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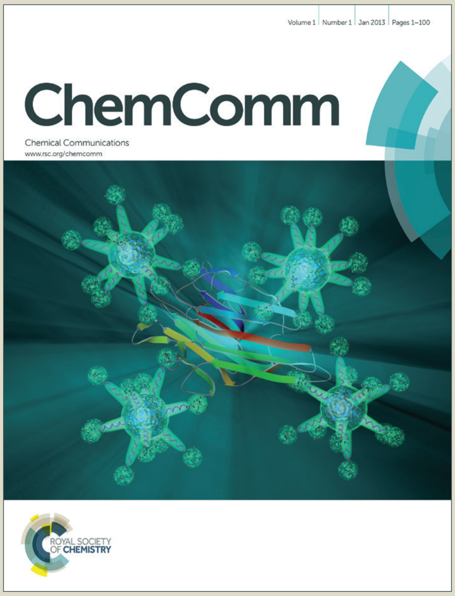

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ARTICLE TYPE

Control over Connectivity and Magnetism of Tetrahedral $FeSe_2$ Chains through Coordination Fe-Amine Complexes

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The synthesis and structural characterization is reported for $[Fe(dien)_2][FeSe_2]_2$ and $[Fe(tren)][FeSe_2]_2$, two new mixed-valence compounds which contain infinite $_\infty^1(FeSe_2)$ tetrahedral chains separated by Fe-amine complexes. The inter- and intra-chain magnetic interactions can be controlled by changing the denticity of the amine while preserving the general structural motif.

Coordination chemistry provides useful tools to control the crystal structures and magnetism of molecular solids and coordination polymers. These materials are often synthesized at relatively low temperatures, as C-, N-, and O-containing ligands play an important role in determining the properties of the magnetic sublattice.[1] Highly-correlated itinerant magnets, which are traditionally considered to be the subject of solid state chemistry or condensed matter physics, are produced through high-temperature syntheses that are incompatible with coordination chemistry ligands.[2-4] Itinerant magnets are sensitive to modifications of the curvature of the density of states at the Fermi level; therefore, aliovalent substitutions and the incorporation of cations are effective ways to alter the magnetic interactions in these materials, as was recently shown by examples of superconducting and antiferromagnetic pnictides and chalcogenides.[2-5]

We have recently demonstrated that a solvothermal approach can yield a highly-correlated itinerant magnet, in which infinite Fe-Se and coordination metal-complex sublattices are both spatially and magnetically separated.[6] In the present work we show how control over the structure and magnetism of the itinerant sublattice can be achieved by adjusting the denticity of the coordinating ligand (Fig. 1). Here we discuss the solvothermal synthesis, crystal structure, and magnetism of two new compounds, $Fe_3Se_4(dien)_2$ and $Fe_3Se_4(tren)$, with dien = diethylenetriamine, and tren = tris(2-aminoethyl)amine.

Solvothermal synthesis has previously been used to produce low-dimensional selenides with new structures and properties.[7] While solid-state syntheses of compounds containing infinite $_\infty^1(FeSe_2)$ tetrahedral chains require high temperatures (1000 K)[2-4] or even a stream of highly toxic H_2Se gas,[8] we have recently shown that similar chains can be stabilized at low temperature with interstitial $Fe(en)_2$ (en = ethylenediamine) complexes (Fig. 1 middle).[6] Nitrogen atoms of the en molecules occupy four equatorial vertices of the octahedral Fe coordination environment, while the complex coordinates to Se atoms from different $FeSe_2$ tetrahedral chains through the apical vertices, with $d(Fe^{complex}\text{-}Se) = 2.70$ Å and $d(Fe^{chain}\text{–}Fe^{complex}) = 4.23$ Å (Fig. 1 middle).

