

Bimetallic Disulfide Complexes

The Reactivity of Fe^{II} and Co^{II} Disulfide Compounds with Dihydrogen PeroxideFeng Jiang,^[a] Maxime A. Siegler,^[b] and Elisabeth Bouwman*^[a]

Abstract: The reactivity of two metal disulfide compounds [M^{II}₂(L¹SSL¹)Cl₄] {M = Fe and Co, L¹SSL¹ = di-2-[bis(2-pyridylmethyl)amino]ethyl disulfide} with dihydrogen peroxide has been investigated. Reaction of the iron(II) disulfide compound [Fe^{II}₂(L¹SSL¹)Cl₄] with H₂O₂ results in the formation of the mononuclear iron(III) sulfonate compound [Fe^{III}(L¹SO₃)Cl₂]. The crystal structure combined with EPR spectroscopy confirms that a high-spin (*S* = 5/2) iron(III) center was generated, which is coordinated by three nitrogen donors and one oxygen atom of

the sulfonate group of the tetradentate ligand, and two chloride ions in an octahedral geometry. In contrast, reaction of compound [Co^{II}₂(L¹SSL¹)Cl₄] with H₂O₂ yielded the mononuclear cobalt(III) sulfinate compound [Co^{III}(L¹SO₂)Cl₂]. The crystal structure and NMR spectroscopy show that in this case a low-spin (*S* = 0) cobalt(III) center was obtained, which is coordinated by three nitrogen donors and one sulfur atom of the sulfinate group of the tetradentate ligand and two chloride ions in an octahedral geometry.

Introduction

Reactions involving dioxygen assisted by metalloenzymes occur in numerous biological systems and play fundamental roles important for health like DNA replication and repair,^[1] as well as the biosynthesis of physiologically vital hormones and neurotransmitters.^[2] A typical example is provided by the non-heme iron enzyme cysteine dioxygenase (CDO), which catalyzes the oxidation of the thiolate of cysteine to a sulfinic acid group. It is believed that some neurological diseases such as Parkinson and Alzheimer are related to the absence of the enzyme CDO.^[3] Another example concerns the cobalt or iron-containing enzyme nitrile hydratase (NHase), where the metal centers are coordinated by two nitrogen atoms from the peptide backbone, one sulfur donor of a cysteine group in the apical position, and two other sulfur donor atoms originating from a sulfenate and a sulfinate group (Figure 1). In this case, dioxygen is most likely the oxidant to modify the cysteine sulfur atoms of the enzyme *in vivo*, which modifies the activity of the enzymes.^[4] As understanding of the degradation pathways of metalloenzymes is of considerable importance, bioinorganic chemists have undertaken the synthesis of Ni^{II}, Cu^{II}, Zn^{II} analogues of N₄S, N₃S, or N₂S₂ ligands, and investigated their reactivity with oxidizing

agents.^[5] The study of the oxidation sensitivity of Fe^{II} thiolate compounds has been described as helpful for the understanding of the role of the metalloenzyme CDO.^[6]

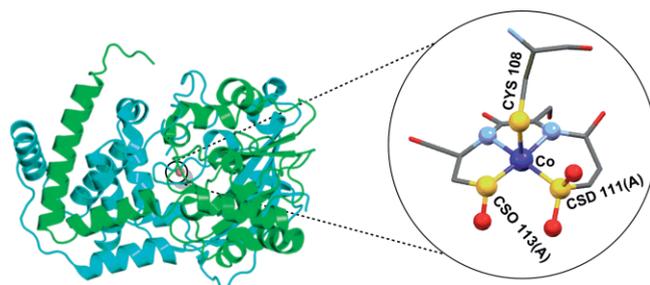


Figure 1. Schematic impression of the Co-factor of nitrile hydratase obtained from *Pseudonocardia thermophila* (yellow, sulfur; purple, cobalt; pale-blue, nitrogen; red, oxygen). The sixth coordination site is normally occupied by water creating an octahedral geometry.^[7]

