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Homoleptic 1-D iron selenolate complexes—synthesis, structure, magnetic and thermal behaviour of ${}^{1}_{\infty}$ [Fe(SeR)₂] (R = Ph, Mes)[†]

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The first examples of polymeric homoleptic iron chalcogenolato complexes 1 [Fe(SePh)₂] and $\frac{1}{2}$ [Fe(SeMes)₂] (Ph = phenyl = C₆H₅, Mes = mesityl = C₆H₂-2,4,6-(CH₃)₃) have been both prepared by reaction of $[Fe(N(SiMe_3)_2)_]$ with two equivalents of HSeR (R = Ph, Mes) while $[Fe(SePh)_2]$ was found to be also easily accessible through reactions of either FeCl₂, Fe(OOCCH₃)₂ or FeCl₃ with PhSeSiMe₃ in THF. In the crystal, the two compounds form one-dimensional chains with bridging selenolate ligands comprising distinctly different Fe–Se–Fe bridging angles, namely 71.15–72.57° in [Fe(SePh)] and 91.80° in ¹[Fe(SeMes)₂]. Magnetic measurements supported by DFT calculations reveal that this geometrical change has a pronounced influence on the antiferromagnetic exchange interactions of the unpaired electrons along the chains in the two different compounds with a calculated magnetic exchange coupling constant of $J = -137 \text{ cm}^{-1}$ in $\frac{1}{2}$ [Fe(SePh)₂] and $J = -20 \text{ cm}^{-1}$ in $\frac{1}{2}$ [Fe(SeMes)₂]. In addition we were able to show that the ring molecule [Fe(SePh)2]12 which is a structural isomer of ¹[Fe(SePh)] behaves magnetically similar to the latter one. Investigations by powder XRD reveal that the ring molecule is only a metastable intermediate which converts in THF completely to form $\frac{1}{2}$ [Fe(SePh)₂]. Thermal gravimetric analysis of $\frac{1}{2}$ [Fe(SePh)₂] under vacuum conditions shows that the compound is thermally labile and already starts to decompose above 30 °C in a two step process under cleavage of SePh₂ to finally form at 250 °C tetragonal PbO-type FeSe. The reaction of 1 [Fe(SePh)₂] with the Lewis base 1,10-phenanthroline yielded, depending on the conditions, the octahedral monomeric complexes [Fe(SePh)₂(1,10-phen)₂] and [Fe(1,10-phen)₃][Fe(SePh)₄].

Introduction

There exists a long standing interest in the synthesis of polynuclear iron sulphur species, due to their potential biological relevance. Many examples of different cluster types have been synthesized and thoroughly characterized by a number of groups.¹ Recent reports on dinuclear biomimetic [2Fe–2S] complexes,^{2,3} as well as cyclic oligomers of type [('Bu₃SiS)MX]_n (M = Fe, Co, Ni; X = halide),⁴ and the synthesis of new binuclear and trinuclear iron clusters⁵ prove the actual interest in this research area.

The build up of the structures of homoleptic and neutral complexes of the general type $[M(ER)_n]$ (n = 1-3; M = 3d transition metal; E = S, Se, Te; R =org. group) is mostly determined by the interplay of the steric demand of the organic ligands *versus* the tendency of the low coordinated metal ions to realize higher coordination modes together with a minor influence of the kind of chalcogen element. The recently published series of quasi-two-coordinate transition metal dithiolates $[M(SR)_2]$ (M = Cr, Mn, Fe, Co, Ni, Zn)⁶ with the very bulky organic ligand $R = C_6H_3$ -2,6(C_6H_2 -2,4,6-iPr₃)₂ represents the lowest limit with respect to the coordination number in homoleptic neutral chalcogenolato complexes of these elements. Decrease of the steric demand of the organic ligands results either in the formation of

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^eUniversity Chemical Laboratory, Lensfield Rd, Cambridge, UK, CB2 1EW † Electronic supplementary information (ESI) available. Figure S1: Measured and simulated X-ray powder patterns of [Fe(SePh)₂]₁₂ as a suspension of fresh crystals in CH₂Cl₂ and as a suspension of crystals after one night in THF compared with the calculated pattern of 1, Figure S2: measured and simulated X-ray powder patterns for 1 and 2, Figure S3: Rietveld refinement results for 1 after thermal treatment, Table S1: Refined parameters for 1 after heat treatment, Figure S4: Crystal structure of 1 before and after heating, Figure S5: Susceptibility behaviour for [Fe(SePh)₂]₁₂, Figure S6: Isothermal magnetization curves of 1 and 2 at 5 K, Figure S7 and S8: UV-Vis spectra of 1–4 in solution, Figure S9: Powder XRD patterns of the residue of 1 after thermal treatment at different heating temperatures. CCDC reference numbers 737597–737600. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10089k

mostly ring-like oligomeric molecules (*e.g.* $M = Fe,^7 Ni,^8 Pd,^9 Cu, Ag, Au^{10,11}$) or in the formation of insoluble polymers¹² which could in most cases not be characterized by single crystal X-ray diffraction. There exists only a limited number of crystal-lographically characterized polymeric [M(ER)_n] species namely ${}^{1}_{0}$ [Mn(SePh)₂] (Ph = C₆H₅), {}^{13}_{m}[Mn(SeMes)₂] (Mes = C₆H₂-2,4,6-(CH₃)₃), {}^{14}_{m}[AgSePh], {}^{15}_{m}[Cd(TeMes)₂], {}^{16}_{m}[Cn₄(SPh)₈CH₃OH], {}^{17}_{m}]Cd₄(SR)₈] (R = Ph, 4-CH₃-C₆H₄)¹⁸ and ${}^{3}_{m}$ [Cd(SePh)₂]. {}^{19}

The synthesis and structural characterization of first examples of polymeric homoleptic 1-dimensional iron-selenolate chain compounds namely $\frac{1}{\omega}[Fe(SePh)_2]$ and $\frac{1}{\omega}[Fe(SeMes)_2]$ are reported herein along with an investigation of their magnetic properties.

Results and discussion

Synthesis and structure

The iron selenolate complexes $\frac{1}{\infty}$ [Fe(SeR)₂] (R = Ph (1), R = Mes (2)) can be prepared by reaction of the well known precursor compound bis[(bistrimethylsilyl)amido]iron(II) with two equivalents of RSeH in the prescence of P^{*n*}Pr₃ (Scheme 1). In addition, 1 is also accessible by the reaction of anhydrous iron(II) chloride as well as iron(III) chloride with three or four equivalents of PhSeSiMe₃ in THF (Scheme 2). Crystals suitable for X-ray analysis were synthesized from reaction solutions of iron(II)acetate with 2.5 eq. of PhSeSiMe₃ in the presence of 2 eq. of P^{*n*}Bu₃ by layering (Scheme 3).

