



SYNTHESIS AND CHARACTERIZATION OF CD COMPLEXES CONTAINING BIDENTATE HETEROCYCLIC NITROGENOUS BASES

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Abstract

Two new Cd(II) complexes of the type [Cd(opd)(dafone)]NO₃(1) and [Cd(phen-dion)(dafone)]NO₃(2) that opd=ortho-phenylenediamine, dafone=4-5 diaza-diazafloren-9-on and phen-dion =1,10-phenanthroline-5,6-dione, have been synthesized. These compounds have been characterized using the IR, UV-Vis, ¹H-NMR spectroscopies and elemental analysis. Also electrochemical behavior of complex (1) and (2) were studied by Cyclic Voltammetric method. The FT-IR results showed that the ligands adduct to metal center as a bidentate ligand by nitrogen atoms.

Keywords: H-NMR spectroscopies; metal center; electrochemical behavior; adduct

1. Introduction

In coordination chemistry, bipyridine, 1,10-phenanthroline, and their derivatives are important chelating agents that are frequently used to synthesize complexes with diverse nuclearity and intriguing properties. These polypyridyl ligands make up important first-row transition metal complexes because they can be used as catalysts, as molecular scaffolding for supramolecular assemblies, as building blocks in the synthesis of metallodendrimers, as building blocks in electrochemistry, and in ring-opening metathesis polymerization. Design and synthesis of physicochemically relevant coordination compounds. Due to the synthetic accessibilities and spectroscopic properties of their own and the complexes derived from them, various dimer ligands are utilized in this direction. Our group has recently reported a number of transition and innertransition metal complexes derived from diimine donors as a partligand.

We now report the syntheses, spectral characterization, and cyclic voltammetric of two coordinate mixed ligand complexes of Cd (II) with Phenanthroline-5,6-dione (phendion), Ortophenylenediaminand, and 4-5 diaza- diazafloren-9-on (dafon), extending our previous research on Metal ion heterocyclic base adducts. As an auxiliary ligand, the bidentate base 1,10-phenanthroline

(phen) was utilized. The synthesis of two brand-new Cadmium(II) addition compounds with the formulas $[\text{Cd}(\text{opd})(\text{dafone})]\text{NO}_3(1)$ and $[\text{cd}(\text{phen-dion})(\text{dafone})]\text{NO}_3(2)$ is described in this research. IR, UV-vis, and NMR spectroscopy were utilized to characterize these complexes. The electrochemical behavior of title complexes was investigated through the use of cyclic voltage metering (CV). The relationship between electronic excitation data and theoretical results was examined. The outcomes were shown and discussed.

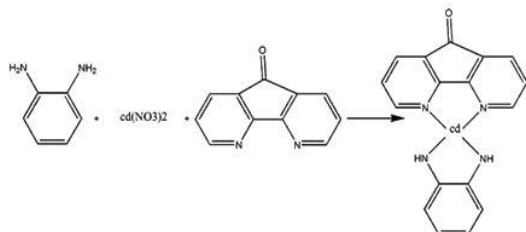
Experimental

Materials and Physical Measurements

Because the raw materials used in this work had purity levels greater than 99 percent, no additional purification was required. Double-distilled, deionized water was used to prepare all of the solutions. An Heraeus rapid analyzer was used to conduct the elemental analysis (C, H, and N). A Bruker tensor 27 spectrophotometer was used to take Fourier transform infrared (FT-IR) spectra in a KBr matrix. A JASCO V-570 spectrophotometer was used to take UV-Vis spectra.

