Reactivity of cobalt(II)-dichalcogenide complexes: correlation between redox conversion and ligand-field strength

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Chapter 1

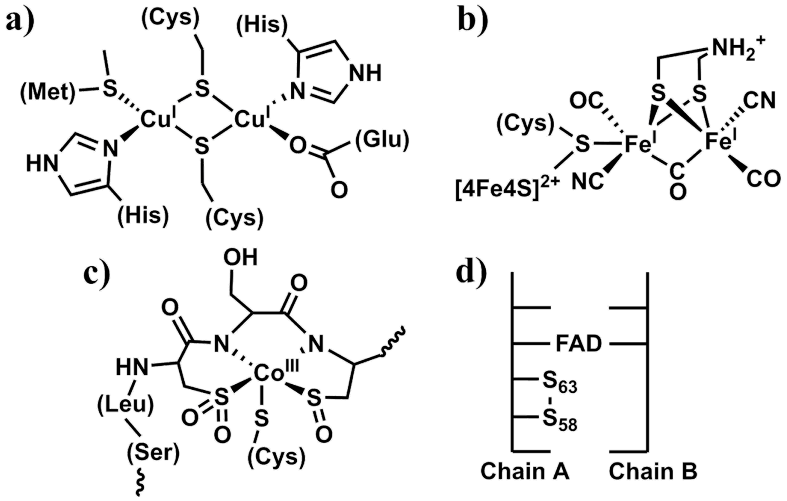
Biomimetic Models of Sulfur-containing Enzymes and a Bioinspired Redox-conversion Reaction

1.1. Introduction

1.1.1. Sulfur-Containing Enzymes

The presence of the element sulfur in biological systems is prominent, in both structural and functional roles. Due to its chemical versatility, in biological systems sulfur can be present as inorganic sulfur (S^{2-}) in iron-sulfur clusters, a thiol group in cysteine (R−SH), a thioether (R–S–R') in methionine, a disulfide e.g. in oxidized glutathione (R−SS−R), or as the partially oxygenated sulfur group (R−SO_x) in e.g. nitrile hydratases.[1, 2]

The sulfur-containing species are utilized by Nature in the form of enzymes, which catalyze various biological processes. Examples of such enzymes are cytochrome *c* oxidase (C*c*O; **Scheme 1.1**.**a**), ferredoxin hydrogenase (**Scheme 1.1**.**b**), nitrile hydratase (NHase; **Scheme 1.1**.**c**), glutathione reductase (GR; **Scheme 1.1**.**d**), and many others.[3-12] The CuA site of cytochrome *c* oxidase contains two copper(I) metal centers, each coordinated to a nitrogen atom of histidine moieties and two bridging cysteine thiolates in a diamond-like structure. The structure of the [Fe−Fe] subunit in ferredoxin hydrogenase in the reduced state consists of two iron(I) centers with a bridging CO and an azadithiolate ligand along with several



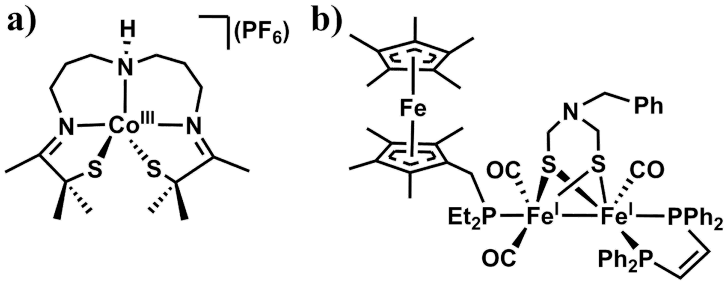
Scheme 1.1. Schematic representations of the a) CuA active site in cytochrome c oxidase (PDB: 5Z62), b) reduced state of the [Fe−Fe] active site in ferredoxin hydrogenase (PDB: 3C8Y and 1HFE), c) cobalt(III)-containing active site of homology model of nitrile hydratase (PDB: 1IRE), and d) simplified active site of glutathione reductase. Figures are adapted from references [3-12].

terminal CO and CN ligands. The [Fe−Fe] subunit is also bound to a $[4Fe4S]^{2+}$ cubane cluster. Nitrile hydratases catalyze the conversion of nitriles to amides. Two types of nitrile hydratases have been reported, one with iron(III) as the metal center and the other with cobalt(III). The structures of cobalt NHases are similar to the structure of iron NHase based on the homology model of Fe-NHases, which contains a cobalt(III) center coordinated by two deprotonated peptide nitrogen atoms and two S-oxygenated cysteines.[13-15] The catalytic cycle of glutathione reductase utilizes the reduction of disulfide bonds into thiols and reoxidation to generate the original species.[16]

1.1.2. Modelling the Active Sites of Sulfur-Containing Enzymes

The generation of understanding of the working mechanism of enzymes is challenging. Ideally the structure of the enzymes needs to be elucidated, which is an arduous job as crystallization of enzymes is difficult. Even when the structures of enzymes can be determined, correlating the structure to the activity is another immense obstacle. Therefore, in bioinorganic chemistry efforts are made to understand the working mechanism of enzymes using synthetic models. Such synthetic models are usually small molecules that are designed to resemble the structure of the active site of the enzyme of interest. Hence, by studying synthetic models one can potentially clarify the working mechanism of the enzyme of interest.[17, 18]

