Polymeric cobalt(II) thiolato complexes – syntheses, structures and properties of $^{1}\infty[\text{Co(SMes)}_{2}]^{+}$ and $^{1}\infty[\text{Co(SPh)}_{2}\text{NH}_{3}]^{+}$

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Reactions of $[\text{Co(N(SiMe}_{3})_{2})_{2}\text{thf}]$ with 2.1 equiv. of MesSH (Mes = C$_{6}$H$_{2}$-2,4,6-(CH$_{3}$)$_{3}$) yield dark brown crystals of the one dimensional chain compound $^{1}\frac{1}{2}[\text{Co(SMes)}_{3}]$. In contrast reactions of $[\text{Co(N(SiMe}_{3})_{2})_{2}\text{thf}]$ with 2.1 equiv. of PhSH result in the formation of a dark brown almost X-ray amorphous powder of ‘Co(SPh)$_{2}$’. Addition of aliquots of CH$_{3}$OH to the latter reaction resulted in the almost quantitative formation of crystalline ammonia thiolato complexes either $[\text{Co(SPh)}_{2}\text{NH}_{3}]_{2}$ or $^{1}\frac{1}{2}[\text{Co(SPh)}_{2}\text{NH}_{3}]$. Single crystal XRD reveals that $^{1}\frac{1}{2}[\text{Co(SPh)}_{2}\text{NH}_{3}]$ forms one-dimensional chains in the crystal via $\mu$_2-SPh bridges whereas $[\text{Co(SPh)}_{2}\text{NH}_{3}]$ consists at a first glance of isolated distorted tetrahedral units. Magnetic measurements suggest strong antiferromagnetic coupling for the two chain compounds $^{1}\frac{1}{2}[\text{Co(SMes)}_{3}] (J = –38.6 \text{ cm}^{-1})$ and $^{1}\frac{1}{2}[\text{Co(SPh)}_{2}\text{NH}_{3}] (J = –27.1 \text{ cm}^{-1})$. Interestingly, also the temperature dependence of the susceptibility of tetrahedral $[\text{Co(SPh)}_{2}\text{NH}_{3}]$ shows an antiferromagnetic transition at around 6 K. UV-Vis-NIR spectra display $d$–$d$ bands in the NIR region between 500 and 2250 nm. Thermal gravimetric analysis of $[\text{Co(SPh)}_{2}\text{NH}_{3}]$ and $^{1}\frac{1}{2}[\text{Co(SPh)}_{2}\text{NH}_{3}]$ reveals two well separated cleavage processes for NH$_{3}$ and SPh$_{2}$ upon heating accompanied by the stepwise formation of ‘Co(SPh)$_{2}$’ and cobalt sulfide.

Introduction

Metal chalcogenolato complexes have attracted interest due to their rich structural chemistry,$^{1–3}$ and their potential use as precursors for M/E (E = S, Se, Te) materials.$^{4,5}$ New developments in the latter respect came from the utilization of small clusters as building blocks for the formation of nanoparticles with controllable size and shape through photolytic decomposition and solvothermal synthesis.$^{6–10}$ For some time metal chalcogenolato complexes have also been investigated due to their relevance as models for active sites of chalcogen-containing metalloproteins.$^{11,12}$ In this respect, recently nickel and cobalt nitrite complexes supported by thiolates like $[\text{Ni(NO)}_{2}\text{SPh}_{2}]$,$^{13}$ $[\text{Ni}_{4}\text{(NO)}_{4}\text{(μ-SPh)}_{4}\text{SPh}_{2}]$,$^{14}$ $[\text{Co(NO)}_{2}\text{SPh}_{2}]$,$^{15}$ and $[\text{Co}_{3}\text{(NO)}_{6}\text{(μ-SPh)}_{3}]$ have been introduced as model complexes for physiological and pathophysiological processes in which nitric oxide plays an important role.$^{13}$ In addition compounds with the general composition ‘MSPh$_{2}$’ (M = Ni$^{2+}$ and Pd$^{2+}$) were for example found to display catalytic properties.$^{14}$ In a different research direction anionic $[\text{Co(SPh)}_{4}]^{4–}$ which is known for over 30 years has recently been shown to display interesting single ion magnetic behavior.$^{15–17}$

