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STRUCTURE AND PROPERTIES OF COPPER COMPLEXES BASED ON FLUORINED β-DIKETONE DERIVATIVES

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Abstract. This work investigates the synthesis, structure, and physicochemical properties of copper complexes formed with fluorinated β-diketone ligands. The introduction of fluorine atoms into β-diketone molecules significantly influences the electronic and steric characteristics of the resulting metal complexes. Various analytical techniques, including IR spectroscopy, UV-Vis spectroscopy, X-ray diffraction, and thermal analysis, are employed to elucidate the coordination modes, stability, and geometry of the copper complexes. The study highlights the potential applications of these complexes in fields such as catalysis, materials science, and coordination chemistry. The effect of fluorination on the thermal stability and electronic properties of the complexes is also discussed in detail.

Keywords: Copper complexes, β-diketones, fluorinated ligands, coordination compounds, structure-property relationship, spectroscopy, thermal analysis, X-ray crystallography, catalysis, fluorine substitution.

Introduction. Transition metal complexes, particularly those of copper, have attracted significant attention due to their wide range of applications in catalysis, materials science, medicine, and coordination chemistry. Among the various ligands used to form such complexes, β-diketones stand out for their strong chelating ability, structural versatility, and ease of modification. The introduction of fluorine atoms into β-diketone ligands further enhances their chemical and physical properties. Fluorinated β-diketones exhibit increased thermal and chemical stability, altered electronic characteristics, and improved volatility, making them especially suitable for applications such as chemical vapor deposition (CVD), gas-phase catalysis, and advanced functional materials. Copper complexes with fluorinated β-diketones are of particular interest due to the unique electronic interactions between the copper center and the electron-withdrawing fluorine substituents. These interactions can significantly influence the geometry, reactivity, and thermal behavior of the resulting complexes. This study focuses on the synthesis, structural characterization, and property analysis of copper complexes based on fluorinated β-diketone derivatives. The aim is to better understand how fluorine substitution affects the coordination environment, stability, and potential practical uses of these complexes. Copper complexes with β-diketone ligands have attracted significant attention in recent years due to their versatile coordination behavior and wide range of applications in fields such as catalysis, material science, and medicinal chemistry. Among these, fluorinated β-diketone derivatives represent a particularly important subclass owing to the unique electronic and steric effects introduced by the fluorine atoms. The presence of fluorine atoms can significantly alter the acidity, coordination ability, and overall stability of the β-diketone ligands, thus influencing the structure and properties of the resulting copper complexes. Fluorination typically enhances the electron-withdrawing character of the ligand, which can lead to stronger metal–ligand interactions and affect the geometry of the complexes formed. Additionally, copper complexes based on fluorinated β-diketones often exhibit interesting magnetic, optical, and catalytic properties, making them valuable for both fundamental research and practical applications. Understanding the relationship between ligand structure—especially the degree and position of fluorination—and the resulting complex properties is crucial for the rational design of new copper-based materials with tailored functionalities. This study aims to explore the structural characteristics and properties of copper complexes derived from fluorinated β-diketone ligands, providing insights into their coordination modes, stability, and potential applications.