The group of Kovacs reported the five-coordinated cobalt(III) compound $[Co^{III}(S_2{}^{Me2}N_3(Pr,Pr))](PF_6)$ (**Scheme 1.2**.**a**) and its analog $[Fe^{III}(S_2{}^{Me2}N_3(Pr,Pr))](PF_6)$ with an accessible binding site for a substrate or inhibitor of the active site of nitrile hydratase.[15,



Scheme 1.2. Schematic representations of synthetic models of a) cobalt NHase,[15] b) [Fe−Fe] hydrogenase.[21]

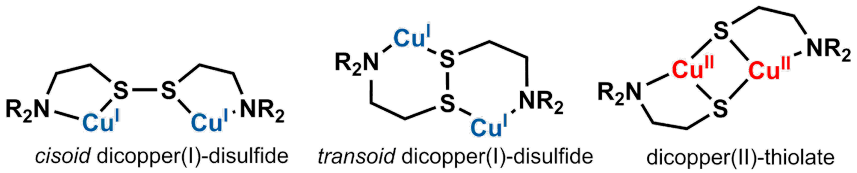
[19, 20] It was reported that several substrates such as azide (NHase inhibitor), ammonia, and thiocyanate (nitrile mimic) can coordinate and subsequently dissociate from the metal center. Other inhibitors such as butyrate or NO (NHase inactivator) did not bind to the cobalt center, but did bind to the iron analog. The results of the study indicated that different mechanisms of enzyme activation and inactivation may be operative for Co-NHase and Fe-NHase, as shown by the binding ability of several biologically relevant substrates towards the model. It was concluded that the thiolate donor *trans* to the vacant site could aid the catalytic process via the *trans* labilizing effect.

An example of a biomimetic model for ferredoxin hydrogenase is depicted in **Scheme 1.2**.**b**. The dinuclear iron site is highly similar to the [Fe−Fe] subunit of the enzyme, containing two iron(I) centers bridged by an azadithiolate ligand, coordinated with CO and a diphosphine ligand.[7, 21] A ferrocene complex modified with a phosphine group coordinated to one of the iron centers was introduced to mimic the function of $[4Fe4S]^{2+}$ group as an electron shuttle. Small molecules such as CO and hydrogen can coordinate to the iron centers, in line with the current proposed catalytic mechanism of [Fe-Fe] hydrogenase.[22, 23]

1.1.3. Mimicking Copper(II)-thiolate Active Sites: The Reaction of Cu(I) Salts with Disulfide Ligands

Inspired by the native enzyme cytochrome *c* oxidase, a number of reports describe efforts to construct a synthetic model of the dinuclear copper-bis-μ-thiolate active site. It is challenging to isolate copper(II)-thiolate species, as generally copper(II) ions in combination with thiolate groups readily undergo an irreversible redox reaction forming copper(I) ions and a disulfide species. The very first dinuclear copper(II)-μ-thiolate complex containing a single thiolate bridge was reported in 1985.[24] A decade later, the group of Tolman reported the first copper(II)-bis-μ-thiolate compounds comprising diamond-shaped Cu_2S_2 cores, using an N_3S donor ligand as well as an N_2S donor ligand.[25]

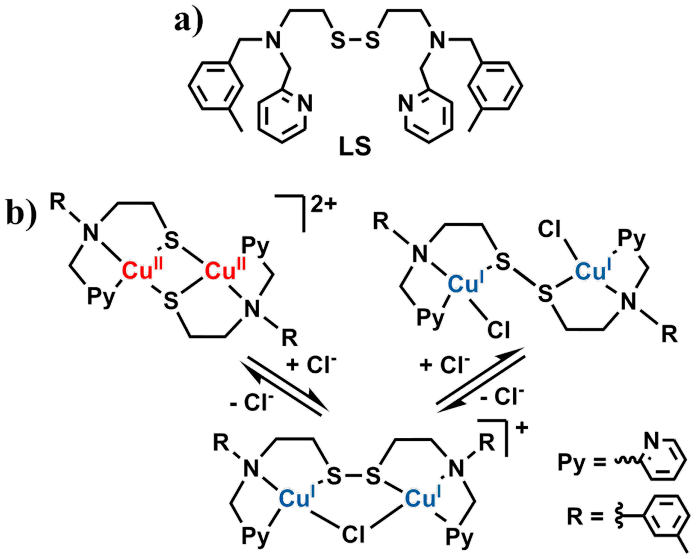
It was not until the early 2000s that the group of Itoh described the unique reverse redox reaction between copper(I) ions and disulfide ligands.[26] It was found that the disulfide bond of a specific chelating ligand can be reduced by copper(I) ions, resulting in the corresponding dicopper(II)-bis-μ-thiolate species.[26] It was described that slight structural changes of the ligand yielded different species with different coordination geometry, namely either a



Scheme 1.3. Different coordination geometries of copper compounds with disulfide and thiolate ligand, adapted from reference [26].

cisoid-dicopper(I)-disulfide, a *transoid*-dicopper(I)-disulfide, or a dicopper(II)-μ-thiolate compound (**Scheme 1.3**). The structural changes in the ligand affect the donor ability of the pyridine nitrogens of the ligand, consequently influencing the electron density at the copper(I) ions and subsequent electron transfer to the disulfide group.

