

# Synthesis and Characterization of Cd Complexes Containing Phenanthroline Derivatives

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## ABSTRACT

Two new Cd(II) complexes of the type  $[Cd(opd)(dafone)]NO_3$  (**1**) and  $[cd(phen-dion)(dafone)]NO_3$  (**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.

**Key words:**  $^1H$ -NMR spectroscopies, metal center, electrochemical behavior, adduct.

## INTRODUCTION

Bidentate heterocyclic nitrogenous bases, for example 1,10-phenanthroline, bipyridine, and their derivatives, are important chelating agents in coordination chemistry and often used to synthesize of complexes with different nuclearity and interesting properties. First-row transition metal complexes containing these polypyridyl ligands not only have important biological properties<sup>1</sup> but are also important because of their versatile use as building blocks in the synthesis of metallo-dendrimers, as molecular scaffolding for supramolecular assemblies, as catalysts, in electrochemistry, and in ring-opening metathesis polymerization<sup>2-16</sup>. Design and synthesis of coordination compounds of physicochemical features. Different diimine ligands are being used in this direction<sup>16-19</sup> because of synthetic accessibilities and spectroscopic properties of their own and the complexes synthesized there from. In recent times a number of transition and inner

transition metal complexes from diimine donors as a part ligand had been reported by our group<sup>20,22</sup>.

In continuation of our previous studies with heterocyclic base adducts of Metal ion, we now report the syntheses, spectral characterization, cyclic voltammetric of two coordinate mixed ligand complexes of Cd (II) with Phenanthroline-5,6-dione (phen-dion), Orthophenylene diamine and 4-5 diaza- diazafloren-9-on (dafon). A bidentate base 1,10-phenanthroline (phen) was used as an auxiliary ligand. In this study we describe the synthesis of the two new Cadmium(II) addition compounds with the formula  $[Cd (opd) (dafone)] NO_3$ (1) and  $[cd(phen-dion)(dafone)]NO_3$ (2). These complexes were characterized using of spectroscopic methods such as IR, UV-vis and NMR. Cyclic Voltammetry (CV) was used to investigate the electrochemical behavior of title complexes. Correlation between theoretical results and electronic excitation data were investigated. The results are presented and discussed.

## EXPERIMENTAL

### Materials and physical measurements

The raw materials used in this work were of purities above 99%, therefore no further purification was required. All solutions were prepared with double distilled deionized water. Elemental analysis (C, H, N) was determined on an Heraeus rapid analyzer. Fourier transform infrared (FT-IR) spectra were recorded using Bruker tensor 27 spectrophotometer in a KBr matrix. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer.

### Synthesis of [Cd (opd)(dafone)]NO<sub>3</sub> (1)

To aqueous solution (20 ml) of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.361 gr, 1 mmole) was added 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. Resulting solution was refluxed for 6 h. The solid (desired product) was collected by suction filtration, washed with acetone, then air dried. The product was dissolved a mixture of CH<sub>3</sub>CN and CH<sub>3</sub>OH and the solvent was left to evaporate slowly at room temperature. (scheme 1) After 5 days, black crystals were isolated (yield 53 %, m.p.(255°C). IR (KBr, cm<sup>-1</sup>): 3419 and 2928  $\nu$  (CH), 1530–1303  $\nu$  (C=C) and  $\nu$  (C=N), 441  $\nu$  (Cd-N), 1710  $\nu$  (C=O), 1300-1400  $\nu$  (NO<sub>3</sub>)<sup>23</sup>. Anal. calc: C, 50.95; H, 3.02; N, 13.98. Found: C, 51.15; Scheme 1.

