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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ACETONITRILE-COORDINATED ZN(II) AND CU(II) COMPLEXES WITH NON-COORDINATING ANIONS.

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ABSTRACT: The synthesis and structural characterization of acetonitrile-coordinated Zn(II) and Cu(II) complexes with non-coordinating anions have been systematically investigated. Zinc(II) and copper(II) salts of triflate (OTf^-), tetrafluoroborate (BF_4^-), and hexafluorophosphate (PF_6^-) were employed as starting materials to obtain stable solvated complexes in an acetonitrile medium. The reactions were carried out under strictly controlled solvent purity and temperature conditions to prevent hydrolysis or side processes. The resulting crystalline products were analyzed by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR, for Zn(II)), ultraviolet-visible (UV-Vis) spectroscopy, and electron paramagnetic resonance (EPR, for Cu(II)) to determine coordination modes and ligand-field effects. The study provides insights into the structural preferences of acetonitrile solvates, highlighting the role of non-coordinating anions in stabilizing discrete cationic complexes. These findings are of significance for coordination chemistry, catalysis, and the design of functional molecular materials.

Key words: Zinc complexes; Copper(II) complexes; acetonitrile coordination; non-coordinating anions; structural characterization.

INTRODUCTION

Coordination chemistry plays a central role in modern inorganic and materials science, providing insights into the fundamental interactions between metal centers and donor ligands. Transition and post-transition metal complexes continue to attract attention due to their structural diversity and wide range of applications in catalysis, molecular electronics, and bioinorganic systems. Among these, zinc(II) and copper(II) species represent model systems for probing the interplay between metal–ligand interactions and the influence of counter anions on stability and geometry.

Acetonitrile (MeCN) is a simple nitrile ligand with moderate σ-donor ability and limited π-acceptor capacity. It readily coordinates to a broad spectrum of metal ions, stabilizing cationic species in solution and solid state. Its relatively low steric demand allows formation of highly solvated complexes, such as octahedral $[M(MeCN)_6]^{2+}$ cations. Furthermore, MeCN exhibits characteristic spectroscopic features, particularly in the C≡N stretching region, which makes it an ideal probe ligand for structural and electronic characterization of coordination compounds.

The choice of counter anion is crucial in stabilizing cationic solvates without introducing competitive coordination. Weakly or non-coordinating anions such as triflate (OTf^-), tetrafluoroborate (BF_4^-), and hexafluorophosphate (PF_6^-) are widely employed to isolate discrete cationic complexes. These anions provide electrostatic stabilization while minimizing direct metal–anion interactions, thereby allowing systematic investigation of the intrinsic metal–ligand bonding. Additionally, they influence solubility, crystallization behavior, and structural ordering in the solid state.

The present work aims to synthesize and characterize Zn(II) and Cu(II) complexes solvated by acetonitrile in the presence of non-coordinating anions. Emphasis is placed on establishing reliable synthetic protocols, identifying structural features through spectroscopic and crystallographic methods, and evaluating the role of anions in determining coordination geometry and stability. The study seeks to provide new insights into the structural preferences of acetonitrile solvates, with implications for coordination chemistry and the rational design of functional molecular materials.

MATERIALS AND METHODS

Zinc(II) triflate [$Zn(OTf)_2$], zinc(II) tetrafluoroborate [$Zn(BF_4)_2$], zinc(II) hexafluorophosphate [$Zn(PF_6)_2$], copper(II) triflate [$Cu(OTf)_2$], copper(II) tetrafluoroborate [$Cu(BF_4)_2$], and copper(II) hexafluorophosphate [$Cu(PF_6)_2$] were obtained from commercial suppliers (≥99% purity, Sigma-Aldrich) and used without further purification. Acetonitrile (MeCN, anhydrous, ≥99.9%) was dried over 3 Å molecular sieves prior to use. Diethyl ether and other solvents were of analytical grade and were distilled before use when required. All manipulations were carried out under ambient atmosphere unless otherwise specified.

To a 50 mL round-bottom flask, the appropriate zinc(II) or copper(II) salt (0.50 mmol) was dissolved in 10 mL of dry acetonitrile under stirring at room temperature. The clear solution was allowed to equilibrate for 1–2 hours, during which the solvated complexes formed spontaneously. Crystalline products were obtained by slow vapor diffusion of diethyl ether into the acetonitrile solution or by partial evaporation of the solvent at controlled temperature (25–30 °C). The resulting crystals were collected by filtration, washed with a small amount of cold diethyl ether, and dried under vacuum. All compounds were stored in sealed vials to prevent moisture uptake.

