast in neutron scattering, with coherent scattering lengths of 6.58 fm (As) and 7.97 fm (Se). Rietveld refinement of the neutron diffraction dataset collected at 100 K confirmed the assignments of As and Se sites in the structure solution based on X-ray diffraction data (Figure S7b). Even though X-ray diffraction data suggested two potential water molecules, one fully occupied and the other partially occupied, only the former water molecule was confirmed by the neutron diffraction data. The discrepancy with X-ray data may be due to certain errors in the Fourier density map that occur for light atoms with small X-ray scattering factors.

$\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ consists of $[\text{Fe}_5\text{Se}_9]$ chains covalently connected by pentagonal $[\text{As}_3\text{Se}_2]\text{-Se}$ motifs forming a 2D layered structure. The $[\text{Fe}(\text{en})_3]^{2+}$ complexes and H_2O molecules

occupy the space between the layers (Figure 1a and 1b). Asymmetric $[\text{As}_3\text{Se}_2]$ -Se rings make the crystal structure polar and chiral. The Fe-As-Se framework is surrounded by Δ -isomers of $[\text{Fe}(\text{en})_3]^{2+}$ complexes arranged in channels parallel and perpendicular to the 2D framework. Several isostructural crystals were solved, half of them were the same chirality as reported here and the other half were of opposite chirality with inverted Fe-Se-As chains and Λ -isomers of $[\text{Fe}(\text{en})_3]^{2+}$. To get a clear picture of the framework and the spacer molecules in the formula unit, the chemical formula can also be written as $[\text{Fe}(\text{en})_3]_2[\text{Fe}_5\text{Se}_9][\text{As}_3\text{Se}_2]\text{-Se}(\text{H}_2\text{O})$. The space-filling H_2O molecules are located in the vicinity of the pentagonal $[\text{As}_3\text{Se}_2]$ -Se segments (Figure 1b). Fe1 and Fe2 atoms form the octahedral $[\text{Fe}(\text{en})_3]^{2+}$ complexes with an average Fe-N bond distance of 2.21(2) Å which is typical for high spin Fe(II) complexes.⁵⁶

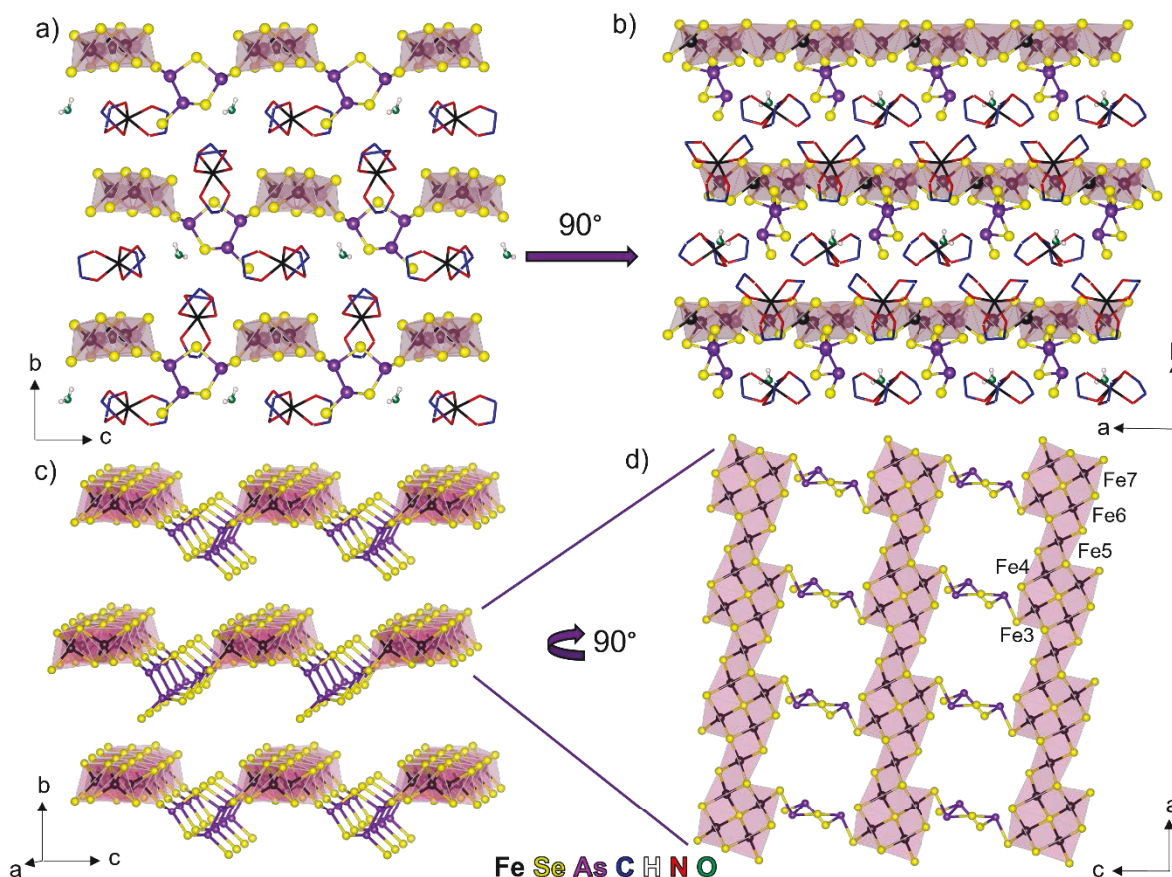


Figure 1. Crystal structure of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O}) = [\text{Fe}(\text{en})_3]_2[\text{Fe}_5\text{Se}_9][\text{As}_3\text{Se}_2]\text{-Se}(\text{H}_2\text{O})$. General view along **a)** [100] and **b)** [001] directions. H atoms in *en* are omitted for clarity. **c)** 2D Fe-As-Se framework showing the $[\text{Fe}_5\text{Se}_9]$ chains connected by $[\text{As}_3\text{Se}_2]$ -Se rings. **d)** Top view of a single Fe-As-Se layer along the [010] direction. Fe: black; Se: yellow; As: purple; N: red; C: blue; O: green.