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

A mixture of 1,10phenanthroline (4.0 g, 19mmol) and KBr (4.0 g, 33mmol) were added to a three necked flask equipped with a dropping funnel. Then ice cold mixture of concentrated H<sub>2</sub>SO<sub>4</sub> (40 mL) and HNO<sub>3</sub>(20 mL) were added to this solution drop wise. The mixture was heated to reflux for 4 h. The hot yellow solution was poured over 600 mL of ice and water and neutralized carefully with NaOH until neutral to slightly acidic pH was attained. Extraction with CHCl<sub>3</sub> was followed by drying with

anhydrous Na<sub>2</sub>SO<sub>4</sub> and removal of solvent and the precipitate was purified further by crystallization from absolute ethanol to give 5.6 g (96%) of 1,10-phenanthroline-5,6-dione<sup>24</sup>. Scheme 1. shows the synthesis of the 1,10-phenanthroline- 5,6-dion (phendion) ligand from 1,10 phenanthroline (phen). Scheme 2

### Synthesis of [cd (phen-dion)(dafone)]NO<sub>3</sub> (2)

First prepare 20 mL solution of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.361 gr, 1 mmole) in water. Then added 20 mL mixture solution of 4-5 diaza-diazafloren-9-on (dafon) (0.176gr, 1 mmole) and 1,10-phenanthroline- 5,6-dion (phendion) (0.210 gr, 1mmol) in methanol to Cd(II) solution. The product was dissolved a mixture of CH<sub>3</sub>CN and CH<sub>3</sub>OH and the solvent was left to evaporate slowly at room temperature. (Scheme 3) After 7 days, yellow crystals were isolated (yield 69%, m.p. (300°C). IR (KBr, cm<sup>-1</sup>): 3419 and 2928  $\nu$  (CH), 1530–1303  $\nu$  (C=C) and  $\nu$  (C=N), 430  $\nu$  (Cd-N), 1675-1700  $\nu$  (C=O), 1300-1400  $\nu$  (NO<sub>3</sub>)<sup>23</sup>. Anal. calc: C, 54.73; H, 2.40; N, 11.10. Found: C, 54.80; H, 2.48; N, 11.21.

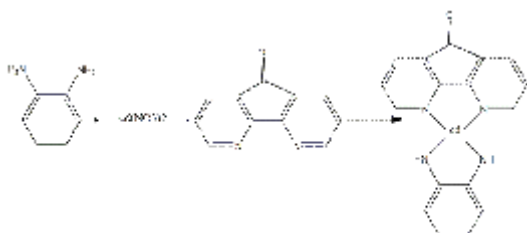
## RESULTS AND DISCUSSION

The ligand and complexes were fully characterized by FT-IR, UV-vis, <sup>1</sup>H-NMR and Cyclic Voltammetric method. The coordination modes of ligands can be classified as two types of bridging and terminal ligands. In Complex (2) phen-dione ligand are coordinated via N moieties to the metal center<sup>25</sup>.

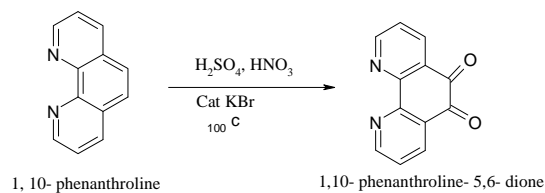
Infrared spectral data of the free ligand and corresponding complex have been compared. On complexation this frequencies shift to a lower wavenumber. The IR frequency shifts (relative to the free ligand) of the amide NH bands exhibited by the diamide complexes were used to establish whether coordination occurs through the amide nitrogen atoms<sup>26</sup> and whether coordination involving nitrogen donors is accompanied by deprotonation in [Cd (opd)(dafone)]NO<sub>3</sub>(1). The IR spectrum of the complexes (1) and (2) show the bands at 441 and 430 cm<sup>-1</sup> associated with the

