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

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Citation

Marvelous, C. (2022, July 5). *Reactivity of cobalt(II)-dichalcogenide complexes: correlation between redox conversion and ligand-field strength*. Retrieved from https://hdl.handle.net/1887/3421554

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Chapter 6

Summary, Conclusions, and Outlook

6.1. Summary

6.1.1. Introduction

Investigations of synthetic models of active sites of enzymes have provided a great deal of understanding in chemical processes occuring in enzymes, such as the catalytic mechanisms or the role of a specific moiety in these active sites.[1-8] During such investigations, some new and unprecedented reactivity of synthetic models are often discovered. One of the many interesting types of reactivity encountered in the last two decades concerns the redox interaction of a disulfide ligand with transition metal ions. The redox interaction can be fine-tuned to change the redox state of the sulfur ligand as well as the transition metal ions, in what is now known as a redox-conversion reaction.[9, 10] These redox-conversion reactions are important as they may shed light on electron-transfer reactions that often occur in Nature.

Despite their importance, so far only a handful of studies have been reported on the redox-conversion reaction of metal-disulfide and metal-thiolate complexes. The majority of these studies were focused on copper-based disulfide/thiolate conversion.[9-16] Recently, several examples of the redox-conversion reaction have emerged concerning cobalt(II)-disulfide and cobalt(III)-thiolate complexes.[17-19] Much like copper-based systems, the cobalt-based disulfide/thiolate conversion is governed by small changes in the coordination environment, though more examples are needed in order to understand the reaction mechanism. In Chapter 1, an extensive discussion concerning the state-of-the-art in redox-conversion reactions is given.

6.1.2. The Importance of Ligand-Field Strength and Ligand Orientation on Redox-conversion of Co(II)-disulfide to Co(III)-thiolate Complexes

In spite of a number of recent examples of cobalt(II)-disulfide to cobalt(III)-thiolate redox-conversion reactions,[17-19] there is limited understanding on how the coordination environment of the metal ion affects this reaction. In Chapters 2 and 3, results are described of our pursuit of understanding the reaction by focusing on the ligand-field strength of the auxiliary ligands used. For this purpose the ligands 2,2'-bipyridine (bpy) and 8-quinolinolate (quin$^-$) were used, both being considered to be strong-field ligands. In addition, the negative charge on the ligand quin$^-$ may help stabilizing the positive charge on the cobalt(III)-thiolate complex.

In Chapter 2 is described how addition of bpy to the cobalt(II)-disulfide compound $[Co_2(L^1SSL^1)(Cl)_4]$ led to the formation of the cobalt(III)-thiolate species $[Co(L^1S)(bpy)]^{2+}$. However, formation of the side products $[Co_2(L^1SSL^1)(bpy)_2(Cl)_2](Cl)_2$ and $[Co(bpy)_3]^{n+}$ was also observed, which was not expected.[20] In Chapter 3 it is shown that a reaction with $quin^-$ leads to the product $[Co(L^1S)(quin)]^+$ in almost quantitative yield without having to remove the chloride ligands.[21] Furthermore, use of the ligand $quin^-$ resulted in the successful conversion of the cobalt(II)-disulfide complex $[Co_2(L^2SSL^2)(Cl)_4]$. Several attempts of using the ligand L^2SSL^2 with cobalt(II) in the redox-conversion reaction have been reported, but so far formation of its Co(III)-thiolate complex was elusive. However, in this case also a side product was unexpectedly found, namely $[Co_2(L^2SSL^2)(quin)_2(Cl)_2]$.

Nevertheless, the formation and the crystal structure of these side products convey valuable insight on how the conversion of the cobalt(II)-disulfide to a cobalt(III)-thiolate compound proceeds. In the structure of the side product $[Co_2(L^1SSL^1)(bpy)_2(Cl)_2]^{2+}$ the nitrogen donors of L^1SSL^1 are in a facial arrangement, hampering the approach of the disulfide group to the cobalt center. In contrast, in the structure of $[Co_2(L^2SSL^2)(quin)_2(Cl)_2]$ the nitrogen donor atoms of L^2SSL^2 are in a meridional orientation, which allows for the disulfide to approach the cobalt center for an efficient electron transfer.