The 2D Fe-As-Se layers are made up of chiral $[\text{Fe}_5\text{Se}_9]$ 1D chains of $\rho 211$ rod symmetry interconnected by pentagonal $[\text{As}_3\text{Se}_2]$ rings with extra terminal Se atoms that swing in between the chains (Figure 1c and 1d). The 2D Fe-As-Se layers are stacked along the [010] direction. Nonplanar and chiral $[\text{As}_3\text{Se}_2]$ -Se linker motifs are superimposed on one another along the [100]

direction with the protruding Se atoms arranged in alternating directionality in adjacent layers (Figure 1c). The top view of a single layer shows each $[\text{Fe}_5\text{Se}_9]$ chain to be made of diagonally arranged fragments of five FeSe_4 edge-sharing tetrahedra labelled as Fe3-Fe7 (Figure 1d). Fe3, Fe4, Fe6 and Fe7 tetrahedra share three edges between adjacent fragments giving a double chain appearance, similar to that in $A\text{Fe}_2\text{Se}_3$ compounds ($A = \text{Rb}, \text{Cs}, \text{Ba}$).^{57–60} In contrast, bridging Fe5 tetrahedra share only two edges within the same fragment. Every fifth tetrahedron of each fragment in one chain is connected to the first tetrahedron of each fragment in the neighboring chain via $[\text{As}_3\text{Se}_2]$ -Se linkers. This gives a ladder appearance to the overall framework. Selenium atoms in the framework exhibit μ_2 , μ_3 , and μ_4 coordination modes. Some of the μ_2 -Se atoms and all the μ_3 -Se atoms are located along the edges of the Fe-Se chains while μ_4 -Se atoms are at the center of the double-chain part comprised of four tetrahedra (Figure 1d). Remaining μ_2 -Se atoms link $[\text{Fe}_5\text{Se}_9]$ chains to $[\text{As}_3\text{Se}_2]$ -Se rings and, hence, connect to one Fe atom and one As atom. Arsenic atoms in the pentagonal linker have different formal oxidation states. As1, connected to three Se atoms, can be assigned a 3+ oxidation state, while As2 and As3, having two As-Se bonds and one As-As bond, have a 2+ formal oxidation state. The average As-Se distance of 2.39(4) Å and As-As distance of 2.465(1) Å are in line with the sum of As and Se covalent radii, 1.22 Å (As) and 1.17 Å (Se).

The *intrachain* Fe-Fe bond distances vary depending on the position of the corresponding Fe atoms in the $[\text{Fe}_5\text{Se}_9]$ chains (Table 1). Within the same chain, Fe-Fe bond distances are longer along the *a*-axis than the Fe3–Fe6 and Fe4–Fe7 distances along the *c*-axis. In the compounds with simple single tetrahedral chains, we have found that the Fe-Fe distance correlates with the type of magnetic exchange.^{17–19} While distances of 2.87–2.98 Å are typical for antiferromagnetic chains, the shorter Fe-Fe distances of 2.72–2.79 Å result in ferromagnetic nearest-neighbor interactions. The distances observed in the present compound are intermediate between these two ranges. Therefore, we may anticipate a competition between antiferromagnetic and ferromagnetic exchange interactions in the $[\text{Fe}_5\text{Se}_9]$ chains.

Table 1. Interatomic Fe-Fe distances in the $[\text{Fe}_5\text{Se}_9]$ chains of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$.

Pair	Distance (Å)
Fe3–Fe4	2.85(1)
Fe3–Fe6	2.80(1)
Fe4–Fe5	2.84(1)
Fe4–Fe7	2.76(1)
Fe5–Fe6	2.83(1)
Fe6–Fe7	2.86(1)

Assigning the formal oxidation states results in the formula $[(\text{Fe}^{2+}(\text{en})_3)_2][(\text{Fe}_5)^{13+}(\text{Se}^{2-})_{12}](\text{As}^{3+})(\text{As}^{2+})_2$, which suggests the Fe atoms in the $[\text{Fe}_5\text{Se}_9]$ chains to be mixed-valent with a net average charge of +2.6. The FeSe_4 tetrahedra are far from being identical, with Fe-Se bond lengths spanning a wide range from 2.329(1) to 2.460(1) Å, giving different tetrahedral volumes (Table 2). Fe5 tetrahedra with only two shared edges have the smallest volume and can be assigned a valence of +3 with certainty. This claim is supported by the

calculated bond valence sums (BVS) of Fe^{chain} atoms in previously reported KFeSe_2 ,⁶¹ $\text{Fe}_3\text{Se}_4(\text{en})_2$,¹⁶ $\text{Fe}_3\text{Se}_4(\text{en})_3$,¹⁸ $\text{Fe}_7\text{Se}_8(\text{en})_9\text{Cl}_2$,¹⁹ $\text{Fe}_3\text{Se}_4(\text{dien})_2$,¹⁷ and $\text{Fe}_3\text{Se}_4(\text{tren})$ ¹⁷ compounds ranging from +3.0 to +3.20 whose valence has been confirmed to be +3 by electron count and ^{57}Fe Mössbauer spectroscopy (Table S2). Calculated BVS of Fe^{2+} in BaFe_2Se_3 was +2.67.⁶² However, mixed-valent compounds such as $\text{Na}_3\text{Fe}_2\text{Se}_4$ ⁶³ and CsFe_2Se_3 ^{57,64} have BVS of +2.75-3.0 which suggest that Fe3, Fe4, Fe6, and Fe7 atoms in $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ may have intermediate valence.

Table 2. Tetrahedral volumes and calculated bond valence sums (BVS) of Fe atoms in $[\text{Fe}_5\text{Se}_9]$ chains of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$.

Fe atom	Tetrahedral volume [$\text{\AA}^3$]	Calculated BVS
Fe3	7.086	+2.87
Fe4	7.009	+2.96
Fe5	6.757	+3.18
Fe6	6.958	+3.02
Fe7	7.065	+2.92

The effects of the composition and the chemical intercalates on the valence state of Fe atoms can be understood when comparing the Fe-Fe connectivity in some of the 1D and 2D Fe chalcogenides reported to date. Flat fully occupied layers of superconducting FeSe^{13} with Fe^{2+} oxidation state gradually transforms into Fe^{3+} with systematic chemical intercalations resulting in cleaving the connectivity between FeSe_4 tetrahedra (Figure 2). Fe^{chain} atoms in 1D single chain compounds always acquire a +3 charge ($\text{Fe}_7\text{Se}_8(\text{en})_9\text{Cl}_2$ ¹⁹, KFeSe_2 ⁶¹) while those in the 1D compounds with double chains ($\text{Fe}_{10}\text{Se}_{12}(\text{en})_7$ ¹⁸, CsFe_2Se_3 ⁵⁷) and 2D compounds with vacancies ($\text{Fe}_9\text{S}_{10}(\text{en})_{3.5}$ ¹⁵) or large voids ($\text{Fe}_{18}\text{Se}_{21}(\text{en})_{12}\text{Cl}_2$ ¹⁹) tend to adopt intermediate oxidation states. In $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$, Fe atoms in the 1D $[\text{Fe}_5\text{Se}_9]$ chains also are mixed-valent as a result of the second type of cations present in the framework.

