Redox Interconversion between Cobalt(III) Thiolate and Cobalt(II) Disulfide Compounds

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Supporting Information

ABSTRACT: The redox interconversion between Co(III) thiolate and Co(II) disulfide compounds has been investigated experimentally and computationally. Reactions of cobalt(II) salts with disulfide ligand L′SSL † (L′SSL † = di-2-(bis(2-pyridylmethyl)amino)-ethyl disulfide) result in the formation of either the high-spin cobalt(II) disulfide compound [CoII(L′SSL †)Cl4] or a low-spin, octahedral cobalt(III) thiolate compound, such as [CoIII(L′)(MeCN)2](BF4)2. Addition of thiocyanate anions to a solution containing the latter compound yielded crystals of [CoII(L′)(MeCN)2](NCS)2. The addition of chloride ions to a solution of [CoIII(L′)(MeCN)2](BF4)2 in acetonitrile results in conversion of the cobalt(III) thiolate compound to the cobalt(II) disulfide compound [CoII(L′SSL †)Cl4], as monitored with UV–vis spectroscopy; subsequent addition of AgBF4 regenerates the Co(III) compound. Computational studies show that exchange by a chloride anion of the coordinated acetonitrile molecule or thiocyanate anion in compounds [CoII(L′)(MeCN)2] and [CoII(L′)(NCS)2] induces a change in the character of the highest occupied molecular orbitals, showing a decrease of the contribution of the p orbital on sulfur and an increase of the d orbital on cobalt. As a comparison, the synthesis of iron compounds was undertaken. X-ray crystallography revealed that structure of the dinuclear iron(II) disulfide compound [FeII(2-L′SSL †)Cl4] is different from that of cobalt(II) compound [CoII(L′SSL †)Cl4]. In contrast to cobalt, reaction of ligand L′SSL † with [Fe(MeCN)3](BF4)2 did not yield the expected Fe(III) thiolate compound. This work is an unprecedented example of redox interconversion between a high-spin Co(II) disulfide compound and a low-spin Co(III) thiolate compound triggered by the nature of the anion.

INTRODUCTION

Sulfur-containing metalloenzymes are ubiquitous in biological systems and play fundamental roles in electron-transfer reactions including oxygen transport, nitrite reduction, and the synthesis of neurotransmitters.1–4 A small number of these metalloenzymes involve thiolate/disulfide interconversion, related to the uptake or release of the metal ions.5–7 For instance, copper delivery to the Cu4 site of cytochrome c oxidase (CcO) involves Sco proteins, and the potential operation principle has been suggested to involve thiolate/disulfide interconversion of two cysteine residues.8,9 Metallothionein Zn-MT-3 has been reported to exchange its Zn(II) ions with Cu(II) centers of amyloid-β peptide (CuAmy). During this exchange four Cu(II) ions are reduced to Cu(I) by four cysteine thiolate groups in MT-3 with the formation of two disulfide bonds.10,11 The essence of the thiolate to disulfide oxidation of cysteines is an electron that shuttles from the cysteine thiolate sulfur to the metal ion in a high oxidation state, after which a disulfide is formed and a geometry change takes place of the reduced metal center in the active site.

However, to the best of our knowledge, the exact mechanism is not well understood of this interconversion in biological systems.1 In the last decades, this phenomenon inspired coordination chemists to synthesize metal thiolate compounds and study their redox interconversion. Since the first publication of a mixed-valence (Cu II Cu I) thiolate compound,12,13 considerable efforts were put in the synthesis and characterization of Cu(II) thiolate compounds, and the investigation of their redox interconversion to the isomeric Cu(I) disulfide compounds.14–20 The chloride-dependent redox interconversion between Cu(II) thiolate and Cu(I) disulfide compounds was first reported by Itoh et al.,20 followed later by the group of Henkel.15 In recent years, our group further investigated the effect of temperature and solvents on the thiolate/disulfide redox interconversion of copper compounds.18 Up until now, several triggers have been reported to influence the copper thiolate/disulfide redox

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interconversion like the addition of halide ions or protons as well as changes in temperature, and the polarity of solvents. In addition, also ligand structure has a distinct influence on the redox interconversion (Scheme 1). As electron-transfer reactions also take place in metalloenzymes containing metal centers other than copper, all of this impressive work inspired us to study whether the thiolate/disulfide redox interconversion could occur for complexes of metal ions like cobalt or iron. Duboc et al. reported the electrochemical synthesis of a triplet-spin state \( S = 1 \) Co(III) thiolate compound and its redox interconversion to a Co(II) disulfide compound triggered by the removal of chloride ions. Herein, we report a low-spin \( S = 0 \) Co(III) thiolate compound, which was formed directly from a reaction of a cobalt(II) salt with ligand \( L^1S \). The effective magnetic moment of compound \( 1Co \) determined in dimethyl sulfoxide solution at 20 °C, revealing a \( \mu_{\text{eff}} \) of 6.53 \( \mu_B \). This value is in agreement with two (weakly interacting) high-spin Co(II) centers (a value of 6.93 \( \mu_B \) is expected for two isolated \( S = 3/2 \) cobalt(II) ions). ESI-MS spectra of purple compound \( 1Co \) dissolved in acetonitrile show a dominant peak \( (m/z) \) at 740.8 corresponding to the fragment \( [Co_{11}^2(L^1SSL^1)_2Cl_4]^+ \) (Figure S1). The \( ^1H \) NMR spectrum of the compound in dimethyl sulfoxide-d<sub>6</sub> shows broad resonances with shifts down to around 75 ppm (Figure S2), indicative of a paramagnetic compound. The effective magnetic moment of compound \( 1Co \) was estimated using Evans’ method in dimethyl sulfoxide solution at 20 °C, revealing a \( \mu_{\text{eff}} \) of 6.53 \( \mu_B \). This value is in agreement with two (weakly interacting) high-spin Co(II) centers (a value of 6.93 \( \mu_B \) is expected for two isolated \( S = 3/2 \) cobalt(II) ions). ESI-MS spectra of compound \( 1Fe \) dissolved in methanol present a peak \( (m/z) \) at 349.1 corresponding to the dicaticionic species \( [Fe_{11}^2(L^1SSL^1)_2Cl_2]^2+ \) (Figure S3). The effective magnetic moment of \( 1Fe \) determined in methanol solution at