DFT calculations were employed to estimate ligand-field strength of the ligands in the compounds. Molecular orbital analyses show that the estimated *d*-orbital splitting energy of a simplified Co(II)-disulfide species is definitively smaller than those of the Co(III)-thiolate complexes. The estimated *d*-orbital splitting energy of $[Co(L^1S)(bpy)]^{2+}$ appears to be smaller than that of $[Co(L^1S)(MeCN)_2]^{2+}$, suggesting that bpy exerts a smaller ligand-field splitting than acetonitrile.[20] Apart from the fact that an excess of acetonitrile is present in the reaction, this result may account for the formation of side products when bpy is employed. The estimated *d*-orbital splitting energy for the complex $[Co(L^1S)(quin)]^+$ appears to be slightly larger than that of $[Co(L^1S)(bpy)]^{2+}$, in agreement with the experimental results. Comparison of the estimated *d*-orbital splitting of $[Co(L^1S)(quin)]^+$ and $[Co(L^2S)(quin)]^+$ indicated that the ligand L^2SSL^2 exerts a weaker ligand field than L^1SSL^1. Despite the electron-donating effect, *ortho*-methylation of pyridine groups on L^2SSL^2 has been reported to reduce the donor ability of the pyridine nitrogen, mostly because of steric hindrance, causing larger metal-nitrogen distances, and thus smaller ligand-field splitting.[9, 18, 20]

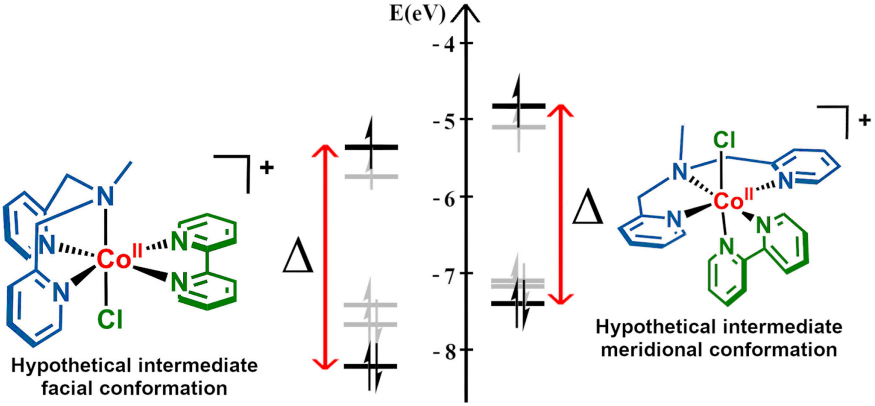

Figure 6.1. Simplified energy diagrams showing the destabilization of the highest SOMO level of the hypothetical intermediate in meridional geometry compared to facial geometry.

The results described in Chapters 2 and 3 reveal that the orientation of the disulfide ligand and the auxiliary ligand also affect the redox conversion.[20, 21] In Chapter 2, the auxiliary ligand bpy is a symmetrical bidentate ligand and thus only the binding mode of the disulfide ligand was investigated using computational methods. It was found that the highest SOMO level of the hypothetical intermediate compound with the nitrogen donor atoms of the disulfide ligand in meridional conformation is more destabilized than that of the facial isomer that was found in the crystal structure (**Figure 6.1**). This indicates that electron transfer from Co to S should be more facile when the nitrogen donor atoms of the ligand L^1S are in meridional arrangement. In contrast, the ligand $quin^-$ used in Chapter 3 is asymmetric and therefore its binding mode to cobalt was investigated. The complex $[Co(L^1S)(quin)]^+$ is more stable energetically when the negatively charged oxygen is *trans* to the sulfur donor than when it is *trans* to the tertiary amine nitrogen. Quantum chemical analyses showed that the coordination of the oxygen of $quin^-$ opposite to sulfur atom of ligand L^1S benefits from more electrostatic interaction between the aromatic rings of $quin^-$ and the positively charged $[Co(L^1S)]^{2+}$ fragment.

