

# **Synthesis, Characterization and Electrochemical Behavior of A Novel Tetradentate Schiff Base Ligand (H<sub>2</sub>L) and Its Cadmium Complex Cd(II)L. the Single Crystal of (H<sub>2</sub>L)DMSO.**

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## **Abstract**

Condensation of primary amines with aldehydes or ketones yield Schiff bases containing imine (C=N) function (CALLIGARIS 1987). Multidentate Schiff base ligands and their metal complexes have been extensively studied for many years (DAIER 2004, MUNRO 2003). However, such Schiff's base molecules decorated with necessary groups are important in various branches of chemistry as potential biomimics, biological activity (XU 2005), catalytic activity (ONES 2008)...

Our group has been involved for quite some time in synthesizing Schiff base derivatives possessing different "O-, N-" cores that are capable of binding transition metal ions (OURARI 2006, 2008). Thus, metal Schiff base complexes such as manganese, iron, cobalt and copper have been synthesized and used in indirect electroreductions of molecular dioxygen. These reactions using electrocatalytic systems could be performed in homogeneous and heterogeneous catalysis in the oxidation of organic substrates as epoxidation of olefins.

In the present work, new symmetrical and unsymmetrical tetradentate Schiff base ligands and their cadmium complexes are synthesized and characterized. We describe also in this paper the single crystal of the symmetrical ligand bridged with benzene, containing an independent molecule of DMSO, as it is shown in the figure, and the electrochemical behavior of its cadmium complex in DMF on a carbon disc electrode.

**Keywords:** Synthesis, Cadmium Schiff base, Single crystal, Electrochemical.

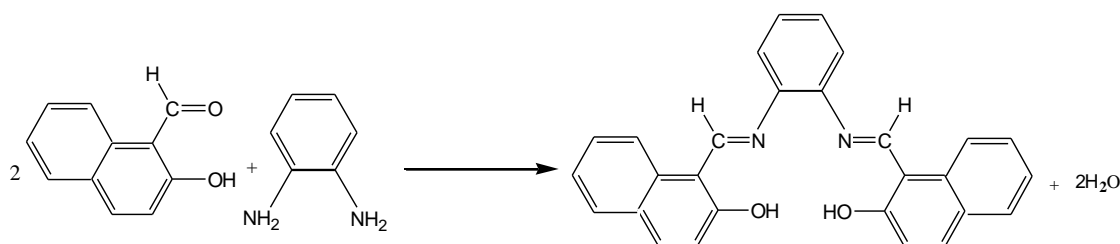
## **Introduction**

During the last decade, the tetradentate Schiff base complexes of transition metals have been extensively studied mainly with manganese, Cadmium, cobalt. Thus, it was demonstrated that such materials might be involved in several applications such as in catalysis or electrocatalysis by activating many small molecules like molecular oxygen.

## Experimental

### Synthesis of the Schiff Base Ligand $H_2L$

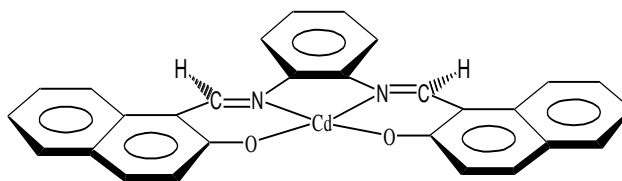
The unsymmetrical  $[N_2O_2]$  tetradentate Schiff base, 2,3-bis(2-hydroxy-1-naphthylmethylene) diaminobenzene was prepared following literature methods (OUARI 2010). To a MeOH solution (15 mL) of 2-hydroxy-1-naphthylmethylene (0.344 g, 2 mmol) was slowly added a MeOH solution (5 mL) of 2,3-diaminobenzene (0.124 g, 1 mmol). The mixture was refluxed with constant stirring under nitrogen atmosphere for 3 h to yield an abundant orange precipitate that was collected by filtration. The product was washed with methanol (3 X 5 mL) then with diethyl ether (3 X 5 mL) and dried under vacuum for 6 h.