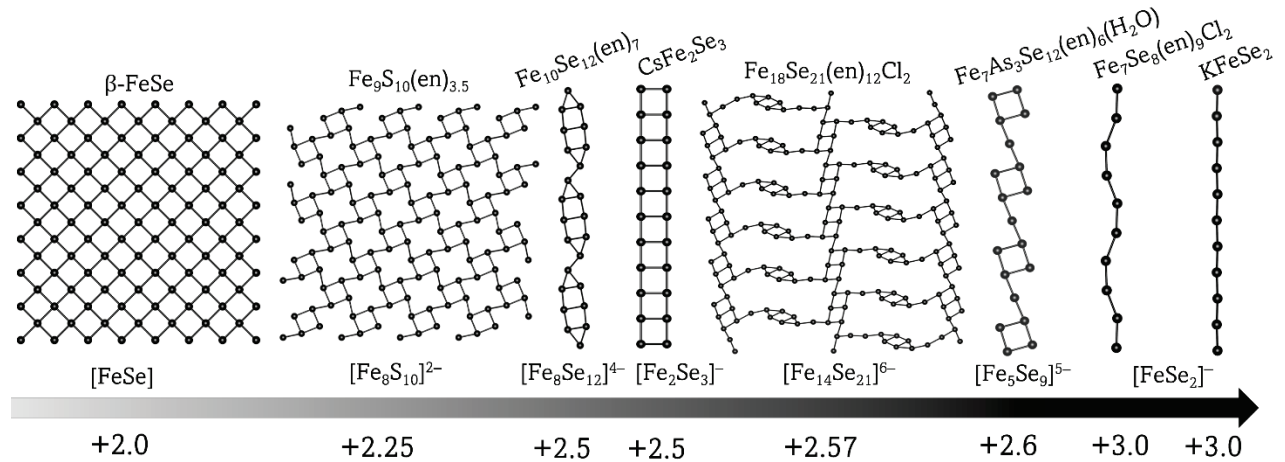


Figure 2. Fe-Fe connectivity in the polyanionic frameworks of 1D and 2D Fe-chalcogenide compounds showcasing the change in the average oxidation state of the Fe atoms. Structural formulae and the polyanionic formulae are given above and below each motif.

Fe $L_{3,2}$ XAS

X-ray absorption spectroscopy (XAS) is an excellent probe for the oxidation state, site symmetry, spin state, and crystal field splitting of Fe ions present in the structure.⁶⁵ Fe- $L_{3,2}$ XA spectra were collected from 300 K to 20 K on a polycrystalline sample mounted on carbon tape glued to Al foil. Before fitting, the spectra were processed for background subtraction and normalized (Figure 3a). At each temperature, the XA spectrum consists of two doublet structures centered ~ 708 eV and ~ 722 eV that correspond to L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) edges respectively.⁶⁶ The broad multiplet nature of the peaks is due to the p - d and d - d Coulomb and exchange interactions.⁶⁷ The peak at ~ 707 eV belongs to the superimposed or combined absorption edges of Fe^{2+} in both octahedral and tetrahedral geometry. Its location is in good agreement with the reported values for O_h Fe^{2+} in $\text{Ba}_9\text{Fe}_3\text{Se}_{15}$ ^{68,69} and T_d Fe^{2+} in FeSe thin films.^{70–73} The peak of similar intensity at a higher photon energy of ~ 709 eV is the main peak of T_d Fe^{3+} L_3 absorption edge occurring in a similar structural environment as in the thiospinel greigite, Fe_3S_4 .^{74,75} To further confirm the presence of +3/+2 oxidation states, control experiments were conducted on centrosymmetric ($P2_1/c$) hydrous salts, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, used as Fe^{3+} and Fe^{2+} references, respectively (Figure S8a).

To analyze the valence of Fe atoms, fittings were performed only on the L_3 absorption edge (Figure 3b, S9) and the count for each valence state was extracted. At 300 K, the Fe^{2+} and Fe^{3+} peaks of the L_3 feature are of comparable intensities which agrees with the $(2\text{Fe}_{\text{oct}}^{2+} + 2\text{Fe}_{\text{tet}}^{2+}) : 3\text{Fe}_{\text{tet}}^{2+}$ ratio determined by electron counting and Mössbauer spectroscopy (*vide infra*). As the temperature decreases from 250 to 50 K, the lower energy Fe^{2+} peak decreases in intensity and gradually becomes a shoulder to the growing main peak of Fe^{3+} (Figure 3c). The relative concentrations of Fe^{2+} and Fe^{3+} may be slightly inaccurate, due to nuances in the normalization procedures.

Assuming the Fe^{2+} in the Fe-amine complex does not undergo any valence state change with temperature, the five crystallographically unique Fe atoms in the chains show a clear increase in the spectral contribution from the 3+ state upon cooling (Figure 3d). At 50 K, essentially all Fe atoms in the chains acquire the 3+ valence state. This result confirms the mixed-valent nature of Fe atoms in the anionic chains and, additionally, reveals that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is strongly temperature-dependent. Room-temperature XAS conducted at lower applied field of 0.5 T showed time dependence of Fe- $L_{3,2}$ spectral signature (Figure S8b). X-rays themselves are known to induce spin state transitions in Fe(II)-containing samples depending on the intensity of X-ray illumination.^{76–78} Nevertheless, the increase in the Fe^{2+} component of the signal during beam exposure (Figure S8b) cannot explain the reduction of Fe^{2+} signal upon cooling.