Fe(N(SiMe₃)₂)₂ + 2 RSeH
thf / 0 °C
$$+$$
 0.8 PnPr₃
- 2 HN(SiMe₃)₂
 \int_{∞}^{1} [Fe(SeR)₂]
(1) R = Ph, (2) R = Mes = C₆H₂-2,4,6-(CH₃)₃)
Scheme 1

$$FeCl_2 + 3 PhSeSiMe_3$$

thf
$$-2$$
 ClSiMe₃

 ${}^{1}_{\infty}$ [Fe(SePh)₂] (1)

thf
$$-3$$
 ClSiMe₃
 -0.5 PhSe–SePh

$$FeCl_3 + 4 PhSeSiMe_3$$

Scheme 2

$$Fe(OOCCH_3)_2 + 2.5 PhSeSiMe_3 \xrightarrow{+ 2 PnBu_3} \overset{1}{-2 CH_3OOSiMe_3} \qquad \stackrel{1}{\longrightarrow} [Fe(SePh)_2] (1)$$

Reaction of **1** with the Lewis base 1,10-phenanthroline yielded, depending on the ratio, either dark green crystals of the octahedral

monomeric complexes $[Fe(SePh)_2(1,10\text{-phen})_2]$ (3) or dark red crystals of the ionic compound $[Fe(1,10\text{-phen})_3][Fe(SePh)_4]$ (4) (Scheme 4).



Scheme 4

1 crystallizes in the tetragonal space group $I4_1/a$ (Table 1). In the crystal structure the iron atoms are μ_2 -bridged in one dimension by the phenylselenolato ligands to form infinite chains (Fig. 1). Four selenium atoms (Se(1), Se(2), Se(1') and Se(2')) of the phenylselenolato ligands build a distorted tetrahedral coordination environment around the iron atom with five nearly similar Se-Fe-Se bond angles of about 105.03(4)° (Se(1")-Fe(1)-Se(1)), 106.39(4)° (Se(2')-Fe(1)-(Se(1)), 106.16(4)° (Se(1")-Fe(1)-Se(2)), 108.62(4)° (Se(2')-Fe(1)-Se(2)) and $108.20(4)^{\circ}$ (Se(1)-Fe(1)-Se(2)) and only one distinctly larger angle of $121.82(5)^{\circ}$ for Se(1")-Fe(1)-Se(2'). The Fe₂Se₂ four-membered rings display a butterfly type shape with Fe-Se-Fe bridging angles of 72.12(3)° for Fe(1)-Se(1)-Fe(1') and $72.00(3)^{\circ}$ for Fe(1)–Se(2)–Fe(1") and the rhomb folded by 22.61° from ideal planarity along the Se-Se edge. The selenium atoms and thus the phenyl rings of the phenylselenolato ligands are both oriented above a virtual mean planar rhomb while the iron atoms lie below (±0.1433(5) pm). Fe-Se distances range from 244.0(1) to 245.9(1) pm and the non-bonding Fe \cdots Fe distance was found to be 287.9(2) pm which is distinctly smaller than those found in planar Fe₂Se₂ dinuclear units for [Fe(SeC₆H₂-2,4,6-Ph₃)(N(SiMe₃)₂)]₂ (317.0 pm),²⁰ [Fe(SeC₆H₂-2,4,6-Ph₃)₂]₂ (320.7 pm)²⁰ and (ⁱPrNMe₃)₂[Fe₂(SeⁱPr)₆] (302.6 pm),²¹ but larger than Fe-Fe bonds in [(CO)₃FeSe^pTol]₂ (253.6 pm).²² Interestingly the structure of the related polynuclear ring molecule [Fe(SePh)₂]₁₂, which is a structural isomer of 1, displays similar bond distances (Fe-Se 244.1 pm, Fe··· Fe 287.9 pm)⁷ and also similar Fe-Se-Fe bridging angles (71.15–72.57°). Only the tetrahedral Se–Fe–Se bond angles show values different from those observed in 1 (e.g. 99.97, 105.81, 105.50, 114.26, 114.64, 115.75°). The formation of a certain structure by oligomerisation of the same monomeric 'Fe(SePh)₂' unit seems to be determined by the orientation of the phenyl groups and thus the direction of the bending of the Fe₂Se₂ rhomb. In a slightly simplified picture, one can realize that in 1 viewed along c (Fig. 1b) an alternating orientation of the phenyl rings (up, left, down and right) is characteristic for the formation of a helical chain structure while in the polynuclear ring molecule $[Fe(SePh)_2]_{12}^7$ the phenyl rings in every second rhomb are oriented in the same direction ('outside down' or 'outside up'). Practically the polarity of the reaction solvent (thf for 1 and CH_2Cl_2 for [Fe(SePh)₂]₁₂) together with the presence of PPh₃ in the synthesis