Structure of  $H_2L$ : N,N'-bis (2-hydroxy naphthalidène)-1,2-diaminobenzène

### Synthesis of the Complex $Cd(II)L$

133 mg (0.5 mmol) of  $Cd(OAc)_2 \cdot H_2O$  were dissolved in MeOH (10 mL). This solution was added dropwise to a stirred methanol solution (5 mL) containing 208 mg (0.5 mmol) of Schiff base ligand  $H_2L$ . The solution turned yellow and a solid precipitated almost immediately. The mixture was refluxed and stirred for 1 h under nitrogen atmosphere. The precipitate was collected by filtration, and washed successively with methanol (3 X 5 mL) and diethyl ether (3 X 5 mL), the product was then recrystallized from DMSO-MeOH and dried under vacuum overnight.



Structure of complex  $CdL$

## Results and Discussion

The main analytical data for the ligand and its complex are given in Table 1.

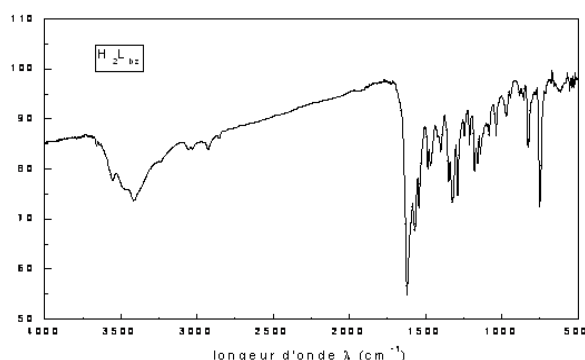
Compound	Color	Yield (%)	R <sub>f</sub> (%)	T <sub>f</sub> (°C)	$\Lambda(\Omega^{-1} \text{ cm}^2 \text{ mole}^{-1})$
H <sub>2</sub> L	orange	43	61	221	11.98
Cd(II)L	yellow	80	51	>300	4.93

R<sub>f</sub> . Retarding factor

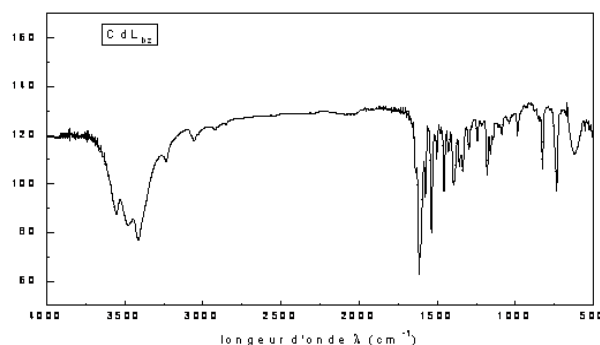
## Spectral Characterization of the Ligand and the Complex

### Infrared Spectra

The IR spectra in KBr discs of H<sub>2</sub>L and Cd(II)L, recorded in the region of 4,000–500 cm<sup>-1</sup>, contain all the characteristic bands of the coordinated tetradentate ligand. The IR spectrum of the complex, compared to its ligand, shows that the  $\nu(\text{C}=\text{N})$  band appearing at 1,610 cm<sup>-1</sup> is shifted to lower energy by 8 cm<sup>-1</sup>, indicating that the ligand is coordinated to the cadmium metal through the nitrogen atoms of the azomethine groups. In addition, the stretching vibration of C–O,  $\nu(\text{C}=\text{O}/\text{phenolate})$ , appears at 1,179 cm<sup>-1</sup> in the ligand form whereas in the complex of Cd(II)L it shifted to higher energy by 7 cm<sup>-1</sup> suggesting that, in this case, the metallic centre causes a drastic increase of the electronic density in the vicinity of the oxygen atoms.



