Comparative Studies of Thiolate and Thiol Ligands in Different Compounds

Introduction

Thiolate and thiol ligands play a crucial role in the field of coordination chemistry, particularly in the formation of metal complexes. These ligands are known for their ability to bind to a variety of metal ions, influencing the properties and reactivity of the resulting complexes. This report delves into the comparative analysis of thiolate and thiol ligands, examining their coordination behavior, electronic effects, and applications in various compounds.

Thiolate vs. Thiol Ligands: Coordination Chemistry

Thiolates, the deprotonated form of thiols, are characterized as soft Lewis bases and exhibit a strong affinity for soft Lewis acid metals (Wikipedia, n.d.). This affinity is particularly evident in the formation of transition metal thiolate complexes, where thiolate ligands often bridge pairs of metals, such as in the case of $Fe2(SCH3)2(CO)6$ (Wikipedia, n.d.). The bond angles in divalent sulfur found in thiolates approach 90°, which is also reflected in the metal-sulfur-carbon angles of metal thiolates. Due to their filled p-orbitals, thiolates act as pi-donor ligands, which is significant in stabilizing high oxidation states in enzymes like cytochrome P450 (Wikipedia, n.d.).

Thiols, on the other hand, are the protonated form of thiolates and are known for their moderate π-acidity. This characteristic is crucial in the stabilization of low metal oxidation states, as seen in thioether-metal complexes (NCBI, 2019). Thioethers, which include thiols, have historically been important in the study of metal complexes due to their ability to coordinate with a variety of metals.

Electronic Structure and Redox Properties

The electronic structure of metal ions is significantly affected by the type of ligand coordinated to them. Thioether ligation, including thiol coordination, has been shown to influence the redox properties of metal complexes. For instance, coordination to thioethers shifts the Cu(II/I) potential to more positive values, enhances the rate of Cu(II/I) redox self-exchange kinetics, and generates unusually intense optical bands (NCBI, 2019). This behavior is attributed to the destabilization of the Cu(II) oxidation state rather than the stabilization of the Cu(I) state.

In contrast, thiolate ligands have been reported to lower the activation barrier to dioxygen binding, increase the ability of $Fe-O2^{\bullet -}$ superoxo compounds to abstract H-atoms from strong C–H bonds, and promote peroxo O–O bond cleavage (NCBI, 2021). The highly covalent nature of iron-thiolate bonds and the redox non-innocence of thiolate ligands facilitate the delocalization of oxidizing equivalents onto the sulfur, which is vital for the function of electron-transfer proteins and non-heme iron enzymes (NCBI, 2021).

Stability and Geometry in Metal Complexes

The stability of metal complexes is greatly influenced by the ligands involved. Thiolate ligands are known for their better stability towards oxidation compared to thiol ligands (NCBI, 2019). This stability is evident in the narrow distribution of stability constants of Cu(I) complexes with thiolate ligands, as opposed to their Cu(II) counterparts. The binding geometry also plays a significant role, with tripodal ligands with mixed nitrogen and sulfur donors affecting the electron-transfer kinetics of Cu(II/I) systems (NCBI, 2019).

In the case of Cd2+ complexes, ligands with two vicinal SH groups, such as DMSA and DMPS, show significantly higher stability constants due to the possibility of forming tetrahedral chelates (NCBI, 2019). This enhanced stability is confirmed by solid-state structures and studies using various techniques like X-ray absorption spectroscopy and density functional theory (NCBI, 2019).

Applications in Sensing and Catalysis

Thiolate and thiol ligands have found extensive applications in various fields, including molecular imaging and catalysis. Thioether coordination chemistry, which encompasses thiol ligands, has been exploited for the selective ligation of copper in biological systems and synthetic chemistry. This type of binding is crucial for pH-independent and oxidation-resistant binding of the cuprous ion, making it valuable in the development of copper-specific recognition moieties for molecular-imaging applications (NCBI, 2019).

Thiolate-protected metal nanoclusters (NCs) are another area where these ligands have shown significant impact. The strong metal-sulfur bond in thiolate-protected NCs allows for fine control of reduction kinetics, which is essential for the successful synthesis of metal NCs (Nature, 2023). Thiolate ligands in metal NCs are also pivotal in dictating the structure, metal-ligand interface, and inducing unique optical and electrochemical properties (Frontiers in Chemistry, 2018).

Conclusion

In summary, thiolate and thiol ligands exhibit distinct coordination behaviors, electronic effects, and stability characteristics that influence the properties of metal complexes. Thiolate ligands tend to form stronger bonds with soft Lewis acid metals, stabilize high oxidation states, and exhibit better stability towards oxidation. They also play a significant role in the function of metalloenzymes and the synthesis of metal NCs. Thiols, with their moderate π-acidity, are crucial in stabilizing low metal oxidation states and are extensively used in copper coordination chemistry.

The comparative analysis of thiolate and thiol ligands reveals that both have unique advantages and applications, making them indispensable in the field of coordination chemistry. Future research and development in this area will continue to uncover new insights and applications for these versatile ligands.

References

- NCBI. (2019). Retrieved from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6602089/
- NCBI. (2021). Retrieved from https://www.ncbi.nlm.nih.gov/pmc/articles/PMC8301228/
- Wikipedia. (n.d.). Transition metal thiolate complex. Retrieved from https://en.wikipedia.org/wiki/Transitionmetalthiolate_complex
- Nature. (2023). Retrieved from https://www.nature.com/articles/s41467-023-38955-y
- Frontiers in Chemistry. (2018). Retrieved from https://www.frontiersin.org/articles/10.3389/fchem.2018.00330/full