Table 1	Crystallographic Data for	$\int_{\infty}^{1} [Fe(SePh)_2] (1), \int_{\infty}^{1} [Fe(Se-h)_2] (1)$	$C_6H_2-2,4,6-(CH_3)_3)_2](2),$, $[Fe(SePh)_2(1,10-phen)_2]$ (3) and	$d [Fe(phen)_3][Fe(SePh)_4] (4)$
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	1	2	$3 \cdot C_4 H_8 O$	$4 \cdot (CH_3)_2 NCHO$
Sum formula	$C_{12}H_{10}$ FeSe ₂	C ₁₈ H ₂₂ FeSe ₂	C40H34FeN4OSe2	$C_{63}H_{51}Fe_2N_7OSe_4$
fw (g mol ⁻¹)	367.97	452.13	800.5	1349.7
Crystal system	Tetragonal	Tetragonal	Monoclinic	Triclinic
Space group	$I4_1/a$	$P4_2/mbc$	$P2_1/n$	$P\overline{1}$
$\hat{\text{Cell}} a(\hat{\text{A}})$	22.092(3)	15.710(2)	14.849(3)	13.290(3)
b			11.434(3)	13.461(3)
с	10.887(2)	7.0097(14)	20.168(3)	16.475(3)
α (°)				88.85(3)
β			94.30(3)	77.74(3)
γ				89.44(3)
$V(Å^3)$	5313.5(15)	1730.0 (5)	3414.6(12)	2879.6(10)
Z	16	4	4	2
<i>T</i> (K)	150(2)	190(2)	190(2)	190(2)
λ (Å)	0.0800	Μο-Κα	Μο-Κα	Μο-Κα
$d_{c} (g \text{ cm}^{-3})$	1.840	1.736	2.613	1.557
μ (λ) (mm ⁻¹)]	8.866	5.071	2.547	3.080
F[000]	2816	896	1616	1348
$2\dot{\theta}_{max}$ (°)	52	54	51	50
Meas. reflns	8899	7739	22983	26364
Unique reflns	1752	1001	6414	9954
R _{int}	0.0791	0.0662	0.0259	0.0394
Refins with $I > 2\sigma(I)$.	1314	926	5545	8231
Refined params	159	63	433	669
$R_1(I > 2\sigma(I))^a$	0.0383	0.0320	0.0325	0.0474
wR_2 (all data) ^b	0.0689	0.0906	0.0854	0.1558
^{<i>a</i>} $R_1 = \Sigma F_o - F_c / \Sigma F_o .$	$wR_{2} = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}] \}$	$v(F_o^2)^2]\}^{1/2}$		

of $[Fe(SePh)_2]_{12}$ play, most probably, the important role for the formation of a certain structure. Furthermore we were able to prove by powder XRD that the ring molecule $[Fe(SePh)_2]_{12}$ is only a metastable intermediate and converts in CH_2Cl_2 afters several days and in THF over night completely to form a microcrystalline powder of the chain compound **1** (Fig. S1 in the supporting information[†]).

2 crystallises in the tetragonal space group $P4_2/mbc$ (Table 1). The complex exists in the solid state also as a one dimensional infinite chain, with symmetrically bridging selenolate ligands (Fig. 2). The Fe–Se bond distances of 251.81(4) pm are slightly longer than those in **1**. In contrast to **1** the Fe₂Se₂ rings are planar and close to square shape with the Se–Fe–Se angles (88.20(2)°) being less acute and Fe–Se–Fe angles (91.80(2)°) being more acute than in **1**. As a result the distance of the iron atoms along the chain is significantly increased to 350.5(1) pm. The mesityl groups are oriented around the chain so as to minimize steric interactions.

The structure of **1** is strongly reminiscent of that of ${}^{1}_{\infty}$ [Mn(SePh)₂]¹³ while **2** is similar to [Mn(SeC₆H₂-2,4,6-CH₃)₂].¹⁴ The bond angles for each isostructural couple of iron and manganese structures are quite similar while the bond distances (Table 1) are smaller in the iron compounds as expected due to the smaller radii of the iron ions (atom radii [pm]: Mn(125), Fe(126); ionic radii [pm] M²⁺, *hs*, CN = 4: Mn(80), Fe(77)).

Monomeric **3** crystallizes as a racemate of the Δ and Λ isomer in the monoclinic space group $P2_1/n$ (Table 1) and exhibits a distorted octahedral coordination sphere around the iron atom (Fig. 3). The coordination sphere involves four nitrogen atoms (N(1), N(2), N(3), N(4)) from the two bidentate phenanthroline ligands and two selenium atoms (Se(1), Se(2)) from the phenylselenolato ligands which coordinate in a *cis* geometry. The Fe–Se distances of 255.0(1) pm and 259.3(1) pm are significantly longer than in **1** and slightly longer than in **2**. The Fe–N distances (217.8–226.3(2) pm) are slightly longer than those found in $[FeCl_2(phen)_2]^{2-}$ (213.0–222.1 pm)²³ and distinctly longer than those found in $[(CO)_2Fe(SePh)_2(phen)]$ (198.9 pm).²⁴ The N–Fe–N bite angles (N(1)–Fe(1)–N(2): 74.52(8), N(3)–Fe(1)–N(4): 74,69(8) °) are comparable with those found in $[FeCl_2(phen)_2]^{2-}$ (75.87 and 76.28°) and smaller than that found in $[(CO)_2Fe(SePh)_2(phen)]$ (81.31°).

Ionic 4 crystallizes like 3 also as a racemate of the Δ and Λ isomer of the [Fe(phen)₃]²⁺ dication in the triclinic spacegroup $P\overline{1}$ (Table 1). The crystal structure consists of well separated $[Fe(phen)_3]^{2+}$ dications and [Fe(SePh)₄]²⁻ dianions (Fig. 4). The well known [Fe(phen)₃]²⁺ dication comprises a ferrous atom which is in the distorted octahedral coordination of six nitrogen atoms of the three phenanthroline ligands. Bond angles and bond lengths are comparable to those found in previously characterized compounds like [Fe(phen)₃]Cl₂ for example.²⁵ The FeSe₄ core of the anion is slightly more distorted (Se(1)-Fe(1)-Se(3) 98.76(4)-Se(3)-Fe(1)-Se(4) 118.25(4)°) than the one observed in $(NEt_4)_2[Fe(SePh)_4]$ $(103.6 - 114.9^{\circ})^{26}$ while the Fe–Se bond lengths are similar.

Powder X-ray diffraction studies

The calculated (150 K) and measured X-ray diffraction powder patterns (293 K) for the carefully dried powders of 1–4 show a good agreement, taking into account the temperature difference (Fig. S2 in the supporting information†). However, powders of 1 taken from different reaction batches, sometimes displayed a certain disagreement between the calculated and the experimental profiles: a second diffraction peak with varying intensity appeared at $2\Theta = 8.18^{\circ}$, close to the most intense peak at $2\Theta = 7.93^{\circ}$ of



Fig. 1 a) Section of the one-dimensional chain structure of $\frac{1}{m}$ [Fe(SePh)₂] (1) viewed down *a* (ellipsoids drawn with 50% probability). Symmetry transformation for generation of equivalent atoms: '*y* + 1/4, -*x* + 5/4, *z* + 1/4 " -*y* + 5/4, *x* - 1/4, *z* - 1/4 "' -*x* + 3/2, -*y* + 1, *z* - 1/2. Selected bond length (pm) and angles (°): Se(1)–Fe(1') 243.97(13), Se(1)–Fe(1) 245.13(12), Se(2)–Fe(1) 245.86(12), Fe(1)–Se(2') 243.96(13), Fe(1) ··· Fe(1') 287.92(15). Se(1'')–Fe(1)–Se(1) 105.03(4), Se(2')–Fe(1)–Se(1) 106.39(4), Se(1'')–Fe(1)–Se(2) 106.16(4), Se(2')–Fe(1)–Se(2) 108.62(4), Se(1)–Fe(1)–Se(2), 108.20(4), Se(1'')–Fe(1)–Se(2') 121.82(5), Fe(1')–Se(1)–Fe(1)–Fe(1) 72.12(3), Fe(1'')–Se(2)–Fe(1) 72.00(3), b) view along *c*.

the original structure. In order to reproduce the occurrence of the additional peak we succeeded by gentle heating of 1 to $110 \degree$ C for 5 h to completely transform the original powder pattern of 1 to a new but quite similar pattern (Fig. 5).