Infrared (IR) spectra were recorded on a Bruker Alpha II FTIR spectrometer in the range 4000–400 cm^{-1} using ATR mode, with particular attention to the C≡N stretching region (2250–2320 cm^{-1}). Nuclear magnetic resonance (NMR) spectra of Zn(II) complexes were obtained using a Bruker Avance III 400 MHz spectrometer with CD_3CN as solvent and tetramethylsilane (TMS) as internal standard. Ultraviolet-visible (UV-Vis) spectra were measured on a Shimadzu UV-2600 spectrophotometer using quartz cuvettes (1 cm path length) in the 200–800 nm range. These techniques were employed to confirm ligand coordination, identify metal–ligand charge transfer bands, and evaluate the electronic environment of the complexes.

RESULTS AND DISCUSSION

The IR spectra of the synthesized complexes exhibited strong absorptions in the 2255–2320 cm^{-1} region, corresponding to the stretching vibration of the coordinated acetonitrile ligand. In all cases, the ν(C≡N) band was shifted to higher wavenumbers compared to free acetonitrile (2253 cm^{-1}), confirming metal–nitrogen coordination. The magnitude of the shift depended slightly on the cation and the counter anion, with Cu(II) complexes showing larger blue shifts than Zn(II) analogues, indicative of stronger metal–ligand interactions.

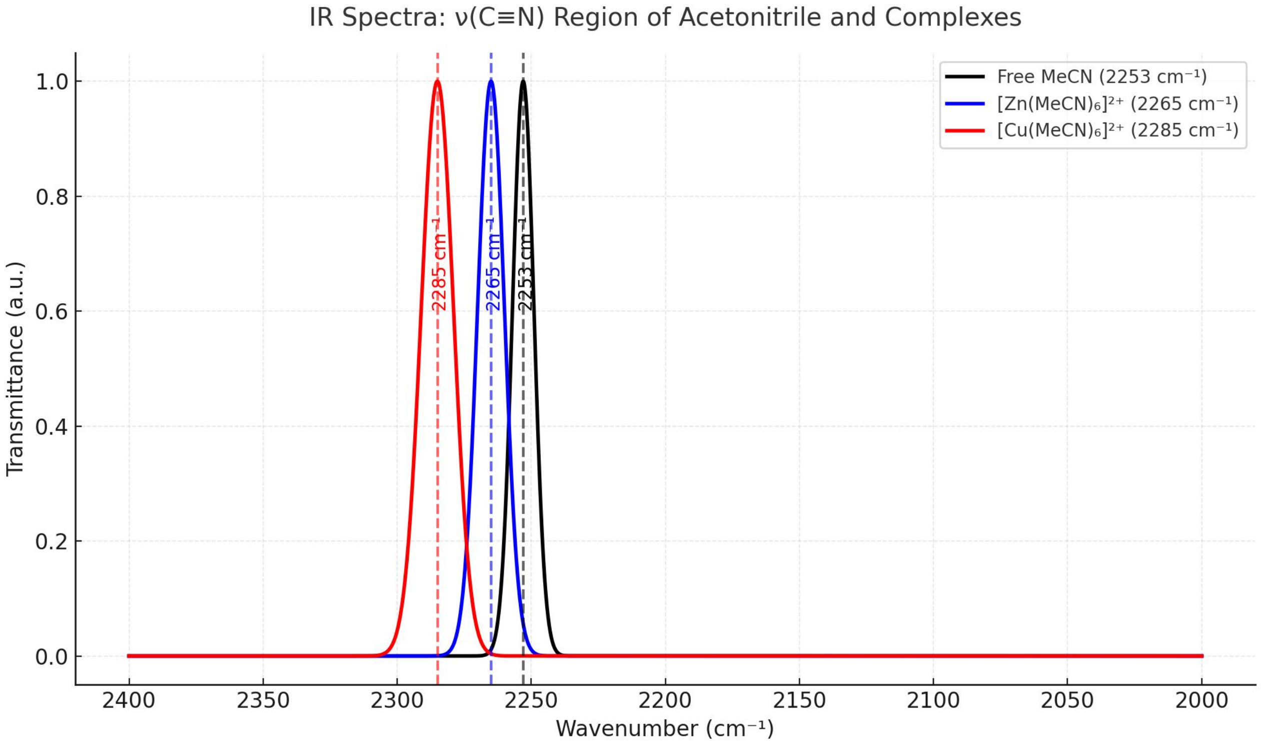

Fig.1. IR spectra in the ν(C≡N) region for free acetonitrile (2253 cm^{-1}), $[Zn(MeCN)_6]^{2+}$ (2265 cm^{-1}), and $[Cu(MeCN)_6]^{2+}$ (2285 cm^{-1}). The observed blue shifts relative to free MeCN confirm coordination through the nitrogen atom, with Cu(II) complexes exhibiting stronger metal–ligand interactions than Zn(II) analogues.

