Redox interconversion between metal thiolate and disulfide compounds

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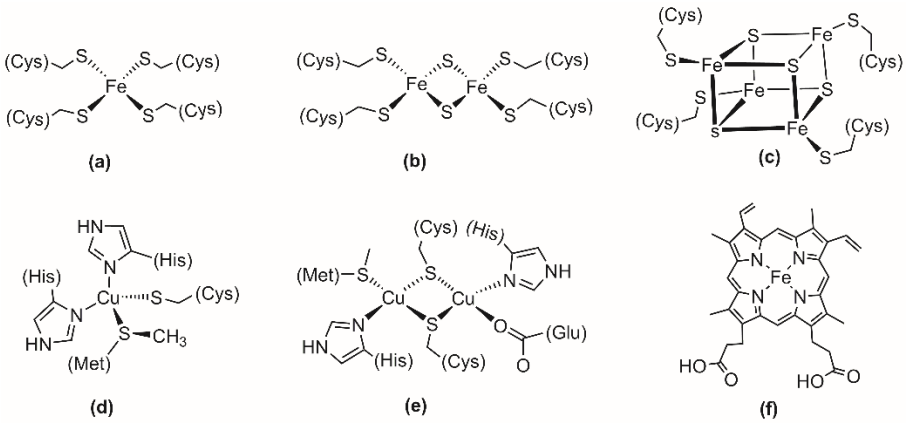
Chapter 1

Introduction

Two types of active sites of copper proteins (Type-1, Cu_A), involved in electron transfer reactions in biological systems, are briefly described. An overview is presented of synthetic models with diamond core [Cu_2S_2] structures that mimic the active sites of Cu_A, including their structure and spectroscopic properties. Furthermore, the redox interconversion reaction of metal thiolate and disulfide compounds is described, which is related to simulation of metal-based thiolate-disulfide interchange occurring in metalloenzymes such as Zn_7MT-3 and ScO.

1.1 General introduction

Electron transfer (ET) reactions promoted by metalloenzymes are of fundamental importance in a large number of biological systems e.g. cellular respiration [1, 2], dioxygen transport [3, 4], and photosynthesis [5]. The dominant redox centers found in ET proteins are iron and copper (Scheme 1.1) [6]. In the last decades, a number copper proteins has been extensively studied using advanced spectroscopic techniques, which provided further insight into the structure and spectroscopic properties of the active sites in these metalloenzymes [7, 8]. Based on the coordination environment, spectroscopic features, and functions of the active sites, copper proteins are classified into six groups, namely, Type-1, Type-2, Type-3, Cu_A, Cu_B and Cu_Z proteins [9]. Among these classes, only Type-1 and Cu_A are involved as ET mediators. Some enzymes containing Type-1 or Cu_A active sites are briefly discussed in the following section [6].



Scheme 1.1. Schematic representation of the active sites of metalloenzymes involved in ET processes (a) mononuclear rubredoxin; (b) binuclear [2Fe-2*S*] ferredoxin; (c) tetranuclear [4Fe–4*S*] ferredoxin; (d) Type–1 active site of plastocyanin; (e) Cu_A active site of cytochrome c oxidase; (f) heme b of cytochromes.

1.2 Copper proteins involved in ET processes

1.2.1 Type–1 active site

The Type-1 copper active site not only is present in mononuclear metalloenzymes such as plastocyanin (Scheme 1.1.d), amicyanin, rusticyanin, and azurin, but also is found in some multicopper proteins, such as nitrite reductase, and ascorbate oxidase. The Type-1 copper center in these metalloenzymes is usually coordinated by two nitrogen atoms of histidines and one sulfur atom of cysteine in a trigonal plane, with another distant axial ligand, which is either a sulfur atom of methionine or an oxygen

atom of glutamine/leucine. The copper–to–nitrogen bond distances range from 1.93 to 2.22 Å, whereas the copper to sulfur bond lengths are between 2.07 and 2.30 Å .The metalloenzymes containing a Type-1 copper center are also called "blue copper proteins" as they show an intense blue color in solution. UV-vis spectra of these solutions usually show a strong and characteristic $Cu^{II} \leftarrow S_{cys}$ charge-transfer transition (LMCT) at 600 nm ($\varepsilon = 5\times10^3\ M^{-1}\ cm^{-1}$), causing the typical blue color. EPR spectra of metalloenzymes containing a Type-1 copper center present a narrow hyperfine coupling probably arising from the covalent nature of the Cu–S bond [8, 10]. Normally, Type-1 copper proteins are involved in long–range ET processes in biological systems [11, 12].