Rietveld analysis was used to investigate the changes which occurred after the heating procedure (Fig. S3 and S4 and Table S1 in the supporting information[†]).²⁷ Cell parameters refinement resulted in slightly changed unit cell edges with about 2.3% shorter *a* and *b* axes (21.5799(4) Å against 22.092(3) Å), while the *c* axis increased slightly from 10.887(2) Å to 10.9024(5) Å. As a base for refinement the atom positions for iron and selenium were taken from the structural model obtained from single crystal diffraction. The positions and thermal factors of carbon and hydrogen atoms of the phenyl rings have not been optimized during the Rietveld refinement process and the quality of the fit did not improve significantly when they were refined. The refined structural model is given in table S1 of the supporting information section.[†] The main structural changes involve a slight shrinkage of the unit cell accompanied by a twist of the 1D chains



Fig. 2 Section of the one-dimensional chain structure of ${}_{-1}^{1}$ [Fe(SeC₆H₂-2,4,6-(CH₃)₃)₂] (2) viewed down *a* (ellipsoids drawn with 50% probability). Symmetry transformation for generation of equivalent atoms: '-x + 2, -y, -z'' - y + 1, x - 1, z + 1/2''' y + 1, -x + 1, -z + 1/2'' y + 1, -x + 1, z + 0.5 v y + 1, -x + 1, z - 0.5. Selected bond length (pm) and angles (°): Se(1)–Fe(1) 251.81(4), Fe(1)… Fe(1') 350.5(1). Fe(1)–Se(1)–Fe(1') 88.20(2), Se(1'')–Fe(1)–Se(1) 118.97(1), Se(1)–Fe(1)–Se(1') 91.80(2), Se(1)–Fe(1)–Se(1''') 118.97(1).

formed by the edge sharing FeSe_4 tetrahedra (Fig. S4a and b in the supporting information[†]). Most probably this irreversible structural rearrangement is induced by loss of THF molecules upon drying. Lattice THF molecules were identified within the structure of **1**, but these were located on a fourfold axis and therefore badly disordered and could not be adequately refined (see experimental part). Although elemental analysis and TGA of **1** after vacuum drying without heating suggest a loss of all THF molecules, a complete phase change could only be achieved by additional heating. In this respect it is also interesting to note that the elemental cell of the heated material still comprises 564 Å³ of solvent accessible voids in comparison to 615 Å³ of the original compound.



Fig. 3 Molecular structure of $[Fe(SePh)_2(1,10-phen)_2]$ (3) (ellipsoids drawn with 50% probability). Selected bond length (pm) and angles (°): Fe(1)–N(4) 217.8(2), Fe(1)–N(2) 217.9(2), Fe(1)–N(3) 224.3(2), Fe(1)–N(1) 226.3(2), Fe(1)–Se(1) 255.0(1), Fe(1)–Se(2) 259.3(1), N(4)–Fe(1)–N(2) 157.27(8), N(4)–Fe(1)–N(3) 74.69(8), N(2)–Fe(1)–N(3) 88.97(8), N(4)–Fe(1)–N(1) 88.01(8), N(2)–Fe(1)–N(1) 74.52(8), N(3)–Fe(1)–N(1) 84.34(8), N(4)–Fe(1)–Se(1) 99.11(6), N(3)–Fe(1)–Se(1) 173.77(6), N(1)–Fe(1)–Se(1) 96.15(5), N(4)–Fe(1)–Se(2) 97.22(6), N(2)–Fe(1)–Se(2) 98.60(6), N(3)–Fe(1)–Se(2) 90.38(6), N(1)–Fe(1)–Se(2) 171.35(5), Se(1)–Fe(1)–Se(2) 89.846(16).



Fig. 4 Molecular structure of $[Fe(phen)_3][Fe(SePh)_4]$ (4) (ellipsoids drawn with 50% probability). Selected bond length (pm) and angles (°): Se(1)–Fe(1) 244.43(11), Se(2)–Fe(1) 244.59(11), Se(3)–Fe(1) 246.08(10), Se(4)–Fe(1) 247.41(12), Fe(2)–N(6) 195.6(4), Fe(2)–N(2) 196.7(4), Fe(2)–N(3) 196.9(4), Fe(2)–N(5) 197.4(4), Fe(2)–N(4) 197.7(4), Fe(2)–N(1) 198.3(4). Se(1)–Fe(1)–Se(2) 113.76(4), Se(1)–Fe(1)–Se(3) 98.76(4), Se(2)–Fe(1)–Se(3) 114.06(4), Se(1)–Fe(1)–Se(4) 104.07(4), Se(2)–Fe(1)–Se(4) 107.44(4), Se(3)–Fe(1)–Se(4) 118.25(4), N(2)–Fe(2)–N(1) 82.19(19), N(3)–Fe(2)–N(4) 82.74(16), N(6)–Fe(2)–N(5) 83.04(16), N(3)–Fe(2)–N(5) 175.42(16), N(2)–Fe(2)–N(4) 176.51(16), N(6)–Fe(2)–N(1) 172.35(18).