The build-up of the structures of homogeneous and neutral complexes of the general type $[\text{M(SR)}_{n}]$ (n = 1–3; M = transition metal; R = org. group) comprising the monodentate thiolato group SR$^{-}$ 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. The recently published series of quasi-two-coordinate transition metal dithiolates $[\text{M(SR)}_{2}]$ (M = Cr, Mn, Fe, Co, Ni, Zn)$^{18,19}$ with the very bulky organic ligand R = C$_{8}$H$_{17}$,6,6(C$_{6}$H$_{5}$)$_{2}$,2,4,6-(Pr)$_{3}$ 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 should result in the formation of either
oligomeric (e.g. ring-like) or polymeric structures. Examples for transition metals include the oligomeric ring structures of 
[[Ni(μ-SPh)2]4] (n = 9, 11),39 [[Ni(μ-SPt)μ-μtmt)]4,40 [[Ni(μ-SBu)μ-μtmt)]10 (μtmt = 4-methylthioethanethiolato)21 and
[[Fe(SPh)]12,22 the 1D chain structures of 1/2[M(SR)2]2,23 and 3/2[ Cd(SR)2]2 (R = Ph, 4-CH3-C6H4)26 and the 3D adamantanoid network structure of 1/3[Zn(SPh)3]2,24 CH3OH,26
1/3[Cd(SR)2]2 (R = Ph, 4-CH3-C6H4)27 and 3/2[Cd(SSePh)2]2.28 In this respect dimeric [(CoSR)2]2 (R = 2,4,6-iPr3C6H2) and hexameric [(Co(SAr)2(tmeda)] (Et = CH3Hs) are the only polynuclear examples for cobalt which have been characterized by single crystal X-ray diffraction.29

In contrast a few more homoletic thiolato complexes of cobalt which areionic have been structurally characterized including the above mentioned [Co(SPh)2]16–30 the dinuclear anions [Co2(SHt)3]− (ref. 31) and [Co2(SPr)3]− (ref. 32) and the cluster anion [Co4(SPh)6]2−.33 The latter ones can be viewed as structural building blocks of oligomeric and polymeric structures mentioned above.

Amine ligated cobalt complexes with monodentate thiolato ligands SR− are rare and include for example [Co(S-2,4,6-Pr3C6H2)2(py)2]34 [Co(S-2,4,6-Pr3C6H2)2(bpy)2]34 [Co(S-2,3,5,6-Me4C6H2)2(bpy)2]34 [Co(S-2,6-Pr3C6H2)2(2,9-Me2phen)]35 [Co(SPh)2(p7-Tol-NNPEt)2]36 [Co(SAr)2(tmeda)]37 (Ar = 2,4,6-Bu3-C6H2) tmeda = tetrathiomethylene diamine) and [Co(SPh)2(phen)]ClO4 (phen = phenanthroline),38 Only four examples of cobalt thiolato complexes with ammonia ligands have been characterized so far namely [Co(Si(SiMe3)2)2(thf)] with 2.1 equivalents of RSH (Scheme 1). The mesityl complex 2 could be obtained from the reaction mixtures as a dark brown crystalline product 1/2[Co(SMes)2] whereas the dark powder of the phenyl-chalcogenolato complex 1a was found to be almost completely X-ray amorphous (Fig. S1, ESIt). The powder pattern of 1 changes if the reaction product is post annealed in solution at 105 °C for approximately 4 h to give 1b. Attempts to suggest a reasonable structural model for 1b based on the powder XRD pattern have so far not been successful.

Upon addition of stoichiometric amounts of methanol to the reaction mixtures of [Co[N(Si(Me)3)2]2(thf)] and PhSH in thf one can isolate the two ammonia complexes [Co(SPh)2(NH3)2] (3) and 1/2[Co(SMes)2(NH3)] (4) (Scheme 2).

