

Impact of Protonation on the Electronic Structure of Metal-Thiolate Complexes

Introduction

Metal-thiolate complexes are pivotal in various fields of chemistry, including biochemistry, catalysis, and materials science. The thiolate ligand, typically derived from a thiol-containing molecule, binds to a metal center through its sulfur atom, forming a metal-sulfur bond that is central to the complex's properties. Protonation, the addition of a proton (H^+) to a molecule, can significantly alter the electronic structure of these complexes, influencing their stability, reactivity, and overall chemical behavior. This report delves into the effects of protonation on the electronic structure of metal-thiolate complexes, drawing on recent research findings to elucidate the underlying chemical principles.

Protonation and Electronic Structure

Protonation of thiolate anions in metal-thiolate complexes can lead to profound changes in their electronic structure. The addition of a proton to the thiolate ligand affects the ligand's charge, which in turn influences the metal-ligand bonding characteristics. Protonation typically reduces the negative charge on the sulfur atom, weakening its ability to donate electron density to the metal center. This can lead to a decrease in the strength of the metal-sulfur bond and may alter the overall geometry of the complex.

Protonation Constants and Biological Implications

The protonation constants of ligands are crucial as they determine the biological properties of a drug, such as solubility, absorption, cell penetration, and bioavailability. For instance, the protonation constants of chelating agents like BAL, DMSA, DMPS, and penicillamine are of primary importance in determining the speciation of complexes formed with toxic metal ions (NCBI, 2023). The protonation constants of mercapto groups in these ligands show variability depending on the number of SH groups present, which significantly impacts the charge distribution and electronic structure of the resulting metal-thiolate complexes.

Metal-Thiolate Bonding and Coordination

The nature of the metal-thiolate bond is influenced by protonation. In metal thiolate complexes, the sulfur atom's nucleophilicity can be enhanced or reduced based on the electronic interactions between the metal d-orbitals and the sulfur p-orbitals. Protonation can lead to " π -repulsion," where the

repulsive interactions between the filled metal d-orbitals and the sulfur lone pairs result in a destabilizing antibonding interaction (NCBI, 2023).

Case Studies of Metal-Thiolate Complexes

Mercury-Thiolate Complexes

Mercury-thiolate complexes exhibit a preference for linear coordination, which can be influenced by protonation. The formation of polynuclear species, such as $\text{Hg}_2(\text{DHLLA})_2$ and $\text{Hg}_4(\text{DHLLA})_4$, is facilitated by the short distance between thiol groups in the chelating agent, and the stability of these complexes is affected by the protonation state of the thiolate ligands (NCBI, 2023).

Cadmium and Lead-Thiolate Complexes

The pCd and pPb values of cadmium and lead complexes with thiol-containing ligands are lower than the corresponding pHg values by more than 20 pM units, indicating differences in stability and electronic structure. The presence of two vicinal SH groups in a ligand, as opposed to a single SH group, can lead to the formation of more stable tetrahedral chelates due to the possibility of forming stronger metal-sulfur bonds (NCBI, 2023).

Group 5 Metal-Thiolate Complexes

Group 5 metal-thiolate complexes, such as those containing vanadium, niobium, and tantalum, exhibit unusual coordination modes of thiolate ligands. The electronic properties of these complexes are significantly affected by the coordination environment, which can be altered by protonation. For example, the formation of a six-membered 1,3,5-trithia-2-vanadacyclohexane ring in a vanadium complex is indicative of the complex's electronic structure and potential reactivity (NCBI, 2023).

Protonation of Porphyrins and Phthalocyanines

Porphyrins and phthalocyanines are planar π -compounds that can be protonated, leading to significant changes in their electronic properties. Protonation at the aromatic nitrogen atoms involved in the π -conjugated system can turn these compounds into electron acceptors, influencing their redox properties and electron-transfer reactions. The rate constants of photoinduced electron-transfer reactions and the reorganization energies of electron transfer are affected by the degree of protonation and distortion of the macrocyclic π -plane (ScienceDirect, 2023).

Conclusion

Protonation plays a critical role in determining the electronic structure of metal-thiolate complexes. By altering the charge distribution and bonding

characteristics of the thiolate ligand, protonation can influence the stability, geometry, and reactivity of these complexes. The protonation constants of ligands are particularly important in biological contexts, where they affect the pharmacokinetics of drugs. The case studies of mercury, cadmium, lead, and group 5 metal-thiolate complexes, as well as protonated porphyrins and phthalocyanines, demonstrate the diverse impact of protonation on the electronic structure of metal-thiolate complexes. Understanding these effects is essential for the rational design of metal-thiolate complexes in various applications, from medicinal chemistry to materials science.

References

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