The discovery of how slight changes of the disulfide ligand affect which copper complex is generated led to a report of the first reversible redox-conversion reaction of a copper(I)-disulfide compound with the corresponding copper(II)-thiolate complex.[27] The reaction in acetone of $[Cu(CH_3CN)_4](ClO_4)$ with the dissymmetric disulfide ligand **LS**, containing pyridyl and m-tolyl groups (**Scheme 1.4.a**) afforded a dicopper(II)-bis-μ-thiolate complex. The clean conversion of the dicopper(II)-bis-μ-thiolate complex to



Scheme 1.4. a) Schematic drawing of the ligand **LS** used in the first reported redox-conversion reaction of a copper(I)-disulfide to a copper(II)-thiolate complex, b) Chloride-induced redox-conversion reaction between copper(I)-disulfide/copper(II)-thiolate with ligand **LS**. [27]

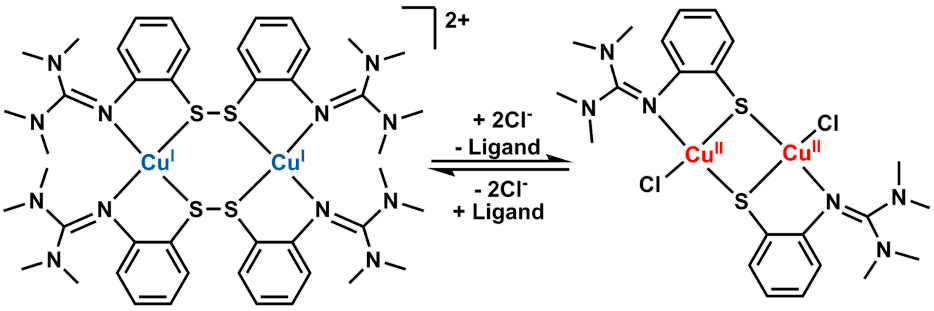
cisoid-dicopper(I)-disulfide complex and further to a *transoid*-dicopper(I)-disulfide complex was achieved by stepwise addition of coordinating chloride ions (**Scheme 1.4.b**). Interestingly, the *transoid*-dicopper(I)-disulfide complex can be reverted to the dicopper(II)-bis-μ-thiolate complex by removal of the chloride ions using a silver salt, showing that this specific redox-conversion reaction is a reversible process.

1.2. The Metal-disulfide to Metal-thiolate Redox-conversion Reaction

1.2.1. Copper-based Systems

Since the report of the novel redox-conversion reaction between the dicopper(I)-disulfide and dicopper(II)-dithiolate compounds by Itoh in 2002, several attempts to obtain reversible redox systems have been successful, using different ligand systems. The Henkel group reported the synthesis of a dinuclear copper(I)-bis-μ-disulfide complex upon the reaction of $[Cu(MeCN)_4]OTf$ with one equivalent of the disulfide ligand $(NGuaS)_2$ in acetonitrile.[28] Upon addition of two equivalents of NEt_4Cl in dichloromethane, blue crystals of the dinuclear copper(II)-bis-μ-thiolate species were obtained. This copper(II)-thiolate species is also obtained upon reaction of the disulfide ligand $(NGuaS)_2$ with two equivalents of copper(I) chloride (**Scheme 1.5**). The reaction from the dicopper(II)-bis-μ-thiolate compound to copper(I)-bis-μ-disulfide complex can be achieved by addition of silver tetrafluoridoborate, but additional disulfide ligand has to be added to replace the chloride ions.

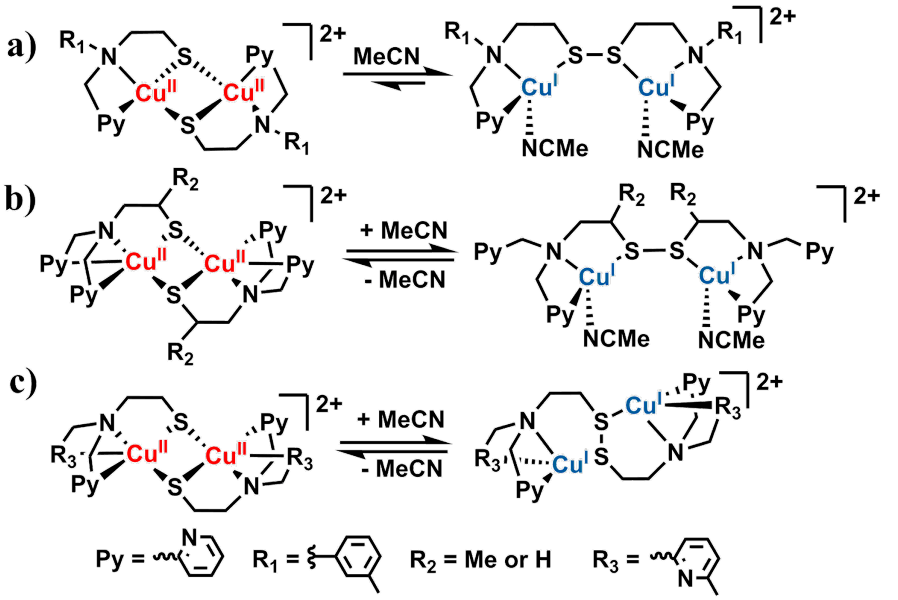
Aside from the addition or removal of chloride ions, the use of solvent has been reported to trigger the redox-conversion reaction between Cu(I)-disulfide and Cu(II)-thiolate complexes. At the time of writing of this Chapter, three reports describe copper compounds of five