Despite the considerable progress made in the last decades, study of the oxidation of sulfur ligands in metal compounds is still important in terms of the following two aspects. First of all, so far most research focused on the study of the oxidation of thiolate compounds of nickel,^[5b,5d,5e,8] or iron,^[6b,6c,6e,8b,9] related to the oxidation sensitivity of hydrogenases, whereas only few studies have been reported concerning the oxidation sensitivity of cobalt compounds as mimics of the metalloenzyme Co-NHase.^[10] Secondly, the redox interconversion between high-valent metal thiolate and low-valent metal disulfide compounds has been studied in the last decade, especially for copper but more recently also for cobalt compounds (Scheme 1).^[6d,11] However, up till now, only a limited number of studies has been reported on the oxidation of metal disulfide compounds.^[12] To the best of our knowledge, only the group of Karlin reported the reactivity of a Cu^I disulfide compound with dioxygen, which was shown to result in the formation of a copper(II) sulfonate

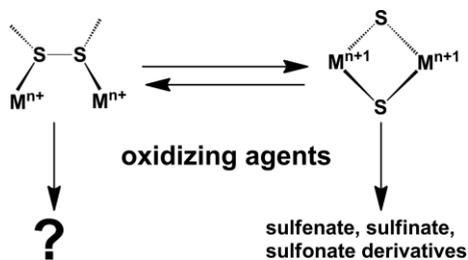
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compound.^[12] In the last few years, Torelli et al.^[13] investigated the mechanism of S–S bond cleavage of a Cu^{II} disulfide compound, and spectroscopic evidence showed that, in aqueous conditions, water acts as the nucleophile to attack the S–S bond, yielding the sulfinate and sulfonate derivatives. Herein we report the reactivity of two metal disulfide compounds [M^{II}₂(L¹SSL¹)Cl₄] (M = Fe, Co; L¹SSL¹ = {di-2-[bis(2-pyridylmethyl)amino]ethyl disulfide}) with dihydrogen peroxide.

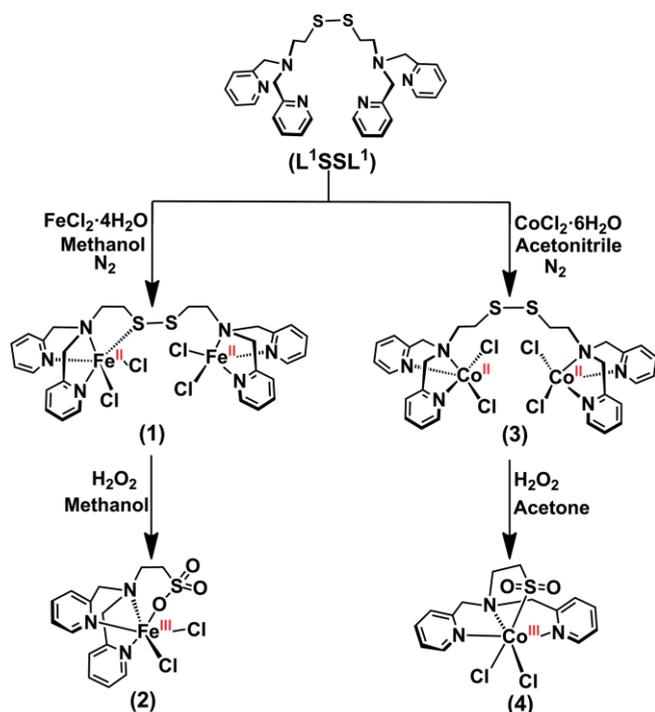


Scheme 1. Overview of the redox interconversion between metal thiolate and disulfide compounds, and the potential oxidative processes.

Results

Synthesis and Characterization of the Oxidized Iron and Cobalt Compounds

The ligand L¹SSL¹ and the coordination compounds [Fe^{II}₂(L¹SSL¹)Cl₄] (**1**) and [Co^{II}₂(L¹SSL¹)Cl₄] (**3**) were synthesized via reported procedures.^[11d,11f,14] The addition of 80 equivalents of H₂O₂ to one equivalent of **1** in methanol resulted in the formation of the compound [Fe^{III}(L¹SO₃)Cl₂] (**2**) in a yield of 58 % (Scheme 2). Similarly, the addition of ≥ 80 equivalents of



Scheme 2. Synthesis scheme of the metal(II) disulfide compounds **1** and **3**, and the oxidation products **2** and **4**.

