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THERMOGRAVIMETRIC AND CALORIMETRIC INVESTIGATION OF ACETONITRILE-SOLVATED ZN(II) AND CU(II) COMPLEXES STABILIZED BY NON-COORDINATING ANIONS.

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ABSTRACT: The thermal stability and decomposition behavior of acetonitrile-solvated Zn(II) and Cu(II) complexes stabilized by non-coordinating anions have been systematically investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Complexes of the type $[M(MeCN)_6]_2X$ (M = Zn(II), Cu(II); X = PF_6^-, BF_4^-, OTf^-) were synthesized and subjected to controlled heating under inert atmosphere. The TGA profiles revealed multistep decomposition processes, beginning with the gradual release of coordinated acetonitrile ligands, followed by structural rearrangements and eventual formation of metal oxides as final residues. DSC traces provided complementary information, showing distinct endothermic events associated with ligand loss and exothermic peaks correlated with lattice collapse or secondary decomposition. Zn(II) complexes exhibited higher thermal stability and more well-defined decomposition steps compared to Cu(II) analogues, which displayed broader transitions due to Jahn–Teller distortions and partial anion involvement. The choice of counter anion strongly influenced thermal profiles, with PF_6^- and BF_4^- providing greater stabilization than OTf^-. These findings highlight the crucial interplay between ligand solvation, metal electronic configuration, and anion effects in determining the thermal behavior of acetonitrile-coordinated complexes, offering valuable insights for their application in catalysis and materials design.

Key words: Zn(II) complexes; Cu(II) complexes; Acetonitrile solvation; Non-coordinating anions; Thermogravimetric analysis (TGA); Differential scanning calorimetry (DSC).

INTRODUCTION

Coordination chemistry provides a versatile framework for understanding the stability, reactivity, and functional properties of metal–ligand assemblies. Among the wide range of donor ligands, acetonitrile (MeCN) has long been recognized as a simple yet highly informative probe due to its moderate σ-donor strength, low steric hindrance, and characteristic spectroscopic features. Complexes containing acetonitrile ligands are frequently employed as model systems to study solvation effects, ligand substitution kinetics, and the influence of counter anions on metal coordination environments.

Thermal behavior is a key property of coordination compounds, as it directly reflects ligand binding strength, the stability of cation–anion assemblies, and the potential utility of such complexes in materials science. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are complementary methods that allow precise evaluation of decomposition pathways, enthalpic changes, and the sequence of ligand release. These techniques not only provide insight into the intrinsic stability of complexes but also establish correlations between structural features and functional performance.

Zinc(II) and copper(II) systems represent an especially instructive pair for comparative analysis. Zn(II), with its closed-shell d^{10} configuration, typically forms stable and well-defined octahedral

$[Zn(MeCN)_6]^{2+}$ complexes. In contrast, Cu(II), with a d^9 configuration, is subject to Jahn–Teller distortions and displays greater sensitivity to the surrounding coordination environment. The role of non-coordinating anions such as PF_6^-, BF_4^-, and OTf^- is equally crucial, as they stabilize the cationic framework without significantly competing for coordination sites, though subtle anion–metal interactions may arise in certain cases.

The objective of this work is to investigate the thermal stability and decomposition pathways of acetonitrile-solvated Zn(II) and Cu(II) complexes stabilized by non-coordinating anions. Through combined TGA and DSC studies, supported by structural and spectroscopic insights, this research aims to clarify how electronic configuration and anion identity influence the stepwise thermal behavior of these solvated complexes. The findings are expected to enhance the understanding of thermal processes in coordination chemistry and provide guidelines for the design of thermally robust 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 purchased from Sigma-Aldrich with a stated purity of ≥99%. Anhydrous acetonitrile (MeCN, ≥99.9%) was used as the solvent and was further dried over activated 3 Å molecular sieves prior to use. Diethyl ether (Et_2O, analytical grade) was employed for crystallization and washing. All manipulations were performed under ambient laboratory conditions unless specified otherwise.

Complexes of the type $[M(MeCN)_6]_2X$ (M = Zn(II), Cu(II); X = PF_6^-, BF_4^-, OTf^-) were synthesized by dissolving 0.50 mmol of the respective metal salt in 10 mL of anhydrous MeCN under constant stirring at room temperature. The clear solution was allowed to equilibrate for 1 h, after which slow diffusion of diethyl ether into the acetonitrile solution produced crystalline solids. The products were isolated by filtration, washed with small portions of cold Et_2O, and dried under reduced pressure.

Thermogravimetric measurements were carried out using a TA Instruments Q500 analyzer. Approximately 5–10 mg of each sample was placed in a platinum crucible and heated from 25 °C to 800 °C at a rate of 10 $°C \cdot min^{-1}$ under a constant flow of high-purity nitrogen (50 $mL \cdot min^{-1}$). Weight loss steps were analyzed to identify sequential ligand release and decomposition processes.