2 crystallizes in the tetragonal space group I4/m (Table 1). In the crystal structure the cobalt atoms are μ2-bridged in one dimension by the two mesitylthiolato ligands to form infinite chains (Fig. 1). Thus 2 resembles the first structurally characterized polymeric cobalt thiolate complex. Four sulfur atoms (S(1), S′(1), S″(1) and S′′′(1)) of the mesitylthiolato ligands build a distorted tetrahedral coordination environment around the cobalt atom with two smaller and four larger S-Co-S bond angles of about 86.50(3)° and 122.04(2)° respectively. The CoS2 rings are planar and close to square shape with a S-Co-S angle of 86.53(3)° and a S-Co-S-Co angle of 93.50(3)°. Co–S distances amount to 233.89(6) pm and the non-bonding Co⋯Co distance was found to be 341.6(2) pm. If viewed along the chain (c axis) the mesityl groups are oriented in a staggered configuration so as to minimize steric interactions. The structure of 2 is strongly reminiscent of that of the selenolato complexes [M(SeC6H2-2,4,6-CH3)2] (M = Mn,23 Fe25). Although the build-up of the 1D chains is almost similar in all three complexes, 2 crystallizes in a different space group with a cell volume which is by 200 Å3 larger for 2 than in the mesityl selenolato complexes mentioned above comprising channels which are filled with solvent molecules (1 eq. due to elemental analysis; solvent potential area of 374 Å2).

3 crystallises in the form of dark blue crystals in the triclinic space group P1 (Table 1). The cobalt atom is coordinated by two phenylthiolate and two ammonia ligands in a distorted tetrahedral fashion (Fig. 2). Bond angles at the cobalt atom range from 104.56(10)–125.87(2)° with the smallest angle

**Results and discussion**

**Syntheses and structures**

The cobalt(II) thiolato complexes of formal composition ‘Co(SR)2’ (R = Ph (1), R = Mes (2)) can be prepared by reaction of [Co(N(SiMe3)2)2(thf)] with 2.1 equivalents of RSH (Scheme 1). The mesityl complex 2 could be obtained from the reaction mixtures as a dark brown crystalline product 1/2[Co(SMes)2] whereas the dark powder of the phenyl-chalcogenolato complex 1a was found to be almost completely X-ray amorphous (Fig. S1, ESIt). The powder pattern of 1 changes if the reaction product is post annealed in solution at 105 °C for approximately 4 h to give 1b. Attempts to suggest a reasonable structural model for 1b based on the powder XRD pattern have so far not been successful.

Upon addition of stoichiometric amounts of methanol to the reaction mixtures of [Co(N(Si(Me)3)2)2(thf)] and PhSH in thf one can isolate the two ammonia complexes [Co(SPh)2(NH3)2] (3) and 1/2[Co(SMes)2(NH3)] (4) (Scheme 2).

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![Scheme 1](image1.png)

**Scheme 1** Syntheses of compounds 1 and 2.

![Scheme 2](image2.png)

**Scheme 2** Syntheses of compounds 3 and 4.
formed by the nitrogen atoms N(1) and N(2) of two ammonia ligands and the largest between the two thiolato ligands S(1), S(2)]. Values of the Co–N (204.6(2), 204.7(2) pm) as well as Co–S (230.25(6), 230.59(6) pm) bond distances are for example comparable to those found in the related mixed thiolato/ammonia cobalt complex [Co(S(Si(OAr)3))2(NH3)] (Ar = 2,6-Pr2C6H3) (Co–N: 205.2(4); Co–S: 228.62(8) pm).10 The planes of the two phenyl rings are almost orthogonal to each other (angle: 87.2°). Short intermolecular S⋯H distances of 259.4–267.7 pm between two of the hydrogen atoms of each ammonia ligand and the sulfur atoms of the phenyl thiolato ligands of neighboring molecules are indicative for hydrogen bonding in the crystal lattice (Fig. S2, ESI†). In addition the shortest intermolecular Co⋯Co distances amount to only 432.3 pm.

