



# Reduction of 2,2'-dinitrophenyl with hydrazine hydrate catalyzed by Pd/C: Cobalt(II), zinc(II) and mercury(II) complexes with benzo[c]cinnoline and $N^2,N^{2'}$ -bis(3-phenylallylidene)biphenyl-2,2'-diamine

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## ABSTRACT

The catalytic reduction of 2,2'-dinitrophenyl with different molar ratios of hydrazine hydrate resulted in two different compounds; benzo[c]cinnoline ( $L^1$ ) and 2,2'-diaminobiphenyl.  $N^2,N^{2'}$ -bis(3-phenylallylidene)biphenyl-2,2'-diamine ( $L^2$ ) has been synthesized by the condensation of 2,2'-diaminobiphenyl with cinnamaldehyde. Complexes of the type  $ML^1_2X_2$  and  $ML^2X_2$  ( $M = Co(II), Zn(II); X = Cl, Br$  or  $I$  and  $Hg(L^2)Cl_2$ ) have been synthesized and characterized by CHN analysis, IR,  $^1H$  NMR and UV–Vis spectroscopy. The crystal structures of  $Co(L^1)_2Cl_2$ ,  $Zn(L^1)_2Br_2$  and  $Hg(L^2)Cl_2$  were determined using single crystal X-ray diffraction. In these three complexes, the coordination polyhedron about the central metal ion is best described as a distorted tetrahedron. The  $Co(L^1)_2Cl_2$ , and  $Zn(L^1)_2Br_2$  complexes exhibit supramolecular structures resulting from  $\pi$ – $\pi$  stacking of the benzo[c]cinnoline ligands. The diimine ligand,  $L^2$ , in the  $Hg(L^2)Cl_2$  complex coordinates to Hg(II) through the two nitrogens of the two phenyl rings to form a seven-membered metallocycle. Furthermore, the ligand prefers a *trans*–*trans* arrangement in the  $Hg(L^2)Cl_2$  complex.

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## 1. Introduction

Transition metal complexes containing nitrogen donor ligands are a major group of coordination compounds, which play an important role in the development of coordination chemistry. Recent years have witnessed a great deal of interest in the synthesis of new chelating functions, such as the mono, bi, tri and tetradentate type nitrogen donor ligands, and their corresponding complexes due to their interesting applications in magnetism, molecular architectures, enzymatic reactions and especially in developing new catalytic systems [1–5]. Moreover, nitrogen based ligands with the metal centers such as zinc and mercury result in supramolecular architectures, designing of biological models and fluorescent compounds [6,7]. Altering and modifying the physical and chemical properties of these systems is easily carried out by varying the number, size and the nature of the substituents on the ligands. This paper deals with the synthesis and spectroscopic characterization of two N-donor ligands, benzo[c]cinnoline ( $L^1$ ) and  $N^2,N^{2'}$ -bis(3-phenylallylidene)biphenyl-2,2'-diamine ( $L^2$ ). The catalytic reduction of 2,2'-dinitrophenyl by changing the molar ratio of the reductant (hydrazine) results in the two products

benzo[c]cinnoline ( $L^1$ ) and 2,2'-diaminobiphenyl (Scheme 1).  $N^2,N^{2'}$ -bis(3-phenylallylidene)biphenyl-2,2'-diamine has been synthesized by the condensation of 2,2'-diaminobiphenyl with cinnamaldehyde (Scheme 1). Also, we wish to report the synthesis and spectral characterization of some new transition metal complexes of Co, Zn and Hg with the synthetic ligands. Structural analysis by X-ray diffraction led to the structural confirmation of these new complexes.