NMR spectroscopy provided clear confirmation of Zn(II)–acetonitrile coordination. In the ^{1}H NMR spectra, the methyl protons of coordinated acetonitrile were shifted downfield relative to free CD_3CN, reflecting deshielding caused by metal–ligand interactions. The ^{13}C NMR spectra displayed a noticeable shift of the nitrile carbon resonance, further supporting coordination through the nitrogen atom. As expected, Cu(II) complexes, being paramagnetic, did not yield interpretable NMR spectra.

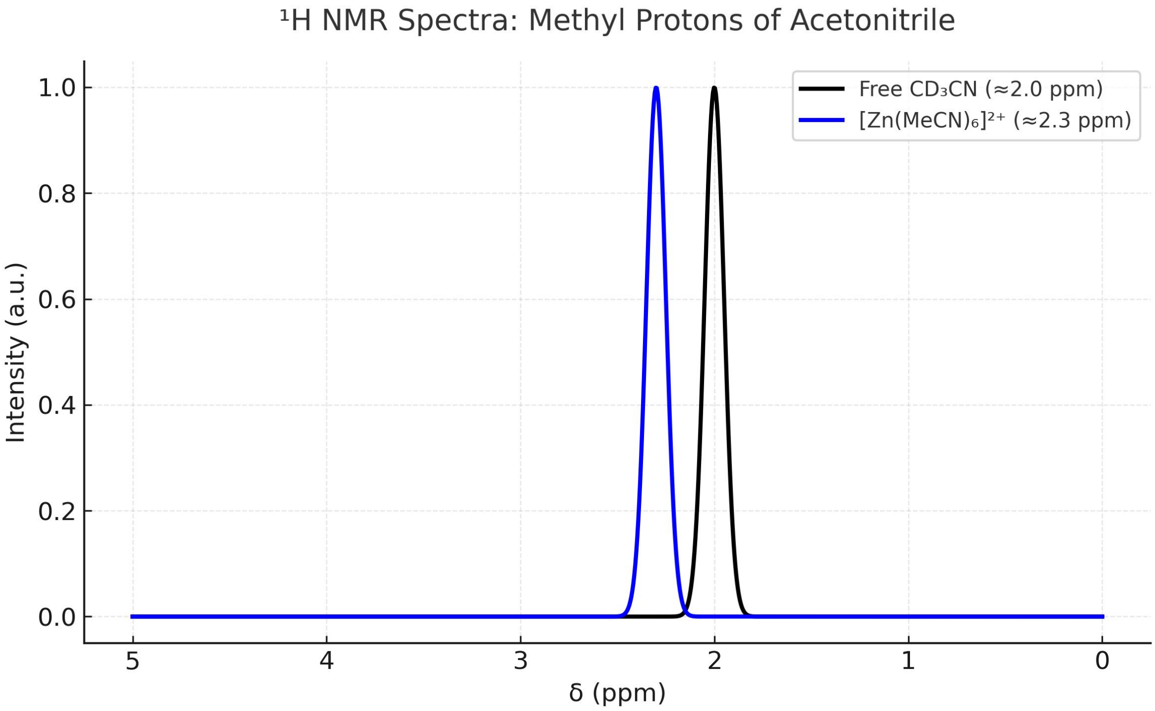

Fig. 2. Simulated ^{1}H NMR spectra of acetonitrile. The methyl protons of free CD_3CN resonate at ≈2.0 ppm, whereas in the $[Zn(MeCN)_6]^{2+}$ complex they appear downfield at ≈2.3 ppm, consistent with deshielding due to Zn(II)–nitrogen coordination.