To decrease the degree of interaction between the Fe-amine complex and the $FeSe_2$ tetrahedral chains, we proposed the tri-dentate ligand dien. Two molecules of dien are able to saturate the Fe coordination environment (Fig. 1 left), preventing the complex from bridging between chains. To strengthen the interactions between the $FeSe_2$ chains and the Fe-amine complexes, we proposed the tetra-dentate ligand tren. Similar to $(en)_2$, tren can saturate four vertices of the octahedral Fe coordination environment, but while $(en)_2$ leaves the apical vertices unoccupied, tren leaves two neighboring vertices unfilled. We hypothesized that these vertices would be filled by Se atoms from one $FeSe_2$ chain (Fig. 1 right).

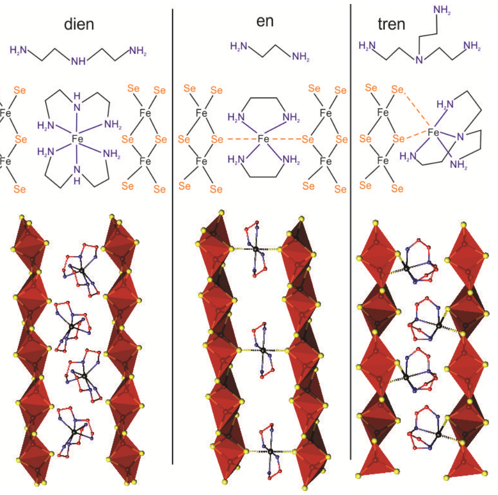

Fig. 1. Diagram of the ligand amine structures (top line), proposed bonding in the compound (middle), and fragments of the actual crystal structure (bottom) for dien- (left), en- (center), and tren- (right) containing compounds. $FeSe_4$ tetrahedra: brown; Fe: black; Se: yellow; N: blue; C: red, H: omitted for clarity.

$Fe_3Se_4(dien)_2$ and $Fe_3Se_4(tren)$ were synthesized through a solvothermal method using the corresponding amine as both a ligand and a solvent. Crystal structure analysis indicated that $Fe(dien)_2^{2+}$ complexes and $FeSe_2$ chains are indeed isolated from each other (Fig. 1 left), as the shortest $d(Fe^{complex}\text{-}Se)$ is 4.71 Å. The proposed bonding motif was also confirmed for $Fe_3Se_4(tren)$ (Figure 1 right), though the tight bonding of Fe(tren) to two Se atoms from the same chain induces bending in the chains (Fig. 2).