H₂O₂ to one equivalent of **3** in acetone led to the formation of the compound [Co^{III}(L¹SO₂)Cl₂] (**4**) in a yield of 83 %. The compounds were characterized with ¹H NMR, UV/Vis, and IR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), elemental analysis and single-crystal X-ray diffraction.

Full characterization of **1** and **3** has been reported in our previous study.^[14] The ESI-MS spectrum of **2** dissolved in methanol presents a dominant peak (*m/z*) at 189.2 assigned to the fragment ¹/₂[Fe(L¹SO₃)(H₂O)]²⁺ (Figure S1). The IR spectrum of **2** shows two intense absorption bands at around 1022 and 1146 cm⁻¹ likely corresponding to the symmetric and asymmetric S=O bond stretching frequencies.^[15] The EPR spectrum of **2** dissolved in dimethyl sulfoxide shows a rather broad, rhombic spectrum with a *g* value of around 4.25, typical for an iron(III) center in a high-spin state (*S* = 5/2; Figure S2).^[16] The magnetic susceptibility of **2** was estimated using Evans' method in dimethyl sulfoxide solution at 20 °C, revealing a μ_{eff} of 5.28 μ_{B} [a value of 5.92 μ_{B} is expected for an *S* = 5/2 iron(III) center].^[17] The ESI-MS spectrum of **4** dissolved in acetonitrile shows a dominant peak (*m/z*) at 425.5 fitting the fragment [Co^{III}(L¹SO₂)Cl(MeCN)]⁺, and a peak at 384.4 corresponding to the fragment [Co^{III}(L¹SO₂)Cl]⁺ (Figure S3). The IR spectrum of **4** shows two strong absorption bands at 1074 and 1173 cm⁻¹ ascribed to vibrations of the sulfinyl group.^[18] The signals in the ¹H NMR spectrum of **4** dissolved in [D₃]acetonitrile are observed in the diamagnetic region, consistent with the cobalt(III) center in this compound being in a low-spin state (*S* = 0; Figure S4).

Single-Crystal X-ray Diffraction Analysis

The crystal structures of **1** and **3** have been reported in our previous study.^[14] Single crystals of **2** and **4** suitable for X-ray structure determination were acquired by slow vapor diffusion of diethyl ether into solutions of the compounds in dimethylformamide and acetone, respectively. Crystallographic and refinement data of the structures are summarized in the Supporting Information Table S1. Projections of the structures are provided in Figure 2, selected bond lengths and angles are given in Table 1. Compound **2** crystallizes in the monoclinic space group *P*2₁/*c* with two crystallographically independent molecules of the compound and one lattice dimethylformamide solvent molecule in the asymmetric unit. The two independent molecules have very similar conformations. The Fe^{III} ion is coord-

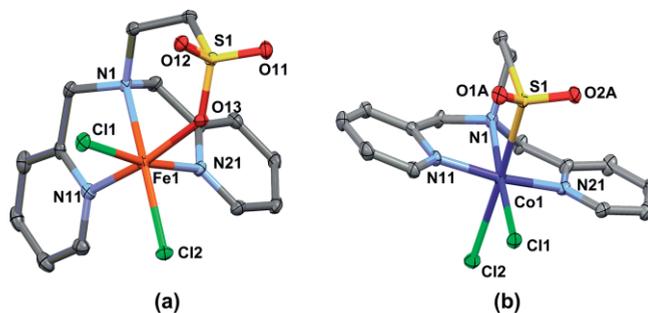


Figure 2. Displacement ellipsoid plots (50 % probability level) of (a) compound **2** and (b) compound **4** at 110(2) K. The lattice solvent molecules and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] from the crystal structure of compounds **2** and **4**.^[a,b]

