# Preparation and Characterization of Some Schiff Base Dioxime Metal Complexes

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**(Recevied on 19/11/2009)** **(Accepted for publication 21/4/2010)**

## Abstract

A dioxime ($LH_2$), [1,4-diaminobenzene-N, N′-bis(2-butylidine-3-one oxime], reacts with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) to yield dinuclear complexes of general formula $[M_2(LH)_2]Cl_2$ with a metal to ligand ratio of 2:2 with M = Co(II) or Cu(II), while Ni(II) forms complex $[Ni_2(LH)_2(H_2O)_2Cl_2]$ with a metal to ligand ratio of 2:2, whereas Zn(II) and Cd(II) form complexes of general formula $[M_2(LH)(H_2O)_2Cl_2]$ with a metal to ligand ratio of 2 :1 . All complexes were characterized by metal content analyses, IR, electronic spectra, magnetic susceptibility and conductivity measurements. The Co(II) and Cu(II) complexes are proposed to be square planar while the Ni(II) complex is proposed to be octahedral and the complexes of Zn(II) and Cd(II) are tetrahedral.

## الخلاصة

يتفاعل الليكاند ثنائي اوكزيم ($LH_2$) ، [ 1 ،4- ثنائي امين بنزين-ن ، ن-بس (2-بيوتيليدين -3- ون اوكزيم)]، مع ايونات الكوبلت ، النيكل ، النحاس، الخارصين والكادميوم الثنائية الموجبة ليعطي معقدات ثنائية النواة ذات الصيغة العامة $[M_2(LH)_2]Cl_2$ عندما M= ايون الكوبلت او النحاس الثنائي الموجب (النسبة المولارية لفلز : ليكاند هي 2 :2)، بينما ايون النيكل (II) يعطي المعقد ذي الصيغة $[Ni_2(LH)_2(H_2O)_2Cl_2]$ (النسبة المولارية لفلز : ليكاند هي 2 :2)، تتكون المعقدات ذي الصيغة العامة $[M_2(LH)(H_2O)_2Cl_2]$ مع كلا من ايوني الخارصين والكادميوم الثنائي الموجب (النسبة المولارية لفلز : ليكاند هي 2 :1). شخصت المعقدات من خلال التحليل الدقيق للفلز ، الاشعة تحت الحمراء ، الطيف الالكتروني ، القياسات المغناطيسية وقياسات التوصيلية المولارية. اعتمادا على هذه القياسات ، يعتقد ان معقدات الكوبلت والنحاس لها شكل مربع مستوي الاكثر احتمالا ، ومعقد النيكل شكل ثماني السطوح الاكثر احتمالا بينما معقدات الخارصين والكادميوم شكل رباعي السطوح الاكثر احتمالا.

## Introduction

The chemistry of oxime metal complexes have been studied and the subject of several reviews(1-3), due to their interesting and important properties, e.g., these class of compounds are used as chelating agents due to their stability of complexes with transition metal(3). Also, their structural importance arising from their specific and selective reactions with metal ions(4). Additionally, they are important in biological(5) and electrochemical applications(6). Many Schiff base derivatives containing substituted oxime have been synthesized, characterized in detail, and used for complexation with some transition metal ions in the literature(3,7). Therefore, it has been found interesting to study of complexes containing Schiff base dioxime derived from 1,4-phenylenediamine with 2,3-butanedionemonoxime.

In our best knowledge, metal complexes of the ligand ($LH_2$), [1,4-diaminobenzene-N, N′ - bis (2-butylidine-3-one oxime)] have not been synthesized. Therefore,we synthesized the complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) of the ligand ($LH_2$) (Figures 1,2 and 3).

## Experimental

### Materials :

All chemicals used in the present work such as 1 , 4 – phenylenediamine ,2,3-butanedionemonoxime and metals chlorides were of Analytical Reagent (A.R.) grade (B.D.H. and Fluka).

### a. Preparation of the ligand ($LH_2$) :

Ethanolic solution of 2,3-butanedionemonoxime (0.02 mol.) was added to ethanolic solution of 1,4-phenylenediamine (0.01 mol.). the mixtures were heated under reflux for 4 hours. The resulting ligand were precipitated, filtered off, washed with ethanol and then dried in air.

### b. Preparation of the Co(II), Ni(II) and Cu(II) complexes :

These complexes were prepared by the same general method as the following :

A hot ethanolic solution of metal chloride (0.02 mol.) was added to an ethanolic solution of the ligand (0.02 mol.), heated under reflux for 7 hours. The complexes were precipitated, filtered off, washed with water, ethanol and then dried in air.