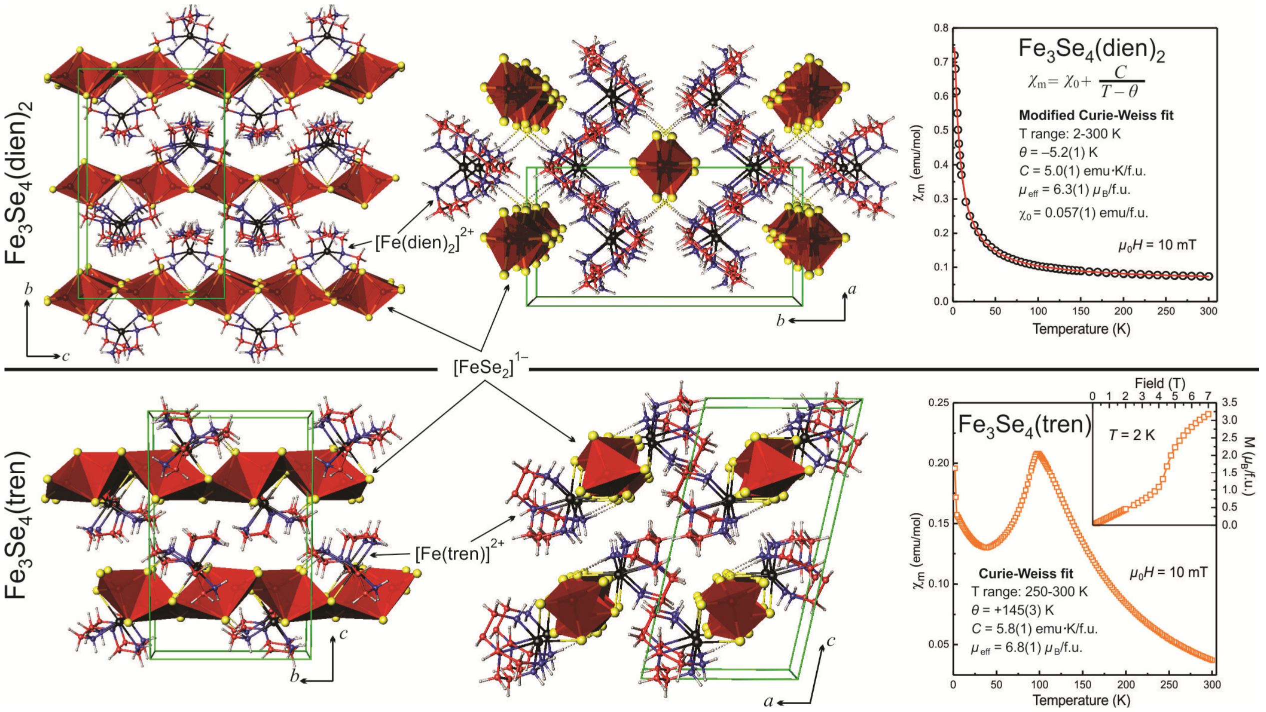

Fig. 2. Left: Crystal structures of (top) $Fe_3Se_4(dien)_2$ and (bottom) $Fe_3Se_4(tren)$. The shortest Se–H interatomic distances, 2.62 Å in $Fe_3Se_4(dien)_2$ and 2.60 Å in $Fe_3Se_4(tren)$, are shown with dashed lines. The unit cell is shown in green. $FeSe_4$ tetrahedra: brown; Fe: black; Se: yellow; N: blue; C: red; H: grey. **Right:** Temperature dependences of molar magnetic susceptibility χ_m for $Fe_3Se_4(dien)_2$ (top) and $Fe_3Se_4(tren)$ (bottom) in an applied field of 10 mT. The red line shows Curie-Weiss fitting for $Fe_3Se_4(dien)_2$. For $Fe_3Se_4(tren)$, lines are shown to guide the eyes. The low temperature upturn is likely due to a small paramagnetic admixture. Inset: isothermal field dependence of the magnetization at 2 K for $Fe_3Se_4(tren)$.

In $Fe_3Se_4(tren)$ the shortest $d(Fe^{complex}\text{-}Se)$ is 2.56 Å; this is shorter than what is found in $Fe_3Se_4(en)_2$, but longer than the Fe^{chain}-Se distances within the tetrahedral chains in all three compounds, which range from 2.33-2.41 Å. The Fe–N distances of 2.20–2.24 Å in $Fe(dien)_2$ and 2.16-2.28 Å in Fe(tren) are typical for the high-spin d^6 state of Fe^{2+}.[1b] In $[Fe(en)_2][FeSe_2]_2$ we have shown that Fe atoms in the $FeSe_2$ chains are Fe^{3+} while Fe atoms in $Fe(en)_2$ are Fe^{2+}.[6] Applying a similar approach with bond valence sum analysis[9] and Mössbauer spectroscopy (ESI Fig. SI 3), we can assign formal oxidation states of +3 for Fe atoms in the $FeSe_2$ chains and +2 for those in the Fe-amine complexes in the reported compounds, resulting in the electron balanced compositions $[Fe^{2+}(dien)_2][(Fe^{3+})_1(Se^{2-})_2]_2$ and $[Fe^{2+}(tren)][(Fe^{3+})_1(Se^{2-})_2]_2$.