**Table 1: Electrochemical data for title complexes in DMF solution**

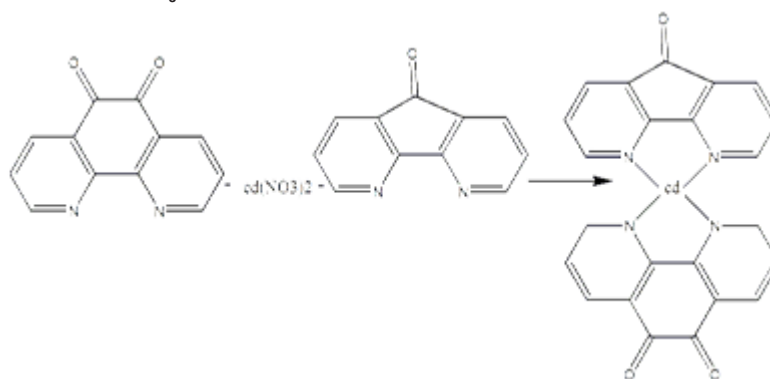
[Cd (opd)(dafone)]NO <sub>3</sub> (1)	Ec/Ea=-0.8/-0.7	Ec/Ea =0.2/0.4
of [cd (phen-dion)(dafone)](2)	Ec/Ea =-0.6/-0.4	Ec/Ea =0.6/1



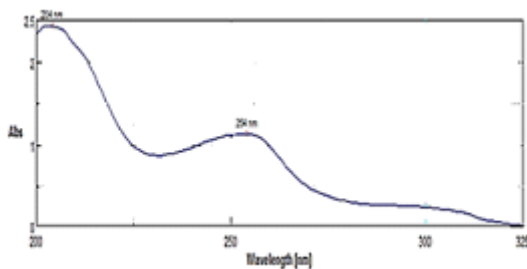
**Scheme 1: Synthesis of [Cd (opd)(dafone)]NO<sub>3</sub> (1)**



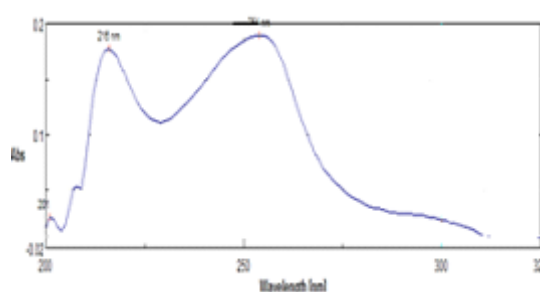
**Scheme 2: Synthesis of the phen-dion ligand**



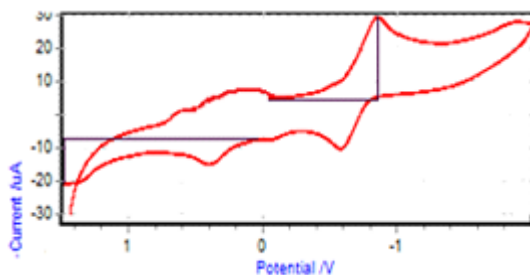
**Scheme 3: Synthesis of [cd (phen-dion)(dafone)]NO<sub>3</sub> (2)**



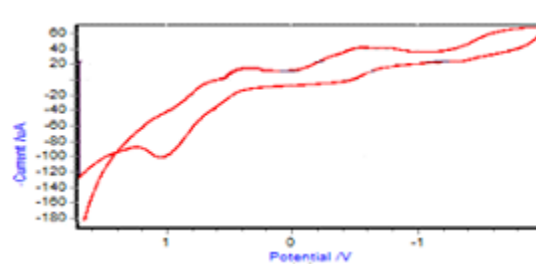
**Fig. 1: Absorption spectrum of [Cd (opd)(dafone)]NO<sub>3</sub> (1) in DMF solution**