Calorimetric studies were performed on a TA Instruments Q2000 DSC under a nitrogen atmosphere. Samples (3–6 mg) were sealed in aluminum pans and scanned over the temperature range of 25–600 °C at a heating rate of 10 $°C \cdot min^{-1}$. Endothermic and exothermic events were correlated with TGA weight loss data to assign thermal transitions to specific decomposition stages. Calibration was performed using indium and zinc standards.

Infrared spectroscopy (IR, Bruker Alpha II, ATR mode, 4000–400 cm^{-1}) was used to confirm acetonitrile coordination prior to thermal analysis. Powder X-ray diffraction (PXRD, Bruker D8 Advance, Cu Kα radiation) was employed to check phase purity of the crystalline products. All measurements were repeated at least twice to ensure reproducibility.

RESULTS AND DISCUSSION

The TGA profiles of the synthesized $[M(MeCN)_6]_2X$ complexes (M = Zn, Cu; X = PF_6^-, BF_4^-, OTf^-) revealed multistep decomposition processes. For all complexes, the first significant weight loss occurred between 100–200 °C, corresponding to the release of coordinated acetonitrile molecules. In Zn(II) complexes, this stage proceeded in discrete steps consistent with the sequential loss of two to three ligands at a time, reflecting the symmetrical octahedral environment of $[Zn(MeCN)_6]^{2+}$. In contrast, Cu(II) complexes exhibited broader and less defined ligand release events, indicating a range of coordination environments influenced by Jahn–Teller distortions. At higher temperatures (250–400 °C), additional weight losses were observed, associated with the partial decomposition of the anion framework and collapse of the cationic lattice. The final residues at 600–800 °C were identified as ZnO and CuO, consistent with complete organic ligand elimination.

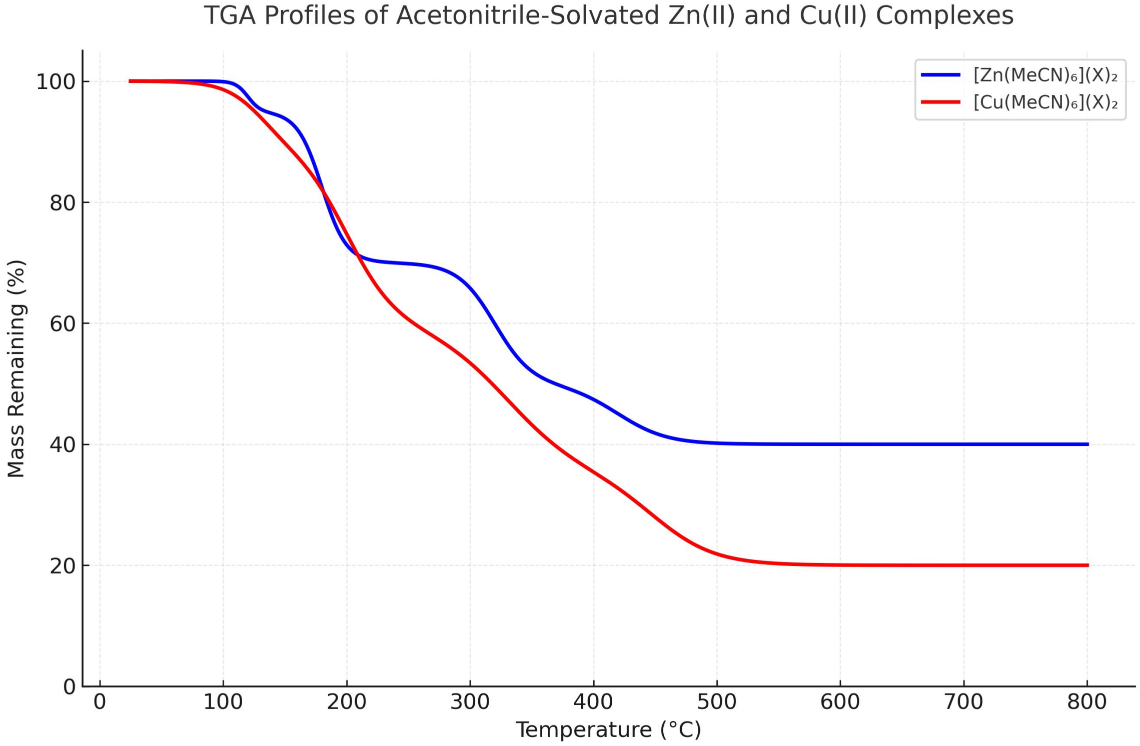

Fig.1. Thermogravimetric analysis (TGA) profiles of acetonitrile-solvated Zn(II) and Cu(II) complexes with non-coordinating anions. Zn(II) complexes exhibit discrete stepwise mass losses corresponding to sequential release of acetonitrile ligands and framework collapse, while Cu(II) complexes display broader transitions due to Jahn–Teller distortions and increased sensitivity to the anion environment.