The $FeSe_2$ chains propagate along [001] in $Fe_3Se_4(dien)_2$ and [010] in $Fe_3Se_4(tren)$ (Fig. 2). Unlike $Fe_3Se_4(en)_2$, both new compounds are characterized by weak inter-chain interactions. In $Fe_3Se_4(dien)_2$ the only interactions between the $Fe(dien)_2$ complexes and different $FeSe_2$ chains are weak Se···H–N bonds in the range of 2.62-3.00 Å. In contrast, each Fe(tren) complex is tightly bound to one $FeSe_2$ chain via two strong Fe–Se bonds and two additional N–H···Se interactions with distances of 2.60 Å and 2.66 Å (Fig. 2 bottom). The only inter-chain interactions are due to longer N–H···Se bonds in the range of 2.76-2.99 Å. To the best of our knowledge, the only reported organometallic compounds containing infinite $FeSe_2$ chains are $FeSe_2(Ar)_2$, Ar = phenyl or mesityl.[10] In these compounds each Se atom forms a strong covalent bond with a carbon atom in the aryl ring.

The shortest Fe–Fe distances are within the $FeSe_2$ chains, with distances of 2.91 Å for $Fe_3Se_4(dien)_2$ and 2.73 Å and 2.80 Å for $Fe_3Se_4(tren)$. In $Fe_3Se_4(tren)$ the shortest Fe^{chain}–$Fe^{complex}$ separation, 3.05 Å, is comparable to the intra-chain Fe–Fe distances. For $Fe_3Se_4(dien)_2$ the Fe^{chain}-$Fe^{complex}$ separations are much longer, with distances of 5.65 Å and 5.88 Å. The $FeSe_2$ chains are well isolated from each other spatially, as the shortest inter-chain Fe–Fe distances are 7.29 Å and 9.04 Å for $Fe_3Se_4(tren)$ and 9.14 Å and 10.15 Å for $Fe_3Se_4(dien)_2$. For $Fe_3Se_4(en)_2$ we have shown that strong magnetic interactions occur in the $FeSe_2$ chains, while the inter-chains interactions are weaker.[6] For $Fe_3Se_4(tren)$ we expect stronger Fe^{chain}–$Fe^{complex}$ magnetic interactions, while for $Fe_3Se_4(dien)_2$ such interactions should be the weakest among all three compounds.

$Fe_3Se_4(dien)_2$ exhibited no magnetic ordering (Fig. 2 top right). A modified Curie-Weiss fit was applied to account for the presence of a temperature-independent paramagnetic contribution (ESI, Fig. SI 4).[11] The values for the asymptotic Curie temperature, θ, and Curie constant, C, depended on the value of χ_0, but for all fittings the sign of θ was negative, indicating antiferromagnetic nearest-neighbor interactions in the $FeSe_2$ chains. A similar type of interactions was observed for $Fe_3Se_4(en)_2$, but in that compound 3D antiferromagnetic ordering occurred through inter-chain interactions mediated by $Fe(en)_2$ complexes. In $Fe_3Se_4(dien)_2$ the complex-chain interactions are significantly suppressed, resulting in the absence of 3D magnetic ordering.

In contrast to $Fe_3Se_4(en)_2$ and $Fe_3Se_4(dien)_2$, Curie-Weiss fitting of the magnetic susceptibility of $Fe_3Se_4(tren)$ yielded a positive value of θ (Fig. 2 bottom right). This indicated that strong ferromagnetic nearest-neighbor interactions were present. While the close proximity of the Fe(tren) complexes to the $FeSe_2$

chains and the resulting bending of the $FeSe_2$ chains altered the type of magnetic interaction in Fe_3Se_4(tren), the 3D magnetic ordering was nevertheless antiferromagnetic, as evidenced by the peak in the susceptibility at 98 K. This is most likely due to antiferromagnetic ordering of the ferromagnetic chains, similar to what was reported for $Ce_2O_2FeSe_2$.[4] This assumption is supported by the metamagnetic transition observed at 2 K and 4.5 T (Fig. 2 bottom right inset). Indeed, for $Fe_3Se_4(en)_2$ with antiferromagnetic coupling within the $FeSe_2$ chains no metamagnetic transition was observed.[6] Preliminary 80 K Mössbauer investigations indicate that Fe_3Se_4(tren) behaves similarly to $Fe_3Se_4(en)_2$: the signal from Fe^{3+} inside the $FeSe_2$ chains is completely split into a sextet, indicating magnetic ordering. In turn, Fe^{2+} is represented by two components, a sextet and a doublet, indicating only partial magnetic ordering for the $[Fe^{2+}$(tren)] sublattice. The Curie constant for Fe_3Se_4(tren), 5.8 emu·K/f.u., was similar to that of $Fe_3Se_4(en)_2$, 5.6 emu·K/f.u. These values indicated that the Fe^{3+} was not in the high spin state ($S = 5/2$), but rather in the intermediate spin state between $S = 1/2$ and 3/2.[6] Similar spin states were observed for Fe^{3+} in $AFeSe_2$ (A = alkaline metal) using neutron diffraction, Mössbauer spectroscopy, and theoretical crystal-field calculations.[8,12]