Scheme 1.5. Schematic representation of the redox-conversion between a Cu(I)-disulfide and a Cu(II)-thiolate compound based on the disulfide ligand $(NGuaS)_2$ influenced by chloride ions.[28]

different ligands that are either in the Cu(I)-disulfide or Cu(II)-thiolate form, depending on the solvent used during the reaction.[29-31] The group of Itoh reported that a copper(II)-bis-μ-thiolate compound can be fully converted to the corresponding copper(I)-disulfide complex by changing the solvent (**Scheme 1.6.a**). The copper(II)-bis-μ-thiolate compound is stable in a relatively nonpolar and non-coordinating solvent such as dichloromethane. Replacement of the non-coordinating solvent by the more polar and weakly coordinating solvent acetone afforded a mixture of the copper(II)-thiolate and copper(I)-disulfide complexes. When the more polar and coordinating solvent acetonitrile (MeCN) was used, the copper(II)-thiolate compound was fully converted to the corresponding copper(I)-disulfide complex.

Similarly, the group of Stack reported the acetonitrile-induced redox-conversion of a Cu(II)-bis-μ-thiolate complex to the corresponding Cu(I)-disulfide complex (**Scheme 1.6.b)**).[30] However, in this reaction two of the coordinating pyridine groups need to

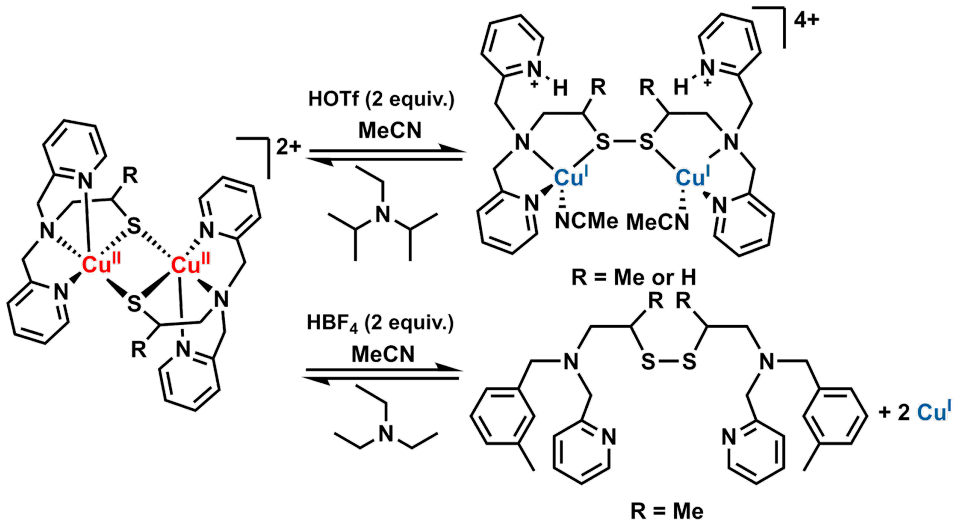


Scheme 1.6. Schematic representations of solvent-induced redox-conversion between copper(I)-disulfide and copper(II)-thiolate compounds from a) group of Itoh,[29] b) group of Stack,[30] c) group of Bouwman.[31]

dissociate, and competition between coordination of the pyridine groups and acetonitrile resulted in equilibrium mixtures of the copper(II)-thiolate and copper(I)-disulfide species.

The acetonitrile-induced redox-conversion between copper disulfide and thiolate compounds has also been reported by our group (**Scheme 1.6.c**).[31] However, for the dissymmetric demethylated ligand used in our studies the conversion was not accompanied by the displacement of pyridyl groups with the solvent. The conformation of the resulting Cu(I)-disulfide compound appeared to be *transoid*, in contrast with previous reports where the resulting Cu(I)-disulfide compound is in the *cisoid* conformation. The DFT-calculated formation energy showed that formation of the *transoid* isomer is indeed possible, although the *cisoid* isomer is thermodynamically more stable.

A rather unexplored manner of triggering the redox-conversion process is by using protons. The group of Stack reported that reaction of the dicopper(II)-bis-μ-thiolate complex shown in **Scheme 1.6.b** with triflic acid (HOTf) in acetonitrile afforded the copper(I)-disulfide complex (**Scheme 1.7**).[30] The reaction was also reported to be reversible using diisopropylethylamine (DIPEA) as a base to deprotonate the pyridinium group, followed by