Distances/Angles	2	4	Distances/Angles	2	4
M–N1	2.2516(15)	1.9724(15)	M–X	1.9666(13)	2.1820(5)
M–N11	2.1998(15)	1.9311(16)	M–Cl1	2.2850(5)	2.2504(5)
M–N21	2.1530(17)	1.9499(16)	M–Cl2	2.2758(5)	2.3274(5)
Cl1–M–Cl2	97.793(19)	91.783(18)	Cl2–M–X	97.13(4)	176.81(2)
Cl1–M–N1	168.37(4)	176.17(5)	N1–M–N11	77.26(6)	85.09(7)
Cl1–M–N11	92.01(4)	96.57(5)	N1–M–N21	77.28(6)	83.17(7)
Cl1–M–N21	96.79(4)	95.23(5)	N1–M–X	87.92(6)	88.90(5)
Cl1–M–X	96.60(4)	87.706(18)	N11–M–X	80.92(6)	168.17(7)
Cl2–M–N1	92.25(4)	91.70(5)	N11–M–X	89.60(5)	88.44(5)
Cl2–M–N11	167.37(4)	88.49(5)	N21–M–X	163.83(6)	92.79(5)
Cl2–M–N21	89.99(4)	90.40(5)			

[a] M = Fe1, X = O13 for **2**, M = Co1, X = S1 for **4**. [b] For compound **2**, the bond lengths and angles are given only for one of the two crystallographically independent Fe complexes (complex A).

minated by the three nitrogen donors from the tetradentate ligand bound in a facial arrangement, one oxygen donor atom of the sulfonate group and two chloride ions in a slightly distorted octahedral geometry with one of the chloride ions bound *trans* to the tertiary amine and the other *trans* to one of the pyridine nitrogen atoms. The Fe–O bond lengths are 1.9666(13)/1.9870(13) Å, and the Fe–N bond lengths range from 2.1421(16) to 2.2516(15) Å. There are no hydrogen-bonding or stacking interactions present in the structure of **2**.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with one molecule of the compound and three lattice water solvent molecules in the asymmetric unit. The hydrogen atoms in two of the three water molecules are disordered over two different orientations. The cobalt(III) ion is coordinated by three nitrogen donors of the ligand bound in a meridional fashion, the sulfur donor of the sulfinate group and two chloride ions in an octahedral configuration. The Co–S bond length is 2.1820(5) Å; the Co–N bond lengths range from 1.9311(16) to 1.9724(15) Å, which are much shorter than the Co–N distances in **3**, and in agreement with a low-spin ($S = 0$) state of the cobalt(III) ion. The Co–Cl1 distance is significantly shorter than the Co–Cl2 distance [2.2504(5) and 2.3274(5) Å, respectively], indicative of the larger *trans* influence of the sulfinate sulfur donor atom. The lattice water molecules are hydrogen bonded to one of the oxygen atoms of the sulfinate group. The crystal packing of **4** does not contain stacking interactions.

Monitoring the Reactivity of **1** and **3** with H₂O₂

UV/Vis spectra of **1** dissolved in methanol show absorption bands at 256, 313 and 390 nm.^[14] UV/Vis spectra of compound **2** dissolved in methanol show an intense absorption band at 258 nm ($\epsilon = 4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) assigned to the $\pi \rightarrow \pi^*$ transitions of the pyridyl groups, as well as two weak bands at 377 nm ($\epsilon = 0.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 485 nm ($\epsilon = 0.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) tentatively ascribed to ligand-to-metal charge transfer transitions (LMCT) (Figure S5).