6.1.3. Resemblance of Selenium and Sulfur in The Redox-conversion Reaction

We expanded the scope of our study to selenium, which is known to have similar properties to sulfur, especially in its redox reactions.[22, 23] The first redox-conversion reaction for a Co(II)-diselenide to Co(III)-selenolate compounds is described in Chapter 4. The

Co(II)-diselenide compound $[Co_2(L^1SeSeL^1)(Cl)_4]$ was obtained using the ligand L^1SeSeL^1, a new ligand analogous with the ligand L^1SSL^1 described in Chapters 2 and 3. The spectroscopic properties of the Co(II)-diselenide compound $[Co_2(L^1SeSeL^1)(Cl)_4]$ resemble those of the disulfide analog $[Co_2(L^1SSL^1)(Cl)_4]$. Formation of Co(III)-selenolate compounds was achieved from the reaction of L^1SeSeL^1 with $Co(SCN)_2$ yielding $[Co(L^1Se)(NCS)_2]$, by removal of chloride ions from $[Co_2(L^1SeSeL^1)(Cl)_4]$ in an acetonitrile solution resulting in $[Co(L^1Se)(MeCN)_2]^{2+}$, or upon addition of $quin^-$ to $[Co_2(L^1SeSeL^1)(Cl)_4]$ giving $[Co(L^1Se)(quin)]^+$; these products resemble the thiolate analogs described in Chapters 2 and 3. However, it appeared that the cobalt(III)-selenolate compounds are rather unstable in solution. DFT calculations indicate that the selenolate donor atom exerts a smaller ligand-field splitting than the thiolate donor atom. In combination with the knowledge acquired in Chapters 2 and 3, the results indicate that the conversion of Co(II)-diselenide to Co(III)-selenolate is not much more difficult to achieve than for the sulfur analogs, but that the selenolate products are less stable in solution. These results show how selenium and sulfur resemble each other in the redox-conversion reaction, but also highlights the differences, which may be relevant to consider for further studies regarding the kinetics of the reaction.

6.1.4. Ligand Modification and Stabilization of Co(III)-thiolate Complexes

In Chapter 5 the results are described of the use of three different disulfide ligands in attempts to obtain Co(III)-thiolate compounds. In the ligand L^3SSL^3 all four pyridine groups of the parent ligand L^1SSL^1 are methylated, while the ligand L^pSSL^p resembles L^1SSL^1 but has two propylene groups between the tertiary amines and the disulfide groups. The ligand $L^{mpz}SSL^{mpz}$ is significantly different from L^1SSL^1, as it contains dimethylpyrazole instead of pyridine groups.

A number of Co(II)-disulfide compounds with these three different ligands were isolated and characterized. The compound $[Co_2(L^{mpz}SSL^{mpz})(Br)_4]$ surprisingly revealed asymmetric coordination of the ligand; one of the disulfide sulfur donor atoms is coordinated to one of the cobalt centers, while the other sulfur donor atom does not coordinate. Reaction of the ligand $L^{mpz}SSL^{mpz}$ with $Co(SCN)_2$ affords cobalt(II)-disulfide compound $[Co_2(L^{mpz}SSL^{mpz})(NCS)_4]$, indicating that the ligand-field strength of the pyrazole ligand is too low to be overcome with the relatively strong-field anions. Unexpectedly, also the reaction of L^pSSL^p with $Co(SCN)_2$ resulted in a cobalt(II)-disulfide compound.