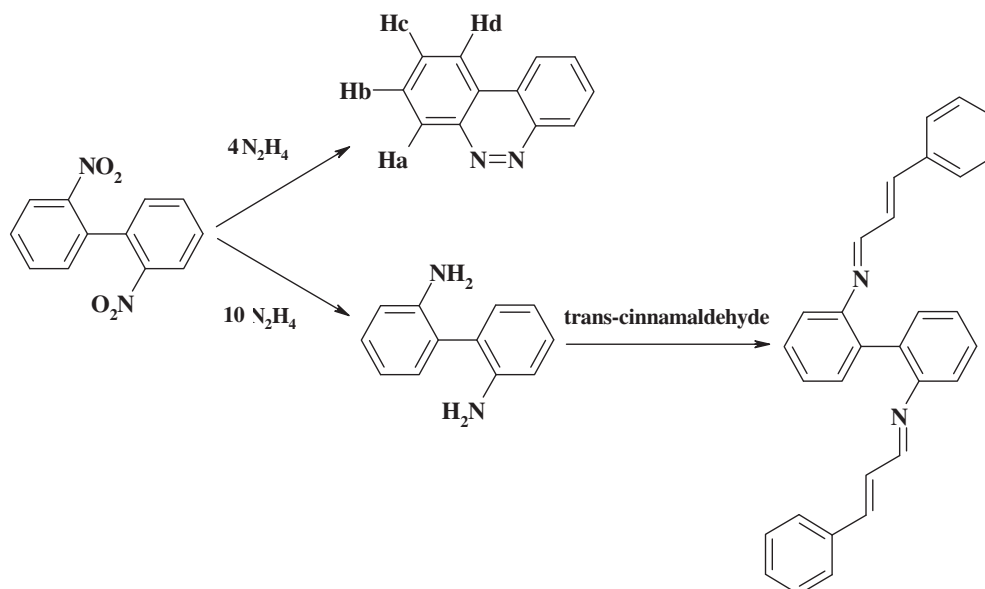
## 2. Experimental

### 2.1. General

All reagents were purchased from commercial sources (Aldrich/Merck) and were used as received without further purification. Solvents used for the reactions were purified and dried by conventional methods [8]. Infrared spectra were recorded as KBr pellets on a Bruker Tensor 27 instrument. NMR spectra were obtained on Bruker AC-250 MHz and AC-500 MHz spectrometers. Proton chemical shifts are reported in part per million (ppm) relative to tetramethylsilane as an internal standard. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer, and the results are given as  $\lambda_{max}$  (log  $\epsilon$ ). Elemental analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer.

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**Scheme 1.** Catalytic reduction of 2,2'-dinitrobiphenyl with different molar ratios of hydrazine hydrate.

## 2.2. Syntheses

### 2.2.1. Benzoc[c]cinnoline ( $L^1$ )

To a solution of 2,2'-dinitrobiphenyl (1 g, 4 mmol) in hot ethanol (15 ml) was added 100 mg 10% Pd/C as a catalyst. About 1.0 ml of 80% hydrazine hydrate (16 mmol) was added dropwise (every 15 min) and the reaction mixture was refluxed for 4 h. After 4 h, the heating was stopped and the catalyst was immediately filtered off. By cooling the yellow filtrate to room temperature, yellow crystals appeared in the solution, which were recrystallized in cold ethanol. Mp 154–156 °C. Yield: 85%. IR (KBr,  $\text{cm}^{-1}$ ): 1463  $\nu(\text{N}=\text{N})$ .  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.67–8.03 (m, 4H, H<sub>b</sub>, H<sub>c</sub>), 8.36–8.87 (m, 4H, H<sub>a</sub>, H<sub>d</sub>). UV–Vis ( $\text{CHCl}_3$ , nm): 384(3.75), 365(3.85), 333(3.97), 313(3.91), 296(4.05), 263(4.44), 254(4.70). *Anal. Calc.* for  $\text{C}_{12}\text{H}_8\text{N}_2$ : C, 79.98; H, 4.47; N, 15.54. Found: C, 80.05; H, 4.41; N, 15.49%.

### 2.2.2. 2,2'-Diaminobiphenyl

To a solution of 2,2'-dinitrobiphenyl (1 g, 4 mmol) in hot ethanol (15 ml) was added 100 mg 10% Pd/C as a catalyst. About 2.5 ml of 80% hydrazine hydrate (40 mmol) was added dropwise sequentially (every 15 min). The reaction mixture was then refluxed for 6 h to complete the reduction (reduction was complete when the solution had become completely colorless). After 6 h, the heating was stopped and the catalyst was immediately filtered off. The volume of the solution was reduced to half of its original volume by heating and then water was added to the filtrate. On adding water, the solution became cloudy and colorless crystals appear in the solution after 30 min. Mp 78–79 °C. Yield: 90%. IR (KBr  $\text{cm}^{-1}$ ): 3384, 3401  $\nu(\text{N}-\text{H})$ .  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.69 (s, 4H, 2-NH<sub>2</sub>), 6.75–6.85 (m, 4H, H<sub>b</sub>, H<sub>c</sub>), 7.09–7.24 (m, 4H, H<sub>a</sub>, H<sub>d</sub>). UV–Vis ( $\text{CHCl}_3$ , nm): 359(1.79), 299(3.49), 256(3.71). *Anal. Calc.* for  $\text{C}_{12}\text{H}_{12}\text{N}_2$ : C, 78.23; H, 6.57; N, 15.20. Found: C, 78.30; H, 6.62; N, 15.25%.