Spectrum of H<sub>2</sub>L



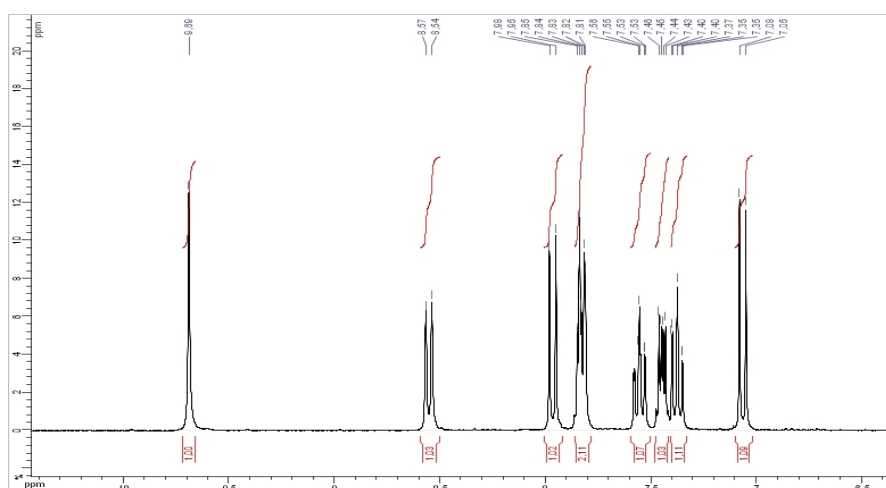
Spectrum of Cd(II)L

### Electronic Spectra

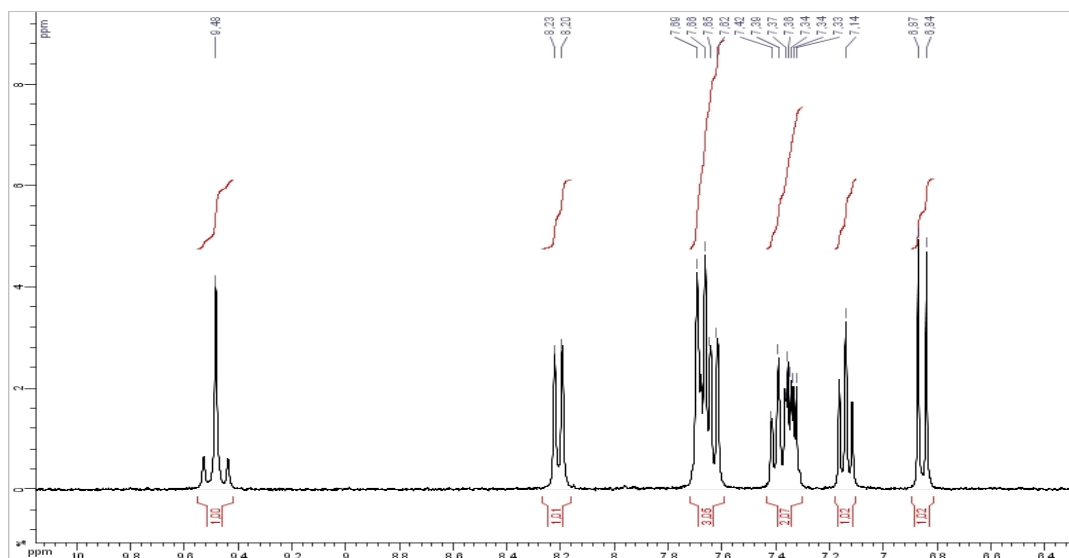
Spectroscopic data UV-Visible of the ligand and the complex Table 2.

Electronic spectra of the free ligands in DMF showed five main absorption bands in the UV range (350–800 nm), attributed to the  $\pi - \pi^*$ ,  $n - \pi^*$  and  $n - \sigma^*$  transitions. Thus, a bathochromic shift for H<sub>2</sub>L was noted when passing from ligand to Cd(II)L. This is due to coordination bonds inducing electronic delocalization through the different sp<sup>2</sup>-hybridization systems in the molecule. New absorption bands in the UV–Vis region of 390–444nm were assigned to  $d - \pi^*$  charge transfer transitions.