Using the knowledge gained from the previous Chapters, attempts were undertaken to form Co(III)-thiolate complexes of the ligand $L^{mpz}SSL^{mpz}$, L^pSSL^p, and L^3SSL^3 by the addition of $quin^-$. The formation of Co(III)-thiolate complexes seemed to be successful as in ESI-MS spectra peaks were present that could be assigned to the expected products. However, in almost all attempts at least one side product was formed, and it appeared not possible to isolate the expected thiolate compounds. Overall, the results indicate that the ligand-field strength of $L^{mpz}SSL^{mpz}$, L^pSSL^p, and L^3SSL^3 is not large enough to be able to convert the Co(II)-disulfide compounds to the corresponding Co(III)-thiolate redox isomers.

6.2. Conclusions and Outlook

Up until now, to the best of our knowledge only three reports describe the redox-conversion of Co(II)-disulfide to Co(III)-thiolate complexes.[17-19] The research field is extended further by some examples that are described in this thesis. From the Co(II)-disulfide and Co(III)-thiolate as well as the Co(II)-diselenide and Co(III)-selenolate complexes that we have investigated, several conclusions can be drawn.

1. The disulfide ligand is the foremost factor in regulating the redox conversion of Co(II)-disulfide and Co(III)-thiolate complexes. Small changes in the disulfide ligand structure have an immense effect on the reactivity of the corresponding Co(II)-disulfide complexes due to steric and ligand-field effects.
2. Inducing an increase in the ligand-field strength of the disulfide ligand most likely will enable the conversion to corresponding Co(III)-thiolate complexes. A smaller ligand-field effect can be counterbalanced by the use of auxiliary ligands that exert strong ligand field.
3. The cleanliness of the redox conversion of Co(II)-disulfide to Co(III)-thiolate complexes is determined by the magnitude of the overall ligand-field splitting energy of the complex, the charge of the exogenous ligand, the arrangement of the ligands in the first coordination sphere of the complex, and the formation constant of side products relative to that of the Co(III)-thiolate complex.

In the research described in this thesis we have employed computational methods in order to estimate the ligand-field strength of the various ligands in a qualitative manner. The DFT computations revealed that the molecular orbitals are a mixture of metal *d*-orbitals and ligand orbitals. Our qualitative picture of the estimated ligand-field splitting has been valuable for understanding the experimental findings.

So far, examples are not known on the effect of addition or removal of protons on the redox conversion of Co(II)-disulfide and Co(III)-thiolate compounds, nor on the influence of temperature in these reactions. Using our current knowledge, it is expected that addition of protons will change the coordinating ability of the ligands, with direct consequences for the ligand-field stabilization of the complex. Lower reaction temperatures most likely will result in stabilization of the low-spin state of the cobalt compounds and might thereby facilitate the formation of cobalt(III)-thiolate compounds. Therefore, in the near future, both experimental and theoretical studies can be directed towards understanding the role of protons, as well as detailed thermodynamic studies of the reaction. Furthermore, additional systematic studies to the design of the disulfide ligand need to be conducted. It was shown that *ortho*–methylation of pyridine rings in the ligands L^2SSL^2 and L^3SSL^3 results in weaker donating ability of these pyridine nitrogen atoms due to steric effects.[9] Thus, it might be interesting to examine functionalization on the *para* position of the pyridine rings to eliminate steric effects and enable a stronger donating ability of the pyridine nitrogens, which may induce the redox-conversion of Co(II)-disulfide to Co(III)-thiolate compounds.

Currently the redox conversion of other metal-disulfide to metal-thiolate complexes is underexplored. Further investigations of redox-conversion reactions based on other transition metals may reveal interesting applications of this redox-conversion, such as for molecular magnetic switches, sensing materials for halide ions, protons, or temperatures. In addition, cobalt(III) complexes with a ligand containing pyridine and thiolate moieties have recently emerged as promising catalysts for electrochemical CO_2 reduction.[24, 25] In this light, the catalytic activity of the Co(III)-thiolate complexes described in this thesis for CO_2 reduction may be worthy of investigation.

6.3. References

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