4 crystallises as a ‘hair-like’ green crystalline precipitate in the monoclinic space group Cc (Table 1 and Fig. 3). The crystal structure of the tiny crystals could only be determined by the help of the ANKA synchrotron source. In the crystal structure the cobalt atoms are μ2-bridged in one dimension by one of the two phenyl thiolato ligands to form infinite chains (Fig. 3). The distorted tetrahedral coordination sphere around the cobalt atoms is completed by two terminal ligands, one being ammonia and the other phenyl thiolato. Bond angles at the cobalt atom range from 94.46(6)–125.94(6)° with the smallest

![Fig. 1 Molecular structure of 1\(^{-}\)[Co(SMes)\(_2\)] (2) (H atoms omitted for clarity). Selected bond length [pm] and angles [°]: Co–S(1) 233.89(6), S(1)–Co(1)–S(1) 86.50(3), S(1)–Co(1)–S(1) 122.04(2), Co(1)–S(1)–Co(1) 93.50(3). Symmetry transformations used to generate equivalent atoms: x, y, z; x + 1, y, z; x, y, z + 1/2; x, −y + 1, −z + 1; y + 1/2, −x + 3/2, −z + 1/2; −y + 1/2, x − 1/2, z − 1/2.

![Fig. 2 Molecular structure of [Co(SPh)\(_2\)(NH\(_3\))]\(_3\) (3) (H atoms omitted for clarity). Selected bond length [pm] and angles [°]: Co(1)–N(1) 204.6(2), N(1)–Co(1)–S(1) 104.56(10), N(1)–Co(1)–N(1) 104.35(6), N(1)–Co(1)–S(1) 106.07(7), N(1)–Co(1)–S(1) 103.81(7), N(1)–Co(1)–S(1) 110.16(8) S(1)–Co(1)–S(1) 125.87(2).

Table 1 Crystallographic data for 1\(^{-}\)[Co(SMes)\(_2\)] (2), [Co(SPh)\(_2\)(NH\(_3\))] (3) and 1\(^{-}\)[Co(SPh)\(_2\)(NH\(_3\))] (4)

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Comparison of bond lengths and angles for 1\(^{-}\)[Co(SMes)\(_2\)] (2), [Co(SPh)\(_2\)(NH\(_3\))] (3) and 1\(^{-}\)[Co(SPh)\(_2\)(NH\(_3\))] (4):

- **Co–S** (233.89(6), 230.25(6), 228.62(8) pm)
- **Co–N** (204.6(2), 204.7(2), 204.2(2) pm)
- **S⋯H** (259.4–267.7 pm)
- **Co⋯Co** (432.3 pm)
A comparison of the measured and calculated X-ray powder diffraction patterns for 2, 3 and 4 reveals the crystalline purity with respect to the formation of other crystalline compounds (Fig. S3–S5, ESI†). Slightly increasing differences in the position of the peaks with increasing detection angle arise from the temperature difference of the data collections (single crystal XRD at 180 K and powder XRD at room temperature).

Optical properties

Electronic spectra of 2–4 have been measured in a region from 350 to 2250 nm (28 571 to 4444 cm\(^-1\)) as grindings of polycrystalline powders in mineral oil between two quartz plates (Fig. 4 and 5). All spectra can be roughly divided into a region with more and less intense bands, the former ones assigned to charge transfer bands and the latter ones most probably belonging to d–d transitions. However, due to the non-validity of the Lambert–Beer law for this kind of sample preparation this assignment has to be taken with care. For a free ion Co\(^{2+}\) the ground state is \(4F_{9/2}\) which in a tetrahedral field of \(T_d\) symmetry splits into \(4A_{+} + 4T_{2} + 4T_{1}\). The first excited quartet term \(4P\) correlates in a tetrahedral ligand field with \(4T_{1}\). In the ideal symmetric tetrahedral Co\(^{2+}\) complexes one would therefore expect three d–d transitions. Complete removal of symmetry should lift the degeneracy of the T representations leading theoretically to a maximum of nine transitions which are expected to partially overlap and comprise different transition dipole moments. Usually the \(4T_{1}(4F) \leftrightarrow 4A(4F)\) and \(4T_{1}(4P) \leftrightarrow 4A(4F)\) transitions appear as multiple absorptions in the near infrared and visible regions respectively.\(^{12}\) A related recent detailed analysis of the UV-vis-NIR spectra of the complex anions \([\text{Co}E\text{Ph}_3]^{2-}\) (E = O, S, Se) can be found in ref. 17 and 43.