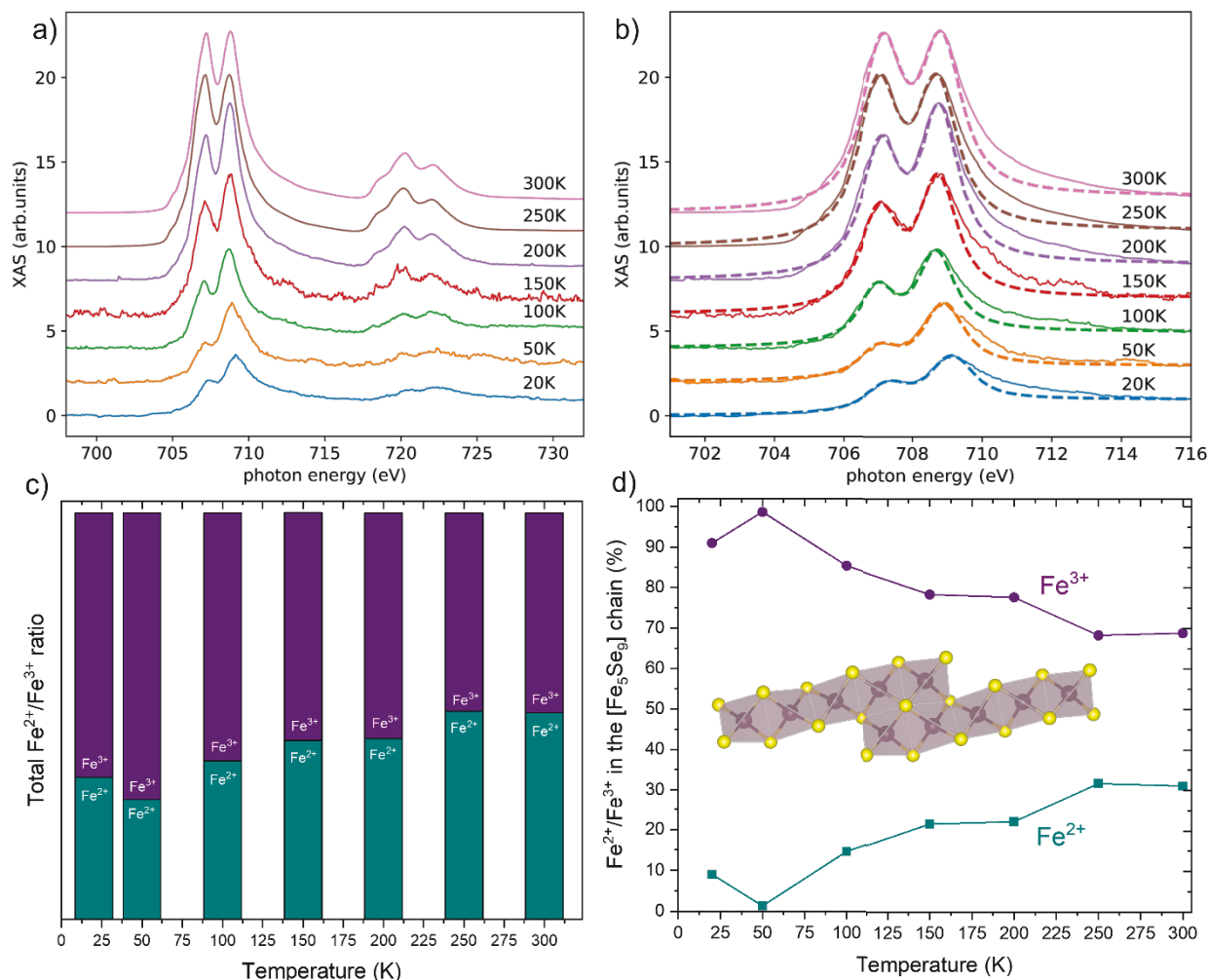


Figure 3. **a)** XA spectra for $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ from 20-300 K with the background subtracted and normalized. **b)** Fittings performed on the Fe L_3 absorption region indicated in dashed lines. **c)** Bar graph showing the change in total $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio with temperature for all seven Fe atoms in the structure. **d)** Scatter plot showing the change in $\text{Fe}^{2+}/\text{Fe}^{3+}$ valence count with temperature for the five Fe atoms in the $[\text{Fe}_5\text{Se}_9]$ chains. For c) and d) Fe^{2+} : cyan; Fe^{3+} : purple.

XMCD spectroscopy

Circular dichroism (CD) is a spectroscopic technique which is commonly used to detect the molecular or solid chirality and reveals important information on different molecular conformations. X-ray magnetic circular dichroism (XMCD) can additionally probe ordered magnetic states due to difference in interaction of spin-up and spin-down electrons with polarized X-rays. In a non-magnetic state, chiral molecules/compounds are capable of interacting with left- and right-polarized electromagnetic radiation and give a non-zero difference signal in the CD measurements.⁷⁹ Presence of homochiral metal-ligand complexes, such as Δ - or Λ - $[\text{Fe}(\text{en})_3]^{2+}$, can render the entire crystal structure chiral, while presence of both Δ - and Λ -isomers related by an inversion center makes the overall structure achiral, as is the case of the majority of hybrid Fe-Se chain compounds.⁸⁰ Magnetic and Mössbauer studies discussed below show that the title

compound is paramagnetic and not magnetically ordered at room temperature. A prominent XMCD signal observed by the L_3 absorption edge under 3.8 T at room temperature (Figure 4), which is much higher than the ordering temperature from Mössbauer spectroscopy. The measurements conducted in proximity to zero field (X-ray natural circular dichroism, XNCD) gave no observable difference signal and displayed no substantial difference to the centrosymmetric Fe^{2+} and Fe^{3+} reference samples. Magnetic hysteresis measurements did not detect any field dependence between ± 0.6 T either. Therefore, we can conclude that the prominent XMCD signal observed at 3.8 T at room temperature is not due to chirality *per se* but is a result of field-induced magnetic polarizability in chiral $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$. Below 200 K, the sample becomes more insulating and the XMCD signal is consequently much weaker, as the TEY measurement relies on the conductivity of the sample. Hence, extracting reliable information becomes rather difficult (Figure S10).

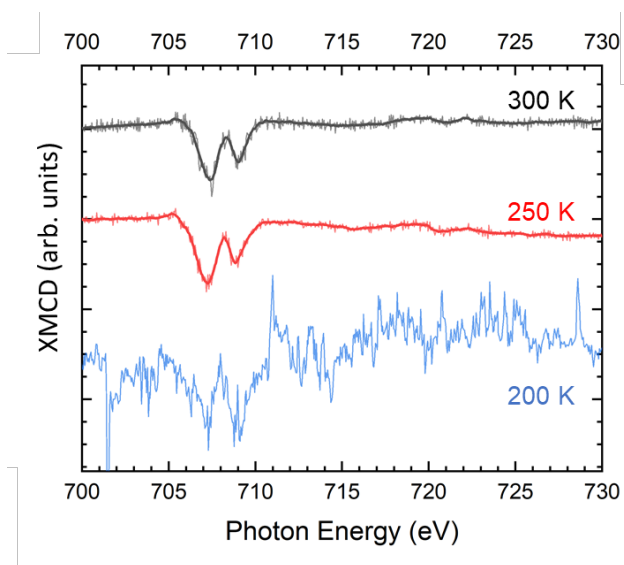


Figure 4. Variable temperature XMCD spectra of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ recorded at the Fe L -edge under a 3.8 T applied magnetic field.

^{57}Fe Mössbauer spectroscopy

To investigate the oxidation states and magnetic properties of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$, ^{57}Fe Mössbauer spectroscopy experiments were performed at 6 K, 50 K, 70 K, 100 K, and 293 K (Figures 5, S10). At 293 K, the spectrum does not show any magnetic ordering and can be fitted with three doublets, Q_1 , Q_2 , and Q_3 , which suggest the 2:5 ratio of octahedral to tetrahedral Fe atoms in the crystal structure. The first component, Q_1 , with the centroid shift (δ) value of 0.96 mm/s and quadrupole splitting (ΔE_Q) value of 0.70 mm/s represents the octahedral high-spin Fe^{2+} ions of the $[\text{Fe}(\text{en})_3]^{2+}$ complexes (Table S3).⁸¹ This finding is consistent with the previously reported room-temperature Mössbauer spectra of $[\text{Fe}(\text{en})_3]_3(\text{FeSe}_2)_4\text{Cl}_2$ that also contains $[\text{Fe}(\text{en})_3]^{2+}$ cations.¹⁹ The other components, Q_2 and Q_3 , can be attributed to tetrahedrally coordinated Fe atoms in the Fe-As-Se framework. The Q_2 component has $\delta = 0.36$ mm/s and $\Delta E_Q = 0.67$ mm/s while for the Q_3 component has $\delta = 0.39$ mm/s and $\Delta E_Q = 1.04$ mm/s. Both isomer shifts and quadrupole splitting of Q_2 and Q_3 are quite different from those reported for high spin