### c. Preparation of the Zn(II) and Cd(II) complexes :

These complexes were prepared by the same method as described above except the ligand was with 0.01 mole.

### Analysis and physical measurements:

The metal contents were determined according to the standard procedure(8). Melting points were determined by using Electrothermal 9300 digital apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001 M dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 $cm^{-1}$ range using KBr disc. Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in DMF at $25^oC$ for 0.001 M solution of the compounds using a 1 cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Faraday method at room temperature using a Bruker BM6 apparatus.

## Results and discussion

Schiff base dioxime ligand ($LH_2$) was obtained by reaction of 1,4-phenylenediamine with 2,3-butanedionemonoxime in the molar ratio 1:2. the resulting solid is dark brown, m.p. 94-$96^oC$ and stable in air. The chemical analytical data of the synthesized Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes are listed in Table 1, suggest that the proposed formula $[M_2(LH)_2]Cl_2$ with a metal to ligand ratio of 2:2 with M = Co(II) or Cu(II), while Ni(II) forms complex $[Ni_2(LH)_2(H_2O)_2Cl_2]$ also with a metal to ligand 2:2 whereas the Zn(II) and Cd(II) form complexes $[M_2(LH)(H_2O)_2Cl_2]$ with a metal to ligand 2:1. the molar conductances of the complexes in DMF are in the range 24-145 ohm$^{-1}$ cm$^2$ mol$^{-1}$ (Table 1), indicating a non electrolytic nature for Ni(II), Zn(II) and Cd(II) complexes, while the electrolytic nature of the Co(II) and Cu(II) complexes with 1:2 ratio(9).

**Table (1) : Analytical and some physical properties of the compounds**

| **Compound** | **m.p C$^0$** | **Colour** | **Yield %** | **% Metal (Found)Calc.** | **$\Lambda_M$ (DMF) cm$^2$ ohm$^{-1}$ mol$^{-1}$** |
|---|---|---|---|---|---|
| $(LH_2)$ | 94-96 | Dark Brown | 71 | ……… | ……… |
| $[Co_2(LH)_2]Cl_2$ | 399 d* | Dark Brown | 77 | 15.22<br>(16.03) | 134 |
| $[Ni_2(LH)_2(H_2O)_2Cl_2]$ | 391 d | Red | 72 | 14.45<br>(15.24) | 24 |
| $[Cu_2(LH)_2]Cl_2$ | 372 d | Dark Brown | 67 | 16.11<br>(17.07) | 145 |
| $[Zn_2(LH)(H_2O)_2Cl_2]$ | 340 d | Brown | 60 | 26.02<br>(25.64) | 29 |
| $[Cd_2(LH)(H_2O)_2Cl_2]$ | 349 d | Brown | 68 | 36.28<br>(37.23) | 28 |

* d = decomposition

## IR spectra

The active site of the free ligand and its bonding to the metal atoms was characterized by comparison of the main infrared absorption bands of the free ligand and its complexes (Table 2). The main characteristic bands located in the ligand spectrum at 3361, 1625 and (1023-976)cm$^{-1}$, which due to the ν(OH) oxime, ν(C=N) and ν(N-O) stretching vibrations(10-14), respectively. Upon complexation, the shift of the ν(N-O) bands to the upper frequencies region, and the shift of the ν(C=N) bands to the lower frequencies region in the IR spectra of Co(II), Ni(II) and Cu(II) complexes (Table 2) may be attributed to N,N-chelation. These both the nitrogen atoms of the azomethine ν(C=N) of imine group and the azomethine ν(C=N) of oxime group to the coordination with the metal(10,12,13-14). The weak bands appeared within the region (2349-2283)cm$^{-1}$ for the Co(II), Ni(II) and Cu(II) complexes, are due to the ν(O-H…….O) stretching for the hydrogen bond (also called H-bridge), in which the ligand looses a proton and a hydrogen bonding will be formed(10,15). The occurrence of new bands in the (429-428) cm$^{-1}$ region in the IR spectra of the Co(II), Ni(II) and