Polymeric 2 displays below 600 nm a shoulder and a maximum centering around 680 nm (14 700 cm\(^-1\)) and further in the near infrared a broad band around 1500 nm (6670 cm\(^-1\)) (Fig. 4). In accordance with spectra of homoleptic Co\(\text{u}\) complexes like \([\text{Co}S\text{Ph}_3]^{2-}\) (ref. 17 and 43) one can assign these bands to transitions to the \(4T_{1}(4P)\) and \(4T_{1}(F)\) states, respectively. For 3 we observe below 500 nm (20 000 cm\(^-1\)) a pair of two bands in the visible between 500 and 750 nm...
(20 000–13 333 cm\(^{-1}\)) and a group of three broad bands in the near infrared between 750 and 1850 nm (13 333–5406 cm\(^{-1}\)) (Fig. 5). In the case of CoL\(_2\)X\(_2\) complexes with \(C_{2v}\) symmetry three bands are usually seen in the near infrared if \(L\) and \(X\) differ significantly in ligand field strength. These bands are suggested to correspond in most cases with the three components of \(^4T_1(\Sigma)\).\(^{42}\) Then the two bands in the visible at 540 nm (18 519 cm\(^{-1}\)) and 644 nm (15 528 cm\(^{-1}\)) should originate from transitions to the split \(^4T_1(\Pi)\) state.

Polymeric 4 displays a similar set of bands in the region above 500 nm comprising two bands in the visible at 590 nm (16 949 cm\(^{-1}\)) and 777 nm (13 771 cm\(^{-1}\)) (Fig. 5). However the maxima in the NIR region are not as distinct as in 3 and can roughly be estimated at 1066 nm (9380 cm\(^{-1}\)), 1320 nm (7576 cm\(^{-1}\)) and 1460 nm (6849 cm\(^{-1}\)). These values indicate an increase of the ligand field splitting ongoing from 2 to 4 to 3 by exchange of one or two thiolato ligands with \(\pi\)-donor properties against the stronger \(\sigma\)-donor ligand NH\(_3\).

**Magnetic properties**

The magnetic behavior of polymeric 2 (Fig. 6) measured between 2 and 300 K in a field of 0.1 T displays a broad maximum in the temperature dependence of \(\chi\) centered around 180 K which is characteristic for strong antiferromagnetic exchange in the chain. A similar behavior has been recently observed for the isostructural chain compounds \(\frac{1}{2}[M(SeMes)\_2]\) (\(M = \text{Mn, Fe}\)).\(^{24,25}\)

In general the magnetic behavior of antiferromagnetic chain compounds has been extensively studied for many years.\(^{44}\) Ideal systems show a broad maximum in the temperature dependence of the magnetic susceptibility (\(\chi\)) as a result of short range ordering. Long range order is not possible in a one-dimensional system. In general two approaches have been taken in order to derive mathematical models for idealized chains. For large moments, such as in our previous work on \(\frac{1}{2}[M(SeR)\_2]\) (\(M = \text{Mn, Fe}; \text{R} = \text{Ph, Mes}\)),\(^{24,25}\) the classical approximation used by Fisher\(^{45}\) is expected to be very good, while for smaller, quantum spin systems, the approach of Bonner and Fisher,\(^{46}\) expanded by Weng,\(^{47}\) is more appropriate, though neither of these models introduce an anisotropy parameter.

For the spin Hamiltonian

\[
\hat{H} = -2J \sum_i S_i \cdot S_{i+1}
\]

these equations have the form:

\[
\chi_M = \frac{N_A S^2 \mu_B^2 S(S+1)}{3k_B T} \left( \frac{1+u}{1-u} \right)
\]

where \(\chi_M\), molar susceptibility; \(N_A\), Avogadro constant; \(\mu_B\), Bohr magneton; \(S\), total spin quantum number; \(k_B\), Boltzmann constant; \(J\), coupling constant; \(T\), temperature and \(u = \coth(2JS(S+1)) - \frac{k_B T}{2JS(S+1)}\).

