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Review of Transition Metal Dithiocarbamate Complexes: Novel Fluorescent Materials for Biosensor Applications

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ABSTRACT

Transition metal complexes with dithiocarbamate ligands have attracted significant attention in recent decades due to their unique electronic and optical properties. This article presents a comprehensive review of transition metal-dithiocarbamate complexes as fluorescent materials and their potential in biosensor development. Focus is given on their chemical structure, fluorescence mechanism, as well as their application in detecting important biomolecules. With the increasing need for sensitive, selective, and low-cost biosensors, these materials offer promising prospects in various biomedical and environmental applications.

Keywords: Fluorescent, Transition Metal, Dithiocarbamate, Biosensor

I. INTRODUCTION

Biosensors are analytical devices that combine biological components with transducer elements to detect specific analytes. One of the main challenges in the development of modern biosensors is finding materials that have high sensitivity, selectivity, as well as good stability. In this context, transition metal complexes with dithiocarbamate emerge as potential candidates thanks to their strong fluorescence properties and ease of chemical modification (Adeyemi & Onwudiwe, 2020). Dithiocarbamates are versatile ligands that can stabilize a wide range of metal ions in different oxidation states (Andrew & Ajibade, 2017). The resulting complexes often exhibit interesting optical properties, including fluorescence, which can be exploited for sensing applications. The fluorescence properties of these complexes can be fine-tuned by varying the metal center, the dithiocarbamate ligand, and the overall molecular structure. The development of fluorescent probes based on metal complexes has been a significant area of research, with applications spanning from biothiol detection to environmental monitoring (Liu et al., 2020). A traditional method of molecular sensor design involves a rational design based on experience, using a pen and paper (Johnson et al., 2019). However, this approach does not guarantee success and can be inefficient for novel problems (Cheng et al., 2013). Therefore, there is a great deal of interest in developing fluorescent biosensors utilizing transition metal-dithiocarbamate complexes.

Metal complexes have found diverse applications in imaging modalities for the diagnosis of diseases such as heart disease, brain disorders, and cancer (Reichert et al., 1999). Metal complexes offer flexible design platforms as enzyme inhibitors, and metals in enzyme active sites can be key drug targets (Mukherjee & Sadler, 2009). The integration of nanomaterials with biomolecules through surface modification techniques allows researchers to create novel diagnostic systems, offering enhanced sensitivity, selectivity, reliability, and practicality (Agasti et al., 2009). Transition metal ions play pivotal roles in diverse biological processes, including oxygen transport, enzymatic catalysis, and gene regulation. However, their dysregulation can lead to various diseases.

II. STRUCTURE AND CHARACTERISTICS OF TRANSITION METAL DITHIOCARBAMATE COMPLEXES

Dithiocarbamate is a bidentate ligand capable of forming stable complexes with various transition metals such as Cu(II), Ni(II), Zn(II), and Fe(III). The general structure of these complexes involves coordination through two sulfur atoms, forming a chelate ring that enhances thermodynamic and kinetic stability. The electronic properties of the center metal and substituents on the dithiocarbamate group affect the optical characteristics, including fluorescence (Andrew & Ajibade, 2017). The versatility of dithiocarbamates stems from the ease of modifying the organic substituents attached to the nitrogen atom, which allows for tuning the electronic and steric properties of the ligand (Saiyed et al., 2021). The coordination chemistry of dithiocarbamate ligands is fascinating, offering a range of possibilities in terms of preparation, solid-state properties, solution behavior, and applications in bioactive materials and luminescent compounds (Tan et al., 2021).

Dithiocarbamates can stabilize a wide variety of oxidation states and coordination geometries, and seemingly small modifications to the ligand can lead to significant changes in the structure and behavior of the complexes formed (Heard, 2005). The preparation of dithiocarbamate ligands usually involves the reaction of a primary or secondary amine with carbon disulfide in the presence of a base, which is typically carried out at low temperatures because the reaction is highly exothermic (Andrew & Ajibade, 2017). This reaction produces dithiocarbamate salts, which can then be used to synthesize metal complexes by reacting them with metal salts in appropriate solvents. The complexes are often characterized by various spectroscopic techniques such as NMR, IR, UV-Vis spectroscopy, and X-ray crystallography to determine their structure and purity. The strong binding affinity of dithiocarbamates to metal ions is advantageous in the context of biosensors because it ensures the stability of the complex under physiological conditions.