Cu(II) complexes were assigned to ν(M-N) stretching, indicating that the imine and oxime nitrogens were involved in coordination with Co(II), Ni(II) and Cu(II) ions(13,14). Two bands display at 3355 and 3346 cm$^{-1}$, attributed to the ν(OH) oxime for the Co(II) and Cu(II) complexes, respectively, while the broad band at 3442 cm$^{-1}$ was observed in the spectrum of Ni(II) complex, indicates the presence of coordinated water(16). The ν(OH) oxime of the Ni(II) complex is not observed in the region 3350 cm$^{-1}$, since it is hidden under the broad band of coordinated water, while the appearance of two bands at 817 and 753 cm$^{-1}$ in the spectrum of Ni(II) complex, attributed to rocking and wagging modes(16), respectively, support the presence of coordinated water. The other new bands located at 559 and 573 cm$^{-1}$ in the spectra of the Co(II) and Cu(II) complexes, respectively, belonging to the chloride groups(16). The positions of these bands suggested the ionic nature and the non-involvement of these groups in coordination, and therefore remained outside the coordination sphere. These observations were in good agreement with the conductance values which have been supported the given formulation of these complexes. The coordination of the chloride ions and the water molecules to the nickel(II) ion could not be inferred from the infrared absorption spectrum since (Ni-Cl) and (Ni-$OH_2$) bands located beyond the limits of our instrument (at the far infrared spectrum).

The stretching bands of C=N at 1625 cm$^{-1}$ in the free ligand, is shifted to lower frequencies region (Table 2) for Zn(II) and Cd(II) complexes and the ν(N-O) in the region (1023-976) cm$^{-1}$ in ligand, is shifted to higher frequencies region (Table 2) for Zn(II) and Cd(II) complexes. Also, there is no O-H …. O peak at the expected region (2350-2280) cm$^{-1}$ for both Zn(II) and Cd(II) complexes. This suggest that the ligand is coordinated through nitrogen and oxygen donors, N,O-chelation(13,17). Assignment of the proposed coordination sites is further supported by the appearance of new bands in the regions (420-418) and (522-517) cm$^{-1}$ which could be attributed to the formation of M-N and M-O bonds(16), respectively . The broad bands at 3443 and 3452 cm$^{-1}$ were observed in the spectra of Zn(II) and Cd(II) complexes, respectively, also the two bands in the regions (824-817) and (756-749) cm$^{-1}$ attributed to rocking and wagging modes, respectively, indicate the presence of coordinated water. These observations support the proposed structures for the Zn(II) and Cd(II) complexes (Figure 3). The coordination of the chloride ions and the water molecules to the Zn(II) and Cd(II) ions could not be inferred from the infrared absorption spectra since (M-Cl) and (M-$OH_2$) bands, M=Zn(II) or Cd(II), located beyond the limits of the instrument (at the far infrared spectra).

**Table 2 : Important IR spectral bands (cm$^{-1}$)**

| Compound | ν (C=N) | ν (N-O) | ν (N-O) | ν (HO…..O) |
|---|---|---|---|---|
| ($LH_2$) | 1625 | 1023 | 976 | --------- |
| $[Co_2(LH)_2]Cl_2$ | 1605 | 1094 | 1015 | 2349 - 2300 |
| $[Ni_2(LH)_2(H_2O)_2Cl_2]$ | 1571 | 1100 | 988 | 2348 - 2285 |
| $[Cu_2(LH)_2]Cl_2$ | 1603 | 1091 | 1014 | 2348 - 2283 |
| $[Zn_2(LH)(H_2O)_2Cl_2]$ | 1609 | 1111 | 982 | --------- |
| $[Cd_2(LH)(H_2O)_2Cl_2]$ | 1612 | 1059 | 1025 | --------- |