Fe^{3+} in FeSe_4 tetrahedra in $[\text{Fe}(\text{en})_2](\text{FeSe}_2)_2$ ($\delta = 0.27$ mm/s, $\Delta E_Q = 0.39$ mm/s),¹⁶ $[\text{Fe}(\text{en})_3]_3(\text{FeSe}_2)_4\text{Cl}_2$ ($\delta = 0.26$ mm/s, $\Delta E_Q = 0.35$ mm/s),¹⁹ and RbFeSe_2 ($\delta = 0.20$ mm/s, $\Delta E_Q = 0.35$ mm/s).⁸² Reduction of the Fe oxidation state from 3+ to an intermediate value of $(3-x)$ is expected to increase the isomer shift, while the asymmetry of the electron cloud increases the quadrupole splitting. Thus, the observed values of δ and ΔE_Q confirm the intermediate valence of the tetrahedral Fe atoms in the structure of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$, as discussed above. Moreover, the chains contain two different types of tetrahedral Fe atoms with non-identical oxidation states. Unlike XAS technique, which has an excited state lifetime of $\sim 10^{-15}$ s, for Mössbauer spectroscopy, the excited state lifetime is $\sim 10^{-9}$ s, which may lead to unresolved mixed valent peaks when electron fluctuation rate between different Fe sites is faster than the lifetime of the excited state.⁸³

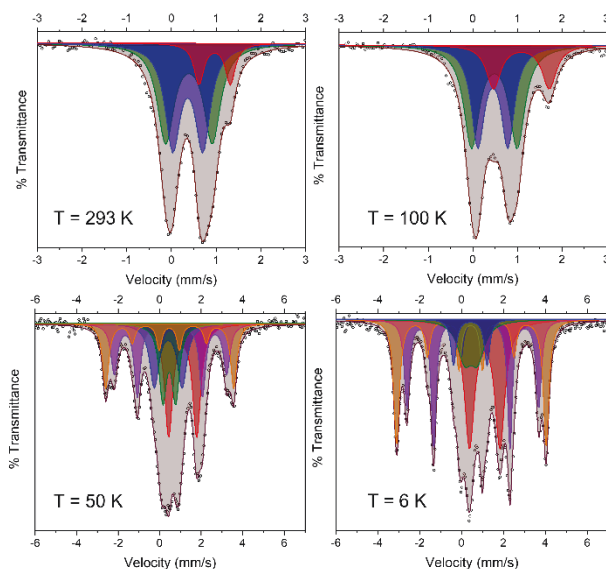


Figure 5. ^{57}Fe Mössbauer spectra for $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ measured at various temperatures. Experimental: black circles; calculated sum of all contributions: maroon; Q₁: red; Q₂: blue; Q₃: green; Q₂₂: yellow; Q₃₃: purple.

The Mössbauer spectrum recorded at 100 K does not show a substantial difference from the room-temperature spectrum, except for the second-order Doppler effect. There is no sign of magnetically split components. A similar spectrum was observed at 70 K (Figure S11). Both 100 K and 70 K spectra can be fitted with only three non-magnetic doublets. A hyperfine splitting of the Mössbauer signal from the Fe atoms in the chains was observed in the 50 K spectrum, indicating a magnetic ordering event which is subsequently enhanced at 6 K. Fitting these two spectra required five components with similar parameters but different relative intensities. The 50 K spectrum is best fitted with three doublets and two hyperfine sextets (Table S3). The Q₁ component attributed to octahedral Fe^{2+} does not undergo hyperfine splitting. Fe atoms in the $[\text{Fe}_5\text{Se}_9]$ chains behave differently; signals from 2/5 of Fe atoms (Q₂ and Q₃ components) remain non-magnetic, while the 3/5 signals are magnetically split (Q₂₂ and Q₃₃ components), indicating a short-range partial magnetic ordering (Figure 6). At 6 K, the octahedral Fe^{2+} signal remains a non-magnetic doublet, while the ratio of magnetic to non-magnetic tetrahedral Fe sites increases from

3:2 to 6:2. The magnetic components show hyperfine splitting values of 22.1 T and 19.5 T. Thus, even at the base temperature the magnetic ordering of tetrahedral Fe atoms is still incomplete.

Previous Mössbauer reports on different Fe coordination environments have indicated the appearance of fully developed sextets with sharp lines when the magnetization relaxation time is orders of magnitude longer than the Larmor precession time of the nuclear moment.^{84,85} In such examples, either external field created by rare-earth cations surrounding Fe centers or strong orbital contribution to momentum in linearly coordinated Fe is present, both are not the case for the reported here compound. *Carling et al.* demonstrated in ferrimagnetic mix-valent $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3]$ layered compounds,⁸⁶ how temperature-dependent hyperfine splitting can be attributed to the lifetime of the magnetic exchange correlations of Fe atoms within a short-range region of 50 Å. Their work stated that the coexistence of broadened sextets and paramagnetic doublets at low temperatures can be a result of the dynamic nature of short-range antiferromagnetic exchange correlations. Spin-correlated and spin-uncorrelated regions can be present within the timeframe of the Mössbauer technique and upon cooling, exchange correlated domains overtake the uncorrelated regions. On the back of this report and the Mössbauer spectra of the previously reported tetrahedral chain compound with $[\text{Fe}(\text{en})_3]^{2+}$ complexes of spinglass nature,¹⁹ we can presume that the hyperfine splitting observed here is not due to slow magnetic relaxation times, but due to short-range magnetic exchange correlations between Fe atoms in Fe_5Se_9 chains.

It is worth mentioning that the intensity of Q_1 , which is the signal for high-spin Fe^{2+} increases upon cooling as opposed to Q_2 and Q_3 (Figure 6). It indicates that recoil-free fraction octahedral Fe^{2+} is increasing much faster than that of tetrahedral Fe^{3+} ions, a similar effect was observed for other hybrid compounds with Fe-Se chains.¹⁹ This trend also applies to the intensities of magnetically split components as well. The decrease in centroid shift values with temperature for Q_1 is caused by second order Doppler effect,⁸⁷ while the decrease in ΔE_Q values is due to the temperature-sensitive nature of the electron density distribution over asymmetrically occupied degenerate orbital states of Fe^{2+} .⁸⁸

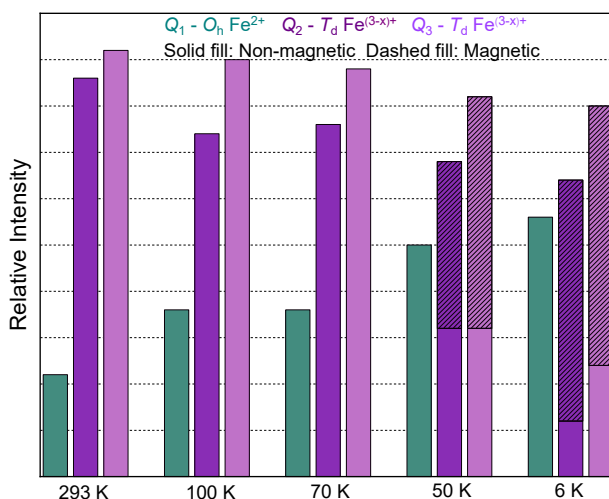


Figure 6. Bar graph comparing the percent intensities of non-magnetic and magnetic components extracted by fitting the Mössbauer spectra for $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ sample at different temperatures.