III. FLUORESCENCE PROPERTIES OF TRANSITION METAL DITHIOCARBAMATE COMPLEXES

Transition dithiocarbamate-metal complexes exhibit fluorescent emission that can be regulated through metal selection and ligand modification. The mechanism of this fluorescence involves transitions between energy levels due to electron excitation, where the effect of the center metal plays an important role in the intensity and wavelength of the emission. Some complexes exhibit emission in a wavelength range suitable for biosensory applications, including in the detection of biomolecules and heavy metal ions (Andrew & Ajibade, 2017). The fluorescence of dithiocarbamate metal complexes can be influenced by the nature of the metal ion, the type of dithiocarbamate ligand, and the presence of other substituents in the complex (Ahmed, 2018). For instance, complexes with copper ions are known to exhibit strong fluorescence due to the metal-to-ligand charge transfer transitions, which are highly sensitive to the electronic environment around the metal center. The ability to tune the fluorescence properties of these complexes by rational design makes them attractive candidates for creating biosensors with tailored sensitivity and selectivity. Furthermore, the photophysical properties of transition metal complexes are significantly influenced by the ligand field effects, which determine the energy levels of the metal d-orbitals and hence the wavelengths of light absorbed and emitted (Collinson & Schröder, 2005). The d electron count of transition metal ions dictates their coordination mode, influencing the spin state of the complexes (Teeuwen et al., 2022).

IV. BIOSENSOR APPLICATIONS

Transition metal-dithiocarbamate complexes have emerged as promising materials for biosensor applications because of their unique fluorescence properties and ability to selectively bind with various biomolecules (Odularu & Ajibade, 2019). These complexes can be designed to detect metal ions with high sensitivity and selectivity, as demonstrated by UV–vis and fluorescence spectroscopic methods (Udhayakumari et al., 2013). The use of dithiocarbamate complexes in biosensors leverages their ability to undergo changes in fluorescence intensity or emission wavelength upon binding to a specific target analyte (El-Nahass et al., 2014). These changes can be readily detected and quantified, providing a means of measuring the concentration of the analyte in a sample. These complexes can also be modified to interact with specific biomolecules, such as proteins, DNA, or enzymes, through affinity interactions. This is crucial in medical diagnostics, where quick and accurate detection is essential for monitoring the progression of diseases such as cancer. Metal complexes have the potential to detect a wide array of cancer biomarkers. Moreover, transition metal complexes can be designed to respond to multiple stimuli, such as pH, temperature, or light, enabling the development of more sophisticated biosensors that can provide real-time information about the biological environment (Tóth et al., 2003). The sensitivity of C2N towards copper and chromium indicates its potential in designing sensors for detecting toxic transition metals (Sohail et al., 2023).

V. ADVANTAGES, LIMITATIONS, AND FUTURE PERSPECTIVES

Transition metal dithiocarbamate complexes offer several advantages in biosensor applications, including high sensitivity, tunable fluorescence properties, and the ability to be modified for specific target analytes. However, there are also limitations that need to be addressed. One significant limitation is the potential toxicity of some metal ions, which can restrict the use of certain complexes in in vivo applications. The toxicity of nanomaterials used in biosensors needs to be considered during the development and disposal phases to minimize environmental and health risks (McCourt et al., 2022). Moreover, the stability of the complexes under physiological conditions can be a concern, as some complexes may degrade or lose their fluorescence properties in the presence of biological fluids. Future research should focus on developing more biocompatible and stable complexes, as well as exploring new strategies for signal amplification and detection. Nanomaterial-enhanced sensors possess diverse types of materials and nanostructures for a multitude of biomarkers (Barbosa et al., 2020). Additionally, the integration of these complexes with microfluidic devices and other advanced technologies can lead to the development of highly sensitive and portable biosensors for point-of-care diagnostics (Akbarzadeh et al., 2012).

Carbon nanomaterials can be utilized in the fabrication of biosensor devices for biomarker detection (Pasinszki et al., 2017). The use of nanoparticle-based sensors in cancer cell detection offers advantages compared to traditional methods, making them relevant for point-of-care cancer diagnostics because they are easy to incorporate into user-friendly sensing platforms (Perfézou et al., 2011). Furthermore, challenges in the development of nanomaterial-based biosensors, such as the need for biocompatibility and controlled synthesis methods, must be addressed to fully realize their potential (Zhang et al., 2009).

VI. CONCLUSION

Transition metal dithiocarbamate complexes hold significant promise as a novel platform for the development of highly sensitive and selective fluorescent biosensors, particularly for phosphate ion detection in cancer diagnostics. Their tunable structures and unique fluorescence properties make them attractive candidates for next-generation biosensing technologies. Despite existing challenges such as toxicity and stability in biological environments, ongoing research continues to make considerable progress in overcoming these limitations. This includes the advancement of label-free sensing mechanisms and the design of sensors that are easier to fabricate. These developments position dithiocarbamate complexes as key components in future biosensor systems that are not only rapid and sensitive but also compatible with physiological conditions and suitable for long-term use. Supported by advancements in materials science and nanotechnology, these transition metal complexes are expected to play an increasingly vital role in enabling early, accurate, and accessible disease detection. This, in turn, lays a critical foundation for improving diagnostic precision, enhancing therapeutic efficacy, and ultimately achieving better clinical outcomes.

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