Scheme 2. Reactions of Ligand \( L^1SSL^1 \) with Different Cobalt(II) and Iron(II) Salts

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Structures of 1Co, 3, Cationic Part of 2, and Theoretical Intermediates [CoIII(L1S)(Cl)(NCS)] (3a) and [CoIII(L1S)Cl2] (4) (MeCN)2+ (Figure S4). The 1H NMR spectrum of brown compound being in a low-spin state (Figure S5). Similarly, the diamagnetic region, consistent with the Co(III) center in this spectra of 2S expected for two isolated [CoIII(L1S)(NCS)]+ (Figure S8).

The Raman spectrum of compound dissolved in acetonitrile show a dominant peak (m/z) at 199.8 for the dicationic species [Co III(L1S)-\(\text{Cl}\)]2+. A projection of the structure of the minor component is shown in Figure 1Co 3.

| bond          | XRD   | DFT   | 2   | XRD | DFT | 3   | DFT | 3a   | DFT | 4   | DFT |
|---------------|-------|-------|-----|-----|-----|-----|-----|------|-----|-----|-----|
| Co1–N1        | 2.311(2) | 2.392 | 1.942 | 1.9558(15) | 1.947 | 1.947 | 1.950 |
| Co1–N11       | 2.064(2) | 2.061 | 1.932 | 1.9235(14) | 1.922 | 1.916 | 1.918 |
| Co1–N21       | 2.084(2) | 2.057 | 1.932 | 1.9332(15) | 1.924 | 1.917 | 1.923 |
| Co1–S1        | 5.9614(8) | 6.004 | 2.206 | 2.2355(5) | 2.211 | 2.208 | 2.202 |
| Co1–X1        | 2.3240(7) | 2.330 | 1.857 | 1.9011(16) | 1.855 | 1.851 | 2.261 |
| Co1–X2        | 2.2716(7) | 2.291 | 1.951 | 1.9934(15) | 1.934 | 2.356 | 2.360 |

See the Discussion section below. X1 = Cl1A, X2 = Cl1B for 1Co; X1 = N41, X2 = N51 for 2 and 3; X1 = N41, X2 = Cl1 for 3a; X1 = Cl1A, X2 = Cl1B for 4. All calculations were performed in the solvent.

| bond          | XRD   | DFT   | 1Co | XRD | DFT | 3   | DFT | 3a   | DFT |
|---------------|-------|-------|-----|-----|-----|-----|-----|------|-----|
| Cl1A–Co1–Cl1B| 100.76(3) | 84.93(5) | S1–Co1–N41 | N51–Co1–N11 | 88.17(6) |
| Cl1A–Co1–N1  | 169.92(6) | 178.43(5) | S1–Co1–N51 | N51–Co1–N21 | 91.59(6) |
| Cl1A–Co1–N11 | 102.96(6) | 90.38(4) | S1–Co1–N1 | N1–Co1–N11 | 84.32(6) |
| Cl1A–Co1–N21 | 97.12(6) | 92.10(4) | S1–Co1–N11 | N1–Co1–N21 | 84.77(6) |
| Cl1B–Co1–N1  | 89.29(5) | 88.44(4) | S1–Co1–N21 | N11–Co1–N21 | 169.09(6) |
| Cl1B–Co1–N11 | 101.81(7) | 89.50(6) | N41–Co1–N51 | 85.70(6) |
| Cl1B–Co1–N21 | 133.71(7) | 179.31(7) | N41–Co1–N1 | 95.65(6) |
| N1–Co1–N11   | 75.42(8) | 95.26(7) | N41–Co1–N21 | 91.18(6) |

20 °C is in agreement with the presence of two high-spin Fe(II) centers in this compound (\(\mu_{\text{eff}} = 7.67\) \(\mu_B\); 8.94 \(\mu_B\) is expected for two isolated S = 2 iron(II) centers). ESI-MS spectra of 2 dissolved in acetonitrile show a dominant peak (m/z) at 199.8 for the dicationic species [CoIII(L’S)-(MeCN)2]+ (Figure S4). The 1H NMR spectrum of brown compound 2 in acetonitrile-\(d_3\) shows resonances in the diamagnetic region, consistent with the Co(III) center in this compound being in a low-spin state (Figure S5). Similarly, the 1H NMR spectrum of compound 3 in acetonitrile-\(d_3\) shows resonances in the diamagnetic region (Figure S6). ESI-MS spectra of brown compound 3 dissolved in acetonitrile show a dominant peak (m/z) at 375.3 corresponding to the fragment [CoIII(L’S)(NCS)]+ (Figure S8).

Confocal Raman spectroscopy using a 476 nm laser was employed to study the disulfide bond in compounds 1Co, 1Fe, 2, and disulfide ligand L’S. The obtained spectra are provided in Figures S9 and S10. The Raman spectrum of ligand L’S shows clear bands at 522 and 550 cm\(^{-1}\), which are attributed to the S–S bond vibration.28 These bands are retained in the Raman spectra of 1Co and 1Fe and as expected are not present in the spectrum of 2.

Attempts were undertaken to investigate the electrochemical properties of the cobalt compounds 1Co, 2, and 3 using cyclic voltammetry in acetonitrile solutions with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte (Figures S11–S14). Unfortunately, the compounds show multiple, poorly resolved redox waves, making it difficult to assign the various processes occurring in the solutions.