## Electronic and magnetic moments

The electronic spectra of the ligand and its complexes were recorded in DMF at room temperature. The electronic spectral data of the ligand and its complexes are given in Table 3. The aromatic band of the ligand at 35971 $cm^{-1}$ is attributed to benzene $\pi \rightarrow \pi*$ transition. The band around 26595 $cm^{-1}$ is due to the $n \rightarrow \pi*$ transition of the non-bonding electrons present on the nitrogen of the imine or oxime group in the lignad. In the spectra of all the complexes, the $n \rightarrow \pi*$ transitions are shifted to higher energy (Table 3). These results indicate that the nitrogen atoms of the imine and oxime groups are coordinated to the Co(II), Ni(II) and Cu(II) ions or may be the nitrogen atom of the imine group is coordinated to the Zn(II) and Cd(II) ions(18). Although the square planar complexes of Co(II) are not very common, the electronic spectrum of Co(II) complex exhibit a band at 16129 $cm^{-1}$ in DMF solution. This is attributable to $^2A_1g \rightarrow ^2B_1g$ transition in square planar geometry. The magnetic moment of Co(II) complex was found to be 2.12 B.M.(per Co ion). This may be to the mixing of the higher ligand field term $^2A_2g$ with $^2A_1g$ ground term on account of spin-orbit coupling whereby the magnetic moment of the cobalt complex goes above the spin value of 1.73 B.M.(19). d-d transitions of the nickel complex at 10373, 18248 and 22222 $cm^{-1}$, corresponding to the transitions of $^3A_2g \rightarrow ^3T_2g(F)(\nu_1)$ , $^3A_2(F) \rightarrow ^3T_1g(F)(\nu_2)$ and $^3A_2g \rightarrow ^3T_1g(P)(\nu_3)$, respectively, in the octahedral field were noted. Magnetic moment value of 3.40 B.M.(per Ni ion), supports the hexacoordinated configuration of the nickel complex(20). The Cu(II) complex shows a d-d absorption band at 24390 $cm^{-1}$, corresponding to $^2B_1g \rightarrow ^2A_1g$ transition. A value of 1.61 B.M. per Cu(II) ion has been observed, which is well within the expected region found for square planar copper(II) complex(21,22). Since the zinc and cadmium ions have $d^{10}$ configuration, the absorption spectra of Zn(II) and Cd(II) complexes shows no bands due to d-d transitions, while the absorptions at 33333 and 32894 $cm^{-1}$ for the zinc and cadmium complexes, respectively, are assigned to $n \rightarrow \pi*$ transitions. The Zn(II) and Cd(II) complexes have diamagnetic character. However, taking into account the spectra and other physio-chemical evidences, four-coordinated tetrahedral geometry is suggested for Zn(II) and Cd(II) complexes(21,22).

**Table (3) : The electronic spectra and magnetic moments of the compounds**

| Compound | Absorption region ($cm^{-1}$) | Possible assignments | Magnetic moment (B.M.) | Geometry |
|---|---|---|---|---|
| ($LH_2$) | 35971 | $\pi \rightarrow \pi^*$ | ----------- | ----------- |
| | 26595 | $n \rightarrow \pi^*$ | | |
| $[Co_2(LH)_2]Cl_2$ | 28409 | $n \rightarrow \pi^*$ | 2.12 | Square planar |
| | 16129 | $^2A_1g \rightarrow {}^2B_1g$ | | |
| $[Ni_2(LH)_2(H_2O)_2Cl_2]$ | 28901 | $n \rightarrow \pi^*$ | 3.40 | Octahedral |
| | 22222 | $^3A_2g \rightarrow {}^3T_1g(P)$ | | |
| | 18248 | $^3A_2g \rightarrow {}^3T_1g(F)$ | | |
| | 10373 | $^3A_2g \rightarrow {}^3T_2g(F)$ | | |
| $[Cu_2(LH)_2]Cl_2$ | 27777 | $n \rightarrow \pi^*$ | 1.61 | Square planar |
| | 24390 | $^2B_1g \rightarrow {}^2A_1g$ | | |
| $[Zn_2(LH)(H_2O)_2Cl_2]$ | 33333 | $n \rightarrow \pi^*$ | Diamagnetic | Tetrahedral |
| $[Cd_2(LH)(H_2O)_2Cl_2]$ | 32894 | $n \rightarrow \pi^*$ | Diamagnetic | Tetrahedral |

## Conclusions

In this paper, we report the preparation, isolation and characterization of a Schiff base dioxime ligand derived from 1,4-phenylenediamine and 2,3-butanedionemonoxime ($LH_2$), and its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The products were characterized by analytical analysis, magnetic and spectroscopic measurements data, one can estimate the stereochemistry of the prepared complexes : octahedral for the $[Ni_2(LH)_2(H_2O)_2Cl_2]$, square planar for the $[M_2(LH)_2]Cl_2$ (M = Co(II) or Cu(II)) and tetrahedral for the $[M_2(LH)(H_2O)_2Cl_2]$ (M= Zn(II) or Cd(II)). the proposed structural formulas of these compounds are presented in Figures 1,2 and 3.