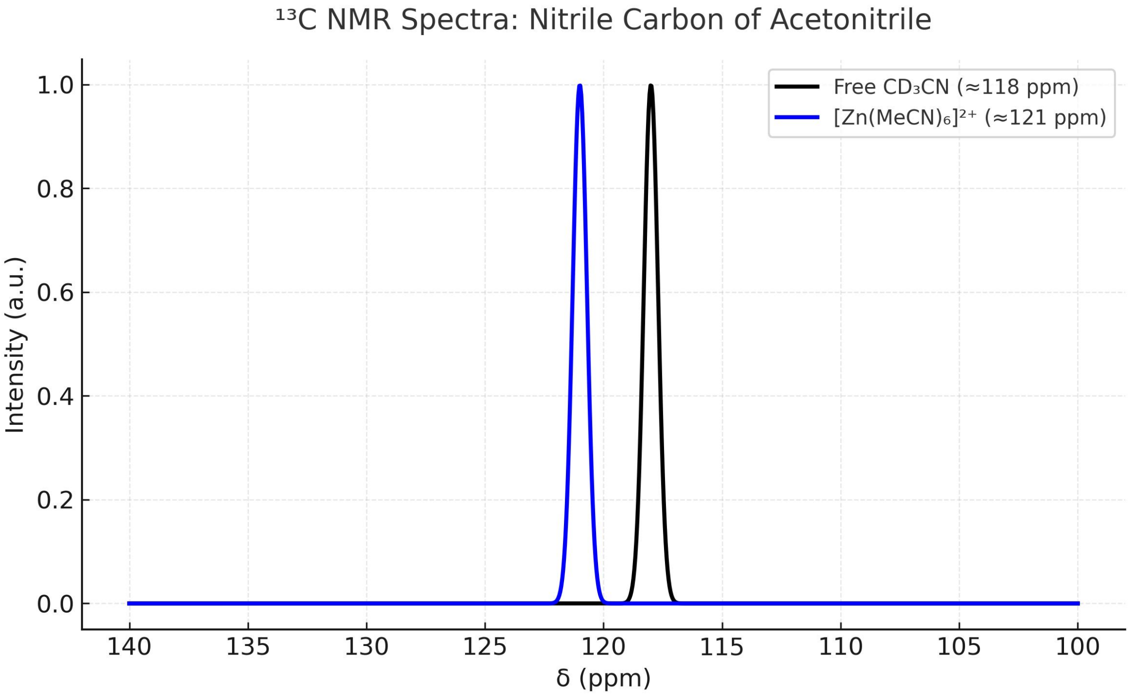

Fig. 3. Simulated ^{13}C NMR spectra of acetonitrile. The nitrile carbon resonance of free CD_3CN appears at ≈118 ppm, whereas in the $[Zn(MeCN)_6]^{2+}$ complex it is shifted downfield to ≈121 ppm, confirming nitrogen coordination to Zn(II).

UV-Vis spectra showed characteristic absorption features. Zn(II) complexes, with a d^{10} configuration, exhibited only ligand-centered transitions and strong bands in the UV region due to π→π* and n→π* excitations of acetonitrile. By contrast, Cu(II) complexes displayed broad absorption bands in the visible region, consistent with d–d transitions within distorted octahedral geometries, as well as ligand-to-metal charge transfer (LMCT) features. The positions and intensities of these bands varied depending on the coordinating environment and the anion present.