Synthesis of $[\text{Cd}(\text{opd})(\text{dafone})]\text{NO}_3(1)$

Mixture of 4-5 diaza-diazafloren-9-on (dafon) (0.176gr, 1 mmole) and opd=orthophenylenediamine (1mmol, 0.108 gr) dissolved in 20 mL methanol was added to an aqueous solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.361 gr, 1 mmole) (20 ml). For six hours, the solution was refluxed. After being collected by suction filtration, the desired product was air dried before being cleaned with acetone. After dissolving the product in a mixture of CH_3CN and CH_3OH , the solvent was allowed to slowly evaporate at room temperature. scheme 1) Black crystals were isolated after five days, yielding 53% at m.p. (255°C). IR (KBr, cm^{-1}): 3419 and 2928 (CH), 1530–1303 (C=C), 441 (Cd-N), 1710 (C=O), and 1300–1400 $\nu(\text{NO}_3)$ (C=N). Anal. calc: C, 50.95; H, 3.02; N, 13.98. Found: C, 51.15; Figure 1



Scheme 1. Synthesis of $[\text{Cd}(\text{opd})(\text{dafone})]\text{NO}_3(1)$

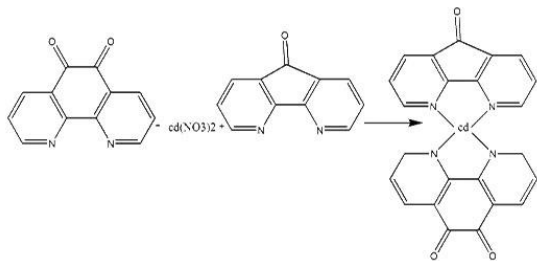
Synthesis of 1,10-phenanthroline- 5,6-dion (phendion)

A three-necked flask with a dropping funnel was filled with a mixture of 1,10phenanthroline (4.0 g, 19 mmol) and KBr (4.0 g, 33 mmol). After that, a drop-by-drop addition of a icy mixture of concentrated H_2SO_4 (40 mL) and HNO_3 (20 mL) was made to this solution. After refluxing for four hours, the mixture was carefully neutralized with NaOH to a pH of neutral to slightly acidic before being poured over 600 milliliters of ice and water. The precipitate was further purified by crystallization from absolute ethanol to yield 5.6 g (96 percent) of 1,10-phenanthroline-5,6-dione²⁴. Schematic 1 depicts the synthesis of the 1,10-phenanthroline- 5,6-dion (phendion) ligand from 1,10 phenanthroline (phen). Extraction with CHCl_3 was followed by drying with anhydrous Na_2SO_4 and solvent removal. Figure 2

Synthesis of $[\text{cd}(\text{phen-dion})(\text{dafone})]\text{NO}_3(2)$

First, dissolve $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.361 gr, 1 mmole) in water to make a 20 mL solution. After that, to the Cd(II) solution, 20 milliliters of a mixture solution of 4-5 diaza-diazafloren-9-on (dafon) (0.176 gr, 1 mmol) and 1,10-phenanthroline- 5,6-dion (phendion) (0.210 gr, 1 mmol) in methanol were added.

After dissolving the product in a mixture of CH₃CN and CH₃OH, the solvent was allowed to slowly evaporate at room temperature. Scheme 3: After seven days, yellow crystals (yielding 69 percent, m.p.) were isolated. IR (KBr, cm⁻¹): 3000. 3419 and 2928 (CH), 1530–1303 (C=C), and 430 (Cd-N), 1675–1700 (O), 1300–1400 ν (NO₃)²³. Anal. calc: C, 54.73; H, 2.40; N, 11.10. Found: C, 54.80; H, 2.48; N, 11.21.



Scheme 3. synthesis of [Cd(phen-dion)(dafone)]NO₃ (2)

Results and Discussion

The ligand and its complexes were thoroughly examined using the cyclic voltametric, FT-IR, UV-vis, and ¹H-NMR techniques. There are two categories of ligands' coordination modes: bridging and terminal ligands. N moieties are used to coordinate phen-dione ligands with the metal center 25 in Complex 2.

