

# Applications of H-bond Donation in Metal-Thiolate Complexes

## Introduction

Hydrogen bonding (H-bonding) is a fundamental interaction in chemistry, playing a crucial role in the structure and function of a wide range of chemical and biological systems. In the context of metal-thiolate complexes, H-bond donation has emerged as a significant factor influencing the stability, structure, and reactivity of these complexes. This report delves into the applications of H-bond donation in metal-thiolate complexes, exploring how this interaction contributes to the development of new materials, catalysts, and energy storage solutions.

## Stabilization of Metal-Thiolate Complexes

Metal-thiolate complexes are pivotal in various biochemical processes and synthetic applications. The introduction of H-bond donors proximal to metal centers has been shown to create specific microenvironments that stabilize these complexes (National Center for Biotechnology Information [NCBI], n.d.). For instance, the stability of  $\text{Co}^{\text{III}}\text{-OH}$  complexes is enhanced by the presence of a symmetrical H-bond network, which can lower the nucleophilicity of the  $\text{Co}^{\text{III}}\text{-OH}$  unit and reinforce the cavity structure, providing a more protective environment (NCBI, n.d.).

## Modulation of Reactivity

The reactivity of metal-thiolate complexes can be modulated by H-bonding networks. For example, the presence of H-bonds directly affects the strength of  $\text{Fe-O(S)}$  bonds, often at the expense of  $\pi$ -bonds. This modulation can lead to the formation of high-spin complexes with longer  $\text{M-O}$  bonds, which are stabilized by H-bonds (NCBI, n.d.). Such effects are crucial in the design of metal complexes for specific catalytic functions, including dioxygen binding and activation.

## Influence on Electronic Structure

H-bond donation to thiolate ligands can have a continuous effect on the electronic structure of metal-thiolate complexes. This is particularly evident in the case of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{SR}$  complexes, where H-bond donation does not significantly alter the electronic structure, but protonation leads to a reorganization resulting in a HOMO that is largely metal in character (PubMed, n.d.). This reorganization is critical for understanding the electronic properties and reactivity of these complexes.

# Catalysis and Energy Conversion

Metal-thiolate complexes with H-bonding capabilities have been investigated for their potential in catalyzing the hydrogen evolution reaction (HER). For instance, heterobimetallic complexes with  $\text{NiN}_2\text{S}_2$  or  $[(\text{NO})\text{Fe}]\text{N}_2\text{S}_2$  donors demonstrate roles for electron delocalization by NO and Fe-S bond dissociation, which facilitate proton uptake and transfer, crucial for dihydrogen formation (Royal Society of Chemistry [RSC], 2017).

## Design of Molecular Conductors

The design of single-component molecular conductors based on metal bis(dithiolene) complexes has been explored with the introduction of H-bonding interactions. These interactions can control the overall structural arrangement and stabilize the same structure despite different electron counts, which is essential for the development of conductive materials (RSC, 2020).

## Bioinspired Applications

Inspired by metalloenzymes, synthetic metal complexes incorporating intramolecular H-bond donors have been developed to mimic enzyme functions. These complexes form specific microenvironments around metal ions, which can promote new functions in synthetic metal complexes, such as dioxygen activation (NCBI, n.d.).

## Conclusion

The applications of H-bond donation in metal-thiolate complexes are multifaceted and have significant implications for various fields, including catalysis, material science, and bioinorganic chemistry. The ability to stabilize metal-thiolate complexes, modulate their reactivity and electronic structure, and design molecular conductors and bioinspired systems underscores the importance of H-bonding interactions in advancing our understanding and utilization of these complexes. As research continues to unravel the complexities of H-bonding in metal-thiolate chemistry, we can expect to see further innovations and applications that leverage these interactions for technological and scientific advancements.

## References

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