Fits to the classical Fisher method of the \(\chi\) vs. \(T\) curve of 2 for the data between 75 and 300 K (eqn (1)) yield \(J = -38.6(9)\) cm\(^{-1}\) suggesting a stronger coupling in 2 than in the related mesitylselfenolato complexes \(\frac{1}{2}[M(SeMes)\_2]\) (\(M = \text{Mn}; J = 11.2\) cm\(^{-1}\); \(M = \text{Fe}; J = -16.2\) cm\(^{-1}\)).\(^{24,25}\)

Deviation from the model at low temperatures which has been also observed for the complexes \(\frac{1}{2}[M(SeMes)\_2]\) (\(M = \text{Mn, Fe}\)) could originate from an increasing influence of zero field splitting where states with low \(J_{\text{eff}}\) may be preferentially populated as the temperature decreases. A paramagnetic tail which is observed below ca. 25 K might be attributed to a small amount of paramagnetic impurities and/or contributions of paramagnetic ends of chains. Isothermal magnetization curves of 2 at 5 K show no saturation up to 4.5 T consistent with an antiferromagnetic behaviour (Fig. S6, ESI†).

The static magnetic behavior of complex 3 was studied between 2 and 300 K in a field of 0.1 T and by magnetization measurements from 0 to 7 T at 2, 3, 4, 6, 10 and 25 K (Fig. 7 and S7, ESI†). A distinct maximum in the \(\chi\) vs. \(T\) curve around

![Fig. 6 Temperature dependence of \(\chi\) (filled squares) and \(\chi T\) (open circles) of \(\frac{1}{2}[\text{Co(SMes)}\_2]\) (2). Solid green lines represent the results of the fitting to Fisher’s equation (eqn (1)).](image)

![Fig. 7 Temperature dependence of \(\chi\) (filled squares) and \(\chi T\) (open circles) of \(\{\text{Co(SeMes)}\_2(\text{NH}_3)\}_2\) (3). Solid green lines represent the results of the simultaneous fittings with the temperature dependent magnetization (Fig. S7, ESI†) according to a spin Hamiltonian (eqn (2)) by the PHI program.](image)
6 K is an indication for the presence of antiferromagnetic interactions in \(3\). The \(\chi T\) vs. \(T\) and \(M\) versus \(H\) curves at different temperatures calculated for a dinuclear unit of \(3\) were therefore simultaneously fitted using the PHI program\(^4\) by means of an isotropic spin Hamiltonian (SH) accounting for the exchange coupling (Heisenberg–Dirac–van Vleck Hamiltonian) and zero-field splitting (ZFS): (eqn (2)).

\[
\begin{align*}
H &= H_{\text{ex}} + H_{\text{zef}} + H_{\text{CF}} \\
H_{\text{ex}} &= -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \\
H_{\text{zef}} &= \mu_B \sum_{i=1}^{3} \mathbf{S}_i \cdot \mathbf{B}_i \\
H_{\text{CF}} &= \sum D_i \left( S_{ij}^2 - \frac{1}{3} S_i (S_i + 1) + \frac{E_i}{D_i} (S_{ij}^2 - S_{jj}^2) \right)
\end{align*}
\]

\(D\): axial ZFS parameter; \(E\): rhombic ZFS parameter; \(S\): spin vector; \(\mathbf{B}\): magnetic field vector; \(g\): g-factor; \(\mu_B\): Bohr magneton.

The fitted curves where found to describe the temperature dependent susceptibility quite well whereas they increasingly deviate for the magnetization curves below the antiferromagnetic transition point around 6 K (Fig. 7 and S7, ESI†). The parameters indicate a weak antiferromagnetic coupling \((J = -1.254 \text{ cm}^{-1})\) and the presence of magnetic anisotropy \((g = 2.205, D = +4.69 \text{ cm}^{-1}, E = \pm 0.057 \text{ cm}^{-1})\) as expected for tetrahedral \(\text{Co}^{2+}\). However, as both effects, antiferromagnetic coupling and ZFS, are known to have virtually the same effect on the temperature dependence of powder averaged data of \(\chi\), the absolute values of the fittings must be taken with care.

The magnetic behavior of polymeric \(4\) (Fig. 8) measured between 2 and 300 K in a field of 0.1 T displays, like polymeric \(2\), a broad maximum in the temperature dependence of \(\chi\) centered around 135 K indicative for strong antiferromagnetic coupling. In main contrast \(4\) comprises one thiolato bridge with a \(\text{Co–S–Co}\) bridging angle of 103.5° instead of two in \(2\) (\(\text{Co–S–Co}\): 93.54°). Fits to the classical Fisher method of the \(\chi\) vs. \(T\) curve of \(4\) (eqn (1)) yield \(J = -27.1(2) \text{ cm}^{-1}\). Magnetic data of comparable thiolato-bridged polymeric cobalt compounds have not been reported so far. In analogy to \(2\) the model deviates at low temperatures from the experimental curve for similar reasons given above. Isothermal magnetization curves of \(4\) at 4 K show no saturation up to 4.5 T consistent with an antiferromagnetic behaviour (Fig. S8, ESI†).

