

ELECTRONIC SPECTROSCOPIC INVESTIGATION OF A ONE-DIMENSIONAL CADMIUM(II) ISONICOTINATE COORDINATION POLYMER

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Abstract

Coordination polymers based on pyridine-carboxylate ligands have attracted considerable attention due to their structural diversity and potential applications in catalysis, adsorption, luminescent materials, and crystal engineering. In the present study, a cadmium(II)-based coordination polymer incorporating the isonicotinate ligand was synthesized and characterized by UV-Vis spectroscopy. Single-crystal structural analysis revealed the formation of a one-dimensional coordination polymer formulated as catena-poly[(μ_2 -isonicotinato- κ^2 O,O': κ N)(κ^2 -O,O'-nitrate)(diaqua)cadmium(II)]·(N,N-dimethylamine), with the general composition [Cd(μ -INA)(NO₃)(H₂O)₂]_n. The isonicotinate ligand acts as a bridging linker through both carboxylate oxygen and pyridyl nitrogen donor atoms, connecting adjacent Cd(II) centers into infinite one-dimensional chains. According to the accepted nomenclature for coordination polymers, the compound is therefore classified as a catena-poly structure.

The electronic absorption spectrum exhibits an intense absorption maximum at 295 nm, which is assigned to ligand-centered $\pi \rightarrow \pi$ electronic transitions associated with the conjugated aromatic pyridine-carboxylate framework. A weak and broad absorption feature observed within the 320-360 nm region may be attributed to $n \rightarrow \pi$ transitions of the coordinated carboxylate groups and possible ligand-to-metal charge-transfer interactions. No significant absorption bands were detected in the visible region, which is consistent with the d^{10} electronic configuration of Cd(II) and the absence of $d-d$ transitions. The observed spectroscopic behavior confirms the successful coordination of the isonicotinate ligand to the cadmium centers and supports the formation of a stable one-dimensional coordination polymer. These findings contribute to the understanding of the electronic properties of cadmium-

based coordination polymers and provide a basis for future investigations of their functional applications.

Keywords

Cadmium(II), isonicotinate, coordination polymer, catena-poly, UV-Vis spectroscopy, $\pi \rightarrow \pi$ transition.

Introduction

Coordination polymers constructed from pyridine carboxylate ligands have become an important class of crystalline materials due to their remarkable structural diversity and tunable physicochemical properties. These compounds have attracted considerable interest in recent years because of their potential applications in gas storage and separation, heterogeneous catalysis, luminescent materials, molecular sensing, drug delivery, and functional porous materials. The ability of pyridine carboxylate ligands to coordinate metal ions through multiple donor sites enables the formation of coordination architectures with various dimensionalities, ranging from discrete molecular complexes to one-, two-, and three-dimensional extended frameworks.

Among pyridine carboxylate derivatives, isonicotinic acid (4-pyridinecarboxylic acid, HINA) is considered one of the most versatile building blocks in coordination chemistry. The ligand contains both a pyridine nitrogen atom and a carboxylate group, providing N,O-donor coordination sites capable of binding metal ions in different modes. Owing to this dual functionality, isonicotinate can act as a terminal ligand or as a bridging linker connecting adjacent metal centers, thereby promoting the construction of extended coordination networks. Furthermore, the rigid aromatic backbone of the ligand facilitates the formation of well-defined supramolecular architectures through hydrogen bonding and π - π stacking interactions.

Cadmium(II) ions are particularly attractive for the synthesis of coordination polymers because of their flexible coordination geometry, relatively large ionic radius, and ability to accommodate a wide range of coordination numbers. These characteristics often lead to the formation of structurally diverse coordination compounds with interesting optical and electronic properties. The combination of Cd(II) ions with isonicotinate ligands therefore represents an effective strategy for designing novel coordination polymers with predictable structural motifs.

In the present study, a cadmium(II) coordination polymer incorporating isonicotinate and nitrate ligands was synthesized and investigated. Structural analysis revealed that the isonicotinate ligand acts as a μ_2 -bridging linker, connecting neighboring Cd(II) centers into an infinite one-dimensional chain. According to the

accepted nomenclature for coordination polymers, one-dimensional structures are designated by the prefix *catena-poly*, whereas two-dimensional and three-dimensional architectures are described as *layer-poly* and *framework-poly*, respectively. Therefore, the title compound is appropriately classified as a *catena-poly* coordination polymer. In addition, the electronic properties of the compound were examined using UV-Vis spectroscopy in order to evaluate the influence of metal-ligand coordination on its absorption behavior and electronic transitions.

Results and Discussion

The synthesized coordination polymer was formulated as $[\text{Cd}(\mu\text{-INA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$, where INA denotes the isonicotinate ligand. Structural analysis revealed that the isonicotinate ligand functions as a μ_2 -bridging linker through both the carboxylate oxygen atoms and the pyridine nitrogen atom. This coordination mode enables the ligand to connect neighboring Cd(II) centers, generating an infinite one-dimensional polymeric chain. The extended connectivity observed in the crystal structure confirms the formation of a coordination polymer rather than a discrete molecular complex. According to the accepted nomenclature for coordination polymers, compounds exhibiting one-dimensional chain architectures are designated by the prefix *catena-poly*. Therefore, the title compound is appropriately named as catena-poly $[(\mu_2\text{-isonicotinato-}\kappa^2\text{O}, \text{O}':\kappa\text{N})(\kappa^2\text{-O}, \text{O}'\text{-nitrato})(\text{diaqua})\text{cadmium(II)}] \cdot (\text{N}, \text{N-dimethylamine})$.