1.2.2 Cu_A active site

The Cu_A active site is found in e.g. cytochrome c oxidase (CcO, Scheme 1.1.e), and nitrous oxide reductase, enzymes that play a vital role in electron-transfer reactions. The Cu_A active site comprises a dinuclear dicopper diamond core [Cu_2S_2], in which both copper centers are in a distorted tetrahedral geometry coordinated by a nitrogen atom of histidine, two bridging thiolate sulfur donors of two cysteines, and a weakly coordinating ligand, which is either a methionine sulfur donor or a backbone carbonyl oxygen atom. The copper–to–nitrogen bond lengths in Cu_A sites range from 1.93 to 2.22 Å, the Cu–S bond distances are around 2.2 Å. Notably, the distance between the two copper centers in the Cu_A site range from 2.43 – 2.60 Å; this rather short distance allows for a direct interaction between the two copper ions. The oxidation state of the two copper centers shuttles between $Cu^{II}Cu^{II}$ and $Cu^{I}Cu^{II}$ during ET. Metalloenzymes containing a Cu_A active site commonly give a purple color in solution. Absorption spectra of these purple solutions show two intense absorbance bands at around 480 and 530 nm arising from Cu ← S charge transfer, and another broad band at around 780 nm ascribed to the charge transfer between the copper ions in the mixed-valent state. EPR spectra of proteins containing a Cu_A active site normally present a seven-line hyperfine splitting pattern, which is caused by delocalization of the electron between the two copper ions. Generally, enzymes containing the Cu_A active site are terminal electron acceptors of ET processes [13].

1.3 Synthetic models for Cu_A sites

To obtain further insight into the operation principle of electron transfer within Cu_A active sites, inorganic chemists synthesize small molecule mimics to simulate the structure and spectroscopic properties of Cu_A active sites [14, 15]. The major challenge of the synthesis of mimics resembling the Cu_A active site is that disulfide bonds tend to be formed from two thiolate ligands when reacted with Cu(II) ions, with

the concomitant reduction of the Cu(II) ions to Cu(I) (equation 1) [16]. Therefore, initial studies focused on the synthesis of dinuclear Cu(I) dithiolate compounds as mimics for the reduced state of Cu_A sites. The first example of a dinuclear Cu(I) compound bridged by two arylthiolate groups was reported over 30 years ago, followed after a few years by a report of a highly similar compound by another group (compounds **C1** and **C2** in scheme 1.2) [17, 18]. Both compounds **C1** and **C2** were synthesized electrochemically starting from copper metal (equation 2). The structures show a $[Cu^{I}_2S_2]$ diamond core with Cu···Cu distances of 2.613(3) and 3.0186(12) Å, respectively. The large difference in the Cu···Cu distances is likely induced by the steric effect of the additional methyl groups in compound **C2**. Although compounds **C1** and **C2** replicate a diamond core $[Cu_2S_2]$ with the desired Cu···Cu distances, the cysteine ligands present in the Cu_A site are mimicked with aromatic rather than aliphatic thiolate ligands. Electrochemical oxidation of **C1** and **C2** failed to generate the corresponding mixed-valent or high-valent compounds with a diamond $[Cu_2S_2]$ core.