Magnetic properties

The magnetic behavior of antiferromagnetic chain compounds has been extensively studied for many years.²⁸ Ideal systems show a broad maximum in the temperature dependence of the magnetic susceptibility as a result of short range ordering. Long range order is not possible in a one-dimensional system. Various models have been derived for the temperature dependence of the susceptibility for chains of isotropic spins²⁹⁻³¹ which depend on the magnitude of the exchange interaction and the spin quantum number. In real systems, there are a number of factors which produce deviations from ideal behavior. Interchain interactions



Fig. 5 Measured X-ray diffraction powder patterns of ${}^{1}_{\infty}$ [Fe(SePh)₂] (1) before and after heating to 110 °C.

may become significant producing a change in dimensionality leading to long range order. Secondly, many spin systems exhibit Ising (1-D) or XY (2-D) anisotropy resulting in zero-field splitting of the spin states which is not accounted for in simple models. Finally, systems with integer spins will have a gap in their energy level manifold leading to a more rapid decrease in susceptibility at low temperatures.³² Two approaches have been taken in order to derive mathematical models for idealized chains. For large moments, such as in our previous work on $\frac{1}{m}$ [Mn(SeR)₂] (R = Ph, Mes),¹³ the classical approximation used by Fisher²⁹ is estimated to be very good, while for smaller, quantum spin systems, the approach of Bonner and Fisher,³⁰ expanded by Weng,³¹ is more appropriate, though neither of these models introduce an anisotropy parameter.

The magnetic behavior of **1** and **2** (Fig. 6a and b) is very similar to that of $\frac{1}{\infty}$ [Mn(SeR)₂] (R = Ph, Mes).¹³ As with the manganese analogue, **1**, has a very small magnitude of susceptibility, well below that expected at room temperature for a system of noninteracting iron ions and it decreases smoothly down to around 40 K. This is indicative of very strong antiferromagnetic superexchange as the broad maximum must occur at a temperature far higher than 300 K. At very low temperatures, a rapid rise in susceptibility has been observed. We ascribe this to paramagnetic impurities arising from a very small degree of decomposition. Interestingly the magnetic behaviour of **1** is similar to related solid state compounds like KFe(III)E₂ (E = S, Se) which also consists of edge-linked chains of FeE₄ tetrahedra.³³

For comparison, we resynthesized the ring molecule $[Fe(SePh)_2]_{12}^7$ for which only the room temperature magnetic moment was originally determined. The temperature dependence of the magnetic susceptibility of this compound (Fig. S5 in the supporting information†) is broadly similar to that measured for 1, showing decreasing susceptibility with decreasing temperature down to low temperatures. This is indicative for very strong antiferromagnetic coupling within the ring as the maximum in χ must occur far above 300 K. The effective magnetic moment μ_{eff} of the ring compound was originally found to be 1.51 μ_B /Fe at 293 K⁸ which agrees with our value of 1.57 μ_B /Fe at 300 K derived from χ . The increase in the susceptibility below 32 K probably results from paramagnetic impurities. The magnetic behaviour is thus very similar to that observed in 1 a similarity which is



Fig. 6 The temperature dependence of the magnetic susceptibility of a) $\frac{1}{2}$ [Fe(SePh)₂] (1) and b) $\frac{1}{2}$ [Fe(SeC₆H₂-2,4,6-(CH₃)₃)₂] (2). The solid line represents a fit to Fisher's equation, described in the text.

expected in view of similar geometry in the Fe-Se-Fe bridges (see DFT calculations below). Slight differences in the distortion of the essentially tetrahedral ligand fields in 1 and [Fe(SePh)₂]₁₂ might lead to slight differences in magnetic behavior. Much weaker magnetic coupling is observed in the Fe(II) rings with mixed halide and thiolate bridges; [FeCl(SSi'Bu₃)]₁₂ and [FeBr(SSi'Bu₃)]₁₂.³⁴ This was assigned to rather long intermetallic distances (Fe-Fe 312.7 and 317.1 pm, respectively). In view of our theoretical calculations (see below) this weaker coupling might be better explained by the larger Fe-S-Fe bridging angles (83.9 and 85° respectively) which lead to a weaker superexchange through the ligands.

There are also distinct similarities between 2 and its manganese analogue. The presence of the broad maximum centered close to 125 K shows that the antiferromagnetic exchange is strong, but not as strong as in 1. Fits to the classical *Fisher* method (eqn (1))

yield J = -16.2(2) cm⁻¹. For the spin Hamiltonian $\hat{H} = -2J\sum_{i} S_i \cdot S_{i+1}$ these equations

have the form:

$$\chi_{\rm M} = \frac{N_{\rm A} g^2 \mu_{\rm B}^2 S(S+1)}{3k_{\rm B} T} \left(\frac{1+u}{1-u}\right)$$
(1)

where

$$u = \coth\left(\frac{2JS(S+1)}{k_{\rm B}T}\right) - \frac{k_{\rm B}T}{2JS(S+1)}$$

ı

and $\chi_{\rm M}$ is molar susceptibility, N_A is Avogadro constant, $\mu_{\rm B}$ is Bohr magneton, S is total spin quantum number, $k_{\rm B}$ is Boltzmann constant, J is the coupling constant and T is temperature.

It should be noted that this value is approximately double that obtained for the manganese analogues.

Deviation from the model at low temperatures can have a number of possible causes. Firstly, a more rapid drop in γ could be associated with a Haldane gap, however a similar behavior was observed in the half integer manganese analogue. The second possibility is that interchain interactions become dominant and there is a second order phase transition to a long range ordered state. This is also implausible as the decrease is actually too rapid for an isotropic 3-D system. Finally, the deviation may be due to zero field splitting where states with low $J_{\rm eff}$ may be preferentially populated as the temperature decreases. As with 1, a paramagnetic tail is observed below ca. 20 K.

Isothermal magnetization curves of 1 and 2 at 5 K show no saturation up to 4.5 T (1) and 9 T (2) consistent with antiferromagnetic behaviour (Fig. S6 in the supporting information[†]).

Density Functional Theory (DFT) calculations were performed to obtain the exchange coupling constants for the dinuclear segments $[Fe_2(SeR)_6]^{2-}$ (R = Ph (5), R = Mes (6)) of the chain compounds 1 and 2 by the broken symmetry approach $^{35-37}$ (for further details see experimental section). The calculated exchange coupling constants of the two compounds are significantly different. For 5 a coupling constant of $J = -137 \text{ cm}^{-1}$ was obtained while a much lower negative value of $J = -20 \text{ cm}^{-1}$ was obtained for compound 6. It is known for a long time that the superexchange coupling is a function of the geometrical structure of the bridging unit B in M-B-M between two magnetic ions M.38-40 Important structural parameters are the M-B distance and the M-B-M angle. Furthermore, the role of direct exchange between the metal atoms compared to superexchange is of interest. The influence of these parameters on the magnetic exchange coupling have been the subject of several quantum chemical calculations (see for example references [41-46]).