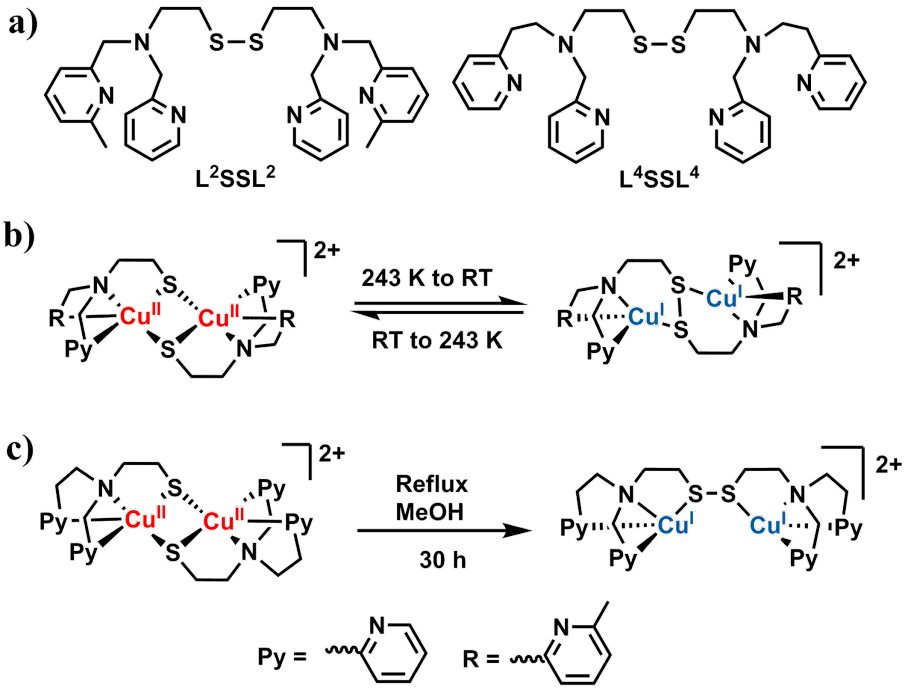


Scheme 1.7. Schematic representation of the reversible redox-conversion of copper(I)-disulfide and copper(II)-thiolate complexes induced by the addition of protons or a base.[30, 32]

re-coordination of the pyridine group to the copper(I), promoting the electron transfer to the disulfide group and yields the initial copper(II)-thiolate complex.

At the same time similar studies were also performed in our group. Addition of tetrafluoridoboric acid (HBF_4) to the Cu(II)-thiolate complex (**Scheme 1.7**) was monitored using UV-Visible and ^{1}H-NMR spectroscopy.[32] The addition of the acid resulted in sharper proton peaks in ^{1}H-NMR spectrum, indicating the formation of Cu(I) species. In contrast to the report of Stack's group, it was observed that the ligand dissociates from the copper centers. DFT studies showed that dissociation of the diprotonated ligand is favored by more than 100 kJ mol^{-1} over the formation of a diprotonated Cu(I)-disulfide complex.

Reaction of L^2SSL^2 (**Scheme 1.8.a**) with $[Cu(MeCN)_4]^+$ in methanol results in formation of an equilibrium mixture of the related copper(II)-thiolate and copper(I)-disulfide compounds. UV-Vis spectroscopy of this mixture showed significant changes in the absorption bands

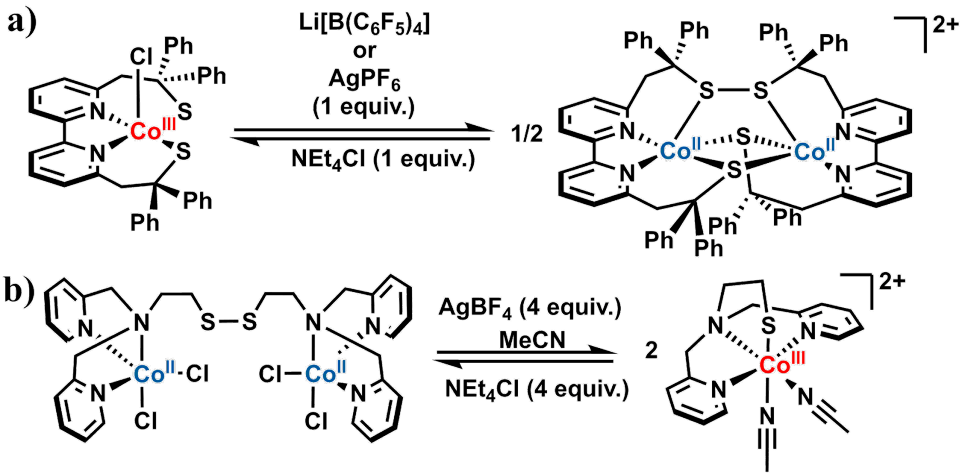


Scheme 1.8. a) Structure of the ligand L^2SSL^2 and L^4SSL^4 used for temperature-induced redox-conversion of copper(I)-disulfide/copper(II)-thiolate; Reaction schemes of temperature-induced redox-conversion of copper(I)-disulfide / copper(II)-thiolate complex of ligand b) L^2SSL^2 and c) L^4SSL^4.[31]

upon cooling the solution, indicating a shift in the equilibrium to the Cu(II)-thiolate compound (Reaction **Scheme 1.8.b**).[31] Heating the solution back to room temperature re-established the original spectra, indicating a temperature-induced redox equilibrium. Heating the solution further resulted in the formation of the Cu(I)-disulfide compound. Thus, the Cu(I)-disulfide / Cu(II)-thiolate conversion is reversible in methanol at low temperatures, but irreversible after exposure to higher temperatures. The use of L^4SSL^4 (**Scheme 1.8.a and Scheme 1.8.c**) resulted in the similar observations, i.e. upon heating the Cu(I)-disulfide compound was irreversibly formed.