$$2Cu(II) + 2LS^- \longrightarrow 2Cu(I) + LSSL \qquad (1)$$

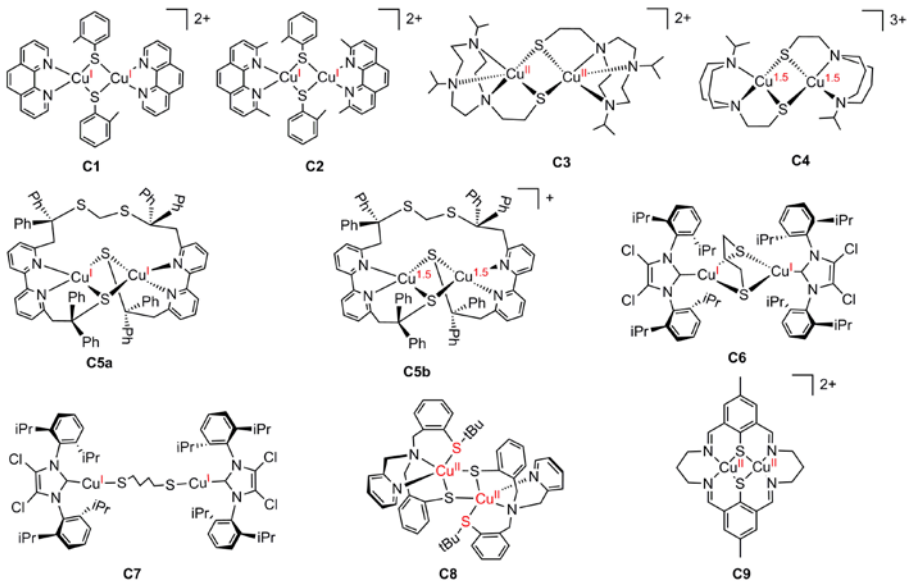
$$2Cu + 2L + 2RSH \longrightarrow (L)_2(RS)_2Cu_2 + 2H^+ + 2e^- \quad (2)$$

The first dinuclear Cu(II) dithiolate compound (**C3**) was reported by Tolman and coworkers [16]. It was shown that compound **C3** presented the desired $[Cu_2S_2]$ diamond core with two Cu(II) centers bridged by two thiolate groups. The S···S distance in **C3** is 3.093(2) Å, which is much longer than a disulfide bond (~ 2.0 Å), indicating that a Cu(II) thiolate rather than a Cu(I) disulfide compound was obtained. The Cu···Cu distance is 3.340(2) Å, which is much longer than the Cu···Cu distance in Cu_A active sites, accounting for the absence of direct interaction between two copper ions. Interestingly, this compound showed different spectroscopic characteristics in different solvents, which is thought to be related to an equilibrium between mononuclear and dinuclear Cu(II) compounds in these solvents.

Following this work, an unprecedented mixed-valent dicopper(I,II) dithiolate compound **C4** was reported by the same group [19]. The ratio of the ligand and Cu(II) salt (3:2) used in the synthesis is essential for obtaining this mixed-valent compound, as the extra ligand acts as reducing agent for one of the Cu(II) ions. Compound **C4** shows a fully delocalized, mixed-valent dicopper diamond core $[Cu^{1.5}_2S_2]$ with a Cu···Cu distance of 2.9306(9) Å. This shorter Cu···Cu distance compared to **C3** suggests that the two copper ions may have a direct interaction. This assumption was later confirmed by the observation of a seven-line hyperfine splitting pattern in the EPR spectra of **C4**. Overall, this is the first mimic that closely replicates the geometry

and spectroscopic properties of the resting-state of the Cu_A active site, also including delocalization of the unpaired electron over two copper ions. However, electrochemical reduction of compound **C4** did not yield the desired dicopper(I) compound.

In 2011, Duboc et al. reported the two dinuclear copper dithiolate compounds **C5a** and **C5b**, which were characterized by X-ray crystallography, UV-vis and EPR spectroscopy [20]. Crystal structures show that the two copper ions in both compounds are in trigonal-pyramidal geometries with a $[Cu_2S_2]$ diamond core. Compound **C5a** contains two Cu(I) centers, whereas **C5b** is mixed-valent, containing a Cu(I) and a Cu(II) center. The Cu···Cu distance in **C5a** is 2.6378(14) Å, which is much shorter than in **C5b** (2.9349(11) Å). EPR spectra of **C5b** revealed a seven-line hyperfine splitting pattern, similar to the EPR spectra of Cu_A active sites.