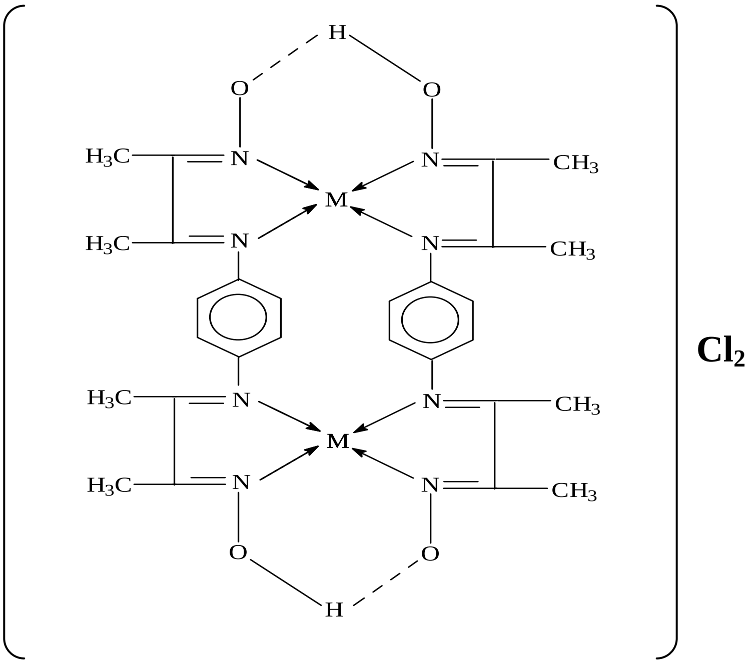

**Fig.1 : The proposed structure of the complexes $[M(LH)_2]Cl_2$ M = Co(II) or Cu(II)**

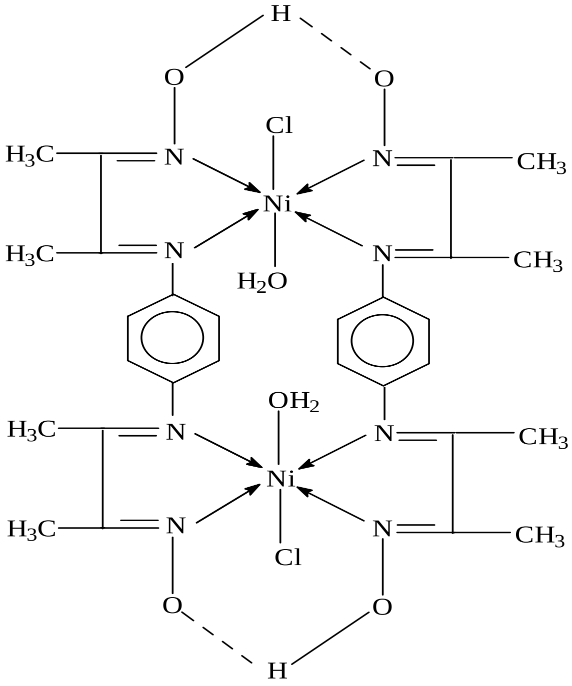

**Fig.2 : The proposed structure of the complex $[Ni_2(LH)_2(H_2O)_2Cl_2]$**

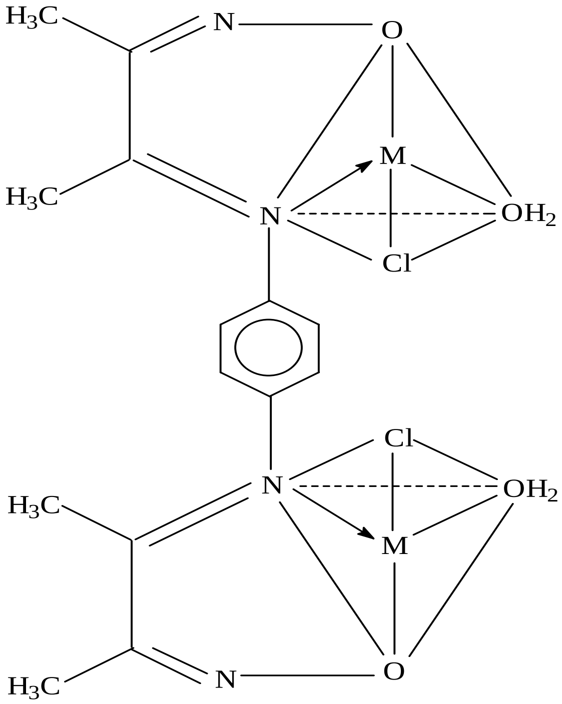

**Fig.3 : The proposed structure of the complexes $[M_2(LH)(H_2O)_2Cl_2]$ M= Zn(II) or Cd(II)**

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