1.2.2. Cobalt-based Systems

In the last few years, the study of the redox-conversion reaction between metal-thiolate and metal-disulfide complexes has progressed to systems containing other redox-active metal centers. One of the interesting metals to study is cobalt, because of its presence in enzymes such as Co-NHase, as described in Section 1.1.1. The redox-conversion between cobalt(II)-disulfide and cobalt(III)-thiolate compounds was first reported by the group of Duboc in 2014.[33] Via electrochemical methods a mononuclear cobalt(III) complex was obtained of a dianionic N_2S_2 donor ligand. This five-coordinate cobalt(III) complex is in an unusual high-spin state ($S = 3/2$). Removal of the axial chloride ions using $Li[B(C_6F_5)_4]$ or $AgPF_6$ generated the (bis-μ-thiolate)-μ-disulfide cobalt(II) complex as shown in

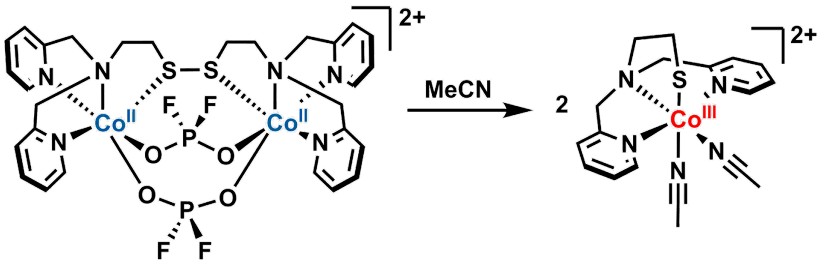


Scheme 1.9. Schematic representations of chloride-induced redox-conversion of cobalt complexes from a) Duboc's group,[33] b) Bouwman's group.[34]

Scheme 1.9.a. This dinuclear, five-coordinate cobalt(II) complex can also be generated by exhaustive electrolysis at 0 V vs Fc^+/Fc of the mononuclear cobalt(II)-thiolate compound in dichloromethane. The Co(II)-disulfide compound reverts to the Co(III)-thiolate complex upon addition of chloride ions, and the reversibility is maintained up to ten cycles without loss of conversion.

The ligand L^1SSL^1, which was first used in the study of copper-based redox-conversion, in a reaction with cobalt(II) chloride resulted in the formation of the cobalt(II)-disulfide complex $[Co_2(L^1SSL^1)Cl_4]$, in which the cobalt(II) ions are in a trigonal bipyramidal geometry.[34] Removal of the chloride ions using $AgBF_4$ in acetonitrile afforded the mononuclear, six-coordinate cobalt(III)-thiolate complex, $[Co(L^1S)(MeCN)_2]^{2+}$ as shown in **Scheme 1.9.b**. This cobalt(III)-thiolate complex can also be generated by the reaction of L^1SSL^1 and $[Co(MeCN)_6](BF_4)_2$ in acetonitrile, and can be converted to the cobalt(II)-disulfide complex by addition of NEt_4Cl. The addition or removal of chloride ions thus has an opposite effect compared to that in Duboc's system.

The cobalt(II)-disulfide compound $[Co_2(L^1SSL^1)(PF_2O_2)_2](PF_6)_2$ containing the unusual bridging $PF_2O_2^-$ anion is stable as such in dichloromethane (nonpolar and non-coordinating solvent) and methanol (polar and weakly coordinating solvent), but converts to the cobalt(III)-thiolate compound $[Co(L^1S)(MeCN)_2]^{2+}$ when dissolved in acetonitrile (polar and coordinating solvent) (**Scheme 1.10**.).[35] In contrast, the partially methylated cobalt(II)-disulfide compound $[Co_2(L^2SSL^2)(PF_2O_2)_2](PF_6)_2$ is stable as such in acetonitrile and does not convert to the corresponding Co(III)-thiolate complex. Similarly, reaction of L^2SSL^2 with $Co(SCN)_2$ did not result in formation of the expected cobalt(III)-thiolate



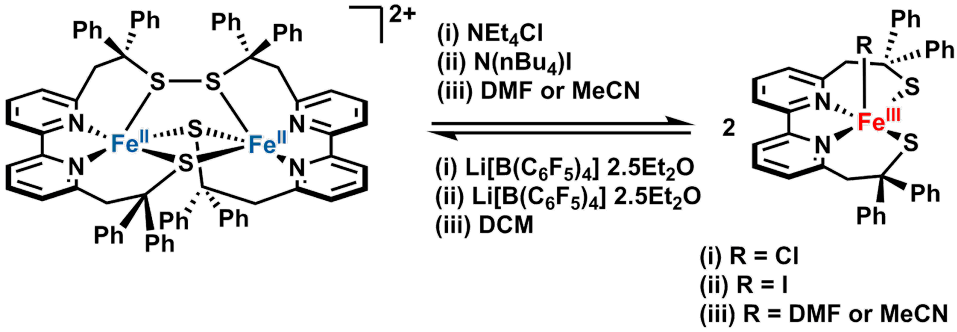
Scheme 1.10. Schematic representation of the redox-conversion of $[Co_2(L^1SSL^1)(PF_2O_2)_2]^{2+}$ in acetonitrile.[35]

complex whereas the cobalt(III)-thiolate complex $[Co(L^1S)(NCS)_2]$ is formed upon reaction of L^1SSL^1 with $Co(SCN)_2$ regardless of the solvent used.[34, 35] The compounds $[Co_2(L^1SSL^1)(NO_3)_4]$ and $[Co_2(L^2SSL^2)(NO_3)_4]$ with the strongly coordinating anion NO_3^- are stable as such in both methanol and acetonitrile. Thus, it appears that coordination of acetonitrile to the cobalt(II)-disulfide compounds leads to redox isomerization, but only as long as relatively stronger coordinating ligands are absent.