To gain more insight into the magnetically ordered phase, neutron powder diffraction measurements were conducted at 100 K and 20 K (Figure S7a). The two patterns did not show significant difference to one another, and no additional magnetic peaks were observed at 20 K. Peaks corresponding to an unidentified trace impurity are clearly visible at low angle at both temperatures. These peaks are not due to the magnetically ordered phase since they are present in both 100 K and 20 K patterns. The incoherent scattering from hydrogen atoms resulted in moderate pattern quality and high background which may mask the magnetic peaks in the 20 K pattern. Deuteration of the sample may give a lower background but doing this to obtain ~1 g of the sample required for a neutron diffraction experiment is not cost effective.¹⁵

Electron specific heat

Prior to conducting electronic specific heat measurements on the sample, an Au standard was run to validate instrument. The reported electron heat capacity value for Au is $0.729 \text{ mJ/mol}\cdot\text{K}^2$.⁸⁹ Linear fit of C_p/T vs T^2 below 20 K^2 using the equation: $C_p/T = \gamma + \beta T^2$, produced a γ coefficient of $0.76(4) \text{ mJ/mol}\cdot\text{K}^2$ (Figure S12), which confirmed the reliability of the data measured by the instrument. Electron heat capacity data collected on a pressed pellet of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ in $H = 0 \text{ T}$ and 7 T did not show any peaks below 100 K. At temperatures ~6 K, the two curves crossover (Figure S13a and b). The C_p/T dependence on T^2 for 0 T gives a upturn at low temperature which could be attributed to the low-temperature (<2 K) Schottky anomaly due to AFM interactions (Figure S13c).^{90,91} This prevents accurate determination of the γ coefficient and Debye temperature. The AFM nature of interactions is supported with suppression (or shifting to even lower temperature) of the anomaly at high applied magnetic field of 7 T (Figure S13d).

Magnetic measurements

The magnetic measurements were conducted on finely ground $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ crystals packed inside a PTFE capsule. A contribution of the empty capsule was subtracted from the raw data to obtain the net moment for the sample. The sample contained 6% elemental arsenic by mass which was considered for mass/mol calculations. Diamagnetic correction (χ_D) was applied to the overall calculated susceptibility (χ_{meas}) to account for the intrinsic diamagnetism of all atoms in the sample along with the elemental arsenic impurity, according to the equation $\chi = \chi_{\text{meas}} - \chi_D$.⁹²

Magnetic susceptibility, $\chi = M/H$, measured under an applied field of 1000 Oe, exhibits a typical paramagnetic behavior with no magnetic ordering down to 5 K (Figure 7a, green). A Curie-Weiss fit, $\chi = C/(T - \theta)$, performed in the 100-350 K range, results in the best-fit values for the Curie constant, $C = 6.28(1) \text{ emu}\cdot\text{K/mol}$, and the asymptotic Weiss temperature, $\theta = -33.9(3) \text{ K}$ ($R^2 = 0.9987$). The latter suggests dominant antiferromagnetic (AFM) nature of the nearest-neighbor interactions in the $[\text{Fe}_5\text{Se}_9]$ chains. The effective magnetic moment derived from this fit is $7.09 \mu_B$ ($2.68 \mu_B/\text{Fe}$). This effective moment is slightly lower than the expected paramagnetic contribution

of two octahedral high-spin $[\text{Fe}(\text{en})_3]^{2+}$ complexes, 7.4-7.8 μ_B , thus indicating that the magnetic moments of tetrahedral Fe atoms is significantly quenched. At 350 K, the magnitude of the χT product reaches ~ 6 emu·K/mol and shows a gradual decrease from 350-75 K, with no anomaly, followed by a substantial drop down to 5 K (Figure 7a, purple). The decrease in the χT product is in line with AFM interactions in the chains. For comparison we synthesized and characterized simple compound with similar complexes, $[\text{Fe}(\text{en})_3]\text{Cl}_2$. For the latter, the χT product shows a flat behavior with $C = 3.45$ emu·K/mol, which is reasonable for high-spin Fe^{2+} complexes (Figure S14).

Isothermal magnetization curves for $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ are shown in Figure 7b. The lowest experimental values for magnetization are observed at 300 K. As the temperature is lowered, the magnetization gradually increases, reaching the highest values at 1.8 K. The drastic increase in magnetization observed from 50 – 1.8 K is evident by the maximum moments of 1.54 μ_B/mol at 50 K and 4.74 μ_B/mol at 1.8 K achieved at the magnetic field of 7 T. The saturated maximum magnetization of 8 μ_B expected for two non-interacting high-spin Fe^{2+} (d^6) atoms in the *tris-en* complexes is not achieved under a 7 T field. However, this is a common observation for $[\text{M}(\text{en})_3]^{2+}$ ($M = \text{Ni}, \text{Co}, \text{Fe}$) complexes as per the reports of *Bensch and co-workers* where nearly half the saturation magnetization expected for three non-interacting Fe^{2+} ions was observed at 5 T.⁹³ To further validate this observation, M vs H measurements were conducted on $\text{Fe}(\text{en})_3\text{Cl}_2$ at 1000 Oe field resulting in a maximum magnetization of 2.67 μ_B at 7 T; far from the expected saturation value of 4 μ_B (Figure S14 Inset).

The FC and ZFC magnetic susceptibility curves under 25 Oe superimpose on each other and do not display any splitting down to 1.8 K (Figure S15). AC magnetic measurements in the 30-120 K range detected no anomalies that would indicate magnetic ordering or spin-glass formation (Figure S16). One can assume that the hyperfine magnetic splitting detected by Mössbauer spectroscopy stems not from long-range magnetic ordering but from short-range AFM correlations along the chain. Under an applied field of 7 T, a clear deflection from the paramagnetic trend is observed for both ZFC and FC susceptibility data at low temperature. (Figure 7c). We hypothesize that there are competing short range AFM or AFM/FM interactions in the Fe-As-Se 2D layers that prevent long range ordering.