Scheme 1.2. Reported synthetic models as mimics of the Cu_A active site. References are provided in the text.

The mimics reported by Duboc are based on "N_2S_2"-type ligands, resulting in coordination geometries different from that of the copper ions in Cu_A active sites, which are in "NS_2" environments with an additional methionine or a backbone carbonyl group at a longer distance. The additional nitrogen donor in the mimics results in different geometries of the copper centers compared to those in Cu_A. Hence, further study of synthetic models for Cu_A active sites centered on reducing the coordination number of the copper centers. In the last few years, Warren et al.

reported the synthesis of a dicopper(I) dithiolate compound **C6** containing a carbene ligand and 1,3-propanedithiolate as a bridging ligand [21]. The length of the dithiolate ligand is crucial for generating the desired [Cu_2S_2] diamond core; the dinuclear **C7** was formed instead with the longer 1,4-butanedithiolate ligand. The Cu···Cu distance in **C6** is 2.8387(15) Å. Oxidation of compound **C6** led to the formation of the desired mixed-valent dicopper(I,II) dithiolate compound, which shows EPR spectra similar to that of Cu_A active sites. Unfortunately, a crystal structure of the oxidized compound could not be obtained.

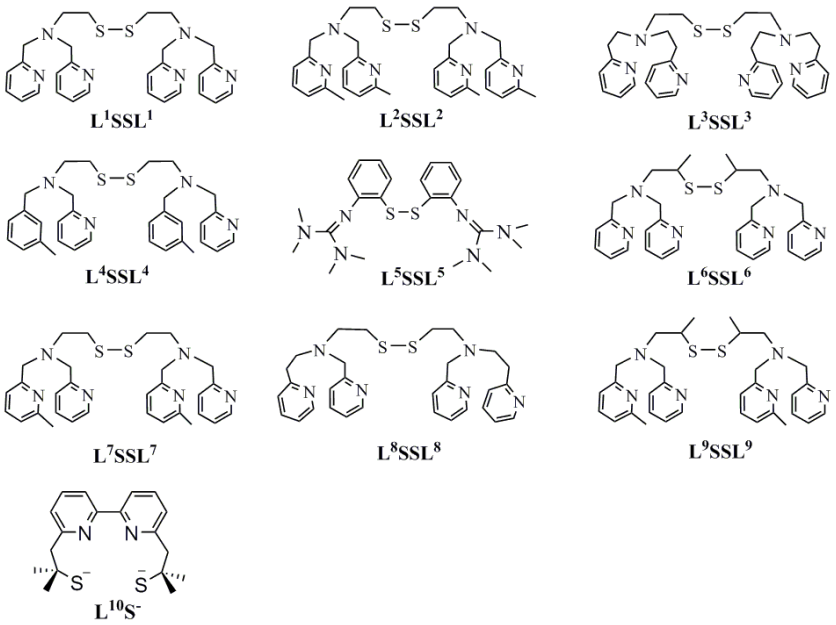
The two other examples **C8** and **C9** with diamond core structures (scheme 1.2) are not further discussed in [22, 23].

1.4 Redox interconversion between metal thiolate/disulfide compounds

1.4.1 General introduction

The study of synthetic models of Cu_A active sites provides useful information on the structure and spectroscopic properties of these copper proteins; however, the operation principle of the electron-transfer reactions occurring in metalloenzymes is still not well understood [24]. In the last decades, several mechanisms have been proposed for the electron-transfer reactions occurring in copper proteins [25-27]. For instance, copper delivery to the Cu_A site of cytochrome c oxidase (CcO) involves Sco proteins; the potential mechanism has been proposed to involve thiolate–disulfide interconversion of two cysteine residues [28, 29]. Metallothionein Zn_7MT-3 has been reported to exchange its Zn(II) ions with Cu(II) centers of amyloid-β peptide (CuAβ). 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 [28, 30].