**Description of the Crystal Structures.** Single crystals of 1Co and 3 suitable for X-ray structure determination were obtained by vapor diffusion of diethyl ether and disisopropyl ether into acetonitrile solutions containing the compounds. Single crystals of 1Fe were grown by vapor diffusion of diethyl
ether into a methanolic solution of the compound. Unfortunately, single crystals of 2 could not be obtained, but after 8 weeks from an acetonitrile solution of compound 2 kept in air, crystals were obtained of the cobalt(III) sulfinate compound \( [\text{Co}^{3+}(L^1\text{SSL}_1)_{2}\text{Cl}_2] \). The crystal structure of 2 has been determined, and a projection of the structure is provided in Figure S15. Crystallographic and refinement data of the structures are provided in Table S1. A projection of the dinuclear structure of 1 is shown in Figure 1a; relevant bond distances and angles are given in Tables 1 and 2. Compound 1 crystallizes in the centrosymmetric space group \( P4_1 \), with one dinuclear complex and one molecule of diethyl ether cocrystallized in the asymmetric unit. The two Co(II) ions are bound to three nitrogen atoms of ligand and two chloride ions in distorted trigonal-bipyramidal geometries with the tertiary amine nitrogen and one of the chloride ions in the apical positions. The calculated \( \tau \) values of the S-geometry are 0.60 and 0.72 for Co1 and Co2, respectively. The \( \tau \) value is determined from the two largest bond angles and is between 0 and 1, where 0 presents a perfect square pyramid. The Fe1—S1 bond length is 2.6925(8) Å, which is much shorter than the Fe2—S2 distance of 3.231(1) Å but longer than the Fe—S bond distances in some reported thioether-Fe(II) compounds (ranging from 2.200 to 2.285 Å). The Fe—N bond distances range from 2.135(2) to 2.270(3) Å for both FeII ions, in agreement with a high-spin state \( (S = 2) \) of both iron(II) centers. One of the two lattice methanol molecules is hydrogen bound to one of the coordinated chloride ions. The crystal packing of this structure shows no stacking interactions.

A projection of the mononuclear structure of 3 is shown in Figure 1b; relevant bond distances and angles are presented in Tables 1 and 2. Compound 3 crystallizes in the orthorhombic space group \( \text{Pbcn} \). The Co(III) ion is coordinated by three nitrogen donor atoms, one thiolate sulfur donor of the tetradentate ligand, and two nitrogen atoms of the thiocyanate anions in an octahedral geometry. The three nitrogen atoms of the tetradentate ligand are bound in a meridional fashion. The Co—S bond length is 2.2353(5) Å; the bond distances between the cobalt center and the five nitrogen donors range from 1.9011(16) to 1.9934(15) Å. The thioionate donor atom N51 is at a significantly larger distance than N41, indicative of a larger trans influence of the thiolate sulfur donor. When finalizing the refinement, a residual electron density peak of 2.47 \( \epsilon \) Å was found at ca. 1.46 Å from S1. This peak is thought to arise from an oxygen atom, and its presence may result from the partial oxidation of S1 occurring during the crystallization process. Single crystals were obtained only after 3 weeks, during which time dioxygen must have diffused into the flask. Such a mono-oxygenated product likely is an intermediate in the oxidation of Co(III)-thiolate compound 2 to dioxygenated product 3 containing a sulfinate ligand (Figure S15). A projection of the compound \( [\text{Co}^{\text{III}}(L^1\text{SO})-(\text{NCS})_{2}] \) (which is present with an occupancy factor of 0.178(5)) is given in Figure S16. Hydrogen-bond or stacking interactions are not present in this compound.

UV—vis Spectroscopy and Reactivity. UV—vis spectra of purple 1 dissolved in acetonitrile show four absorption bands (Figure 3a, black line). The absorption band at 261 nm \( (\epsilon = 4.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \) is assigned to the \( \pi \rightarrow \pi^* \) transition of the pyridyl groups, whereas the three low-intensity bands at 524 \( (\epsilon = 0.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \), 570 \( (\epsilon = 0.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \), and 640 \( (\epsilon = 0.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \) nm likely correspond to \d→\p transitions that are partially spin-allowed by \p orbital mixing, combined with a \Cl→\Co charge-transfer transition (LMCT). Absorption bands for the solid sample appear at 216, 253, 508, 595, and 797 nm (Figure S17). UV—vis spectra of brown compound 2 dissolved in acetonitrile reveal three absorption bands (Figure 3a, blue line). The band at 262 nm \( (\epsilon = 8.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \) is ascribed to the \( \pi \rightarrow \pi^* \) transition of the pyridyl groups, whereas the two absorption bands at 287 nm \( (\epsilon = 6.9 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \) and 441 nm \( (\epsilon = 0.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \) are tentatively ascribed to ligand-to-metal charge-transfer transitions (LMCT). UV—vis spectra of compound 3 dissolved in acetonitrile present four absorption bands (Figure S18). The absorption bands at 238 and 279 nm are assigned to the \( \pi \rightarrow \pi^* \) transitions of the pyridyl groups, whereas the two absorption bands at 325 and 515 nm likely correspond to LMCT transitions.3,34 The UV—vis spectrum of 3 in the solid state presents four absorption bands at 268, 336, 514, and 667 nm (Figure S19). UV—vis spectra of 1 dissolved in methanol show one strong absorption band at 256 nm \( (\epsilon = 8.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}) \) corresponding to the \( \pi \rightarrow \pi^* \) transition of pyridyl...
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The reaction of 1Fe with AgBF4 in methanol solution was investigated as well, monitored by UV–vis spectroscopy under anaerobic conditions; the results are shown in Figure S23. With the addition of AgBF4, the absorption at 313 nm decreases and fully disappears after the addition of 2 equiv of chloride ion per cobalt center, while three new absorption bands appear at 524, 570, and 640 nm. The intensity of the absorption band at 441 nm gradually decreases until this band completely disappears after the addition of 2 equiv of chloride ion per cobalt center, while three new absorption bands appear at 524, 570, and 640 nm. The final spectrum equals the absorption spectrum of Co(II) compound 1Co.