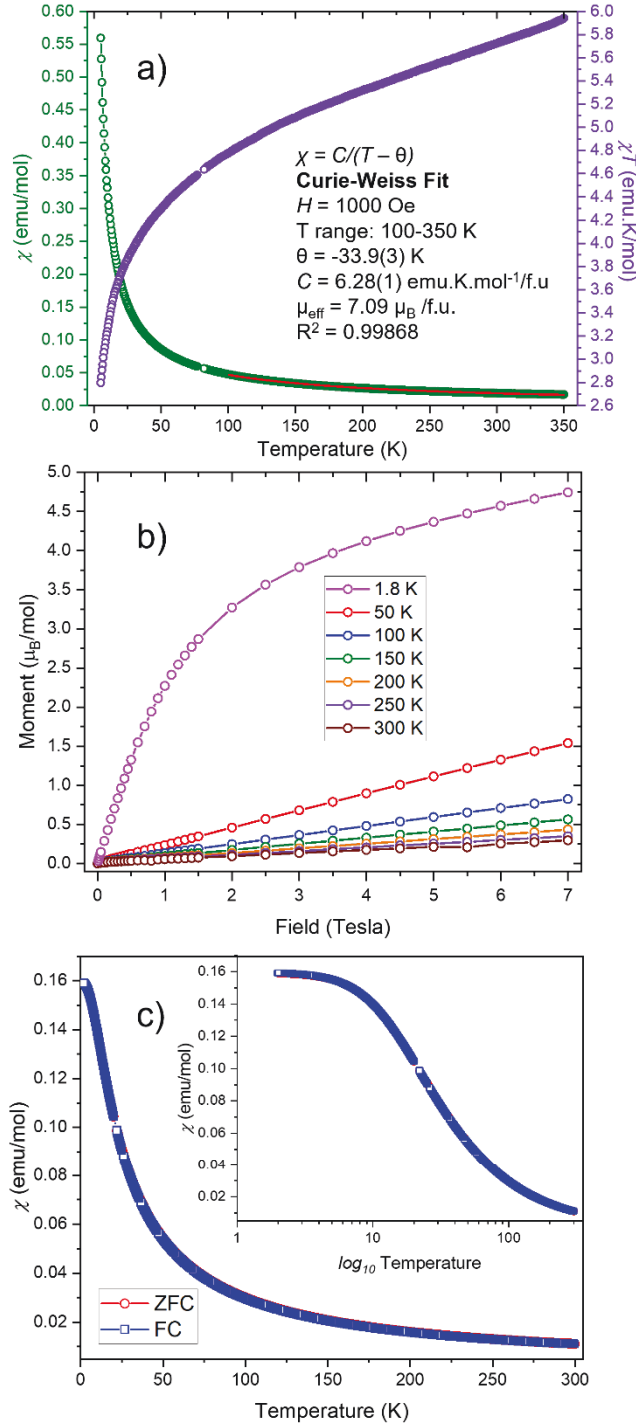
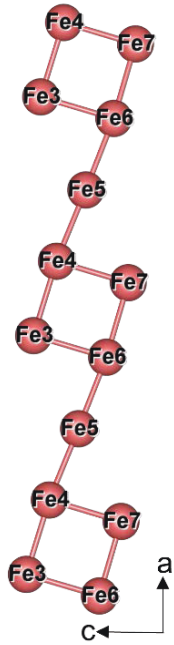


Figure 7. Magnetic properties of $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$: **a)** Temperature dependence of magnetic susceptibility, χ (green circles) and χT (purple circles) measured under an applied field of 1000 Oe. Curie-Weiss fitting for χ vs T plot is shown as a red line. **b)** Isothermal M vs. H curves at 300-1.8 K. **c)** Field-cooled (FC) and zero-field-cooled (ZFC) curves for $\text{Fe}_7\text{As}_3\text{Se}_{12}(\text{en})_6(\text{H}_2\text{O})$ measured under an applied field of 7 T. Inset: Same plot with temperature on log scale emphasizing low-temperature part.

DFT calculations

To probe our hypothesis DFT calculations were performed. The $[\text{Fe}(\text{en})_3]^{2+}$ sublattice was replaced by Ba^{2+} ions for the simplicity of calculations keeping the unit cell neutral. The magnetic ground state of the system was explored by calculating the total energy of various magnetic configurations of the Fe-As-Se framework in the unit cell ($Z = 2$): $\text{Fe}_{10}\text{As}_6\text{Se}_{12}$. The effective *intrachain* and *interchain* exchange interactions were estimated. The magnetocrystalline anisotropy energy (MAE) was estimated by calculating the total energies of the ground magnetic structure with the spin along different directions. $\text{Fe}_{10}\text{As}_6\text{Se}_{24}$ sublattice consists of two symmetrically equivalent layers. Within a unit cell, each layer contains five Fe atoms that form a pseudo-one-dimensional chain along *a*-direction (Figure 8). Fe3, Fe4, Fe6 and Fe7 atoms form a square on the *ac*-plane; and the Fe5 atom connects with Fe4 and Fe6 atoms, bridging two neighboring four-Fe squares (Table 3 image).

Table 3. The magnetic moments M (μ_B/cell) and total energies E (meV/cell) of various *intra-chain* spin configurations. The numbering of Fe atoms in the chains is as in the fragment shown in the rightmost column.

SCs	Fe3	Fe4	Fe5	Fe6	Fe7	M (μ_B/cell)	ΔE (meV/Fe)	
1	↑	↑	↑	↑	↑	27.01	+295	
2	↑	↑	↓	↑	↑	16.22	+120	
3	↑	↓	↓	↓	↑	-4.27	+71	
4	↓	↓	↑	↓	↑	-5.42	+13	
5	↑	↓	↑	↓	↓	-5.38	+6	
6	↑	↓	↑	↓	↑	6.49	0	

First the magnetic ground state of the pseudo-1D chain was explored considering six different spin configurations (SCs, Table 3). All five ferrimagnetic SCs have lower energies than the ferromagnetic configuration. The SC2, where Fe3-Fe4 and Fe6-Fe7 pairs of the four-Fe square are spin up and the connecting Fe5 being spin down, has the second highest energy. The SC6 configuration with antiparallel pairing of adjacent spins has the lowest energy. Note that this allows AFM pairing of spins between the atoms with shortest interatomic distances, Fe3-Fe6 (2.80 Å) and Fe4-Fe7 (2.76 Å). SCs 4 and 5 with a ferromagnetic component for either Fe3-Fe4 or Fe6-Fe7

have only slightly higher energies <13 meV/Fe than the ground state. The energy differences between these SCs 4, 5, 6 are relatively subtle, suggesting competing *intrachain* FM/AFM magnetic interactions which leads to magnetic frustration. Note that we cannot rule out the possibility of an even lower energy configuration. However, this result implies that the tetrahedral chains are more inclined towards the antiferromagnetic arrangement of spin magnetic moments.