The formation of Cu(I) disulfide compounds from the reaction of thiolate ligands with Cu(II) salts provides a potential chemical strategy to investigate the thiolate–disulfide interconversion reaction. In the last decade, a number of dinuclear Cu(II) thiolate compounds have been synthesized, and the redox interconversion of these Cu(II) thiolate compounds to their isomeric Cu(I) disulfide compounds have been investigated (scheme 1.3). Until now, several triggers have been found to influence the thiolate/disulfide interconversion, such as the addition of halide ions or protons, as well as changes in temperature, or the polarity of the solvents used. In addition, also the ligand structure has a distinct influence on the redox interconversion reaction.



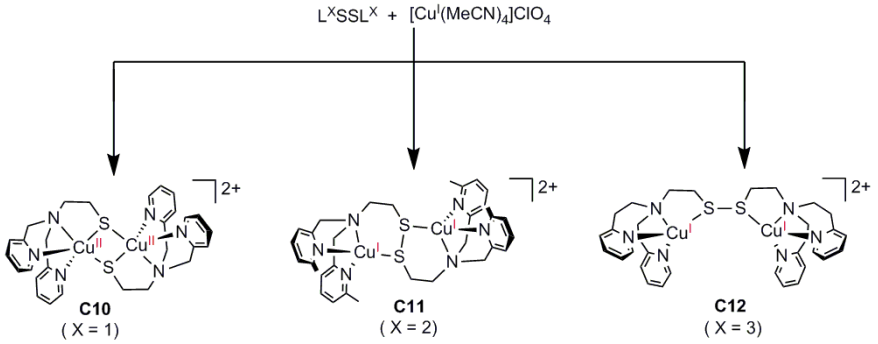
Scheme 1.3. Reported ligands for the synthesis of Cu(II) thiolate or Cu(I) disulfide compounds.

1.4.2 Ligand-induced redox interconversion

Thiolate ligands proved to be efficient reductants for the synthesis of Cu(I) compounds [16, 31]. As discussed above, the ratio of thiolate ligand and Cu(II) salt is crucial to yield the mixed-valent compound **C4** [19].Another mononuclear Cu(I) compound was synthesized from a Cu(II) salt, with the ligand acting as the reductant [31]. The first paper reporting the synthesis of dinuclear Cu(II) thiolate and Cu(I) disulfide compounds starting from disulfide ligands was published by the group of Itoh in 2001 (Scheme 1.4) [32]. Slight modification of the structure of the disulfide ligand yielded different compounds: use of L^1SSL^1 resulted in the Cu^{II} μ-thiolate compound **C10**, L^2SSL^2 resulted in the Cu^{I} *transoid*-disulfide compound **C11**, whereas L^3SSL^3 yielded Cu^{I} *cisoid*-disulfide compound **C12**.

Compound **C10** reveals a $[Cu_2S_2]$ diamond core with a Cu···Cu distance of 2.96 Å, which is shorter than that in **C3** [16], but similar to that in the mixed-valent dicopper(I,II) compound **C4** [19]. Compound **C10** is EPR silent, indicating a strong antiferromagnetic interaction between the Cu(II) ions. The *transoid*-disulfide dicopper(I) compound **C11** was formed when the ligand L^2SSL^2 was employed. The copper ions in **C11** are in a trigonal pyramidal geometry with a long Cu···Cu distance of 5.16 Å; the two Cu(I) ions are in *transoid* positions relative to the disulfide bond. A

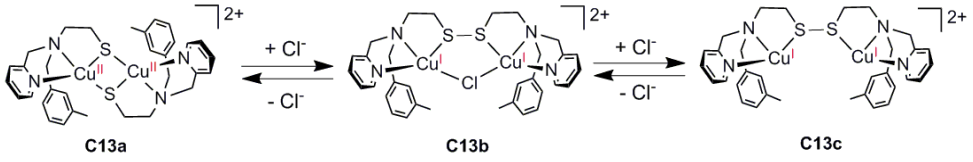
cisoid disulfide Cu(I) compound **C12** was formed when the ligand L^3SSL^3 was used. The copper ions in **C12** are also in a trigonal pyramidal geometry, with a shorter Cu···Cu distance of 3.91 Å. UV-vis and EPR spectra of both compounds **C11** and **C12** do not present any characteristic bands, in agreement with the presence of Cu(I) rather than Cu(II) centers. Generally, a *transoid* structure as found in **C11** can be regarded as a potential intermediate in the conversion of a *cisoid* structure present in **C12** to the dithiolate structure as present in **C10**, and vice versa.