To investigate the potential redox interconversion between the cobalt(II) disulfide compound and the cobalt(II) thiolate compound (Scheme 3), tetraethylammonium chloride was titrated into the acetonitrile solution containing Co(III) compound and the cobalt(III) thiolate

**Table 3. Selected Bond Distances (Å) and Angles (deg) in the Crystal Structure of [FeII(LSSL)L]Cl4 (1Fe) as well as from DFT-Optimized Structures of the Compound with Different Spin States (S = 2 and 0 for Both Iron Centers)**

| distances | XRD | DFT (S = 2, 2) | DFT (S = 0, 0) | angles | XRD | angles | XRD |
|-----------|-----|---------------|---------------|--------|-----|--------|-----|
| Fe1–N1    | 2.270(2) | 2.355 | 1.970         | ClIA–Fe1–ClIB | 100.40(3) | ClIA–Fe1–ClIB | 101.45(3) |
| Fe1–N11   | 2.198(2) | 2.129 | 1.942         | ClIA–Fe1–N1   | 93.12(6)  | ClIA–Fe1–N1   | 65.76(6)  |
| Fe1–N21   | 2.187(2) | 2.131 | 1.969         | ClIA–Fe1–N11  | 93.08(6)  | ClIA–Fe1–N31  | 103.69(7) |
| Fe1–S1    | 2.6925(8) | 3.506 | 2.105         | ClIA–Fe1–N21  | 93.56(6)  | ClIA–Fe2–Cl2B | 102.55(6) |
| Fe1–ClIA  | 2.4228(8) | 2.415 | 2.413         | ClIB–Fe1–N1   | 166.05(6) | ClIB–Fe2–N2   | 92.79(6)  |
| Fe1–ClIB  | 2.3419(7) | 2.297 | 2.323         | ClIB–Fe1–N11  | 108.65(6) | ClIB–Fe2–N31  | 94.52(6)  |
| S1–S2     | 2.0570(9) | 2.030 | 2.979         | ClIB–Fe1–N21  | 99.94(6)  | ClIB–Fe2–N41  | 93.26(6)  |
| Fe2–N2    | 2.253(2) | 2.355 | 1.969         | N1–Fe1–N11    | 73.77(8)  | N2–Fe2–N31    | 75.26(8)  |
| Fe2–N31   | 2.141(2) | 2.129 | 1.943         | N1–Fe1–N21    | 75.57(8)  | N2–Fe2–N41    | 75.98(8)  |
| Fe2–N41   | 2.135(2) | 2.132 | 1.968         | N11–Fe1–N21   | 148.92(8) | N31–Fe2–N41   | 150.51(9) |
| Fe2–S2    | 3.321(1) | 3.509 | 2.106         | ClIA–Fe1–S1   | 170.91(3) | ClIA–Fe1–S1   | 86.37(3)  |
| Fe2–Cl2A  | 2.3035(8) | 2.293 | 2.324         | ClIB–Fe1–S1   | 86.37(3)  | ClIB–Fe1–S1   | 86.37(3)  |
| Fe2–Cl2B  | 2.4241(8) | 2.416 | 2.414         | ClIB–Fe1–N1   | 79.83(6)  | ClIB–Fe1–N1   | 79.20(6)  |
| Fe1–Fe2   | 6.0567(6) | 7.150 | 6.433         | ClIA–Fe1–N11  | 79.83(6)  | ClIA–Fe1–N11  | 79.20(6)  |

**Scheme 3. Redox Interconversion Reaction of Co(II) Compound 1Co and Co(III) Compound 2 with the Addition or Removal of Chloride Anions**

![Scheme 3](image-url)

Figure 3. (a) UV–vis spectra of 1Co (black) and 2 (blue). UV–vis spectra were recorded using solutions 1 mM in [Co] with a transmission dip probe path length of 1.8 mm. The inset shows the UV–vis spectra of compounds recorded of solutions 2 mM in [Co]. (b) UV–vis spectra recorded upon addition of Et4NCl to a solution of the compound [CoIII(L1S)(MeCN)2](BF4)2 (1Fe) and the cobalt(III) thiolate

The reactivity of 1Fe with AgBF4 in methanol solution was investigated as well, monitored by UV–vis spectroscopy under anaerobic conditions; the results are shown in Figure S23. With the addition of AgBF4 the absorption at 313 nm decreases and fully disappears after addition of 2 equiv of AgBF4, while the absorption band at 390 nm shifts to 368 nm. ESI–MS spectra of the final reaction mixture show the presence of a large number of species, including a peak at m/z 734.8 for [Fe2(L1SSL1)Cl4]2+, indicating that the reaction does not simply yield the anticipated Fe(III) thiolate compound. As described above, the direct reaction of L1SSL1 with Fe-

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(MeCN)₆][BF₄]₂ yielded a tetracovalent Fe(II) compound of the disulfide ligand with bridging fluoride ions.²⁵