<sup>1</sup>H-NMR spectra in DMSO-d<sub>6</sub> showed the aromatic protons as multiplet in the range 6.83–8.55 ppm. The intrinsically unsymmetrical tetradentate Schiff base possesses two azomethine groups, both azomethine protons (CH=N) appearing at 9.38 and 10.38 ppm.



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<sup>1</sup>H-NMR spectrum of CdL complex in DMSO-d<sub>6</sub> at 300 MHz

## Elemental analyses

The elemental analysis of the synthesized compounds were in good agreement with the proposed chemical formulae for H<sub>2</sub>L and Cd(II)L. However, the complex shows a ligand–metal stoichiometric ratio of 1:1 affording mononuclear compound.

Compound	%C	%H	%N
	trouvé (calculé)		
H <sub>2</sub> L. MeOH	78.47 (77.66)	5.14 (5.39)	6.29 (6.25)
CdL	63.51 (63.83)	3.68 (3.44)	5.20 (5.32)

## Diffraction RX sur le monocristal H<sub>2</sub>L.DMSO

The ligand crystallizes in the monoclinic space group P2<sub>1</sub>/c.

Crystal data and refinement parameters for the ligand **H<sub>2</sub>L**

<b>Molecular formula moiety</b>	<b>C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>S</b>
<b>Molecular weight</b>	<b>494.59</b>
<b>Temperature (K)</b>	<b>173(2)</b>
<b>Radiation <math>\lambda</math></b>	<b>Mo-K<math>\alpha</math> (0.71073 Å)</b>
<b>Crystal system</b>	<b>Monoclinic</b>
<b>Space group</b>	<b>P2<sub>1</sub>/c</b>
<b><i>a</i>/Å</b>	<b>13.3535 (4)</b>
<b><i>b</i>/Å</b>	<b>7.5618(2)</b>
<b><i>c</i>/Å</b>	<b>24.3500(8)</b>
<b><i>alpha</i>°</b>	<b>90.00</b>
<b><i>Beta</i>°</b>	<b>90.9590(10)</b>
<b><i>gamma</i>°</b>	<b>90.00</b>
<b><i>V</i>/Å<sup>3</sup></b>	<b>2458.43(13)</b>
<b><i>Z</i></b>	<b>4</b>
<b><i>D</i><sub>calc</sub> (g cm<sup>-3</sup>)</b>	<b>1.336</b>
<b>Crystal size (mm<sup>3</sup>)</b>	<b>0.40 x 0.38 x 0.28</b>
<b>Crystal description</b>	<b>Prism</b>
<b>Crystal colour</b>	<b>Red</b>
<b>Absorption coefficient (mm<sup>-1</sup>)</b>	<b>0.168</b>
<b><i>F</i>(0 0 0)</b>	<b>1040</b>
<b>Reflections collected/unique</b>	<b>17304/5917 [<i>R</i><sub>int</sub> = 0.0173]</b>
<b>Range/indices (<i>h</i>, <i>k</i>, <i>l</i>)</b>	<b>-16, 17; -9, 9; -32, 32</b>
<b><i>T</i><sub>limit</sub></b>	<b>1.53 – 28.01</b>
<b>No. of observed data, <i>I</i> &gt; 2<i>Sigma</i>(<i>I</i>)</b>	<b>4939</b>
<b>No. of variables</b>	<b>328</b>
<b>No. of restraints</b>	<b>0</b>
<b>Goodness of fit on <i>F</i><sup>2</sup></b>	<b>1.032</b>
<b>Largest diff. Peak and hole (e Å<sup>-3</sup>)</b>	<b>0.302 and -0.380</b>
<b><i>R</i><sub>1</sub>, <i>wR</i><sub>2</sub> [<i>I</i> ≥ 2<i>Sigma</i>(<i>I</i>)]<sup>a</sup></b>	<b>0.434, 0.1090</b>
<b><i>R</i><sub>1</sub>, <i>wR</i><sub>2</sub> (all data)<sup>a</sup></b>	<b>0.0543, 0.1196</b>