Scheme 1.4. Schematic representation of the three copper compounds that were obtained from the reaction of three similar disulfide ligands with Cu(I) salt.

1.4.3 Halogen-induced redox interconversion

Treatment of the disulfide ligand L^4SSL^4 with two equivalents of $[Cu^I(CH_3CN)_4](ClO_4)$ in acetone under inert atmosphere yields the dark brown-colored bis(μ-thiolato)-dicopper(II) compound **C13a** [33]. The structure of **C13a** shows that both Cu(II) ions are in a square-pyramidal geometry with a S···S distance of 3.13 Å, which is much longer than in a disulfide S–S bond. The Cu···Cu distance is around 2.80 Å, indicating a potential interaction between the two Cu(II) ions.

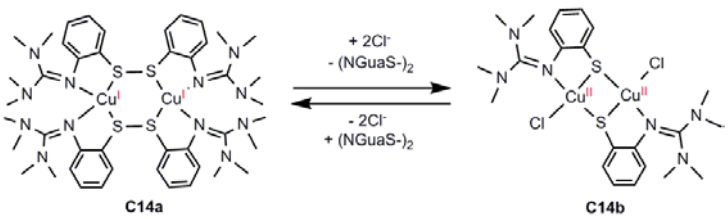


Scheme 1.5. Schematic representation of the redox interconversion between dicopper(II) thiolate **C13a** and disulfide dicopper(I) compound **C13c** mediated by chloride ion.

Upon addition of one equivalent of chloride anion to a dichloromethane solution of **C13a**, the dicopper(I) disulfide compound **C13b** was obtained, which further converted to **C13c** upon addition of another equivalent of chloride (scheme 1.5). The

removal of chloride ions from **C13c** led to the regeneration of compound **C13a** via the intermediate **C13b**.

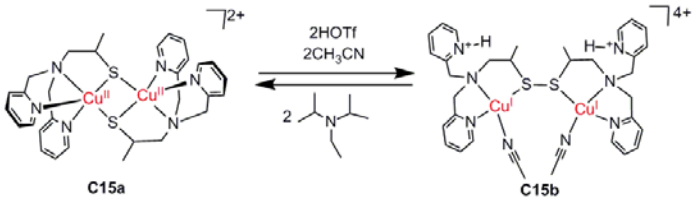
Another example of halogen-induced redox interconversion was reported by the group of Henkel in 2012 (Scheme 1.6) [34]. The Cu(I) disulfide compound **C14a** was synthesized from the disulfide ligand L^5SSL^5, in which the Cu(I) ions are in four-coordinate tetrahedral geometries. In contrast to the results reported by Itoh, addition of chloride anions (in the form of Et_4NCl) to the dichloromethane solution of compound **C14a** led to the formation of the dicopper(II) dithiolate compound **C14b** with the loss of one of the ligands. Removal of chloride anions from **C14b** in the presence of additional ligand resulted in the regeneration of **C14a**. Further experiments showed that this interconversion can also be triggered by bromide anions.



Scheme 1.6. Schematic representation of the redox interconversion of compounds **C14a** and **C14b** induced by chloride ions.

