Redox interconversion between metal thiolate and disulfide compounds

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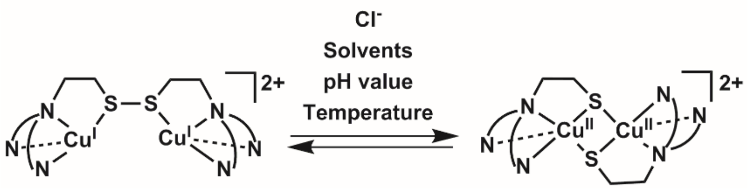
Chapter 7

Summary, Conclusion and Outlook

7.1 Summary

7.1.1 Introduction

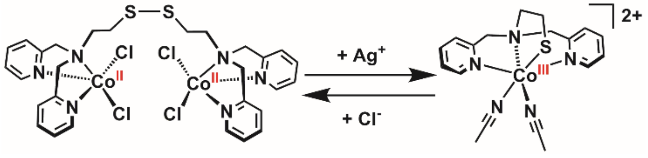
Electron-transfer reactions assisted by metalloenzymes are ubiquitous and play fundamental roles in biological systems such as dioxygen transport, nitrite reduction, as well as the synthesis of neurotransmitters [1-4]. However, understanding the exact mechanism of electron-transfer reactions occurring in metalloenzymes is still a long-term challenge [2]. In the last decades, synthetic models of enzyme active sites by well-designed ligands provided a chemical perspective into how these reactions take place [5-8]. Among them, tremendous efforts have been put in the synthesis of copper(II) thiolate compounds with a diamond core [Cu_2S_2] structure, and in the investigation of the redox interconversion of these copper(II) thiolate compounds to their isomeric copper(I) disulfide compounds (Scheme 7.1) [9-14]. These studies aimed to simulate the structure, spectroscopic properties, and electron-transfer processes of Cu_A active sites.



Scheme 7.1. Schematic representation of the redox interconversion between copper(II) thiolate and copper(I) disulfide compounds.

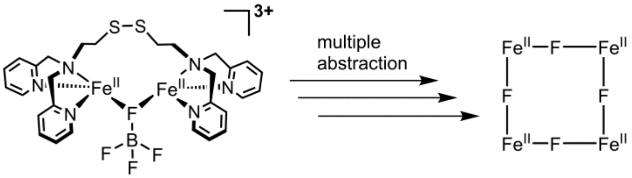
7.1.2 Redox interconversion between cobalt thiolate/cobalt(II) compounds

As described in Chapter 1, redox interconversion between copper(II) thiolate and copper(I) disulfide compounds has been extensively studied. However, only few studies have been reported concerning other transition metal compounds with disulfide/thiolate ligands. In Chapter 2, the synthesis is described of one cobalt(II) disulfide and two cobalt(III) thiolate compounds starting from the disulfide ligand L^1SSL^1 in reaction with different cobalt(II) salts. Cobalt(III) thiolate compounds were formed when cobalt(II) salts with BF_4^-, PF_6^-, or NCS^- anions were employed, whereas use of $CoCl_2$ resulted in a cobalt(II) disulfide compound. Further investigation revealed that the addition of chloride ions to a solution of the cobalt(III) thiolate compound in acetonitrile results in conversion to the cobalt(II) disulfide compound, as monitored with UV-vis spectroscopy (Scheme 7.2); subsequent addition of $AgBF_4$ regenerates the Co(III) thiolate compound. Computational studies revealed that substitution of the coordinated acetonitrile molecule or thiocyanate anion in cobalt(III) thiolate compounds by a chloride anion induces a change in the character of the highest occupied molecular orbital, showing a decrease of the contribution of the *p* orbital on sulfur and an increase of the contribution of the *d* orbital on cobalt.



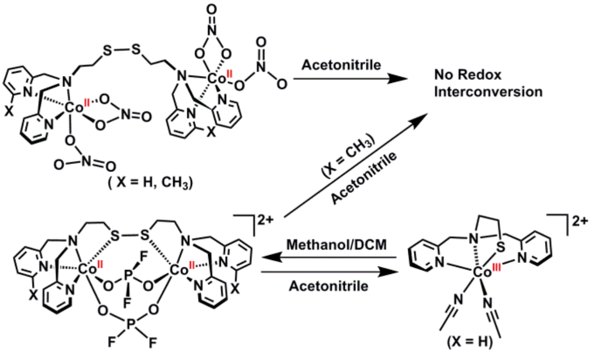
Scheme 7.2. Redox interconversion between cobalt(III) thiolate and cobalt(II) disulfide compounds induced by addition/removal of chloride anions in acetonitrile solution.