**Thermal decomposition**

Thermogravimetric analysis (TGA) of \(3\) and \(4\) in a helium gas flow as well as under vacuum conditions (\(~10^{-6} \text{ mbar}\)) shows that the thermal decomposition occurs in well separated two-step processes in a temperature range between 35 and 255 °C (Fig. 9, S9, ESI† and Table 2). Under vacuum conditions the centers of the cleavage processes are shifted by 40–60 °C to lower temperatures. The mass change of the decomposition reactions corresponds to the calculated cleavage of two \(\text{NH}_3\) (calcd 10.9%) and one \(\text{SPh}_2\) (calcd 59.8%) for \(3\) and one \(\text{NH}_3\) (calcd 5.8%) and one \(\text{SPh}_2\) (calcd 63.3%) in case of \(4\). Thus the black solid residues of the TGA of \(3\) and \(4\) heated above 260 °C have the formal composition ‘CoS’. The XRD powder patterns of samples of \(4\) heated to 550 °C in vacuum (Fig. S10, ESI†) are in agreement with the theoretical peak pattern of the cobalt pentlandite structure with the formal composition ‘Co$_5$S$_{18}$’.\(^{50}\) It is presently not clear whether the sulphur (1.21 mass %) which should in theory be additionally cleaved is contained in the volatile decomposition products or as an amorphous product in the residue. Samples heated up to 260 °C are almost amorphous.

Based on the fact that the cleavage of \(\text{NH}_3\) takes place in a well separated step from further decomposition to CoS we also investigated the intermediate product of polymeric 3 with the formal composition ‘Co(SPh)$_3$‘ with respect to its crystallinity by powder XRD. Powders from vacuum thermolysis up to 110 °C displayed after 1 h of isothermal treatment a pattern of an almost amorphous product with one broad reflection feature around 7° in 2θ (Fig. S11, ESI†). The pattern is similar to that obtained for \(1\) (Fig. S1, ESI†). Post annealing of this product at 260 °C for 1 h resulted in an almost amorphous pattern with two broad signals around 20° (Fig. S12, ESI†). The main peak at 2θ = 24° (calcd 22.77°) can be assigned to the pentlandite structure with the formal composition Co$_5$S$_{18}$ (calcd 22.82°). The difference in the 2θ values indicates the retention of the CoS$_2$ pentlandite structure in the amorphous product. The observed signal at 2θ = 17° could be assigned to CoS (calcd 16.5°).
residue at 150 °C for 3–4 h under N₂ atmosphere resulted in powders which display reasonable well-shaped reflection peaks (Fig. S11, ESIF). However, the pattern does not agree with the one obtained for 1b (Fig. S1, ESIF) and those simulated for the structures of the polymeric compounds \(^1\alpha\)M(SePh)\(_2\) \((M = \text{Mn, Fe}^{2,25}\) or \(^1\alpha\)Cd\(_2\)(SPh)\(_3\)\(^1\)). Attempts to suggest an appropriate structural model for subsequent refinement of the powder data proved to be not successful.

### Conclusion

The first examples of polynuclear Co(II) thiolato complexes have been successfully synthesized and structurally characterized namely \(^1\alpha\)[Co(SMes)\(_2\)] and \(^1\alpha\)[Co(SPh)\(_2\)NH\(_3\)]. Both complexes display strong antiferromagnetic coupling along the chains. In contrast [Co(SPh)\(_2\)(NH\(_3\))\(_2\)] consists of isolated distorted tetrahedral units which are stabilized in the crystal lattice by secondary S⋯H and Co⋯Co interactions giving rise to a weak antiferromagnetic coupling. The ammonia complexes [Co(SPh)\(_2\)NH\(_3\)] and \(^1\alpha\)[Co(SPh)\(_2\)NH\(_3\)] were obtained in almost quantitative yields by \textit{in situ} generation of NH\(_3\) in reactions of [Co(N(SiMe\(_3\))\(_2\)](thf) with 2 equiv. of HSPh upon addition of aliquots of CH\(_3\)OH. Microcrystalline products of formal composition ‘Co(SPh)\(_2\)’ can be obtained either from direct reactions of [Co(N(SiMe\(_3\))\(_2\)](thf) with 2 equiv. of HSPh in toluene at 105 °C or thermal cleavage of NH\(_3\) from \(^1\alpha\)[Co(SPh)\(_2\)NH\(_3\)]. However, attempts to solve the structure of them on the basis of the X-ray powder data were so far unsuccessful.

