

Assessing Donor Properties of Thiolate Ligands in Chemical Complexes

Introduction

Thiolate ligands are sulfur-containing ligands that play a crucial role in the structure and function of various chemical complexes, particularly those involving transition metals. These ligands are known for their strong ability to donate electrons to metal centers, influencing the electronic, geometric, and reactivity properties of the complexes they form. The donor properties of thiolate ligands are of significant interest in the field of catalysis, materials science, and bioinorganic chemistry, as they are integral to the function of many metalloenzymes and catalytic processes. This report aims to provide a comprehensive assessment of the donor properties of thiolate ligands in chemical complexes, drawing on recent experimental and computational studies.

Mechanistic Insights from Experimental Studies

Recent experimental studies have shed light on the role of thiolate ligands in ligand-assisted catalysis using first-row metals. For instance, a mechanistic study of the dihydroboration of nitriles catalyzed by a Mn(I) complex featuring thioether, imine, and thiolate donors revealed the importance of the bifunctional thiolate donor and the coordinative flexibility of the ligand in accessing low-energy intermediates during catalysis (Royal Society of Chemistry, 2022). This study highlighted the necessity of UV light for catalysis and the loss of two CO ligands, indicating the dynamic nature of the thiolate ligand in the catalytic cycle.

Computational Studies and Ligand Exchange Dynamics

Computational studies, particularly density functional theory (DFT) calculations, have been instrumental in understanding the electronic influence of thiolate donors. DFT calculations support the experimental observations by showing that thiolate ligands can significantly influence the redox potential of metal centers and facilitate the formation of reactive intermediates (National Center for Biotechnology Information, 2021). For example, the electronic absorption spectra of iron complexes with thiolate ligands exhibit intense charge transfer bands, indicative of optimal orbital overlap and significant electron donation from the thiolate to the metal center.

Ligand Shell Fragility and Rigidity

The addition or elimination of thiolate ligands can dramatically influence the structure and properties of nanoclusters. Tandem mass spectrometry and nuclear magnetic resonance (NMR) analysis have demonstrated that the addition of one excess thiolate ligand to [Au₂₅MHA₁₈] species results in a more fragile surface structure, while maintaining a similar composition (Nature Communications, 2020). This finding underscores the delicate balance between ligand number and the stability of the ligand shell in nanoclusters.

Reversible Conversion Processes

The reversible addition and elimination of thiolate ligands on gold nanoclusters have been successfully demonstrated, with oxidative etching and CO-reduction driving the interconversion between [Au₂₅MHA₁₈]⁻ and [Au₂₅MHA₁₉]⁰ species. This process highlights the dynamic nature of thiolate ligands and their ability to undergo redox chemistry, which is crucial for applications in nanotechnology and catalysis (Nature Communications, 2020).

Influence on Structural and Physical Properties

Thiolate ligands have been shown to systematically influence the structural and physical properties of metal complexes. For instance, a series of iron(II) complexes with varied thiolate donors allowed for the assessment of the influence of the thiolate on the Fe-O and O-O bond strengths in Fe^{III}-OOR species. The nature of the thiolate donor significantly impacted the Fe^{III}/Fe^{II} potential, supporting the idea that thiolate ligands play a major role in controlling the iron redox potential (National Center for Biotechnology Information, 2021).

Ligand Exchange Mechanisms

Ligand exchange reactions involving thiolate ligands are critical for modifying the surface properties of nanoparticles. Single-crystal X-ray structures and DFT computations have provided insights into the associative mechanism of thiolate-for-thiolate ligand exchange, revealing the importance of solvent accessibility and the covalent nature of the metal-thiolate bond (National Center for Biotechnology Information, 2015).

Conclusion

The donor properties of thiolate ligands are multifaceted and have profound implications for the design and function of chemical complexes. Experimental and computational studies have demonstrated that thiolate ligands can modulate the electronic structure, facilitate catalytic processes,

and enable dynamic ligand exchange reactions. The ability of thiolate ligands to donate electrons to metal centers is central to their role in influencing the reactivity and stability of complexes. Future research should continue to explore the nuances of thiolate chemistry to harness their full potential in various applications.

References

- Royal Society of Chemistry. (2022). Mechanistic study of dihydroboration of nitriles catalyzed by Mn(I) complex. Retrieved from <https://pubs.rsc.org/en/content/articlelanding/2022/sc/d2sc04339d#!>
- Nature Communications. (2020). Control of single-ligand chemistry on thiolated Au₂₅ nanoclusters. Retrieved from <https://www.nature.com/articles/s41467-020-19327-2>
- National Center for Biotechnology Information. (2021). Influence of thiolate donors on iron complexes. Retrieved from <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8312276/>
- National Center for Biotechnology Information. (2015). Ligand exchange on gold nanoclusters. Retrieved from <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4624284/>