1.4.4 Solvent- and proton-induced redox interconversion

Already in 2004, the group of Itoh reported that either a Cu(I) disulfide or the corresponding Cu(II) thiolate compound was formed depending on the coordinating abilities of the used solvent [35]. Recently, the group of Stack reported the Cu(II) thiolate compound **C15a** to be formed from a reaction of the ligand L^6SSL^6 with a Cu(I) salt. (Scheme 1.7) [36]. UV-vis combined with X-ray absorption spectroscopy (XAS) showed that in acetonitrile solution the Cu(I) species **C15b** is formed, whereas the Cu(II) compound **C15a** is the dominant species in less-coordinating solvents such as acetone. Addition of two equivalents of trifluoromethanesulfonic acid (HOTf) into a solution of **C15a** in acetonitrile leads to full conversion of the Cu(II) thiolate compound to the corresponding Cu(I) disulfide compound **C15b**, and this reaction can be reversed by addition of a base such as N,N-diisopropylethylamine (DIPEA). This redox reaction also occurs for the disulfide ligand L^1SSL^1 in presence of copper salts.

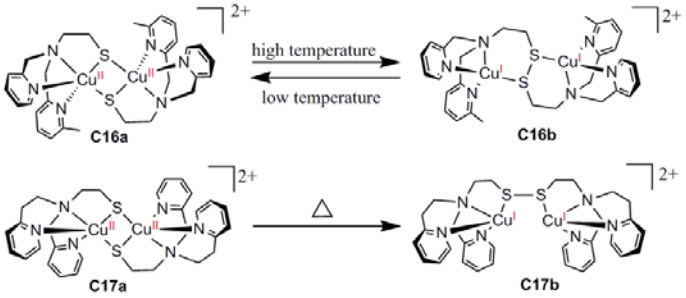


Scheme 1.7. Schematic drawing of the redox interconversion between a Cu^{II} thiolate species to a Cu^{I} disulfide species upon addition of HOTf/DIPEA.

Recently, a similar study was conducted by our group using the disulfide ligands L^6SSL^6, L^7SSL^7, L^8SSL^8, and L^9SSL^9 [37, 38]. It was found that use of polar solvents such as acetonitrile generally results in the formation of Cu(I) disulfide compounds, whereas the use of less polar solvents like acetone stabilize the corresponding Cu(II) thiolate compounds. In contrast to the study reported by the group of Stack , it was found that addition of acid into a solution of the Cu(II) thiolate compound of the ligand L^6SSL^6 leads to the protonation and dissociation of the disulfide ligand with the release of Cu(I) ions. This result was corroborated by DFT calculations.

1.4.5 Temperature-induced redox interconversion

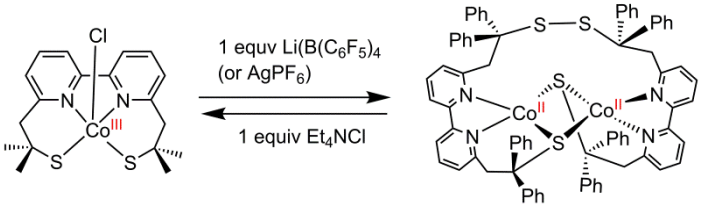
The first temperature-induced redox interconversion between Cu(II) thiolate and Cu(I) disulfide compounds was reported by our group in 2014 [38]. Compound **C16a** obtained from L^7SSL^7 was shown to undergo solvent-dependent redox interconversion to **C16b**, but in addition showed a temperature-induced redox interconversion. At low temperatures in methanolic solutions, the Cu(II) compound **C16a** is the dominant species, whereas at higher temperatures, the Cu(I) disulfide **C16b** is predominant. However, this interconversion is only reversible below room temperature; at higher temperatures a Cu(I) species is irreversibly formed, presumably with a transoid conformation. Furthermore, Cu(II) compound **C17a** was obtained from the disulfide ligand L^8SSL^8 in methanolic solution [38]. Increasing the temperature of the solution containing compound **C17a** until reflux led to the formation of Cu(I) disulfide compound **C17b**, but reduction of the temperature did not lead to recovery of **C17a**, as confirmed by X-ray structure and UV-vis spectroscopy. Apparently, **C17a** is a kinetic product, which is converted to the thermodynamic Cu(I) disulfide compound **C17b** at higher temperatures.