A dinuclear iron(II) disulfide compound was formed from the ligand L^1SSL^1 in reaction with $FeCl_2·4H_2O$. The two iron(II) centers in this compound are found in two different geometries, which are different from the related cobalt(II) disulfide compound. Reaction of the ligand L^1SSL^1 with $[Fe(MeCN)_6](BF_4)_2$ yielded an iron(II) fluoride cluster rather than the expected Fe(III) thiolate compound (Scheme 7.3). The novel tetranuclear cluster comprising both terminal and bridging fluoride ions reveals a unique and nearly planar $[Fe_4F_4]$ core, as is described in Chapter 5.



Scheme 7.3. Schematic representation of the formation of an iron(II) fluoride cluster comprising a unique, nearly planar $[Fe_4F_4]$ core.

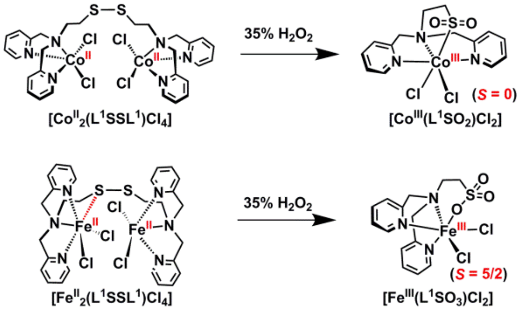
Four cobalt(II) disulfide compounds with different disulfide ligands (L^1SSL^1, L^2SSL^2) and different anions ($PO_2F_2^-$, NO_3^-) were isolated and characterized using various methods, as reported in Chapter 3 (Scheme 7.4); the ligand L^2SSL^2 has a methyl group at two of the pyridine rings. The cobalt(II) compounds with $PO_2F_2^-$ anions were unexpectedly formed from an old batch of $AgPF_6$, but were successfully reproduced using the solid salt $LiPO_2F_2$. Single crystal X-ray crystallography showed that in all cobalt(II) compounds the cobalt(II) ions are in octahedral geometries. Solution studies revealed that the cobalt(II) disulfide compound with the ligand L^1SSL^1 and $PO_2F_2^-$ anions is stable as such in the solvents dichloromethane and methanol, but in acetonitrile redox interconversion occurs with the formation of the cobalt(III) thiolate compound $[Co^{III}(L^1S)(MeCN)_2]^{2+}$. This interconversion does not occur for the compound with NO_3^- anions. Further investigation revealed that both cobalt(II) disulfide compounds of the disulfide ligand L^2SSL^2 also do not show this redox interconversion in any of the investigated solvents.



Scheme 7.4. Schematic representation of the redox interconversion between cobalt(III) thiolate and cobalt(II) disulfide compounds.

7.1.3 Reactivity of Fe^{II} and Co^{II} disulfide compounds with dihydrogen peroxide

Investigation of the reactivity of metal thiolate compounds with dioxygen has attracted considerable attention in the last decades, aimed at the understanding of oxidation sensitivity of metalloenzymes in biological system [15-22]. However, the study of the oxidation of metal disulfide compounds is still rare [19]. It was found that oxidation of the iron(II) disulfide compound described in Chapter 2 resulted in the formation of a mononuclear high-spin (S = 5/2) sulfonato-Fe(III) compound as the final product, whereas oxidation of the related cobalt(II) disulfide compound yielded the low-spin (S = 0) sulfinato-cobalt(III) derivative (Scheme 7.5). ESI-MS spectra of the reaction mixture in combination with the results of a previous study indicated that oxidation of the cobalt compound proceeds via a relatively stable sulfenato-cobalt(III) compound [23].



Scheme 7.5. Schematic representation of oxidation of metal disulfide compounds.