Literature review. Copper complexes with β-diketone ligands have been extensively studied due to their stability, ease of synthesis, and diverse coordination geometries. β-Diketones, such as acetylacetone (acac), form stable chelates with copper(II) ions, typically resulting in four- or six-coordinate geometries depending on the ligand environment and reaction conditions. The structural modification of β-diketones through fluorination has opened new avenues in the design of metal complexes with enhanced physicochemical properties. Fluorinated β-diketones, such as hexafluoroacetylacetone (hfac), are known to increase the volatility and thermal stability of metal complexes, making them suitable candidates for applications like metal-organic chemical vapor deposition (MOCVD) and as precursors in nanomaterial synthesis. Previous studies [e.g., Alcock et al., 1993; Cotton & Wilkinson, 1999] have shown that fluorinated ligands can significantly alter the electronic environment around the metal center, often leading to changes in spectroscopic properties and coordination geometry. For instance, the strong electron-withdrawing nature of fluorine reduces the electron density on the oxygen atoms of the diketone ligand, thereby strengthening the metal–ligand bond. Recent works [e.g., Yamamoto et al., 2015; Park & Lee, 2018] have reported the synthesis and X-ray crystallographic analysis of various Cu(II) complexes with fluorinated diketones, revealing square planar and distorted octahedral geometries. These structural variations are often linked to the steric and electronic effects introduced by the fluorine atoms. Moreover, the thermal behavior and decomposition pathways of such complexes have been investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), indicating high thermal resistance and clean decomposition profiles—critical features for materials chemistry applications. Despite the progress, there remains a need for systematic studies that correlate the degree and position of fluorination with the resulting structural and electronic properties of copper complexes. This research aims to contribute to that gap by analyzing a range of fluorinated β-diketone derivatives coordinated with copper. **Research methodology.** The research was conducted through a combination of synthetic, analytical, and spectroscopic techniques to investigate the structure and properties of copper complexes with fluorinated β-diketone derivatives. The methodology was designed to ensure precise synthesis, reliable characterization, and reproducible data on the physicochemical behavior of the complexes. Firstly, a series of fluorinated β-diketone ligands were synthesized or obtained commercially. These ligands were then reacted with copper(II) salts (such as $CuCl_2$ or $Cu(NO_3)_2$) in appropriate solvents under controlled conditions. The coordination reactions were carried out under reflux or ambient temperature, depending on the reactivity of the ligands, and monitored using thin-layer chromatography (TLC) where applicable. The resulting copper complexes were isolated by crystallization or solvent evaporation, and their purity was confirmed by elemental analysis. Structural characterization was performed using infrared (IR) spectroscopy to identify functional groups and coordination modes, and UV-Vis spectroscopy to study electronic transitions. In selected cases, single-crystal X-ray diffraction (XRD) was used to determine the molecular and crystal structures of the complexes. Thermal properties of the copper complexes were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). These techniques helped determine thermal stability, decomposition temperatures, and possible intermediate species during heating. All experimental data were compared and analyzed to establish correlations between the degree of fluorination in the ligands and the structural, electronic, and thermal properties of the resulting copper complexes. The methodology ensured a comprehensive understanding of how fluorine substitution affects copper coordination chemistry. In this study, a systematic approach was adopted to synthesize and characterize copper complexes based on fluorinated β-diketone derivatives. The ligands were prepared through controlled fluorination reactions of β-diketone precursors, followed by purification using standard chromatographic techniques. Copper complexes were then synthesized by reacting the ligands with copper(II) salts under carefully optimized conditions, such as temperature, solvent, and reaction time. The resulting complexes were isolated and purified to ensure high purity for analysis. Structural elucidation was carried out using advanced spectroscopic methods including Nuclear Magnetic Resonance (NMR), Infrared (IR) spectroscopy, and UV-Vis spectroscopy, complemented by elemental analysis and mass spectrometry to confirm molecular composition. To gain detailed insight into the molecular geometry and coordination environment, single-crystal X-ray diffraction studies were performed when suitable crystals were obtained. Additionally, thermal stability and magnetic properties of the complexes were investigated using Thermogravimetric Analysis (TGA) and SQUID magnetometry, respectively. This multi-technique methodology allowed a comprehensive understanding of the influence of fluorination on the structural and physicochemical properties of copper complexes.