1.2.3. Systems Based on Other Metal Ions

Redox-conversion in manganese and iron systems has been reported by the group of Duboc, using the same ligand as described in Section 1.2.2 for cobalt.[36, 37] The conversion of (bis-μ-thiolate)-μ-disulfide dimanganese(II) (isostructural to the cobalt(II) compound shown in **Scheme 1.9.a**) to the mononuclear Mn(III)-dithiolate compound was achieved by addition of halide ions in the non-coordinating solvent dichloromethane; however, the reaction did not go to completion, as approximately 30% of the manganese(III)-thiolate compound was obtained after 16 hours. The ease of the redox-conversion reaction of the manganese system was estimated by computing the Gibbs free energy of the thiolate compounds at 0 K. The Gibbs free energy of the Mn(III)-thiolate compound is significantly higher both in the gas phase (+3.6 kcal/mol) and in CH_2Cl_2 solution (+7.9 kcal/mol) than that of the cobalt(III) system (−31.0 kcal/mol and −15.1 kcal/mol, respectively), indicating that the redox-conversion in the manganese system is less favorable compared to the cobalt system.

A redox-conversion system based on iron is interesting as generally iron(II) is more readily oxidized than cobalt(II) or manganese(II). The dinuclear, (bis-μ-thiolate)-μ-disulfide diiron(II) complex, isostructural with the cobalt(II) compound in **Scheme 1.9.a,** was shown to convert to the corresponding iron(III)-dithiolate compound upon addition of chloride ions in dimethylformamide in a quantitative yield (**Scheme 1.11**).[37] The reaction was shown to be reversible up to three times without loss of efficiency. Different results were obtained when iodide was employed, as the iodide-coordinated iron(III)-dithiolate is particularly stable and only partially reverts to the initial iron(II) complex in presence of a large excess of lithium salt (**Scheme 1.11**).[37, 38] In addition, a solvent-dependent redox-conversion for the same iron(II) complex was also reported. In non-coordinating and nonpolar solvents such as dichloromethane, the iron(II)-disulfide form is stable, whereas in more polar and



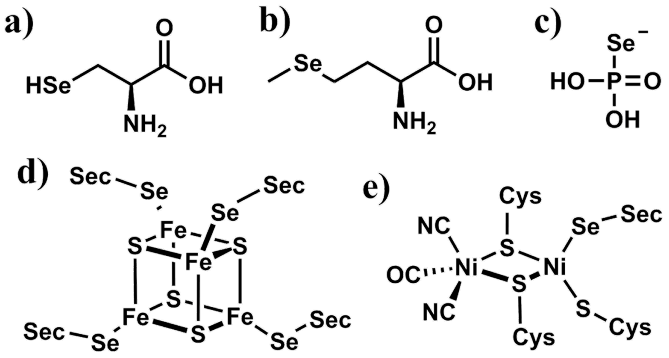
Scheme 1.11. Schematic representations of the redox-conversion between iron(II)-disulfide and iron(III)-thiolate compounds induced by chloride ions, iodide ions, or solvent molecules. Reaction conditions for (i) 2 equiv. NEt_4Cl in DMF and 2 equiv. $Li[B(C_6F_5)_4]2.5Et2O$ in DCM; for (ii) 2 equiv. $N(nBu_4)I$ in DCM and 20 equiv. $Li[B(C_6F_5)_4]2.5Et2O$.[37, 38]

coordinating solvents such as dimethylformamide (DMF) or acetonitrile the iron(III)-thiolate is formed with a coordinated solvent molecule (**Scheme 1.11**). However, the use of acetonitrile did not result in full conversion, possibly due to a lower affinity of Fe(III) for acetonitrile than for DMF.[37]

To our knowledge, currently other examples of manganese- and iron-based redox-conversion systems have not been reported. It seems that redox-conversion of manganese- and iron-based systems are also ligand-dependent. Utilization of L^1SSL^1 (shown to give redox-conversion with copper in **Scheme 1.7**, and with cobalt in **Scheme 1.9**) in combination with iron salts afforded a dinuclear iron(II)-disulfide complex; so far attempts to convert this compound to the corresponding iron(III)-thiolate complex were unsuccessful.[34]

1.3. The Analog of Sulfur: Selenium

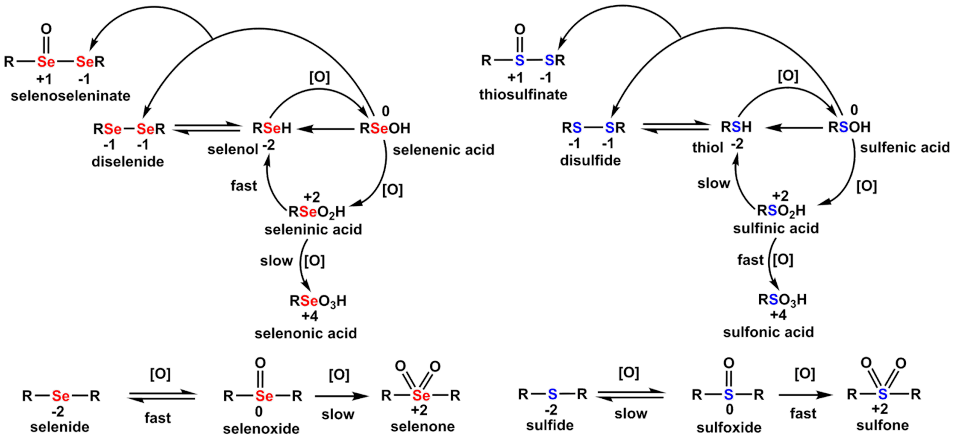
Located below sulfur in the periodic table, selenium is an element that is often described only briefly in chemistry textbooks. Selenium and its compounds, however, are extremely important and selenium is one of the most essential trace elements in the human body.[39] In the 1930s, selenium compounds were found to cause poisoning of livestock.[40] About forty years later, the very same element was discovered to be present in the 21st amino acid, selenocysteine.[41-43] Since then, the significance of selenium in biology is the topic of many investigations. Several examples of selenium in biomolecules are depicted in