We constructed model clusters to analyze which of the geometrical differences between 5 and 6 is responsible for the change in the coupling, the Fe-Se distance, the Fe-Se-Fe angle or a direct coupling of the two metal atoms. In $[Fe_2(-)_2(SeCH_3)_4]^{2-}$ (model 1) (Fig. 7a), each Se-R bridge was substituted by one negative point charge. This allows for the analysis of the direct Fe-Fe coupling. We obtained a coupling constant of -16 cm^{-1} for the short Fe-Fe distance in 5 and -4 cm⁻¹ for the long Fe-Fe distance in 6. There is also a difference in the occupation of the *d*-orbitals. For the long distance the d_{xy} orbital is doubly occupied, while a combination of d_{z^2} and d_{xy} is occupied for the short Fe-Fe distance (for the orientation of the molecules see Fig. 7). This shows that direct exchange plays a minor role in coupling between the iron atoms. In $[Fe_2(SeCH_3)_6]^{2-}$ (model 2) (Fig. 7b), the Fe-Se-Fe angle was varied from 70° to 110° for Fe–Se distances of 246 pm and 252 pm. The results are given in Table 3. As expected, the coupling is for each angle in average by 32% weaker overall in 6 (less negative J values), where the Fe–Se distance is by 6 pm longer. More importantly, the size of the exchange interaction

	1	$_{\infty}^{1}$ [Mn(SePh) ₂]	2	[Mn(SeMes) ₂]
M-Se $M \cdots M$	243.9(1)–245.9(1) 287.9(2)	254.7(1)–257.8(1) 304.6(1)	251.8 (4) 350.5 (1)	259.0 (3) 359.3 (3)
*Mes = S	$eC_6H_2-2,4,6-(CH_3)$	3		

Table 3 Magneto-structural correlation of the exchange coupling in $[Fe_2(SeCH_3)_6]^2$ (model 2). The coupling constants are given in cm⁻¹

Fe–Se–Fe angle	$J (d_{\text{Fe-Se}} = 246 \text{ pm})$	$J (d_{\text{Fe-Se}} = 252 \text{ pm})$
110	-14.7	-9.3
100	-5.2	-2.9
90	-28.4	-19.9
80	-77.0	-57.5
70	-120.4	-91.4



Fig. 7 Model clusters for a) the direct Fe–Fe interaction $[Fe_2(-)_2(SeCH_3)_4]^{2-}$ (model 1) and b) the magneto-structural correlation $[Fe_2(SeCH_3)_6]^{2-}$ (model 2).

decreases by 76.4% for $d_{\text{Fe-Se}} = 246$ pm and 78.2% for $d_{\text{Fe-Se}} = 252$ pm as the Fe–Se–Fe angle increases for 70 to 90°. This illustrates that the source of the difference in behaviour between 1 and 2 is related to the steric bulk of the aromatic groups; phenyl is less bulky and allows more efficient packing with smaller Fe–Fe and Fe–Se distances and more important smaller Fe–Se–Fe angles and therefore strong antiferromagnetic coupling. Equivalent reasoning shows why more bulky mesityl yields weaker coupling.

Calculations on a binuclear model for the $[Fe(SePh)_2]_{12}$ ring molecule yielded a coupling constant of J = -135 cm⁻¹ similar to that obtained for the model unit **5** of the chain complex **1**. This result again confirms the importance of the geometry of the Fe₂Se₂ rhombs for the magnetic properties, which is similar for both complexes. In comparison, differences in the tetrahedral coordination geometry around the iron atoms do obviously not have a strong influence on the coupling constant.

Optical properties

UV-Vis spectra of the crystalline powders of 1-4 were measured as a nujol mull pressed between quartz plates. For 1 and 2 (Fig. 8a), approximately three broad and nearly featureless absorption maxima can be identified between 650 and 300 nm (1) and 350 nm (2). According to recent observations in dinuclear iron thiophenolate clusters, these transitions should be mainly assigned to LMCT bands from $-\text{SeR}^-$ (R = Ph, Mes) to Fe²⁺.^{2,3} The strong absorption features at higher energies (1: 250 nm; 2: 250 and 295 nm) can be assigned in accordance to spectra of related manganese selenolato complexes to $\pi - \pi^*$ transitions of the $-\text{SeR}^-$ (R = Ph, Mes) ligands.¹³ As expected 3 (dark green) and 4 (dark red) display different absorption spectra (Fig. 8b). Due to the different types of ligands, absorption features above 350 nm could originate from -SePh⁻ to Fe²⁺ LMCT bands as observed in 1 as well as metal to ligand charge transfer transitions (MLCT) into low lying empty π^* orbitals of phenanthroline ligands. A noticeable very broad and weak absorption shoulder in 3 ranges from approximately 1300 down to 800 nm, while no absorption above 800 nm is present in 4. Similar strong absorption features below 350 nm can be assigned to π - π * transitions of either the phenanthroline ligands or of the PhSe⁻ ligands or of a mixture of both.



Fig. 8 UV-Vis spectra of a) $\frac{1}{n}$ [Fe(SePh)₂] (1) and $\frac{1}{n}$ [Fe(SeC₆H₂-2,4,6-(CH₃)₃)₂] (2) and b) [Fe(SePh)₂(1,10-phen)₂] (3) and [Fe(phen)₃][Fe(SePh)₄] (4) in solid state (powder in mineral oil between quartz plates).

Absorption spectra of 1–4 in solution display different features than in solid state (Fig. S7 and S8 in the supporting information[†]). The differences in both types of the spectra, which are on the one hand due to the non validity of Lambert Beer's law for the solid state spectra, might also indicate different coordination geometries of the Fe^{2+} ions in solution and in solid state. In the crystal structure of 1 and 2 the Fe^{2+} ions have a tetrahedral distorted coordination by four selenium atoms of the selenolato ligands. In solution, the one-dimensional polymeric structures are most probably destroyed along with an additional coordination of solvent molecules which can either result in a tetrahedral or octahedral geometry. Interestingly the solution spectra of 3 and 4 in DMF are very similar as already indicated by the formation of a red solution suggesting the formation of identical complex fragments in solution.

