Redox interconversion between metal thiolate and disulfide compounds

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Citation

Jiang, F. (2018, December 7). *Redox interconversion between metal thiolate and disulfide compounds*. Retrieved from https://hdl.handle.net/1887/68029

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Title: Redox interconversion between metal thiolate and disulfide compounds
Issue Date: 2018-12-07

Chapter 3

Solvent-dependent Redox Interconversion of Cobalt(III) Thiolate and Cobalt(II) Disulfide Compounds

In this chapter, we describe the synthesis of the cobalt(II) disulfide compounds $[Co^{II}_2(L^XSSL^X)(PO_2F_2)_2](PF_6)_2$ *and* $[Co^{II}_2(L^XSSL^X)(NO_3)_4]$ *from two different disulfide ligands* L^XSSL^X *in reaction with cobalt(II) salts (X = 1, di-2-(bis(2-pyridylmethyl)amino)-ethyl disulfide; X = 7, di-2-((6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amino)-ethyl disulfide). The redox interconversion of these cobalt(II) disulfide compounds to their related cobalt(III) thiolate compounds has been investigated. It was found that the compound* $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ *is stable as such in methanol and dichloromethane solution, but in acetonitrile redox interconversion occurs with the formation of the cobalt(III) thiolate compound* $[Co^{III}(L^1S)(MeCN)_2]^{2+}$*. The other disulfide compounds do not show this solvent-dependency and remain in the disulfide form in all investigated solvents. This is a rare example of redox interconversion between cobalt(II) disulfide and cobalt(III) thiolate compounds controlled by solvents.*

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3.1 Introduction

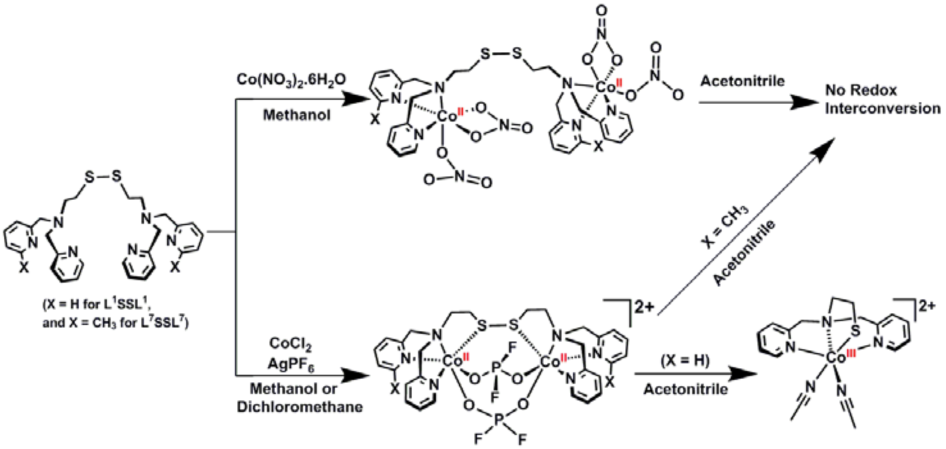
Electron-transfer reactions involving thiolate-disulfide interconversions occur in a number of biological processes and play fundamental roles in e.g. copper transport, regulation of gene expression, and protein folding and stability [1-4]. However, until now, the exact mechanism of these electron-transfer reactions in vivo is not well understood [2]. To gain more insight into the operation principle of the thiolate-disulfide interconversion occurring in metalloenzymes such as metallothionein Zn_7MT_3 [5-7], in the last decades tremendous efforts have been put in the synthesis of copper(II) thiolate compounds and the study of their redox interconversion to the corresponding copper(I) disulfide compounds [8-13]. So far, several triggers have been found to tune this redox interconversion such as protons [10, 12], halide ions [9, 13], as well as the polarity of solvents [11, 12], and changes in temperature [11].

In the last few years, the study of the redox interconversion between metal thiolate and disulfide compounds has progressively moved from copper to other metal ions. The group of Duboc reported the electrochemical synthesis of a cobalt(III) thiolate compound and its redox interconversion to the related cobalt(II) compound induced by the removal of chloride anions [14]. Recently, our group presented the synthesis of a cobalt(III) thiolate compound by the reaction of a disulfide ligand with a cobalt(II) salt containing non-coordinating anions, and the redox interconversion to the isomeric cobalt(II) disulfide compound triggered by the addition of chloride anions [15]. However, to the best of our knowledge, other triggers, such as the polarity of solvents, have not yet been reported to affect the redox interconversion of cobalt(III) thiolate and cobalt(II) disulfide compounds. In this chapter, we report the solvent-dependent formation of cobalt(III) thiolate and the related cobalt(II) disulfide compounds using the rather unique $PF_2O_2^-$ anion.