The formation of the mononuclear sulfonato-iron(III) compound **2** by the reaction of **1** with H₂O₂ in methanol was monitored using UV/Vis spectroscopy at room temperature. The addition of an excess of 35 % H₂O₂ (0.2 mmol, 40 equiv. to **1**) to the solution containing **1** resulted in a color change from yellow

to dark brown, and then back to yellow immediately. The reaction is very fast, UV/Vis spectra showed a new band at 375 nm appearing instantly after addition of H₂O₂ and increasing in intensity during the whole process, while the band at 394 nm decreases rapidly until it disappears (Figure S6). Isosbestic points are not observed, suggesting that more than one compound is formed during this process. Attempts have been undertaken to trap the intermediates, first by lowering the temperature to –41 °C, but the spectra were nearly identical with those obtained at room temperature (Figure S7). Upon further reduction of the temperature to –78 °C, the reaction slows down and the spectra show the formation of a new band at 375 nm with a gradual decrease of the band at 394 nm (Figure 3). At this reaction temperature an isosbestic point is observed. An ESI-MS spectrum recorded of this reaction mixture shows peaks at m/z 381.1, 397.1 and 429.2, corresponding to the fragments $[\text{Fe}^{\text{III}}(\text{L}^1\text{SO}_2)\text{Cl}]^+$, $[\text{Fe}^{\text{III}}(\text{L}^1\text{SO}_3)\text{Cl}]^+$, and $[\text{Fe}^{\text{III}}(\text{L}^1\text{SO}_3)\text{Cl}(\text{CH}_3\text{OH})]^+$, respectively (Figure S8). This clearly shows that the sulfinato-iron(III) compound is an intermediate; the observation of the sulfonate-compound in the MS is ascribed to the high rate of the reaction at room temperature while transferring the solution to the mass spectrometer. An absorption band that could potentially be ascribed to interactions of the iron center with dihydrogen peroxide [e.g. a hydroperoxido-to-iron(III) LMCT] was not found.^[19] Unfortunately, additional information could not be obtained in further attempts to slow down the oxidation process, by titration of small amounts of H₂O₂ into the methanolic solution of **1** (Figure S9). An attempt was made to trap a potential alkylperoxido-iron(III) intermediate by the reaction of **1** with *t*BuOOH at –41 °C, but this attempt was also not successful (Figure S10).

Compound **3** is stable in air. UV/Vis spectra of **3** dissolved in acetonitrile show absorption bands at 261, 524, 570, and 640 nm.^[14] UV/Vis spectra of **4** dissolved in acetonitrile present several absorption bands, the one at 236 nm is attributed to $\pi \rightarrow \pi^*$ transitions of the pyridyl groups ($\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), whereas two bands at 327 ($\epsilon = 9.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 525 nm ($\epsilon = 0.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) likely correspond to LMCT transitions (Figure S11).^[6d,14]

The reaction of **3** with H₂O₂ in acetonitrile was monitored using UV/Vis spectroscopy at room temperature. The addition of 35 % H₂O₂ (0.8 mmol, 80 equiv. to **3**) to a solution of **3** in

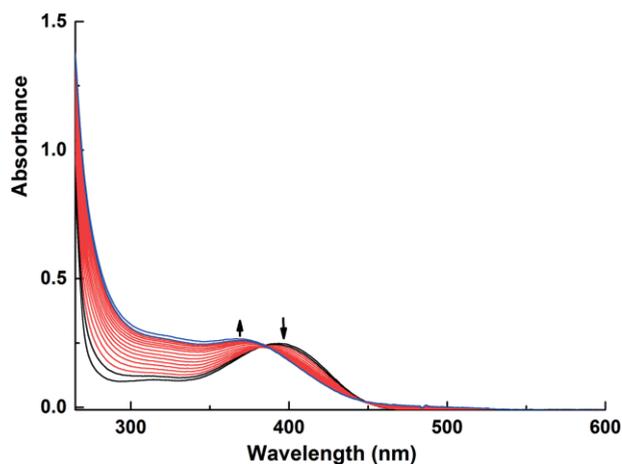


Figure 3. The change in UV/Vis spectra upon addition of H_2O_2 (0.8 mmol, 80 equiv. to **1**) to compound **1** in methanolic solution at -78°C . UV/Vis spectra were recorded using a solution 2 mm in [Fe] (10 mL) with a transmission dip probe path length of 1.2 mm. Spectra were recorded every 30 seconds over a period of 10 min.