Scheme 1.8. Schematic drawing of the redox interconversion between a Cu(II) thiolate species to a Cu(I) disulfide species triggered by temperature.

1.4.6 Redox interconversion between cobalt thiolate/disulfide compounds

In the last few years, the study of redox interconversion reactions between metal thiolate and disulfide compounds has gradually switched from copper to other first-row transition metals. The first examples of the interconversion reaction between Co(III) thiolate and Co(II) disulfide compound was reported by the group of Duboc [39, 40]. The unusual triplet-spin (S = 1) Co(III) thiolate compound **C18a** was synthesized electrochemically. It was shown that removal of chloride anions from this Co(III) compound by addition of $Li(B(C_6F_5)_4)$ or $AgPF_6$ resulted in the formation of the Co(II) disulfide compound **C18b**, whereas addition of chloride anions to compound **C18b** led to the regeneration of **C18a**. Similar reactivity was reported for the Mn(III) thiolate compound based on the same ligand [41].



Scheme 1.9. Schematic representation of the redox interconversion between mononuclear Co(III) compound **C18a** and dinuclear Co(II) compound **C18b** induced by removal or addition of chloride ions.

1.5 Aim and outline of this thesis

The synthesis of Cu(II) thiolate compounds and the investigation of their redox interconversion to the corresponding Cu(I) disulfide compounds has been extensively studied in the last decade, providing improved understanding of the mechanism of electron-transfer reactions occurring in metalloenzymes. However, until now, only limited research focused on metals other than copper, whereas especially cobalt, iron

and manganese redox processes may be similarly important. The goal of the research described in this thesis is to extend the study of redox interconversion reactions from copper to other first-row transition metal ions. In Chapter 1, several types of metalloenzymes are introduced, which are involved in electron-transfer reactions in biological systems. An overview is provided of synthetic models of Cu_A active sites, including their structural and spectroscopic properties. Finally, the state-of-the-art in redox interconversion reactions between metal thiolate and disulfide compounds has been described.

In Chapter 2, our investigation is reported of redox interconversion between Co(II) disulfide and Co(III) thiolate compounds, induced by chloride anions. The formation of mononuclear rather than dinuclear Co(III) compounds is discussed, and supported by DFT calculations. Moreover, the possible formation of iron(II) disulfide and iron(III) thiolate compounds has been explored and the results are compared with that of the cobalt compounds.

In Chapter 3, the redox interconversion reaction between Co(II) disulfide and Co(III) thiolate compounds tuned by solvents is described. In contrast to the redox interconversion between Cu(II) thiolate and Cu(I) disulfide compounds, Co(III) compounds are formed in coordinating solvents such as acetonitrile, whereas Co(II) disulfide compounds are obtained in weakly- or non-coordinating solvents like acetone and dichloromethane.

The study of the oxidation of Co(II) and Fe(II) disulfide compounds is described in Chapter 4. Oxidation of a Co(II) disulfide compound with dihydrogen peroxide yielded a Co(III) sulfinate compound as the final product. It was found that a Co(III) sulfenato derivative is generated as an intermediate, as confirmed by X-ray structure and ESI-MS spectrometry. Oxidation of an iron(II) disulfide compound with dihydrogen peroxide resulted in the formation of an iron(III) sulfonato compound, and studies at low temperature indicated that sulfenato and sulfinato compounds are generated as intermediates.

In Chapter 5, the synthesis and characterization of a novel tetranuclear fluorido-bridged iron(II) compound is described. This compound was obtained from a reaction of a disulfide ligand with iron(II) tetrafluoridoborate, during which the iron(II) center abstracts fluoride ions from the tetrafluoridoborate anion.

The synthesis and characterization of a series of mononuclear transition metal compounds is described in Chapter 6. Their structure and spectroscopic properties are compared with those of related dinuclear compounds.

Finally, in Chapter 7 a summary is presented of the main findings described in this thesis, followed by an outlook, and suggestions for further research in this field is given.

Parts of this thesis have been published (Chapters 2, 4, 5 and 6) [42-45], or is in preparation for submission (Chapter 3).

1.6 References

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