### 2.2.3. $N^2,N^2$ -bis(3-phenylallylidene)biphenyl-2,2'-diamine ( $L^2$ )

To a solution of 2,2'-diaminobiphenyl (1 g, 5 mmol) in ethanol (15 ml) was added a solution of *trans*-cinnamaldehyde (1.634 g, 10 mmol) in ethanol (2 ml) and the resulting mixture was stirred at room temperature for 1 h. The ligand ( $L^2$ ) was obtained as a yellow microcrystalline precipitate. It was then filtered off, washed with cold diethylether and dried in air. Yield: 90%. IR (KBr): 1624  $\text{cm}^{-1}$

$\nu(\text{C}=\text{N})$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.89–6.99 (m, 6H, 2-C=CH-C-, 4-ortho H of ArH), 7.31–7.45 (m, 16H, 2PhCH=C-, ArH), 8.09 (d, 2H,  $^3J_{\text{HH}} = 5$  Hz, 2-CH=N-). UV–Vis ( $\text{CHCl}_3$ , nm): 340(4.41), 295(4.75). *Anal. Calc.* for  $\text{C}_{30}\text{H}_{24}\text{N}_2$ : C, 87.35; H, 5.86; N, 6.79. Found: C, 87.40; H, 5.80; N, 6.83%.

### 2.2.4. $\text{Co}(L^1)_2\text{Cl}_2$ (**1a**)

To a solution of anhydrous  $\text{CoCl}_2$  (50 mg, 0.385 mmol) in 5 ml acetonitrile was added a solution of  $L^1$  (139 mg, 0.77 mmol) in 5 ml acetonitrile, and the mixture was stirred at room temperature for 3 h. On slow evaporation of the solution, blue crystals were obtained, which were collected by filtration, washed with a mixture of diethylether–acetonitrile (9:1, v/v) and dried under vacuum. Yield: 85%. IR (KBr,  $\text{cm}^{-1}$ ): 1455  $\nu(\text{N}=\text{N})$ . UV–Vis ( $\text{CHCl}_3$ , nm): 678(2.05), 635(1.88), 615(1.86), 367(3.44), 353(3.54), 312(4.27), 303(4.26), 256(5.27). *Anal. Calc.* for  $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{CoN}_4$ : C, 58.80; H, 3.29; N, 11.43. Found: C, 58.86; H, 3.34; N, 11.49%.

### 2.2.5. $\text{Co}(L^1)_2\text{Br}_2$ (**2a**)

This complex was synthesized by a procedure similar to that for **1a** using anhydrous  $\text{CoBr}_2$  (50 mg, 0.23 mmol). Yield: 65%. IR (KBr,  $\text{cm}^{-1}$ ): 1453  $\nu(\text{N}=\text{N})$ . UV–Vis ( $\text{CHCl}_3$ , nm): 682(2.10), 639(1.90), 619(1.81), 369(3.42), 350(3.56), 315(4.25), 306(4.21), 259(5.30). *Anal. Calc.* for  $\text{C}_{24}\text{H}_{16}\text{Br}_2\text{CoN}_4$ : C, 49.77; H, 2.78; N, 9.67. Found: C, 49.83; H, 2.81; N, 9.60%.

### 2.2.6. $\text{Co}(L^1)_2\text{I}_2$ (**3a**)

This complex was synthesized by a procedure similar to that for **1a** using anhydrous  $\text{CoI}_2$  (50 mg, 0.16 mmol). Yield: 69%. IR (KBr,  $\text{cm}^{-1}$ ): 1450  $\nu(\text{N}=\text{N})$ . UV–Vis ( $\text{CHCl}_3$ , nm): 685(2.09), 638(1.85), 622(1.78), 368(3.40), 345(3.55), 316(4.23), 310(4.25), 260(5.31). *Anal. Calc.* for  $\text{C}_{24}\text{H}_{16}\text{CoI}_2\text{N}_4$ : C, 42.82; H, 2.40; N, 8.32. Found: C, 42.87; H, 2.35; N, 8.39%.

### 2.2.7. $\text{Zn}(L^1)_2\text{Cl}_2$ (**4a**)

To a solution of  $\text{ZnCl}_2$  (50 mg, 0.367 mmol) in acetonitrile (5 ml) was added a solution of  $L^1$  (132 mg, 0.733 mmol) in acetonitrile (5 ml), and the mixture was stirred for 1 h. On slow evaporation of the solution, yellow crystals were obtained, collected by filtration, washed with a mixture of diethylether–acetonitrile (9:1, v/v) and dried under vacuum. Yield: 90%. IR (KBr,  $\text{cm}^{-1}$ ): 1454  $\nu$

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