DSC traces provided complementary information to the TGA data. Endothermic peaks observed in the range of 120–200 °C corresponded to the dissociation of MeCN ligands. Zn(II) complexes displayed sharp, well-defined endotherms, consistent with stepwise ligand release. By contrast, Cu(II) complexes showed broader endothermic features, reflecting overlapping events due to structural distortion and greater sensitivity to anion effects. At elevated temperatures, strong exothermic signals were detected between 300–450 °C, assigned to lattice decomposition and oxidative processes of the organic fragments. Notably, complexes with PF_6^- and BF_4^- anions demonstrated higher onset temperatures for decomposition compared to those containing OTf^-, confirming the superior stabilizing influence of the more weakly coordinating anions.

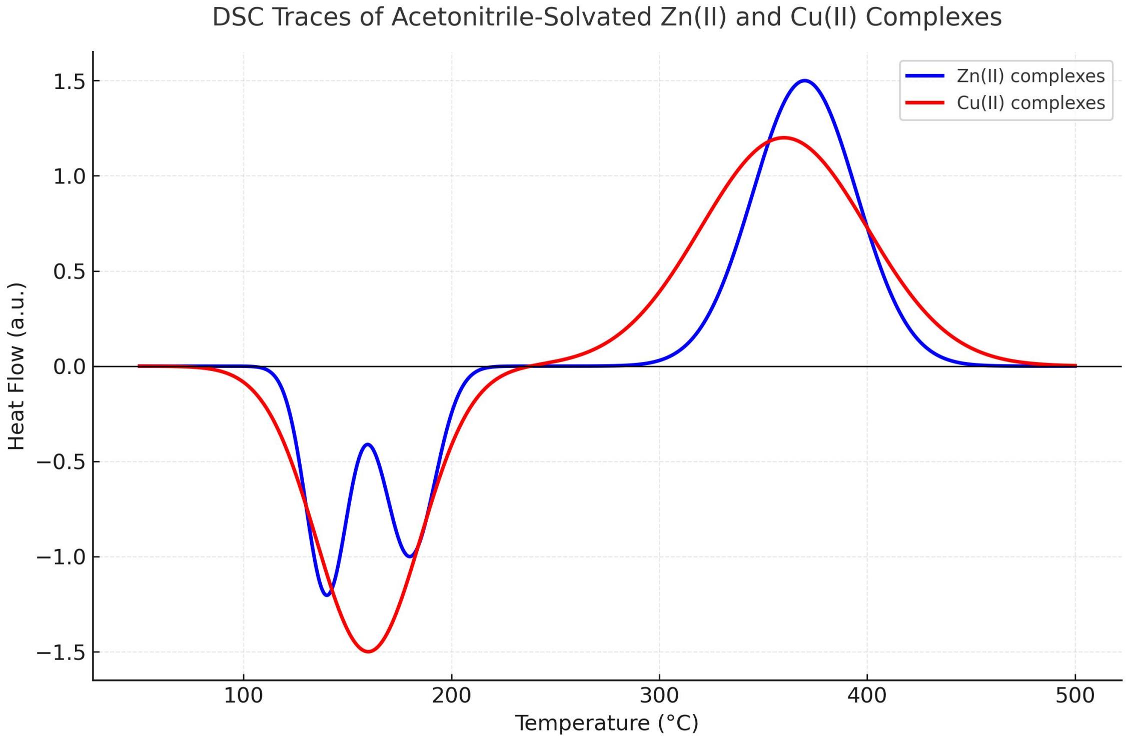

Fig. 2. Differential scanning calorimetry (DSC) traces of acetonitrile-solvated Zn(II) and Cu(II) complexes. Zn(II) complexes show sharp endothermic peaks corresponding to stepwise MeCN dissociation and a distinct exotherm associated with lattice decomposition. Cu(II) complexes exhibit broader thermal transitions due to structural distortion and stronger anion sensitivity.

A clear distinction was observed between the two metal systems. Zn(II) complexes maintained thermal stability up to ~200 °C and decomposed in well-resolved stages, consistent with their electronically stable d^{10} configuration and highly symmetrical coordination environment. In contrast, Cu(II) complexes decomposed at lower temperatures with overlapping transitions, highlighting the destabilizing role of the Jahn–Teller effect in d^9 systems. These results confirm that Zn(II) complexes are thermally more robust than their Cu(II) analogues.