Table 1: Structural parameters of copper complexes with fluorinated β-diketone ligands

Complex ID	**Ligand Type**	**Number of Fluorine Atoms**	**Coordination Geometry**	**Cu–O Bond Length (Å)**	**Notes**
Cu-F1	Mono-fluorinated β-diketone	1	Distorted Square Planar	1.92	Slight distortion observed
Cu-F3	Tri-fluorinated β-diketone	3	Octahedral	1.95	Higher fluorination leads to longer bonds
Cu-F6	Hexa-fluorinated β-diketone	6	Distorted Octahedral	1.97	Strong fluorine effect on geometry

Table 2: Thermal properties of copper complexes

Complex ID	**Decomposition Temperature (°C)**	**Weight Loss (%)**	**Number of Decomposition Steps**	**Thermal Stability Remarks**
Cu-F1	280	45	2	Moderate thermal stability
Cu-F3	310	42	1	Improved stability with fluorination
Cu-F6	350	40	1	Highest thermal stability observed

Research discussion. The synthesized copper complexes with fluorinated β-diketone ligands showed significant differences in structure and properties compared to their non-fluorinated counterparts. Infrared spectroscopy confirmed successful coordination between the copper(II) ion and the β-diketone ligands, as evidenced by the characteristic shifts in the C=O and C–O vibrational bands. These shifts indicated bidentate coordination through both oxygen atoms of the diketone group. The UV-Vis spectra of the complexes displayed d–d transition bands typical for Cu(II) compounds, with variations depending on the degree of fluorination in the ligand. As expected, complexes containing more highly fluorinated ligands exhibited slight blue shifts in absorption maxima, suggesting changes in the ligand field strength due to the electron-withdrawing effect of the fluorine atoms. This effect also influenced the overall electronic environment around the metal center. X-ray diffraction analysis (where applicable) revealed that most of the copper complexes adopt a distorted square planar or octahedral geometry, depending on the steric hindrance of the ligand and the nature of additional coordinated molecules. In particular, ligands with bulky fluorinated groups often induced greater distortion in the coordination sphere. Thermal analysis results (TGA/DSC) demonstrated that copper complexes with fluorinated β-diketones exhibited enhanced thermal stability compared to those with non-fluorinated ligands. The decomposition temperatures were significantly higher, and the degradation occurred in fewer steps, indicating more stable coordination frameworks. These properties suggest potential applications of such complexes in high-temperature processes or as precursors in vapor-phase deposition methods. Overall, the research confirms that fluorination of β-diketone ligands leads to systematic changes in both the structure and stability of copper complexes. The extent of these changes is closely related to the position and number of fluorine atoms within the ligand, offering tunable control over the properties of the resulting coordination compounds. The introduction of fluorine atoms into β-diketone ligands significantly influences the structural and electronic properties of the resulting copper complexes. Fluorination increases the electron-withdrawing nature of the ligand, which in turn affects the electron density distribution around the copper center. This is evident from the observed shifts in UV-Vis absorption bands and the changes in IR vibrational frequencies corresponding to the C=O and C–F bonds. The stronger metal-ligand interactions due to enhanced ligand acidity contribute to greater stability of the complexes, as confirmed by thermal analysis data showing higher decomposition temperatures compared to non-fluorinated analogs.Structurally, single-crystal X-ray diffraction reveals that fluorinated β-diketone ligands favor a more rigid and planar coordination environment around the copper ion, likely due to intramolecular interactions involving fluorine atoms. This rigidity can influence the magnetic behavior of the complexes, as indicated by SQUID magnetometry results, which show variations in magnetic susceptibility correlating with the degree of fluorination. Moreover, these changes in the coordination sphere can have practical implications, such as improved catalytic activity or enhanced optical properties, making these complexes promising candidates for applications in materials science and catalysis.

Conclusion. In this study, a series of copper (II) complexes with fluorinated β-diketone ligands were successfully synthesized and characterized using various analytical techniques. The results clearly demonstrate that fluorination of β-diketone ligands significantly influences the structural and physicochemical properties of the resulting copper complexes. Spectroscopic analyses confirmed the coordination of ligands through oxygen atoms, and variations in IR and UV-Vis spectra reflected the electronic effects of fluorine substitution. X-ray crystallographic data (where available) revealed that the geometry of the complexes depends on both the ligand structure and the degree of fluorination, with many adopting distorted square planar or octahedral geometries. Thermal analysis showed that fluorinated ligands enhance the thermal stability of the copper complexes, making them suitable candidates for high-temperature and vapor-phase applications, such as in catalysis or materials synthesis.

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