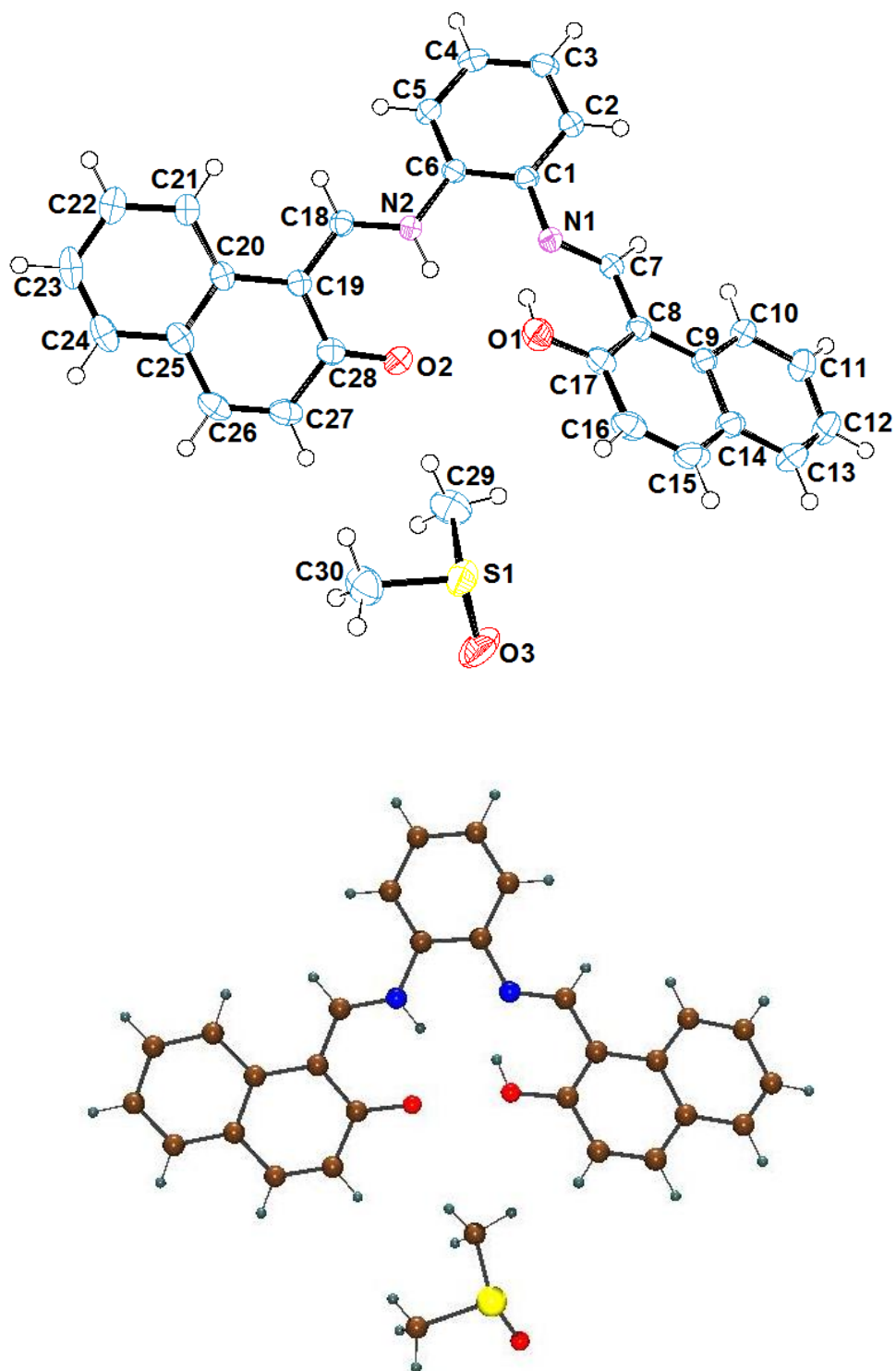
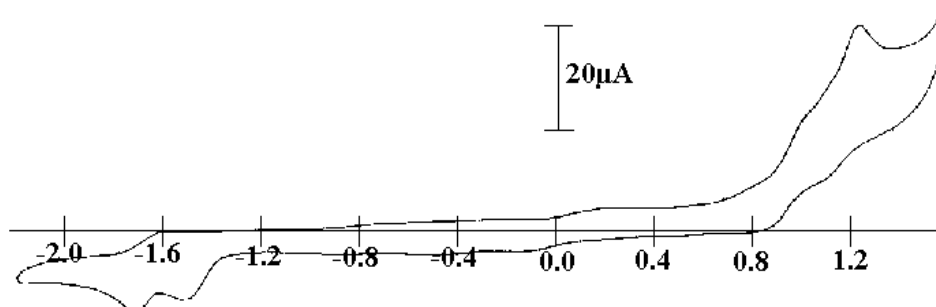