### Experimental section

#### Synthesis

Standard Schlenk techniques were employed throughout the syntheses using a double manifold vacuum line with high purity dry nitrogen (99.9994%) and a MBraun Glovebox with high purity dry argon (99.9990%). The solvent THF (tetrahydrofuran), diethyl ether and toluene were dried over sodium-benzophenone, and distilled under nitrogen. CH\(_3\)OH (H\(_2\)O < 0.001%) obtained from Aldrich was degassed, freshly distilled and stored under nitrogen. HSPh was purchased from Aldrich and distilled prior to use. [Co(N(SiMe\(_3\))\(_2\)](thf) was prepared according to ref. 51.

<table>
<thead>
<tr>
<th>1(^{\text{st}}) step</th>
<th>2(^{\text{nd}}) step</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Co(SPh)(_2)(NH(_3))(_2)</strong></td>
<td><strong>Co(SPh)(_2)(NH(_3))(_2)</strong></td>
</tr>
</tbody>
</table>

### Table 2: Temperatures of the 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) cleavage step taken from the TGA analysis of [Co(SPh)\(_2\)(NH\(_3\))\(_2\)] (3) and \(^1\alpha\)[Co(SPh)\(_2\)NH\(_3\)] (4) (Fig. 6)

<table>
<thead>
<tr>
<th>Region</th>
<th>Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>75–135</td>
</tr>
<tr>
<td>vac</td>
<td>35–105</td>
</tr>
</tbody>
</table>

### 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 2 and 3 were collected using graphite-monochromatised MoKα radiation (\(\lambda = 0.71073 \text{ Å}\)) on a STOE IPDS II.
Solid state UV-Vis spectra were measured as micron sized crystalline powders in mineral oil between quartz plates with a Labsphere integrating sphere.

Thermogravimetric analyses were run in Al₂O₃ crucibles on a thermobalance STA 409 from Netzsch in a dynamic helium gas flow (25 ml min⁻¹) and under vacuum conditions 1.5 × 10⁻⁶ mbar at a heating rate of 2 °C min⁻¹. The crucibles were filled (20-35 mg) inside an argon glove box, transferred in Schlenk tubes and mounted under a stream of argon to the balance. Caution should be taken with respect to the bad smelling volatile products formed in the TGA.

Zero–Field–Cooled (ZFC) temperature dependent susceptibilities were recorded for 2 in dc mode using a MPMS-III (Quantum Design) SQUID magnetometer over a temperature range from 2 to 300 K in a homogeneous 0.1 T external magnetic field. The magnetization curves were measured on the same instrument up to a dc field of 7 T. ZFC temperature dependent susceptibilities were recorded for 3 in RSO mode using a MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range from 5 to 300 K in a homogeneous 0.1 T external magnetic field. The magnetization curves were measured on the same instrument up to a dc field of 4.5 T.

Ac susceptibility measurements of 3 have been performed at 2 K using a MPMS-XL (Quantum Design) SQUID magnetometer with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. There is no indication for a relevant signal of the out-of-phase component of the ac susceptibility (χ″) even under applied dc fields up to 1000 Oe which indicates that under these conditions the spin lattice relaxation is faster than the timescale of the experiment.

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 samples were transferred in sealed Schlenk tubes from the glove box to the magnetometer and then rapidly transferred to the helium-purged sample space of the magnetometer. The data were corrected for the sample holder including the gelatine capsule and for diamagnetism using Pascal’s constants.58–60

Author contributions


Conflict of interest

The authors declare no financial interests.

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References