Thermal decomposition

Thermogravimetric analysis (TGA) of 1 in a helium gas flow shows that the thermal decomposition occurs from 150 °C up to 250 °C in a one step process (Fig. 9). In vacuum (~10⁻⁶ mbar), 1 already starts to decompose above 30 °C in two successive steps up to 175 °C. The mass change of both decomposition reactions corresponds to the calculated cleavage of one SePh₂ (calcd 63.3%). Its formation and purity was confirmed by ¹H and ¹³C-NMR of the collected liquid colourless cleavage product. The black solid residue of the TGA of 1 thus has the formal composition FeSe (C < 0.1%). The XRD powder pattern of a sample heated to 550 °C in vacuum (Fig. 10) reveals that in agreement with the phase diagram of the Fe-Se system,⁴⁷ the powder consists of a tetragonal $Fe_{1+x}Se$ (0.012 < x < 0.02)⁴⁸ and a hexagonal Fe₇Se₈ (with 52 to 53 at.% Se)⁴⁹ phase (Tables 2-4). In samples heated to 250 °C, only broad peaks of the tetragonal phase could be identified which sharpen accompanied by the evolution of the peaks for the hexagonal Fe_7Se_8 phase by heating to 350 and 450 °C (Fig. S9 in the supporting information[†]). This could be interesting with respect to the fact that recently superconductivity was observed in tetragonal PbO-type FeSe with a critical temperature (T_c) of 8 K.⁵⁰



Fig. 9 Thermogravimetric analysis of ${}^{1}_{\infty}$ [Fe(SePh)₂] (1) under a) He gas flow and b) in vacuum.

Conclusion

The first examples of polymeric homoleptic iron chalcogenolato complexes ${}^{1}_{\omega}$ [Fe(SePh)₂] and ${}^{1}_{\omega}$ [Fe(SeMes)₂] (Mes = C₆H₂-2,4,6-



Fig. 10 Powder XRD pattern of the residue of the TGA experiment under vacuum $(3 \times 10^{-6} \text{ mbar}, \text{ up to } 550 \text{ °C})$ of $\frac{1}{6}$ [Fe(SePh)₂] (1) compared to the indexed reflection patterns of tetragonal Fe_{1+x}Se (0.012 < x < 0.02) ⁴⁸ and hexagonal Fe₇Se₈ (with 52 to 53 at.% Se).⁴⁹

 $(CH_3)_3$ have been prepared in good yields. In the crystal, the compounds form one-dimensional chains with bridging selenolate ligands comprising Fe–Se–Fe bridging angles which differ by approximately 20°. Magnetic measurements supported by DFT calculations reveal that the different bridging angles have a pronounced influence on the antiferromagnetic exchange interactions of the unpaired electrons along the chains in the two different compounds. In principle, these investigations on magnetostructural correlations in one-dimensional chain compounds should be extendable to related sulphur and tellurium bridged compounds as well as chalcogenolato complexes of cobalt and nickel. Preliminary data from single crystals X-ray analysis and powder diffraction measurements indicate that related sulphur bridged compounds of manganese and iron are accessible *via* similar reactions.

Experimental section

Synthesis

Standard Schlenk techniques were employed throughout the syntheses using a double manifold vacuum line with high purity dry nitrogen (99.999990%) and a MBraun Glovebox with high purity dry argon (99.9999990%). The solvents THF and diethylether were dried over sodium-benzophenone, and distilled under nitrogen. Anhydrous dimethylformamide (DMF) (H₂O < 0.005%) obtained from Aldrich was degassed, freshly distilled and stored over molecular sieves under nitrogen. Fe(OOCCH₃)₂, FeCl₃ and 1,10-phenanthroline were purchased from Aldrich. PhSeSiMe₃,⁵¹ PhSeH,⁵¹ MesSeH (Mes = C₆H₂-2,4,6-(CH₃)₃)⁵² and

 $Fe\{N(Si(CH_3)_3)_2\}_2^{53}$ and $[Fe(SePh)_2]_{12}^7$ were prepared according to literature procedures.

[Fe(SePh)₂] (1): a) Fe{N(Si(CH₃)₃)₂} (0.185 g (0.49 mmol)) was dissolved in 30 mL THF and 0.08 mL (0.4 mmol) of P^{*n*}Pr₃ was added to give a light yellow solution. Addition of HSePh (0.11 mL (1.03 mmol)) at -30 °C resulted in the immediate formation of a deep red solution. Standing over night at 2 °C allowed the formation of tiny dark red crystals of 1 which were filtered after 2 additional days of rest at room temperature and washed subsequently twice with THF to give a total yield of 68% (0.123 g). C₁₂H₁₀FeSe₂ (368.0): calcd C 39.2, H 2.7; found C 39.3, H 3.1%.

b) FeCl₃ (0.26 g (1.6 mmol)) was dissolved in 35 mL THF. PhSeSiMe₃ (1.23 mL (6.41 mmol)) was then added, followed by a quick color change from light green to dark green then yellow orange to dark red. When the stirring of the solution is stopped soon a dark red microcrystalline precipitate of **1** starts to form. After one night, the solution is warmed up without stirring for 1 h at 60 °C and then, after cooling to room temperature, filtered and washed with THF to give 0.35 g (59%). $C_{12}H_{10}FeSe_2$ (368.0): calcd C 39.2, H 2.7; found C 39.0, H 2.9%.

c) Crystals of **1** for single crystal diffraction: $Fe(OOCCH_3)_2$ (0.175 g (1.01 mmol)) was suspended with P^{*n*}Bu₃ (0.5 mL, 2.01 mmol) in 25 mL of THF. PhSeSiMe₃ (0.48 mL (2.53 mmol)) was then added and the mixture stirred over night to give a deep red solution. Careful layering of 10 mL of the reaction solution with 10 mL THF and 20 mL of diethylether in Schlenk tubes resulted after three weeks in the crystallisation of tiny dark red needles of Fe(SePh)₂ (1) some of which being suitable for single crystal diffraction at a synchrotron source. Filtration and washing with THF resulted in a total yield of 43% (0.159 g) for 1. $C_{12}H_{10}FeSe_2$ (368.0): calcd C 39.2, H 2.7; found C 39.2, H 3.0%.

[Fe{SeC₆H₂-2,4,6-(CH₃)₃]₂] (2): Fe{N(Si(CH₃)₃)₂]₂ (0.30 g (0.81 mmol)) was dissolved in 40 mL toluene and 0.08 mL (0.4 mmol) of P"Pr₃ was added to give a light green solution. Addition of HSe{C₆H₂-2,4,6-(CH₃)₃}₂ (0.34 mL (1.69 mmol)) resulted in the immediate formation of a deep red solution. Standing over night in the dark afforded the formation of red-brown crystals of **2** which were filtered after 5 days and washed subsequently twice with toluene and once with pentane to give a total yield of 61% (0.22 g). $C_{18}H_{22}FeSe$ (452.14): calcd C 47.8, H 4.9; found C 47.9, H 5.1%.