Fig. 1. The molecular structure of the ligand, showing the atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are omitted for clarity

## Electrochemical Study

In this study, we have, recorded the voltammograms of the ligand and the complex under nitrogen atmosphere.

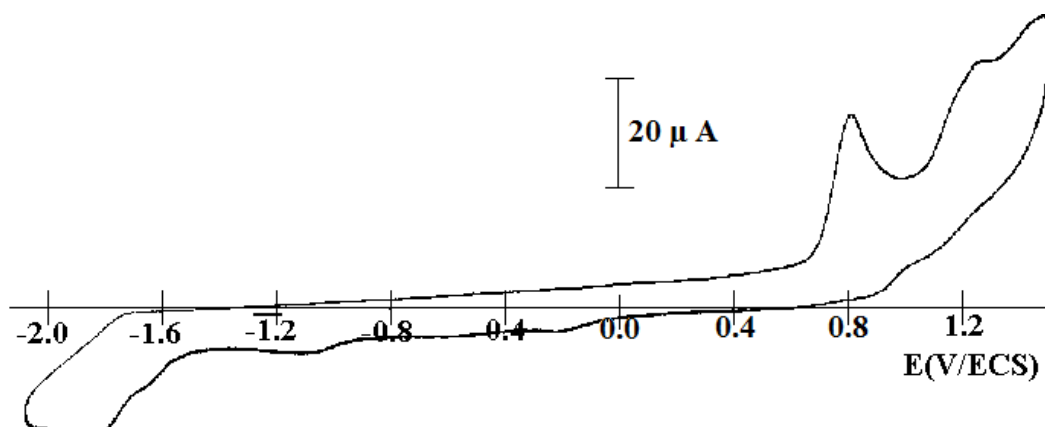
### 4.1. Ligand



The cyclic voltammetry of  $H_2L$  was achieved in DMF solutions in the -2200 to +1600mV range. We observe two anodic waves, Epa1 -1600 and Epa2 +1120 mV. Only Epa1 shows its reduction wave, giving a redox system, the Epa2 not reversible. These irreversible anodic waves are attributed to the para- and ortho-oxidations of phenol moieties and of the phenol groups themselves. During the back sweep, we observe two cathodic waves at Epc1-1500 and Epc2 -1680 mV. However, the redox system observed at  $E_{1/2}$  -1635mV.

### Complex Cd(II)L

At anodic potentials, shows three waves at Epa1-1680, Epa2 +800 and Epa3 +1200 mV. The first wave and the third are irreversible and due to oxidation of the ligand. The second represents oxidation of Cd(II). For cathodic potentials, we observe one reduction wave at Epc1-1700 mV due to reduction of the ligand.





## Conclusion

The work described in this paper involved the synthesis and structural characterization of ligand and its complex. This is confirmed by X-ray diffraction on one of the ligand. Electrochemical studies revealed that the first oxidation process Cd(II) is irreversible.

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