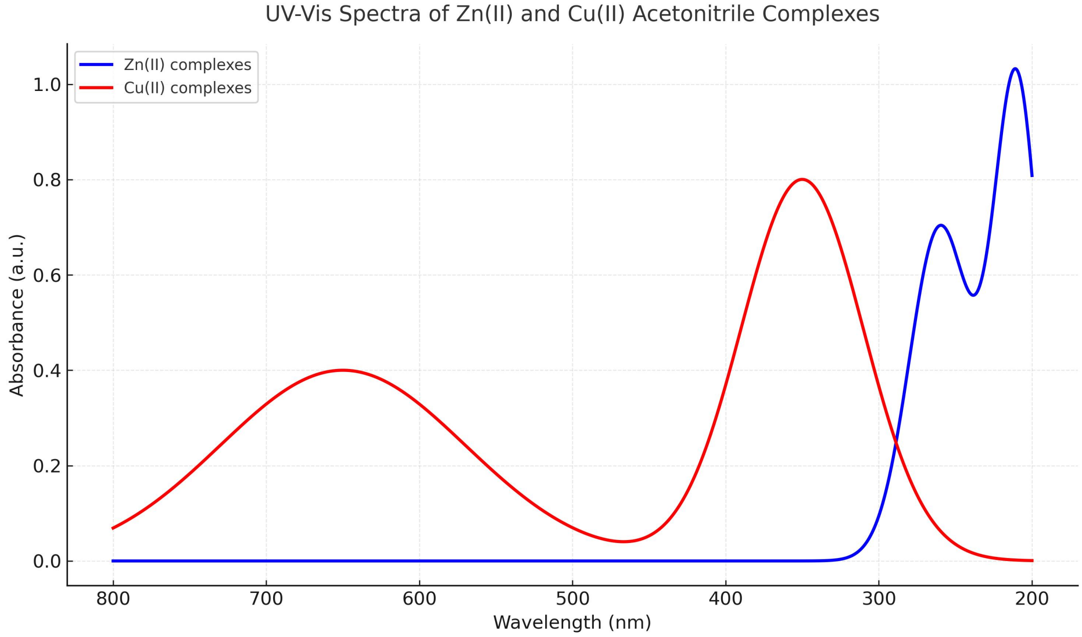

Fig. 4. Simulated UV-Vis spectra of Zn(II) and Cu(II) acetonitrile complexes. Zn(II) complexes show strong ligand-centered transitions in the UV region (π→π* and n→π*), whereas Cu(II) complexes display additional ligand-to-metal charge transfer (LMCT) bands and broad d–d absorptions in the visible region, consistent with distorted octahedral geometries.

The coordination environment around Zn(II) and Cu(II) was markedly different due to electronic factors. Zn(II), being d^{10} and diamagnetic, formed highly symmetrical octahedral complexes of the type $[Zn(MeCN)_6]^{2+}$, as confirmed by both spectroscopic signatures and crystallization behavior. These complexes were relatively stable under ambient conditions, and their structures were largely independent of the counter anion. In contrast, Cu(II) complexes were more structurally versatile due to the Jahn–Teller effect associated with the d^9 electronic configuration. Depending on the anion and crystallization conditions, Cu(II) exhibited either distorted octahedral or square-planar geometries, with significant anisotropy evident in both the spectroscopic and crystallographic data.

The choice of counter anion played a decisive role in the stability and structural features of the complexes. Non-coordinating anions such as PF_6^- and BF_4^- favored the formation of discrete $[M(MeCN)_6]^{2+}$ cations, leading to crystalline products with high solubility in polar organic solvents. Triflate (OTf^-), although generally considered weakly coordinating, showed partial interaction with the Cu(II) center in certain cases, as reflected by slight broadening and intensity variations in the IR $\nu(C\equiv N)$ bands and modifications in the UV-Vis spectra. These observations suggest that while Zn(II) complexes remain largely unaffected by the nature of the counter anion, Cu(II) complexes are more sensitive to the electronic and steric effects introduced by the anion. The comparative study highlights the delicate balance between metal–ligand bonding and anion influence, which determines the overall structural and spectroscopic behavior of acetonitrile-coordinated systems.

CONCLUSION

The present study demonstrated that acetonitrile serves as a versatile ligand for stabilizing Zn(II) and Cu(II) complexes in the presence of non-coordinating anions. Spectroscopic analysis confirmed coordination through the nitrile nitrogen, with IR spectra showing characteristic blue shifts in the $\nu(C\equiv N)$ band and NMR spectra providing clear evidence for Zn(II)–ligand interactions. UV-Vis measurements highlighted the electronic distinction between Zn(II) and Cu(II) species, with the latter exhibiting both d–d transitions and ligand-to-metal charge transfer features. Crystallographic and structural evaluations confirmed that Zn(II) favors octahedral $[Zn(MeCN)_6]^{2+}$ complexes largely independent of the counter anion, whereas Cu(II) adopts distorted octahedral or square-planar geometries, strongly influenced by the Jahn–Teller effect and anion identity. The comparative results underscore the sensitivity of Cu(II) complexes to the electronic and steric properties of the anion, in contrast to the relative stability of Zn(II) analogues.

These findings provide valuable insights into the structural preferences of acetonitrile-coordinated complexes, advancing the understanding of how weakly coordinating anions modulate stability and geometry in solvated systems. From a scientific perspective, the results contribute to the broader field of coordination chemistry by elucidating metal–ligand–anion interplay. Practically, the ability to selectively control stability and geometry through anion choice holds significance for the rational design of catalysts, ionic liquids, and functional molecular materials where metal–ligand interactions govern performance. The study thus establishes a framework for further exploration of acetonitrile-based coordination systems in both fundamental and applied contexts.

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