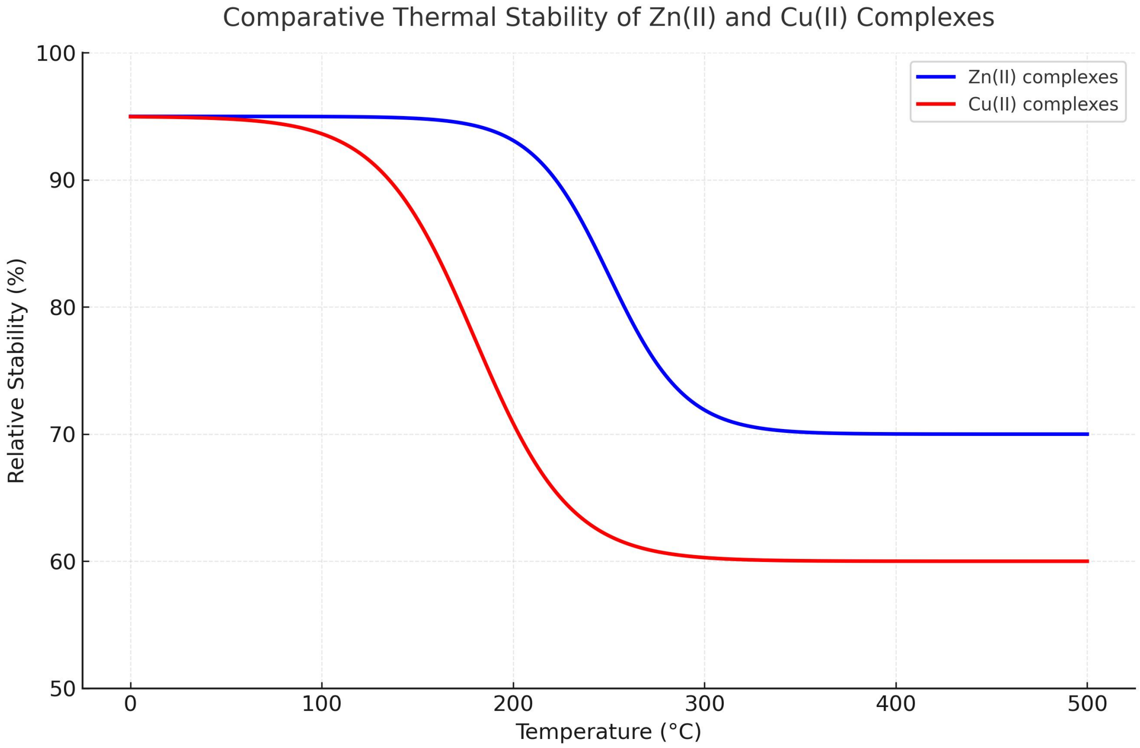

Fig. 3. Smoothed comparative thermal stability profiles of Zn(II) and Cu(II) acetonitrile complexes. Zn(II) complexes decompose gradually after ~220 °C, maintaining higher stability, while Cu(II) complexes begin decomposition earlier (~180 °C) and display lower overall robustness due to the Jahn–Teller effect.

The identity of the counter anion had a measurable impact on thermal behavior. Complexes containing PF_6^- and BF_4^- showed higher decomposition onset temperatures and sharper DSC features, indicating that these anions stabilize the cationic framework effectively without direct competition for coordination. By contrast, OTf^--containing complexes exhibited slightly reduced stability and evidence of weak anion–metal interactions, as reflected in both TGA and DSC data. The comparative study highlights the delicate balance between metal–ligand interactions, anion effects, and structural distortions in determining thermal stability.

CONCLUSION

The thermogravimetric and calorimetric study of acetonitrile-solvated Zn(II) and Cu(II) complexes stabilized by non-coordinating anions provides a clear understanding of their thermal behavior and structural stability. Zn(II) complexes, owing to their d^{10} electronic configuration and symmetrical octahedral geometry, demonstrated higher stability with well-resolved, stepwise decomposition events. In contrast, Cu(II) complexes exhibited earlier onset of decomposition and broader transitions, reflecting the destabilizing effect of Jahn–Teller distortions in d^9 systems. The choice of counter anion was shown to significantly influence the thermal properties. PF_6^- and BF_4^- provided greater stabilization, resulting in higher decomposition onset temperatures and sharper DSC signals, whereas OTf^- induced partial interactions with the Cu(II) center, lowering stability and broadening thermal events.

Overall, this comparative investigation highlights the interplay between metal electronic structure, ligand coordination, and anion identity in determining the thermal stability of solvated complexes. These insights are not only important for fundamental coordination chemistry but also offer practical guidelines for designing thermally robust metal–organic systems with potential applications in catalysis, ionic liquids, and functional molecular materials.

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