3.2 Results

3.2.1 Synthesis and characterization of cobalt(II) compounds

The ligands di-2-(bis(2-pyridylmethyl)amino)-ethyl disulfide (L^1SSL^1) and di-2-((6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amino)-ethyl disulfide (L^7SSL^7) were synthesized via reported procedures [8, 13]. Treatment of the ligand L^1SSL^1 with $CoCl_2$ and $AgPF_6$ in methanol resulted in a pink solution from which crystals of $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ were isolated (Scheme 3.1). The unexpected presence of the $PO_2F_2^-$ anion is ascribed to the use of an old batch of $AgPF_6$ that apparently was partly hydrolysed. The compound was successfully reproduced in a yield of 30% using a mixture of fresh $AgPF_6$ and commercially available $LiPO_2F_2$ [16]. Similarly, the compound $[Co^{II}_2(L^7SSL^7)(PO_2F_2)_2](PF_6)_2$ was isolated from the old batch of $AgPF_6$, and then was reproduced in a yield of 52% using a mixture of $AgPF_6$ and $LiPO_2F_2$. The addition of $Co(NO_3)_2·6H_2O$ to a methanolic solution of the ligands L^1SSL^1 or L^7SSL^7 led to the formation of similar pink solutions from which the compounds $[Co^{II}_2(L^1SSL^1)(NO_3)_4]$ and $[Co^{II}_2(L^7SSL^7)(NO_3)_4]$ were isolated in a yield of 81% and 41%, respectively. All compounds were characterized by single crystal X-ray crystallography, electrospray ionization mass spectrometry (ESI-MS), elemental analysis, IR, UV–vis and nuclear magnetic resonance (NMR) spectroscopy.



Scheme 3.1. Synthetic scheme of the cobalt(II) disulfide compounds $[Co^{II}_2(L^1SSL^1)(NO_3)_4]$, $[Co^{II}_2(L^7SSL^7)(NO_3)_4]$, $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ and $[Co^{II}_2(L^7SSL^7)(PO_2F_2)_2](PF_6)_2$.

3.2.2 Single crystal X-ray crystallography

Single crystals of $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$, $[Co^{II}_2(L^1SSL^1)(NO_3)_4]$ and $[Co^{II}_2(L^7SSL^7)(PO_2F_2)_2](PF_6)_2$ suitable for X-ray structure determination were obtained by slow vapor diffusion of diethyl ether into the solutions of these compounds. The crystals of $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ obtained from methanol and dichloromethane are isomorphous, as confirmed by single X-ray diffraction. The structure of the crystals obtained from dichloromethane solution is discussed. Projections of the structures of $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ and $[Co^{II}_2(L^1SSL^1)(NO_3)_4]$ are given in Figure 3.1; a projection of the structure of $[Co^{II}_2(L^7SSL^7)(PO_2F_2)_2](PF_6)_2$ is provided in Appendix II, Figure AII.1. Selected bond distances of all three compounds are provided in Table 3.1, selected angles of $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ and $[Co^{II}_2(L^1SSL^1)(NO_3)_4]$ are given in Table 3.2, and the refinement data of the structures are summarized in Appendix II, Tables AII.1 and AII.2. The compound $[Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2$ crystallizes in the triclinic space group *P*–1 with 3.3 molecules of dichloromethane co-crystallized in the asymmetric unit. The two Co(II) ions are bound to three nitrogen donor atoms and one sulfur atom of the ligand and two oxygen atoms of separate difluoridophosphate anions in a distorted octahedral geometry. The three nitrogen donor atoms of the ligand are coordinated in a facial arrangement and the two difluoridophosphate ligands are bridging between the two cobalt(II) centers. The Co–O bond lengths range from 2.0264(13) to 2.0991(13) Å, the Co–S bond lengths are 2.5927(5) and 2.6190(5) Å. The Co-N bond distances are between 2.0797(15) and 2.1405(15) Å, and the S–S bond length is 2.0531(6) Å. The structure of $[\mathrm{Co^{II}_2(L^7SSL^7)(PO_2F_2)_2](PF_6)_2}$ is highly similar (Appendix II, Figure AII.1).

Compound $[\mathrm{Co^{II}_2(L^1SSL^1)(NO_3)_4}]$ crystallizes in the monoclinic space group $P2_1/n$. Both Co(II) ions are coordinated by three nitrogen donors of the ligand and three oxygen atoms of one monodentate and one bidentate nitrate anion in distorted trigonal-bipyramidal geometries if the two coordinated oxygen atoms from the bidentate nitrate ligand are regarded to occupy one coordination site. The three nitrogen donors are bound in a facial fashion. The Co–O bond distances are between 2.071(3) and 2.354(2) Å; the cobalt-to-nitrogen bond lengths range from 2.060(3) to 2.249(3) Å. The disulfide sulfur atoms are non-coordinating and the S–S bond length is 2.0372(1) Å, which is slightly shorter than in $[\mathrm{Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2}$. Stacking interactions are not present in the structures, despite the presence of the aromatic pyridine groups.

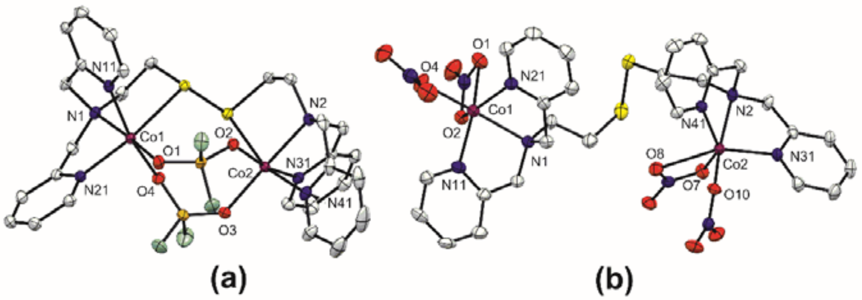


Figure 3.1. Displacement ellipsoid plot (50% probability level) of (a) the cationic part of $[\mathrm{Co^{II}_2(L^1SSL^1)(PO_2F_2)_2](PF_6)_2}$ and (b) $[\mathrm{Co^{II}_2(L^1SSL^1)(NO_3)_4}]$ at 110(2) K. Lattice solvent molecules, non-coordinating PF_6 anions (for a) and hydrogen atoms are omitted for clarity.