**Fig. 2: Absorption spectrum of [cd (phen-dion)(dafone)]NO<sub>3</sub> (2) in DMF solution**



**Fig. 3: Cyclic voltammogram of [Cd (opd)(dafone)]NO<sub>3</sub> (1) in DMF solution**



**Fig. 4: Cyclic voltammogram of [cd (phen-dion)(dafone)]NO<sub>3</sub> (2) in DMF solution**

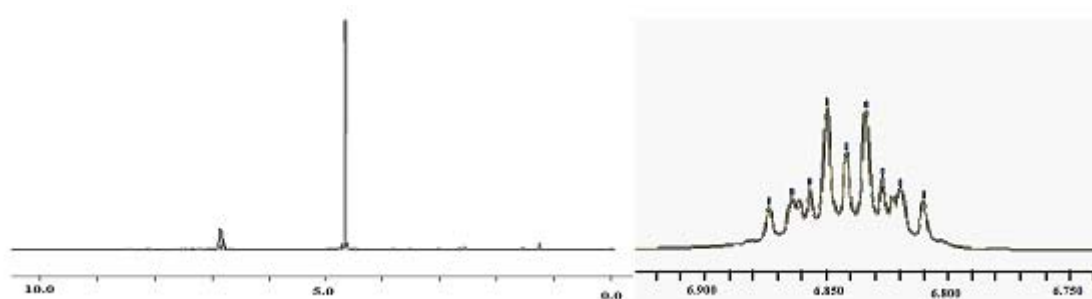


Fig. 5:  $^1\text{H-NMR}$  spectrum of of  $[\text{Cd}(\text{phen-dion})(\text{dafone})]\text{NO}_3$

stretching frequency of the Cd-N bond in **(1)** and **(2)** respectively<sup>23</sup>. The IR spectrum of the free phen-dione showed a sharp band at  $1675\text{cm}^{-1}$ , which associated with the stretching frequency of the C=O band of the ligand. The observed band did not shift significantly in comparison with the corresponding complexes. This was reasonable since the C=O moieties were far from the coordination site of the ligand with the metal ion<sup>27</sup>. The IR spectrum of the complex **(2)** showed a band around  $1689.5\text{cm}^{-1}$ , which was assigned to the  $\nu(\text{C=O})$  band of an O-quinoid group of the phen-dione ligand. In general, the carbonyl stretching frequency was relatively insensitive to changes in the metal center, a reflection of the fact that the effect of the metal center and its coordination environment on the carbonyl stretch was a secondary one<sup>5</sup>. The variation band at  $1530\text{cm}^{-1}$  was assigned to  $\nu(\text{C=N})$ <sup>28-29</sup>.

Electronic spectrum of the title complexes, in DMF solution show in Figs 1 and 2. UV-vis spectra show two absorption bands approximately in 204, 254 nm that attributed to the intra ligand transitions ( $\pi \rightarrow \pi^*$ ) and ( $n \rightarrow \pi^*$ ) of ligands (Fig 1). Fig 2 the bands at 201, 216 and 254 nm corresponding to transition of ligands in complex **(2)**<sup>30</sup>. Cd(II) ion have  $d^0$  arrangement therefore no d-d transitions and UV-vis spectrum of title complexes don't show any  $d \rightarrow d$  transition of central ion.

The cyclic voltammograms of title complexes were obtained at  $25^\circ\text{C}$  under an argon atmosphere using DMF solution containing 0.1M TBAH as supporting electrolyte with scan speed of  $500\text{ mVs}^{-1}$  (Fig.3 and Fig.4). Voltammograms show

cathodic and anodic steps which are corresponding to the oxidation and reduction of the ligands<sup>31,32</sup> Table.1.

#### $^1\text{H-NMR}$ spectra

$^1\text{H-NMR}$  is a very powerful tool for characterization of compounds in solution. Figs. 5 show the  $^1\text{H NMR}$  spectra of complexes **(2)** in  $\text{D}_2\text{O}$  solution at  $25^\circ\text{C}$ . The signals observed in the region of 6.80-6.90 ppm are corresponding to phenanthroline groups in complex **(2)**.

#### CONCLUSION

In summary, we have successfully prepared complexes of Cd with bidentate heterocyclic ligands. These compounds have been characterized using FT-IR, UV-Vis,  $^1\text{H-NMR}$ , elemental analysis and Cyclic voltammetry (CV) techniques. The IR spectra suggest involvement of unsaturated nitrogen atoms of the C=N moieties groups in bonding with the central metal ions. Cyclic voltammetry technique show title complexes have good electrochemical behavior. The complexes **(1)** and **(2)** are air-stable and can be readily recrystallized. Presence pyridine type ligands in these compounds causes catalytic and electron transfer properties. Also this compound can be used to form an electrochemical polymer.

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