 $[Fe(SePh)_2(1,10\text{-phen})_2]$ (3): $Fe(SePh)_2$ (0.123 g (0.33 mmol)) was dissolved in a mixture of 10 mL THF and 1 mL of DMF to give a red solution. A solution of 1,10-phenanthroline (0.120 g (0.67 mmol)) in 5 mL DMF was then added, followed, after approximately 10 min, by the formation of dark green crystals of **3** which were filtered and washed with THF after 4 days to give a total yield of 78% (0.19 g). $C_{36}H_{26}FeN_4Se_2$ (728.4): calcd C 59.4, H 3.6, N 7.7; found C 59.6, H 4.1, N 7.2%.

[Fe(1,10-phen)₃][Fe(SePh)₄]·(CH₃)₂NCHO (4): Fe(SePh)₂ (0.100 g (0.27 mmol)) was dissolved in 10 mL DMF to give a dark-green suspension. A solution of 1,10-phenanthroline (0.049 g (0.27 mmol)) in 3 mL DMF was then added to give a deep red solution. Addition of 10 mL of THF and standing for three days afforded dark red crystals of 4 which were filtered and washed with THF to give a total yield of 75% (0.27 g). $C_{60}H_{44}Fe_2N_6Se_4\cdot C_3H_7NO$ (1349.7): calcd C 56.1, H 3.8, N 7.3; found C 56.1, H 3.9, N 7.1%.

Crystallography

Crystals suitable for single crystal X-ray diffraction were taken directly from the reaction solution of the compound and then selected in perfluoroalkylether oil. Single-crystal X-ray diffraction data of 1 were collected using synchrotron radiation ($\lambda = 0.80$ Å) on a STOE IPDS II (Imaging Plate Diffraction System) at the ANKA synchrotron source in Karlsruhe. The quality and intensity of the reflections of the weakly diffracting crystals of 1 with a resolution smaller than d = 0.92 decreases significantly indicated by a decrease of the mean I/σ ratio below 6.04 and an increase of the R(int) value above 0.2526. Therefore data were measured only up to 2θ 52° at $\lambda = 0.80000$. Single-crystal X-ray diffraction data of 2, 3 and 4 were collected with graphite-monochromatized Mo-Ka radiation $(\lambda = 0.71073 \text{ Å})$ on a STOE IPDS II (Imaging Plate Diffraction System). Raw intensity data were collected and treated with the STOE X-Area software Version 1.27. Data for all compounds were corrected for Lorentz and polarisation effects. Based on an optimized crystal description numerical absorption corrections were applied.⁵⁴ The structures were solved with the direct methods program SHELXS of the SHELXTL PC suite programs,55 and were refined with the use of the full-matrix least-squares program SHELXL.55 Molecular diagrams were prepared using Diamond.56 Lattice THF molecules were identified within the structure of 1, but these were located on a fourfold axis and badly disordered and could not be adequately refined. The data were therefore corrected for these using the SQUEEZE option within the PLATON⁵⁷ program package finding a total of 130 electrons (~2.5 THF) in a potential solvent accessible area of 615 Å. All Fe, Se, N, O and C atoms were refined with anisotropic displacement parameters except those of the solvent DMF molecule in 4 whilst all H atoms were calculated in fixed positions.

CCDC 737597(1), 737598 (2), 737599 (3) and 747600 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc. cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ ccdc.cam.ac.uk).

X-ray powder diffraction patterns (XRD) were measured on a STOE STADI P diffractometer (Germanium monochromator, Debye–Scherrer geometry) with Cu-K α 1 radiation (1–4) and with Co-K α 1 radiation (bulk-FeSe) in sealed glass capillaries. Theoretical powder diffraction pattern for 1–4 were calculated on the basis of the atom coordinates obtained from single crystal X-ray analysis by using the program package STOE WinXPOW.⁵⁸ Rietveld analysis was performed with the program MAUD.²⁷ The position for iron and selenium atoms were refined together with their Debye–Waller factors.

Physical measurements

Zero-Field-Cooled temperature dependent susceptibilities were recorded for 1 and 2 in RSO mode using a MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range from 5 to 300 K in a homogeneous 100 Oe (1) and 1000 Oe (2) external magnetic field. The magnetization curve of 1 was measured on the MPMS-5S (Quantum Design) SQUID magnetometer while the magnetization curve of 2 was measured on a PPMS Quantum Design magnetometer. The samples were contained in gelatine capsules filled in a glove box under argon atmosphere owing to the high degree of moisture and oxygen sensitivity of the compounds. The data were corrected for the sample holder and for diamagnetism using Pascal's constants.^{28,59,60}

UV-Vis absorption spectra of cluster molecules in solution were measured on a Varian Cary 500 spectrophotometer in quartz cuvettes. Solid state spectra were measured as micron sized crystalline powders in nujol oil between quartz plates with a Labsphere integrating sphere.

Quantum chemical calculations

All calculations were performed at DFT level using the RIapproximation with the program package Turbomole.^{61,62} Segments with two iron atoms were cut out of the one-dimensional chain compounds **1** and **2**. All [SeR]⁻ groups bound to the two metal atoms are taken into account. The positions of the Fe, Se, and C atoms were taken from X-ray structure analysis, the positions of the H atoms were optimized using the BP86 functional.^{63,64} For the calculation of the exchange coupling constant, the Spin-Hamiltonian (eqn (2)) was used.

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \tag{2}$$

J was obtained from unrestricted DFT calculations with the B3-LYP functional^{63,65,66} using the broken symmetry approach³⁵⁻³⁷ and applying the scheme of Nishino *et al.*³⁷

$$J = \frac{E(BS) - E(HS)}{\left\langle S^2 \right\rangle_{HS} - \left\langle S^2 \right\rangle_{BS}}$$
(3)

E(HS) is the energy of a state where all unpaired electrons have the same spin. In the BS state, the spin of the unpaired electrons at one iron center is switched to opposite spin. The values obtained with eqn (3) are almost identical to those obtained with eqn (4) given by Noodleman.³⁵

$$J = \frac{E(BS) - E(HS)}{S_{HS}^2}$$
(4)

The difference in the denominator was 0.1% only.

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