**Computational Characterization.** To explore the electronic structures of 1Co, 1Fe, 2, and 3 geometry optimizations were performed for all the compounds starting from the coordinates of the crystal structures. Quartet-spin (S = 3/2) and doublet-spin states (S = 1/2) of the Co(II) centers were considered for 1Co. High-spin (S = 2) and low-spin (S = 0) states of iron(II) centers were taken into account for 1Fe and for the Co(III) center in the cationic parts of 2 and 3. The obtained results are presented in Tables 1, 3, and S3–S6 and Figures S24–S27. Comparison of the experimental and computed structures shows that the geometry of the cobalt centers in 1Co with quartet-spin states (two S = 3/2 ions) is more consistent with the crystallographic data. Furthermore, 1Co with quartet-spin states also has the lowest Gibbs free energy in the solvent, namely, 13 kcal/mol lower than for doublet-spin states (two S = 1/2 ions). The optimized (solvation) structure for 1Fe has the lowest Gibbs free energy with high-spin states (1Fe(2,2,sol,fixation), S = 2 FeII centers), which is 31 and 10 kcal/mol lower than for the compound with two low-spin iron(II) centers (1Fe(0,0,sol,fixation), S = 0) and the compound with mixed-spin states (1Fe(0,2,sol,fixation), S = 0 for one iron(II) center and S = 2 for the other iron(II) center). The optimized geometry of 1Fe with two high-spin iron(II) centers is roughly similar to the crystallographic data; however, both Fe(II) ions are in a five-coordinate configuration, with Fe–S bond distances of 3.509 and 3.506 Å. For optimized compound 1Fe(0,0,sol,fixation) in the low-spin state (S = 0 for both FeII ions), the S–S bond length is 2.979 Å, which is much longer than in the crystal structure of 1Fe, whereas the Fe–S bond distances are much shorter than those in the crystal structure. Therefore, as the computations did not reproduce the Fe–S distances, the geometry was optimized while keeping the distance between Fe2 and S2 fixed. The structure in the high-spin state (1Fe(0,2,sol,fixation), S = 2 for both FeII centers) still has the lowest Gibbs free energy and the acquired structure is consistent with the crystallographic data. Furthermore, the Gibbs free energy of 1Fe(0,2,sol,fixation) is nearly the same as that of 1Fe(2,2,sol,fixation). Apparently, the interaction between Fe2 and S2 is weak, and does not significantly affect the stability of the compound.

Both Co(III) compounds 2 and 3 have the lowest Gibbs free energy in the solvent with a low-spin Co(III) center, namely, 25 and 23 kcal/mol lower than those with a high-spin Co(III) center. The selected bond lengths in the optimized structures of compounds 2 and 3 with the lowest energy are provided in Table 1. The Co–S bond lengths in the optimized structures of 2 and 3 are 2.206 and 2.211 Å, respectively, comparable to the Co–S bond length of 2.2355(5) Å found in the crystal structure of 3. The calculations conducted in the gas phase show similar results with those in the solvent.

The addition of chloride anions to a solution containing cobalt(III)–thiolate compound 2 results in formation of cobalt(II)–disulfide compound 1Co. To investigate this process computationally, the acetonitrile molecules in 2 and the thiocyanate anions in 3 were displaced by chloride ions one by one. The geometries of the theoretical intermediates [CoIII(L1S)(Cl)(MeCN)]⁺ (2a), [CoIII(L1S)(Cl)(NCS)]⁻ (3a), and [CoIII(L1S)Cl₂]⁻ (4) were optimized and their highest occupied molecular orbitals (HOMOs) were analyzed and compared with those of 2 and 3 (Scheme 4). The Gibbs free energies of the two isomeric intermediates (with the chloride ion placed in the position trans to the amine nitrogen donor) are slightly higher than those of intermediates 2a and 3a (1 and 2 kcal/mol, respectively). This small difference may be caused by the trans influence of the thiolate donor, but this was not investigated in detail. Interestingly, the HOMOs of compounds 3, 3a, and 4 consist mainly of p orbitals on sulfur and d orbitals on cobalt with the same total percentage (89% for all of the compounds). It was found that the HOMO gradually consists more of the d orbital on cobalt and less of the p orbital on sulfur, as the number of chloride anions increases and the number of coordinated thiocyanate anions decreases. Similarly, displacement of the acetonitrile molecules in 2 by chloride anions effect the same change on HOMOs (Figure S28).

It has been shown that depending on the experimental conditions dinuclear Cu(II) thiolate compounds [CuII₂(L1S)₂]²⁺ with bridging thiolate donor atoms may be generated when LSSL⁺ or similar disulfide ligands react with Cu(I) salts.¹⁴,¹⁸–²⁰,³⁵ However, mononuclear rather than dinuclear Co(III) thiolate compounds are formed in our study. In order to understand this difference in reactivity, both the hypothetical dinuclear compounds [CoII₃₁(L1S)₂]₄⁺ (5) and [Co₃II₁(L1S)₂(MeCN)₂]₄⁺ (6) with different spin states (S = 0, 1, or 2 for both Co(III) ions) were investigated computationally. As a comparison, the hypothetical mononuclear copper compound [CuII₁(L1S)(MeCN)]⁺ (7) and the actual dinuclear copper compound [CuII₃₁(L1S)₂]²⁺ (8) were optimized as well. The octahedral mononuclear copper(II) compound [CuII₁(L1S)(MeCN)]⁺ and the dinuclear copper(II) compound [CuII₃₁(L1S)₂(MeCN)₂]²⁺ have also been computed but are not discussed here as acetonitrile moved away from the Cu(II) center during the geometry optimization. The obtained results show that 5 has the lowest Gibbs free energy in the solvent with two low-spin cobalt(III) centers (two S = 0 ions); two high-spin states (two S = 2 ions) or two triplet-spin states (two S = 1 ions) result in energies that are 40 and 3 kcal/mol higher. The energies of the antiferromagnetically coupled (S = 0) species were considered for the dinuclear copper(II) (two S = 1/2 ions) and cobalt(III) (two S = 2 ions in 5 or 6, as well as two S = 1 ions) in 5 compounds (see the “Computational Characterization” section). Antiferromagnetic coupling (S = 0) is not beneficial to stabilize 5, for S = 2 or 1 states result in Gibbs free energies being 29 and 24 kcal/mol higher than that of the uncoupled systems. The distance between cobalt(III) ions in optimized geometries of 5 with two high-spin, two triplet-
spin, and two low-spin states are 3.66 S, 3.276, and 3.097 Å, respectively (Figure S29). Similarly, 6 with two $S = 0$ Co$^{III}$ centers has the lowest Gibbs free energy in solvent. Optimization of 6 with two high-spin Co$^{III}$ centers results in dissociation of the dinuclear structure (see Figure S30). Our computational study reveals that dimerization of mononuclear compound 2 to dinuclear compound 5 results in a slight decrease of the Gibbs free energy by 6 kcal/mol; however, formation of 6 leads to an increase of the Gibbs free energy by 19 kcal/mol (Figure 4). The formation of dinuclear copper compound 8 from mononuclear compound 7 leads to stabilization, lowering the Gibbs free energy by 33 kcal/mol (Figure 4, Tables S6 and S7).