Next, the *interchain* magnetic interaction was estimated. Starting with the lowest-energy SC6 *intra-chain* configuration and using a $1 \times 1 \times 2$ supercell, four SCs with different *interchain* magnetic ordering were constructed (Figure 8, Table 4). They are ferromagnetic (FM), *C*-type, *G*-type, and *A*-type antiferromagnetic (AFM) SCs, respectively. The *A*-type AFM SC has the lowest energy while the *C*-type SC has the highest energy, suggesting the effective *interchain* coupling is AFM along *c*-direction but FM along *b*-direction. Note that, comparing Tables 3 and 4, the energy difference between various *interchain* SCs are generally orders of magnitude smaller than those within different *intrachain* SCs.

Table 4. Magnetization and total energy (with respect to the FM *interchain* ordering) of SCs with different *interchain* orderings.

SC	M (μ_B/cell)	ΔE (meV/Fe)
FM	6.49	+0.581
<i>C</i> -type AFM	0	-0.214
<i>G</i> -type AFM	0	-0.470
<i>A</i> -type AFM	0	0

Magnetocrystalline anisotropy can play a critical role in stabilizing the long-range magnetic ordering in lower-dimensional systems by gapping the spin-wave excitations.⁹⁴ Here, MAE was calculated as the total energy difference between different magnetic states in which the magnetization is along the three crystallographic axis directions. The lowest-energy SC6 *intra-chain* structure is employed. We found that, among these three directions, [001] is the easiest direction while [010] is the hardest direction with $E[010] - E[001] = 3.495$ meV/cell. The [100] direction is slightly harder than [001] with $E[010] - E[001] = 0.268$ meV/cell.

The DFT calculations shed light on the magnetic interactions in the Fe-As-Se framework. [Fe₅Se₉] chains are composed of mixed valent Fe atoms. The interactions between different types of Fe atoms in the single chains are ferrimagnetic with a competition between several types of the interactions. This supports the hypothesis on coexisting spin-correlated domains and spin-uncorrelated regions in the layers of this compound as well. The valence state of Fe atoms is highly temperature dependent. Upon cooling the chains became enriched with Fe³⁺ which leads to partial local magnetic ordering at ~ 50 K. When these chains are connected into a 2D framework, the *interchain* magnetic interactions favor weaker AFM coupling facilitated by the [As₃Se₂]-Se pentagonal linkers. The discrete 2D layers stacked along *b*-axis incline towards FM coupling of moments. However, *interchain* coupling is much weaker when compared to *intrachain* coupling. Applying of the high magnetic field of 7 T suppresses AFM interactions and favors FM ones, however, this field is still not sufficient to completely transform *intrachain* interactions to be

ferromagnetic. Due to the complexity of the system, predicting the Néel temperature is tricky as the Mean-Field Estimation, or the Monte Carlo simulations are not accurate for the low-dimensional situations. Further investigations applying renormalized spin-wave theory need to be conducted to better understand how cold the Néel temperature would be.

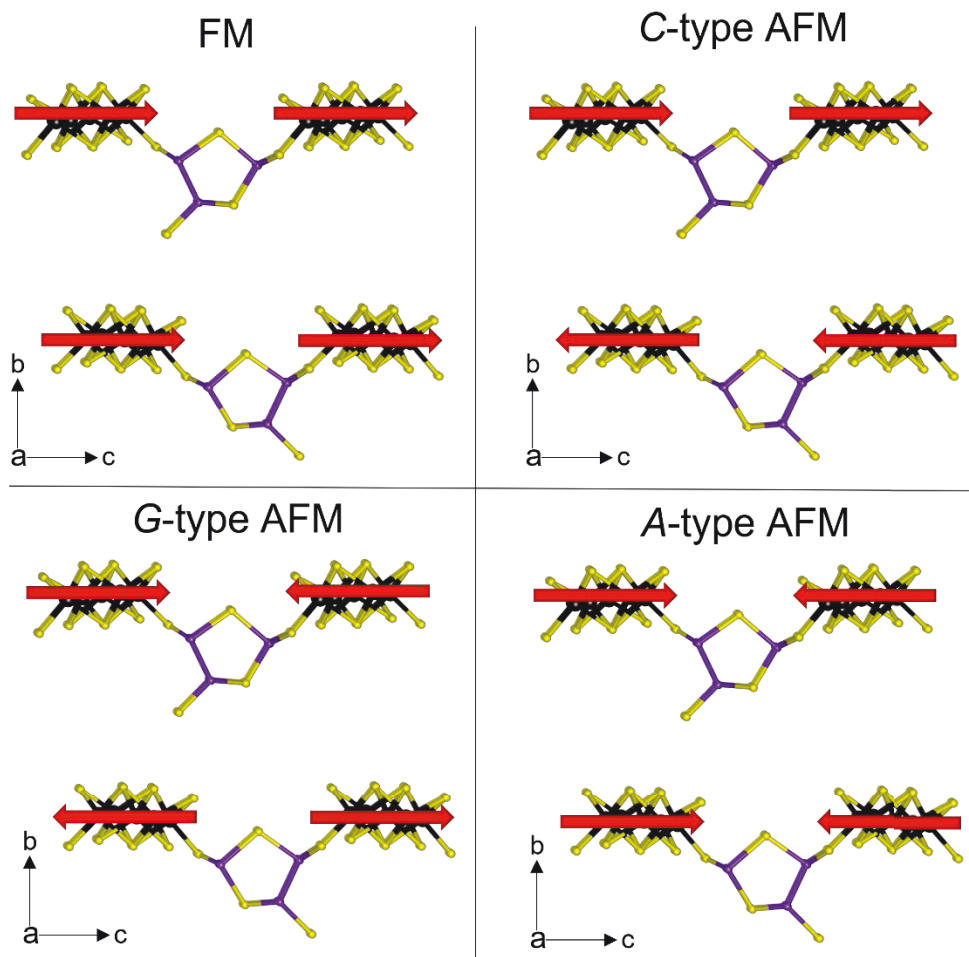


Figure 8. *Interchain spin configurations with FM, C-type, G-type, and A-type AFM states. The red arrows represent the direction of Fe magnetic moments on the same type of Fe atoms in different chains. Note that the arrows are indicated along the easy axis $+c$ and $-c$. Fe: black; Se: yellow; As: purple.*

Conclusions

A novel way to induce chirality and polarity in hybrid compounds was demonstrated by using covalent pentagonal As-Se linker. In the resulting chiral Fe_5Se_9 chains Fe atoms have mix-valent oxidation state as evidence by XAS and Mössbauer spectroscopy. Moreover, the Fe oxidation state is temperature dependent. DFT calculations pointed out to competing intrachain and interchain ferrimagnetic interactions which resulted in the hidden local magnetic ordering which was

observed by Mössbauer spectroscopy. Research probing the tunability of covalent linkers and their impact on the resulting crystal structure is currently underway.

ASSOCIATED CONTENT

Supporting Information.

Details of synthesis and characterization procedures, crystallographic files, additional X-ray diffraction, neutron diffraction, XAS, XMCD, heat capacity, FTIR, magnetic measurement figures, sample photographs, EDS spectra, SEM images, and bond valence sum table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors.

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