acetonitrile resulted in a gradual color change from purple to brown-yellow over a period of 1.5 hours. UV/Vis spectra showed the appearance of two new absorption bands at 311 and 421 nm. At the same time the peaks at 524, 570, and 640 nm assigned to Co^{II} $d-d$ transitions combined with $\text{Cl} \rightarrow \text{Co}^{\text{II}}$ charge transfer transitions (LMCT) decreased in intensity (Figure 4). The spectra are slightly different from the UV/Vis spectrum of the isolated product, indicating the possibility of multiple products formed in this oxidative process. Again, attempts to trap potential intermediates in the oxidation process by titration of small aliquots of H_2O_2 into the solution of **3** unfortunately were unsuccessful (Figure S12). Notably, an ESI-MS spectrum of the reaction mixture of the compound **3** and H_2O_2 recorded after around one hour presents a dominant peak (m/z) at 368.1, which can be assigned to the mono-oxygenated fragment $[\text{Co}^{\text{III}}(\text{L}^1\text{SO})\text{Cl}]^+$ (Figure S13).

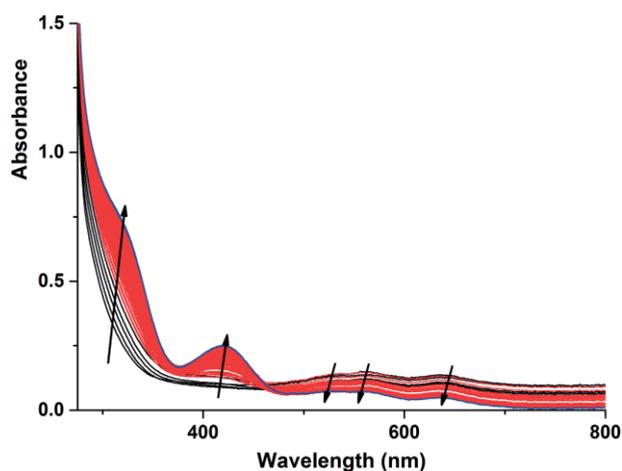


Figure 4. The change in UV/Vis spectra of **3** in acetonitrile solution upon addition of H_2O_2 . UV/Vis spectra were recorded using a solution 2 mm in [Co] with a transmission dip probe path length of 2 mm; spectra were recorded every 30 seconds.

Discussion

Synthesis of transition metal compounds and investigation of their reactivity with oxidizing agents has attracted considerable attention in the last decades. Different S -oxygenated metal derivatives can be formed, depending on the nature of the ligand, coordination environment, oxidizing agents, and the frontier orbitals of the metal centers.^[20] Reaction of the iron(II) compound $[\text{Fe}^{\text{II}}_2(\text{L}^1\text{SSL}^1)\text{Cl}_4]$ (**1**) with H_2O_2 is very fast yielding the high-spin ($S = 5/2$) sulfonato-iron(III) compound $[\text{Fe}(\text{L}^1\text{SO}_3)\text{Cl}_2]$ (**2**). UV/Vis spectroscopy showed the reaction to be complete within several minutes, and analysis of a reaction carried out at -78°C showed that a sulfinato-iron(III) compound is formed as the first intermediate. Unfortunately, a potential μ -peroxido-diiron(III) intermediate such as reported in another study was not observed in our reactions.^[21]

The reactivity of iron(II) or iron(III) thiolate compounds with dioxygen has been extensively studied,^[20a] but to the best of our knowledge, the oxidation of iron(II) disulfide compounds has not been investigated. Oxidation of iron(II) or iron(III) thiolate compounds generally results in the formation of sulfinate derivatives,^[22] but the formation of a sulfenato-iron(III) compound was reported by Kovacs and co-workers.^[23] Rare examples have been reported of high-spin ($S = 2$) iron(II) and low-spin ($S = 1/2$) iron(III) sulfonate compounds, which were obtained by controlled oxidation of the iron(II) center or thiolate sulfur atom.^[9d,15]