![Figure 4. Optimized structures (at the ZORA-OPBE/TZ2P level of theory) of the compounds 2 and 5-8, and the change in Gibbs free energy (in kcal/mol) upon formation of the dinuclear metal compounds in acetonitrile. The acetonitrile molecules liberated in the reactions were taken into account but are omitted from the drawings for clarity.](image)

### DISCUSSION

The redox interconversion between metal thiolate and disulfide compounds has received considerable attention in the past decade. In this manuscript, we report the synthesis of four new cobalt and iron compounds $\left[\text{Co}^{III}\left(L^5\text{SSL}^1\right)\text{Cl}_4\right]$ (1$_{\text{Co}}$), $\left[\text{Fe}^{III}\left(L^5\text{SSL}^1\right)\text{Cl}_4\right]$ (1$_{\text{Fe}}$), $\left[\text{Co}^{III}\left(L^5\text{S}\right)(\text{MeCN})_2\right]\left(\text{BF}_4\right)_2$ (2), and $\left[\text{Co}^{III}\left(L^5\text{S}\right)(\text{NCS})_2\right]$ (3) from reactions of the disulfide ligand L$^5\text{SSL}^1$ with different Co(II) and Fe(II) salts. Whereas the Co(II) disulfide compound is air-stable, the Co(III) thiolate compounds are slightly air-sensitive. The crystal structure of 3 showed the presence (with low occupancy factor) of a complex containing a mono-oxygenated sulfenate ligand, and crystallization of 2 in air after 8 weeks resulted in crystals of oxidized compound 2$_{\text{ox}}$ comprising a dioxygenated sulfinate ligand. ESI-MS spectra of solutions containing 3 taken after 2 h in air did not show any oxidation products, confirming that this oxidation process is very slow and thus that the effect on the redox studies is negligible. Using UV-vis spectroscopy, we showed that the addition of chloride anions to cobalt(III) compound 2 results in a redox interconversion reaction yielding cobalt(II) disulfide compound 1$_{\text{Co}}$; whereas removal of the chloride anions from 1$_{\text{Co}}$ regenerates compound 2. In 2001, the group of Itoh reported the synthesis of a Cu(II) thiolate compound from a similar disulfide ligand. 20 The addition of chloride anions to this Cu(II) thiolate compound led to the redox interconversion reaction to the corresponding Cu(I) disulfide compound, whereas removal of the chloride anions resulted in the regeneration of the Cu(II) thiolate compound. In contrast, the group of Henkel reported a Cu(I) disulfide compound that upon addition of chloride ions resulted in the formation of a Cu(II) thiolate compound. 25 Similarly, the group of Duboc recently reported a Co(III) thiolate compound that upon removal of chloride ions resulted in a Co(II) disulfide complex. 24 Clearly, the formation of metal thiolate or disulfide compounds cannot be predicted based on the anions only.

For comparison the synthesis of the related iron(II) compounds has been investigated. Reaction of ligand L$^1\text{SSL}^1$ with FeCl$_2$·4H$_2$O results in the formation of the iron(II) disulfide compound $\left[\text{Fe}^{II}\left(L^1\text{SSL}^1\right)\text{Cl}_4\right]$ (1$_{\text{Fe}}$), showing a structure that is slightly different from that of $\left[\text{Co}^{II}\left(L^1\text{SSL}^1\right)\text{Cl}_4\right]$ (1$_{\text{Co}}$). However, instead of the expected Fe(III)-thiolate compound similar to 2, reaction of 1$_{\text{Fe}}$ with AgBF$_4$ did not give conclusive results, and reaction of ligand L$^1\text{SSL}^1$ with $\left[\text{Fe(MeCN)}_6\right]\left(\text{BF}_4\right)_2$ resulted in the formation of a fluoride-bridged tetrinuclear iron(II) compound. 23 Thus, the redox interconversion in the iron compound appears to be more difficult despite the fact that one of the thioether sulfurs in 1$_{\text{Fe}}$ is coordinating.

In order to understand the reactivity observed for our compounds, DFT calculations were employed to further explore the electronic structure of 1$_{\text{Co}}$, 1$_{\text{Fe}}$, 3, and the cationic part of 2. The obtained results show that 1$_{\text{Co}}$ has the lowest energy with two high-spin Co(II) centers (two $S = 3/2$ ions), consistent with the crystal structure and the observed effective magnetic moment, whereas low-spin Co(III) centers ($S = 0$) yield the lowest energy structures in compounds 2 and 3, in agreement with the crystal data and the diamagnetic NMR spectra. Similarly, 1$_{\text{Fe}}$ has the lowest energy with both iron centers in high-spin states ($S = 2$), in line with the crystal structure and the magnetic susceptibility in solution.