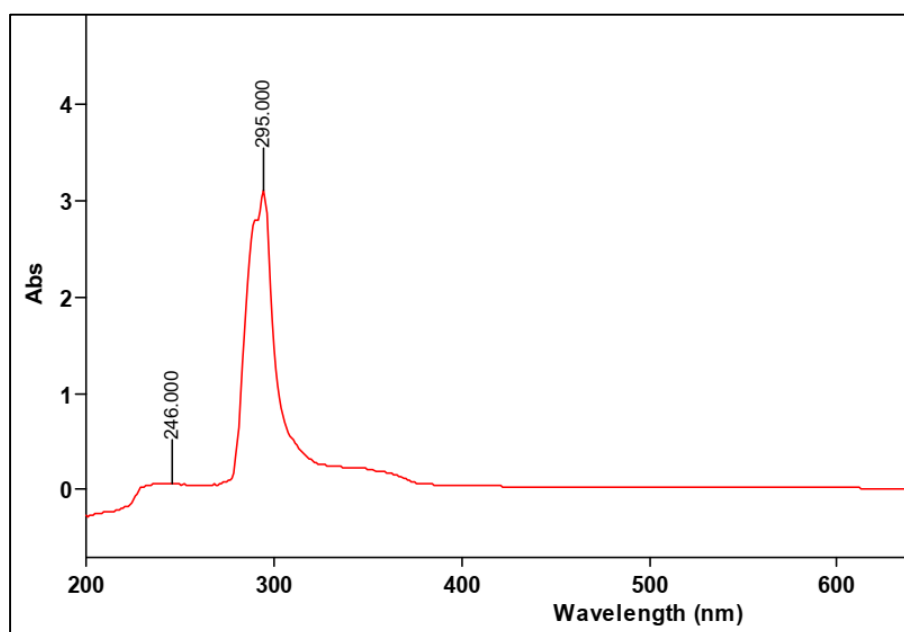


Figure 1. Electronic absorption (UV-Vis) spectrum of the one-dimensional cadmium(II) isonicotinate coordination polymer $[\text{Cd}(\mu\text{-INA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$

The electronic absorption spectrum of the compound was recorded in the range of 200–500 nm and is presented in Figure 1. The spectrum exhibits a strong and intense absorption maximum centered at 295 nm. This absorption band is attributed primarily to ligand-centered $\pi \rightarrow \pi$ electronic transitions within the aromatic pyridine ring and the conjugated carboxylate system of the isonicotinate ligand. The relatively high intensity of this band indicates efficient electron delocalization throughout the aromatic framework and suggests that the ligand retains its conjugated character after coordination to the metal center.

In addition to the principal absorption peak, a weak and broad shoulder extending from approximately 320 to 360 nm can be observed. This feature may be associated with $n \rightarrow \pi$ electronic transitions involving the nonbonding electron pairs of the coordinated carboxylate oxygen atoms. Furthermore, the appearance of this band may indicate the presence of ligand-to-metal charge-transfer (LMCT) interactions arising from electron donation from the ligand orbitals to the vacant orbitals of the Cd(II) center. Such transitions are commonly observed in cadmium coordination compounds containing aromatic carboxylate ligands and contribute to the overall electronic behavior of the material.

No significant absorption bands were detected in the visible region above 400 nm. This observation is consistent with the electronic configuration of Cd(II), which possesses a completely filled d^{10} shell. As a result, $d-d$ electronic transitions are forbidden and cannot contribute to the absorption spectrum. The absence of visible-region absorption bands further confirms the closed-shell nature of the cadmium center and indicates that the observed spectral features originate predominantly from ligand-based transitions and charge-transfer processes.

UV-Vis spectral data provide strong evidence for the successful coordination of the isonicotinate ligand to Cd(II) ions and support the formation of a stable one-dimensional coordination polymer. The observed absorption behavior is characteristic of cadmium-isonicotinate systems and is in good agreement with the proposed crystal structure and coordination environment.

Conclusion

A one-dimensional cadmium(II) coordination polymer based on the isonicotinate ligand, formulated as $[\text{Cd}(\mu\text{-INA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$, was successfully investigated by UV-Vis spectroscopy. Structural considerations indicate that the compound adopts

an infinite chain arrangement and is therefore appropriately classified as a *catena-poly* coordination polymer. The UV-Vis spectrum is characterized by an intense absorption band at 295 nm, which is attributed to ligand-centered $\pi \rightarrow \pi$ electronic transitions associated with the aromatic isonicotinate framework. A weak and broad absorption feature observed at longer wavelengths is likely related to $n \rightarrow \pi$ transitions and possible ligand-to-metal charge-transfer interactions.

The absence of d–d transitions in the visible region is consistent with the closed-shell d^{10} electronic configuration of the Cd(II) ion. The spectroscopic results confirm the successful coordination of the isonicotinate ligand to the cadmium center and support the proposed polymeric structure. These findings contribute to the understanding of the electronic properties of cadmium-isonicotinate coordination polymers and may serve as a basis for further investigations of their structural, optical, and functional characteristics.

References

1. Batten, S. R., Neville, S. M., & Turner, D. R. *Coordination Polymers: Design, Analysis and Application*. Royal Society of Chemistry, 2009.
2. Leong, W. L., & Vittal, J. J. One-dimensional coordination polymers: complexity and diversity in structures, properties, and applications. *Chemical Reviews*, 2011, 111, 688–764.
3. Kreno, L. E., et al. Metal–organic framework materials as chemical sensors. *Chemical Reviews*, 2012, 112, 1105–1125.
4. Wang, C., Zhang, T., & Lin, W. Rational synthesis of noncentrosymmetric metal–organic frameworks for second-order nonlinear optics. *Chemical Reviews*, 2012, 112, 1084–1104.