The reaction of $[\text{Co}^{\text{II}}_2(\text{L}^1\text{SSL}^1)\text{Cl}_4]$ (**3**) with H_2O_2 yielded the low-spin sulfinato-cobalt(III) compound $[\text{Co}^{\text{III}}(\text{L}^1\text{SO}_2)\text{Cl}_2]$ (**4**). Attempts to crystallize the sulfenato intermediate that was observed in ESI-MS unfortunately were not successful. However, we have shown in our previous study that such a mono-oxygenated intermediate indeed exists, as the compound $[\text{Co}^{\text{III}}(\text{L}^1\text{SO})(\text{NCS})_2]$ was trapped during the crystallization of the cobalt(III) thiolate compound $[\text{Co}^{\text{III}}(\text{L}^1\text{S})(\text{NCS})_2]$, due to partial oxidation.^[14] In the last decades, quite some research has been performed on the synthesis of S -oxygenated cobalt(III) compounds by reactions of cobalt(III) salts with S -oxygenated ligands, or via oxidation of cobalt(III) thiolate compounds.^[22,24] Dutta et al. reported the reactivity of a cobalt(II) thiolate compound of a tetradentate N_2S_2 ligand with dioxygen.^[10] The results indicated that oxidation of the cobalt(II) thiolate compound involved two steps. First, one of the thiolate donors is oxidized to a sulfinate group, which is a fast step, upon which the cobalt(II) ion is slowly oxidized to cobalt(III). Still, our case is the first example of the oxidation of a cobalt(II) disulfide compound, where both the cobalt(II) center and the disulfide sulfur atoms are oxidized, yielding a low-spin cobalt(III) sulfinate compound.

Conclusions

In this manuscript, we report the reactivity of the two metal disulfide compounds **1** and **3** with H_2O_2 , which were shown to result in the mononuclear high-spin ($S = 5/2$) sulfonato-iron(III) compound **2**, and the low-spin ($S = 0$) sulfinato-cobalt(III) derivative **4**, respectively. This study provides a rare example of the oxidation of metal disulfide compounds. Although new insight has been gained on the formation of different S -oxygenated

metal derivatives by the reactions of iron(II) or cobalt(II) disulfide compounds with H₂O₂, additional studies are required to unravel the mechanism of the oxidation of metal disulfide compounds.

Experimental Section

General Procedures: All chemicals were acquired from commercial vendors and used as received unless noted otherwise. Acetonitrile and diethyl ether were obtained from a solvent purification system (PureSolv 400), and methanol, dimethylformamide (DMF) were purchased from commercial sources and stored on 3 Å molecular sieves. The syntheses of transition metal disulfide compounds were carried out by standard Schlenk-line techniques under an atmosphere of dinitrogen. ¹H NMR and ¹³C NMR spectra were carried out on a Bruker 300 DPX spectrometer at room temperature and chemical shifts were referenced against the solvent peak. Mass spectra were recorded on a Finnigan Aqua mass spectrometer with electrospray ionization (ESI). IR spectra were recorded on a PerkinElmer UATR spectrum equipped with single reflection diamond (resolution 4 cm⁻¹, scan range 400 cm⁻¹ to 4000 cm⁻¹). Ultraviolet-visible (UV/Vis) spectra were collected using a transmission dip probe with variable path length on an Avantes Avaspec-2048 spectrometer with Avalight-DH-S-BAL light source. Elemental analyses were performed by the Microanalytical Laboratory Kolbe in Germany.

Single-Crystal X-ray Diffraction Analysis: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Mo-K_α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 and was refined on F² with SHELXL-2014/7.^[25] Numerical absorption correction based on Gaussian integration over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) 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 structure of **2** is ordered. The structure of **4** is mostly ordered except for some H atoms from the lattice water solvent molecules.