Combination of experimental results and DFT calculations confirm the formation of a low-spin ($S = 0$) mononuclear Co(III)-thiolate compound in contrast to the dinuclear dithiolate-bridged structure reported for Cu(II) and the dinuclear Co(II) compounds with quartet-spin state (two $S = 3/2$ ions) reported by the group of Duboc. 19,24 The antiferromagnetic interaction between the two Cu(II) ions or the strong antiferromagnetic coupling between two $S = 3/2$ cobalt(II) ions reported by the group of Duboc are likely beneficial for the stabilization of the dinuclear compounds. Our computations show that antiferromagnetic coupling does not stabilize dinuclear cobalt(III) thiolate compounds 5 and 6. Formation of dinuclear cobalt(III) compound 5 from mononuclear 2 seemingly results in a slightly lower Gibbs free energy, which suggests that in solution 2 and 5 may be in equilibrium. However, the compound that crystallizes from the solution is mononuclear 2, and the question remains why the cobalt(III) ions in our ligand L$^5\text{S}^-$ prefer a low-spin configuration in contrast to the intermediate spin occurring in the Duboc system.

The character of the HOMOs of compounds 2 and 3 and theoretical intermediates 2a, 3a, and 4 was investigated to explore the potential dependence of the electron distribution in the HOMO on the presence of different anions, as well as the potential transfer of electron density between cobalt and
sulfur. The HOMO of these compounds has mainly character of p orbitals on sulfur and d orbitals on cobalt, and a small shift of the character of the HOMOs from p orbitals on sulfur to d orbitals on cobalt is found upon substitution of the thiocyanate by chloride anions. Our computational investigation on the potential shift of electron density from sulfur to cobalt upon coordination of chloride anions were not conclusive to help understand the experimental finding of the formation of a Co(II) disulfide compound upon addition of chloride ions.

**SUMMARY AND CONCLUSIONS**

In this manuscript, we report the synthesis of low-spin mononuclear Co(III) thiolate compounds and high-spin dinuclear Co(II) and Fe(II) disulfide compounds from a disulfide ligand \( \text{L}^1 \text{SSL}^1 \) in reaction with Co(II) and Fe(II) salts. It is shown that the redox interconversion of this Co(III) thiolate and the corresponding Co(II) disulfide compound is triggered by the addition or removal of chloride ions. DFT calculations show that the HOMO consists gradually more of the d orbital on cobalt and less of the p orbital on sulfur when the thiocyanate molecules in the compound \([\text{Co}^{\text{III}}(\text{L}^1\text{SSL}^1)-(\text{NCS})_2]\) are substituted with chloride ions. This is the first example of a redox interconversion reaction between low-spin Co(III) thiolate and high-spin Co(II) disulfide compounds.

Despite the new information that is gained including our computational studies, still more research needs to be done to predict accurately the conditions that trigger the redox interconversion reactions for metal thiolate and disulfide compounds.

**EXPERIMENTAL SECTION**

**General Procedures.** All the reagents were purchased from commercial sources and used as received unless noted otherwise. Dry acetonitrile and diethyl ether were obtained from a solvent dispenser (PureSolV 400), and methanol was acquired from commercial vendors and stored on 3 Å molecular sieves. The synthesis of metal compounds was carried out using standard Schlenk-line techniques under a nitrogen atmosphere. \(^1\)H NMR spectra were recorded on a Bruker 300 DPX spectrometer at room temperature. Mass spectra were recorded on a Finnigan Aqua mass spectrometer with electrospray ionization (ESI). IR spectra were acquired on a PerkinElmer UATR spectrometer equipped with a single reflection diamond (scan range 400–4000 cm\(^{-1}\); resolution 4 cm\(^{-1}\)). UV–vis spectra were collected using a transmission dip probe with variable path lengths and reflection probe on an Avantes Avaspec-2048 spectrometer with Avalight-DH-S-BAL light source. A WITEC alpha300R-Confocal Raman Imaging with the laser wavelength of 476 nm was used to record the Raman spectra, and all of the measurements were carried out under ambient conditions at room temperature. Elemental analyses were performed by the Microanalytical Laboratory Kolbe in Germany. Cyclic voltammetry (CV) was performed on an Autolab PGStat10 potentiostat controlled by GPES4 software. A three-electrode system was used including an Ag/AgCl double junction reference electrode, a glassy carbon working electrode (3 mm diameter), and a Pt wire counter electrode in a solution containing 0.1 M NButPF\(_6\). In these conditions the Fe/Fc couple was found to be located at +0.428 V with a peak-to-peak separation of 91 mV in acetonitrile. Potentials are given relative to the Ag/AgCl electrode.

**Single Crystal X-ray Crystallography.** All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) under the program CrysAlisPro (version 1.171.36.32 Agilent Technologies, 2013) was used for \(I_{\text{Cu}}\), \(2\omega\), and \(I_{\text{K}}\;\text{C}^2\) version CrysAlisPro 1.171.39.29c, Rigaku OD, 2017 was used for compound 3). The same program was used to refine the cell dimensions and for data reduction. The structures were solved with the program SHELXS-2013 or SHELXS-2014/7 and were refined on \(F^2\) with SHELXL-2013 or SHELXS-2014. Analytical numeric absorption correction based on a multifaceted crystal model or numerical absorption correction based on Gaussian integration over a multifaceted crystal model were applied using CrysAlisPro. The temperature of the data collection was controlled using the system Csys/Csys (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 23, AFIX 43, or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 \(U_{eq}\) of the attached C atoms. The H atoms attached to O1S and O2S (lattice methanol solvent molecules) for \(I_{\text{Cu}}\) were found from difference Fourier maps, and their coordinates were refined freely. The structures of \(I_{\text{Cu}}\), \(2\omega\), \(I_{\text{K}}\;\text{C}^2\), and 3 are mostly ordered.