The free ligand and the associated complex's infrared spectral data have been compared. These frequencies shift to a lower wavenumber during complexation. In order to determine whether coordination occurs through the amide nitrogen atoms²⁶ and whether coordination involving nitrogen donors is accompanied by deprotonation in [Cd(opd)(dafone)]NO₃, the IR frequency shifts of the amide NH bands exhibited by the diamide complexes were used. The free phen-dione's IR spectrum revealed a sharp band at 1675 cm⁻¹, which was linked to the ligand's C=O band stretching frequency²³. The IR spectrum of the complexes (1) and (2) also reveals bands at 441 and 430 cm⁻¹, respectively, which correspond to the stretching frequency of the Cd-N bond. In comparison to the corresponding complexes, the observed band did not change significantly. Since the C=O moieties were far from the ligand's metal ion²⁷ coordination site, this was reasonable. The complex(2)'s IR spectrum revealed a band around 1689.5 cm⁻¹ that was identified as the (C=O) band of the phen-dione ligand's O-quinoid group. Due to the fact that the metal center and its coordination environment had a secondary effect on the carbonyl stretch, the carbonyl stretching frequency was generally insensitive to changes in the metal center⁵. The 1530cm⁻¹ variation band was given the designation (C=N)²⁸⁻²⁹.

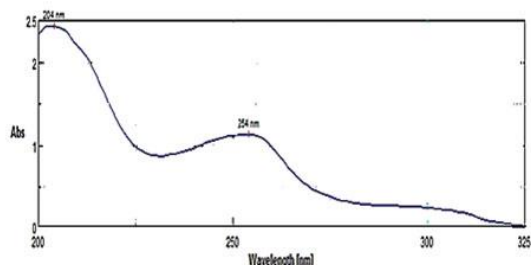


Fig 1. Absorption spectrum of [Cd(opd)(dafone)]NO₃ (1) in DMF solution

Figures 1 and 2 depict the electronic spectrum of the title complexes in DMF solution. In the UV-vis spectrum, there are two absorption bands around 204 and 254 nm that correspond to the intra ligand transitions ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) of ligands (Fig 1). The transition of ligands in complex (2)³⁰ is

represented by the bands at 201, 216, and 254 nm in Figure 2. The Cd(II) ion has a d0 arrangement, so there are no d-d transitions, and the UV-vis spectrum of title complexes does not show any d-d transition of the central ion.

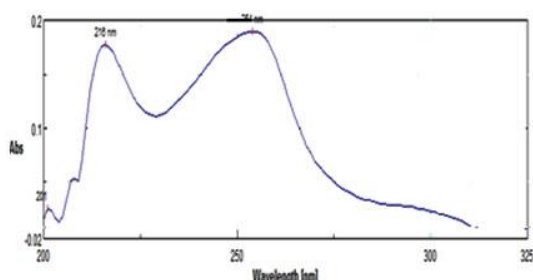


Fig 2. Absorption spectrum of [cd (phen-dion)(dafone)]NO₃ (2) in DMF solution

Using a DMF solution containing 0.1M TBAH as the supporting electrolyte and a scan speed of 500 mvs-1, the cyclic voltammograms of the title complexes were taken at 25°C in an argon atmosphere (Fig. 3 and Fig. 4). Voltammograms display anodic and cathodic steps that correspond to the ligands' oxidation and reduction Table.1.

Table 1: Electrochemical data for title complexes in DMF solution

[Cd (opd)(dafone)]NO ₃ (1)	E _c /E _a =-0.8/-0.7	E _c /E _a =0.2/0.4
[cd (phen-dion)(dafone)](2)	E _c /E _a =-0.6/-0.4	E _c /E _a =0.6/1

¹H-NMR spectra

For the purpose of characterizing compounds in solution, ¹H-NMR is a very effective technique. Figs. 5 depict the complexes' D₂O solution ¹H NMR spectra at 25°C. The complex's phenanthroline groups are represented by the signals found between 6.80 and 6.90 ppm (2).

Conclusion

In conclusion, we have made complexes of Cd with bidentate heterocyclic ligands that work well. The methods of FT-IR, UV-Vis, ¹H-NMR, elemental analysis, and cyclic voltammetry (CV) were used to characterize these compounds. The IR spectra indicate that the C=N moieties groups' unsaturated nitrogen atoms were involved in the bonding with the central metal ions. Title complexes exhibit favorable electrochemical behavior, as demonstrated by the cyclic voltammetry method. (1) and (2) complexes are air-stable and readily recrystallisable. Presence pyridine type ligands in these mixtures causes synergist and electron move properties. Additionally, this substance can be utilized to make an electrochemical polymer.

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