CCDC 1838981 {for [Co^{III}(L¹SO₂)Cl₂]} and 1838983 {for [Fe^{III}(L¹SO₃)Cl₂]} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of the Compounds

[Fe^{III}(LSO₃)Cl₂] (2): The compound [Fe^{II}₂(L¹SSL¹)Cl₄] (38.5 mg, 0.05 mmol) was dissolved in 10 mL of dry and degassed methanol and cooled in an ice bath. To this solution 345 μL 35 % (4.0 mmol) H₂O₂ was added, leading to a color change from yellow to dark brown, and then back to yellow. The obtained yellow solution was stirred for another 4 h, after which time the solvent was evaporated to yield a yellow precipitate. The yellow precipitate was recrystallized from a mixture of methanol and diethyl ether, yielding a light-yellow powder. Yield: 25.0 mg, 0.06 mmol, 58 %. Crystals suitable for X-ray structure determination were acquired by slow vapor diffusion of diethyl ether into a dimethylformamide (DMF) solution containing this compound, yielding single crystals after approximately 12 days. IR: $\tilde{\nu}$ = 476 (m), 504 (m), 551 (m), 541 (m), 591 (s), 653 (m), 645 (m), 721 (w), 746 (s), 771 (s), 782 (s), 814 (w), 841 (w), 897 (w),

919 (w), 932 (s), 969 (s), 984 (s), 1003 (s), 1020 (s), 1046 (w), 1057 (w), 1076 (w), 1096 (m), 1146 (vs), 1189 (w), 1235 (m), 1263 (s), 1288 (m), 1359 (w), 1430 (m), 1448 (m), 1462 (m), 1476 (w), 1571 (w), 1606 (s) cm⁻¹. ESI-MS found (calcd) for 1/2[M - 2Cl + H₂O]⁺ m/z 189.2 (190.0). C₁₄H₁₆Cl₂FeN₃O₃S (433.11): calcd. C 38.83, H 3.72, N 9.70; found C 38.85, H 3.84, N 9.25.

[Co^{III}(LSO₂)Cl₂] (4): The compound [Co^{II}₂(L¹SSL¹)Cl₄] (40.6 mg, 0.05 mmol) was suspended in 5 mL of dry acetone. To this suspension 402 μL 35 % H₂O₂ (4.6 mmol) was added, upon which the color of the suspension changed from purple to brown and the suspended solid gradually dissolved. The final solution was stirred for another 3 days, yielding a purple precipitate. The obtained precipitate was washed with diethyl ether (4 × 15 mL). Yield: 15 mg, 0.04 mmol, 34 %. Crystals suitable for X-ray structure determination were obtained by slow vapor diffusion of diethyl ether into an acetone solution containing this compound, yielding crystals after about 1 week. ¹H NMR (300 MHz, [D₆]DMSO, r.t.): δ = 8.66 (d, 2 H, Py-H⁶), 8.12 (t, 2 H, Py-H⁴), 7.63 (t, 2 H, Py-H³), 7.54 (d, 2 H, Py-H⁵), 5.11 (d, 2 H, Py-CH₂), 4.57 (d, 2 H, Py-CH₂), 3.05 (d, 2 H, S-CH₂-CH₂), 2.90 (t, 2 H, S-CH₂-CH₂), 3.33 (H₂O), 2.50 (DMSO). IR: $\tilde{\nu}$ = 531 (s), 572 (m), 654 (w), 686 (m), 719 (m), 771 (s), 797 (w), 820 (w), 912 (s), 947 (s), 996 (w), 1059 (s), 1074 (vs), 1164 (m), 1177 (m), 1180 (s), 1210 (s), 1228 (s), 1238 (s), 1286 (m), 1433 (w), 1444 (m), 1462 (m), 1483 (m), 1609 (m) cm⁻¹. ESI-MS found (calcd) for [M - Cl]⁺ m/z 384.4 (384.7), [M - Cl + MeCN]⁺ m/z 425.5 (425.8). C₁₄H₁₆Cl₂CoN₃O₂S·1/2H₂O (429.02): calcd. C 39.18, H 3.99, N 9.79; found C 39.16, H 3.91, N 9.73.

Supporting Information (see footnote on the first page of this article): The supporting information contains crystallographic data of the compounds, UV/Vis spectra of all compounds and oxidation reactions, EPR spectrum of [Fe^{III}(L¹SO₃)Cl₂], ¹H NMR spectrum of [Co^{III}(L¹SO₂)Cl₂].

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