A simple change in ligand denticity is an effective method for modifying the magnetic interactions in itinerant $_{\infty}^{1}(\mathrm{FeSe}_2)$ tetrahedral chains. This exemplifies the great potential of a coordination chemistry approach to the development of novel magnetic materials, as coordination metal complexes are much more tunable than traditional solid state metal or metal oxide cations. Solvothermal synthesis is a suitable method for combining infinite magnetic fragments and varying coordination complexes to form new crystalline compounds with interesting structures and magnetism.

Conclusions

Two new compounds containing $_{\infty}^{1}(\mathrm{FeSe}_2)$ tetrahedral chains and Fe-amine complexes were synthesized. We have shown that magnetic interactions within the chains can be changed from antiferromagnetic to ferromagnetic by simple alterations in the denticity of the amine ligand, without affecting the general structural motif. Moreover, the Fe-amine complex plays an important role in mediating magnetic inter-chain interactions, leading to behaviors ranging from Curie-Weiss paramagnetism to strong antiferromagnetism. Extension of this approach to other infinite Fe-chalcogenide magnetic systems is currently underway.

Notes and references

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† Electronic Supplementary Information (ESI) available: crystallographic tables and .CIFs, powder X-ray diffraction data, χT magnetic plots, Mössbauer spectra, SEM images and EDX spectra. See DOI: 10.1039/b000000x/

‡ $Fe_3Se_4(dien)_2$ and Fe_3Se_4(tren) were synthesized through a solvothermal method. Chemicals were purchased from Alfa Aesar (AA) and Acros Organics (AO) and used as received. Elemental Fe and Se (AA, both 99.998%) were mixed together in a 3:4 molar ratio with a total weight of 50 mg. 100 mg of NH_4Cl (AA, >99.5%) was added to the reaction mixture as a mineralizer. 30 mL of dien (AA, 99%) or tren (AO, 96%) was used as the solvent. Reactions were performed in 45-mL PTFE-lined stainless steel autoclaves (Parr Instrument Company) with a filling fraction of 67% at 473 K for 5 days. The reaction products were filtered, washed with ethanol and acetone, and stored in an Ar-glovebox. The reaction products appeared as shiny, black needle-like crystals.

The samples were characterized by powder X-ray diffraction using a Rigaku Miniflex 600 diffractometer employing Cu-K_α radiation (ESI Fig. SI1). Elemental analysis of selected crystals (Hitachi S4100T scanning electron microscope with Oxford INCA energy-dispersive X-ray microanalysis, confirmed the presence of Fe and Se as the only heavy elements (ESI, Fig. SI 2). No traces of chlorine were detected. Single crystal X-ray diffraction experiments were performed using a Bruker Smart Apex II diffractometer with Mo-K_α radiation. Crystals of both samples exhibited a tendency for twinning. The solution and refinement of the crystal structures were carried out using the SHELX suite of programs.[13] Final refinements (ESI, Table SI1) were performed 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 numbers CCDC 1029630 and 1029631. Magnetic measurements were performed on polycrystalline samples with a Quantum Design SQUID magnetometer MPMS-XL. Samples were placed between two long strips of Kapton tape to ensure minimal contribution from the sample holder.

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