Scheme 1.12. Examples of selenium in biomolecules. a) Selenocysteine (Sec),[41] b) Selenomethionine, c) Monoselenophosphate, a product of selenide and ATP (Adenosine TriPhosphate) catalyzed by SelD (Selenide, water dikinase) enzyme,[45] d) Sec as a ligand in an iron-sulfur cluster in methionine sulfoxide reductase (MsrB) homolog,[46] e) Sec as a ligand in [NiFeSe] hydrogenases.[47]

Scheme 1.12. [41, 44-47] Selenium is mostly found in selenocysteine (Sec) and acts as ligand for the metal ion in the active site of several enzymes.

The oxidation states and different oxygenated species that are known for selenium, are similar to those of sulfur (**Scheme 1.13**). However, selenium is a heavier element than sulfur, which causes a number of differences in its properties. For instance, selenium is less basic than



Scheme 1.13. Structures of several selenium and sulfur species with different oxidation states. Arrows show chemical transformation between species, and [O] symbolizes two-electron oxidation processes.[49]

sulfur,[48, 49] therefore, at the same pH, selenolates usually are better leaving groups than thiolates.[50] The π-donation of selenium compounds is usually weaker than that of sulfur compounds due to the larger ionic radius of selenium. These properties of selenium imply that its compounds are more reactive than sulfur compounds, for example the rate of the selenolate-diselenide exchange reaction is 10^7 times faster than that of the thiol-disulfide exchange reaction.[51]

The enhanced reactivity of selenium in comparison to sulfur compounds does not always make selenium a good choice as an alternative for sulfur in chemical reactions. Although several studies show that selenium compounds have antioxidant activity by scavenging reactive oxygen species (ROS),[49, 52, 53] selenium compounds are known to be more toxic than sulfur compounds, i.e. selenolates can react with dioxygen to produce superoxide radicals.[54] Selenium compounds are also more difficult to handle due to its faster redox reactions, e.g. selenolate (in the form of CH_3Se^-) is oxidized to the selenenate ion (CH_3SeO^-) using H_2O_2 with a calculated rate constant of 3.6×10^4 M^{-1} s^{-1}, whereas the rate constant for thiolate oxidation to sulfenate is only 10.2 M^{-1} s^{-1}.[55] The lower basicity of selenium compounds means that they may not be better ligands than their sulfur analogues, depending on the solvent and the pH.[48, 56]

1.4. Aim and Outline of This Thesis

The goal of the research described in this thesis is to extend the study of redox-conversion reactions in cobalt-based systems, with the aim to provide further understanding of electron transfer in the cobalt-based system and how it acts differently from the copper-based system. In this Chapter, an overview is provided of the redox-conversion reaction, starting from the first report to the state-of-the-art of these reactions. A brief introduction is also provided on selenium and its properties. The challenges and obstacles in this field of research have also been described briefly.

In Chapter 2, the results are described of experimental as well as DFT studies concerning the effectivity of the external ligands 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) in inducing a redox-conversion reaction of the cobalt(II)-disulfide complexes $[Co_2(L^1SSL^1)X_4]$ (X = Cl, Br) to the corresponding cobalt(III)-thiolate compounds. The ligands bpy and phen

were selected based on the hypothesis that redox-conversion of cobalt(II)-disulfide to cobalt(III)-thiolate may be induced by strong-field ligands.

In Chapter 3, the results are described of employment of the anionic ligand 8-quinolinolate ($quin^-$) as an external ligand, which partially compensates for the dicationic charge of the cobalt(III)-thiolate compounds. The larger estimated ligand-field strength of 8-quinolinolate compared to that of bpy might aid to obtain clean conversion of the cobalt(II)-disulfide compounds $[Co_2(L^xSSL^x)X_4]$ (x = 1 or 2) to the cobalt(III)-thiolate complexes $[Co(L^xS)(quin)]^+$.

The study of redox-conversion was taken further to the selenolate and diselenide system in order to assess potential differences with the thiolate to disulfide conversion. The synthesis of the diselenide ligand L^1SeSeL^1 is described in Chapter 4, as well as the formation of the cobalt(II)-diselenide complex $[Co_2(L^1SeSeL^1)Cl_4]$. The formation of several cobalt(III)-selenolate complexes from the cobalt(II)-diselenide $[Co_2(L^1SeSeL^1)Cl_4]$ complex were described.

The synthesis of a new pyridine-containing disulfide ligand with longer bridges between the disulfide and tertiary amines is described in Chapter 5. The reactions of this new ligand as well as two other previously reported ligands with different cobalt(II) salts were investigated. The formation of dinuclear cobalt(II)-disulfide complexes of all the ligands is reported. Combining the knowledge that we obtained from Chapters 2 – 4, the reactivity of the formed cobalt(II)-disulfide complexes was tested using the $quin^-$ ligand as an external influence.

Finally, in Chapter 6 a summary of this research is provided, as well as an outlook and suggestions for further research. Parts of this thesis have been published (Chapter 2),[57] submitted (Chapter 3)[58] or are in preparation for publication (Chapters 4 and 5).

1.5. References

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