7.1.4 Synthesis and characterization of a series of transition metal compounds of thioether and disulfide ligands

In Chapter 6, the synthesis and characterization has been described of a series of transition metal compounds $[M^{II}(L^1SCH_3)Cl_2]$ (M = Co, Cu, Mn, Fe) of a tetradentate ligand containing a thioether donor. The structural and spectroscopic properties of these compounds are compared to those of the related dinuclear disulfide compounds $[M^{II}_2(L^1SSL^1)Cl_4]$. The crystal structures combined with the magnetic susceptibility data confirmed that the metal centers in these compounds all are in high-spin states. The geometries of the central ion in the series $[M^{II}(L^1SCH_3)Cl_2]$ show an interesting continuous trend: whereas the iron(II) center in $[M^{II}(L^1SCH_3)Cl_2]$ is in an octahedral geometry with coordination of the thioether sulfur (at 2.6972(6) Å), going via the manganese(II) (2.8325(4) Å) and copper(II) (2.9961(4) Å) to cobalt(II) (5.8887(8) Å) the thioether sulfur progressively is at a larger distance from the metal center. This results in distorted square-pyramidal geometries for the copper(II) and manganese(II) centers and a trigonal-bipyramidal geometry for the cobalt(II) center. This trend is also partly visible in the structures of the dinuclear compounds $[M^{II}_2(L^1SSL^1)Cl_4]$. Generally, the dinuclear compounds generally show longer M-S distances than the related mononuclear compounds, indicating that the disulfide sulfur atom is a slightly weaker ligand than the thioether sulfur donor.

7.2 Conclusions and outlook

In the last decade, the redox interconversion between metal thiolate and disulfide compounds has been extensively investigated for copper, but not for other transition metal ions. In this thesis, our investigations are described of the possibility to extend the metal thiolate/disulfide redox interconversion reactions to cobalt or iron compounds. A number of cobalt(II) disulfide and cobalt(III) thiolate compounds of different ligands and different anions are reported in this thesis. It was revealed that the anion of cobalt(II) salts, the structure of disulfide ligands, and the type of solvent influence the formation of either cobalt(II) disulfide or cobalt(III) thiolate compounds. However, a consistent trend cannot be provided to predict which of the species is generated.

- The interconversion is not related to the binding strength of the anion: whereas the coordinating chloride ion leads to the formation of cobalt(II) disulfide compounds, use of the coordinating thiocyanate ion leads to the formation of cobalt(III) thiolate compounds.
- The interconversion is not related to the polarity of the solvent, nor on the potential binding strength of the solvent: the solvents chloroform (non-polar and non-coordinating) and methanol (highly polar and coordinating) lead to formation of cobalt(II) disulfide compounds, whereas acetonitrile (medium polarity and coordinating) leads to the corresponding cobalt(III) thiolate compound (for L^1SSL^1 as the ligand in combination with the $PF_2O_2^-$ anion).

One general observation is that the cobalt(II) ions in the disulfide compounds are in the high-spin state in all cases reported in this thesis, whereas the cobalt(III) ions in the thiolate compounds are in a low-spin state. An important conclusion of this work therefore is that the cobalt(II) disulfide to cobalt(III) thiolate interconversion reaction might be related to the ligand field strength of the ligand, and the binding strength and ligand field strength of the anions and solvent used. A larger ligand field splitting of the ligand in combination with a large ligand-field splitting caused by the anion or coordinating solvent will ultimately lead to the formation of low-spin cobalt(II) ions. In an octahedral geometry this results in the presence of a single electron in a high-energy anti-bonding *d* orbital; transfer of this high-energy electron to a *p* orbital of a nearby disulfide sulfur atom then effectively results in the oxidation of the cobalt center with the reduction of the disulfide to thiolate groups.

Indeed, computational studies revealed that exchange of the coordinated acetonitrile molecule or thiocyanate anion in cobalt(III) thiolate compounds by a chloride anion induces a change in the character of the highest occupied molecular orbital, showing a decrease of the contribution of the *p* orbital on sulfur and an increase of the contribution of the *d* orbital on cobalt; however, this effect appeared to be rather small. Ultimately this should result in the formation of the cobalt(II) disulfide compound, although this was not found to occur in the minimization process. Thus, in the future, more computational studies should be conducted to clarify the mechanism of these redox interconversion reactions in detail.

Further systematic studies should be undertaken to investigate the subtle balance of the redox interconversion and its dependence on the combinations of ligand field strengths of the ligand and anions or coordinating solvents. Thus, the effect may be studied of different halogen anions (F^-, Br^-, I^-) or other coordinating co-ligands on the position of the redox interconversion reactions.

Although the cobalt thiolate/disulfide redox interconversion reactions have been largely extended in this thesis, the effect of the addition/removal of protons, and changes in temperature to these redox reactions is still worthy of investigation.

Apart from the cobalt compounds, two iron(II) disulfide compounds were reported in this thesis (Chapter 2 and 5). However, so far we were not able to trigger the conversion of these compounds to their respective iron(III) thiolate compounds. Further studies are necessary to reveal what would trigger such a redox interconversion. Non only would this be interesting for the iron(II)/iron(III) redox couple, but similar studies can also be done for the manganese(II)/manganese(III) couple.

7.3 References

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