For \(I_{\text{Cu}}\), the absolute configuration was established by anomalous-dispersion effects in diffraction measurements on the crystal, and the Flack and Hooft parameters refine to 0.006(5) and 0.010(6), respectively. While finalizing the refinement of 3, one residual electron density peak of 2.47 eÅ\(^{-3}\) was found at ca. 1.46 Å from S1. This peak is thought to be an oxygen atom, and its presence may result from the partial oxidation of S1 occurring during the crystallization process. Its occupancy factor was set to refine freely, and its final value is 0.178(5). Another peak of 0.42 eÅ\(^{-3}\) was found at ca. 1.12 Å from S1. The nature of this peak is not entirely clear.

**Density Functional Theory (DFT) Calculations.** All calculations were performed with the Amsterdam Density Functional (ADF) program version r479531,37,38 using relativistic DFT at ZORA OPBE/TZ2P for geometry optimization and energies.39 Solvation in acetonitrile was simulated using the conductor-like screening model (COSMO).40–42 All stationary points in the gas phase and in the condensed phase were verified to be minima on the potential energy surface (PES) through vibrational analysis. The energies of the singlet state of the Cu\(^{\text{II}}/\text{Co}^{\text{III}}\) μ-thiolate complexes \((E^1)\) have been obtained from the unrestricted broken-symmetry singlet energies \((E^0)\) and the energy of the triplet \((E^0)\) with the approximate projection method of Noodleman: \(E^0 = 2E^0 + E^1 + 446\).43 The Gibbs free energies \((\Delta G = \Delta H - T\Delta S)\) were evaluated with the following procedure. Enthalpies at 298.15 K and 1 atm \((\Delta H_{298})\) were calculated from electronic bond energies \((\Delta E)\) in the solvent and vibrational frequencies using standard thermochemistry relations for an ideal gas, according to

\[
\Delta H_{298} = \Delta E + \Delta E_{\text{trans},298} + \Delta E_{\text{rot},298} + \Delta E_{\text{vib},298} + \Delta (\mu_{\text{E}},298) + \Delta (\mu_{\text{V}})_{298}
\]

(1)

Here, \(\Delta E_{\text{trans},298}\), \(\Delta E_{\text{rot},298}\), and \(\Delta E_{\text{vib},298}\) are the differences between the two complexes in translational, rotational, and zero-point vibrational energy, respectively; \(\Delta (\mu_{\text{E}},298)\) is the change in the vibrational energy resistance, as one goes from 0 to 298.15 K. The vibrational energy corrections are based on our frequency calculations in the gas phase. The molar work term \(\Delta (\mu_{\text{E}})\) is \(\Delta nRT\) with \(n = 0\). Thermal corrections for the electronic energy are neglected. The entropy \(\Delta S\) was also obtained from the gas phase calculations. Most systems were optimized in C\(_3\) symmetry. CH\(_2\)CN was optimized with C\(_3\) symmetry.

**Synthesis of the Compounds.** \([\text{Co}^{\text{II}}(\text{L}^1\text{SSL}^1)L]^+ (1)\). Ligand \(L^1\text{SSL}^1\) (107.0 mg 0.207 mmol) was dissolved in 3 mL of dry acetonitrile, and separately CoCl\(_2\)-6H\(_2\)O (98.5 mg 0.214 mmol) was dissolved in 3 mL of dry acetonitrile. The two solutions were mixed resulting in a purple solution, which was stirred for about 30 min. Then, 8 mL of diethyl ether was added, and a purple precipitate was obtained which was washed with diethyl ether (5 × 5 mL); Yield: 99.1 mg, 0.13 mmol, 64%. Single crystals suitable for X-ray diffraction were obtained by slow vapor diffusion of diethyl ether into the acetonitrile solution containing the compound; single crystals were obtained after 2 days at room temperature. IR (cm\(^{-1}\)): 1606s, 1571w, 1480m, 1442s, 1092w, 1022m, 766vs, 648s, 478w. ESI-MS found (calcld) for \([\text{M}–\text{Cl}]^+\): m/z 740.8 (740.9). Elemental analysis calcld (%) for \(\text{C}_{34}\text{H}_{27}\text{Cl}_{3}\text{Co}_{3}\text{N}_{13}\text{S}_{5}^2\text{H}_{2}\text{O}\): C: 41.40, H: 4.47, N: 10.3; found: C: 41.71, H, 4.57, N, 9.80. UV–vis (acetonitrile at 1 mM [Co]): \(\lambda_{\text{max}}\) (e

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in M⁻¹ cm⁻¹⁻¹: 261 nm (4.6 × 10³), 524 nm (0.1 × 10³), 570 nm (0.1 × 10³), 640 nm (10⁻⁴). 

[Co(L²(Si)(MeCN))(BF⁴)]⁺ (2). To a yellow solution of ligand L⁴SS (17.2 mg, 0.138 mmol) in 4.6 mL of dry and degassed acetonitrile, solid [Co(MeCN)⁶](BF⁴) (131.7 mg, 0.275 mmol) was added, resulting in a brown yellow solution. The acquired solution was stirred for 3 h, and then the volume was reduced to 0.5 mL. Addition of 15 mL of diethyl ether led to the formation of a yellow oil material. 

The obtained yellow oil material was washed with diethyl ether (3 × 15 mL). Yield: 103.0 mg, 0.18 mmol, 65%. Single crystals of 2 could not be obtained, but from an acetonitrile solution of compound 2 kept in air, after 8 weeks crystals were obtained of the cobalt(III) sulfide complex [Co(L²(Si)(MeCN))(MeCN)]⁺ (2); δ(CN) 810 ppm (1H NMR (300 MHz, DMSO-d₆), 524 nm (0.1 × 10⁻³)).

Raman, UV-vis, ¹H NMR, ¹³C NMR, and ESI-MS spectra and the cyclic voltammograms of the compounds; Cartesian coordinates of the calculated structures, calculated energies and plots of the HOMOs (PDF)

Accession Codes
CCDC 1496381, 1496385, 1827153, and 1850287 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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ASSOCIATED CONTENT

Supporting Information

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