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### The Synthesis and Ni(II), Co(II), Cu(II), Zn(II), and Cd(II) Complexes of Two Novel Tetraoximes

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## THE SYNTHESIS AND Ni(II), Co(II), Cu(II), Zn(II), AND Cd(II) COMPLEXES OF TWO NOVEL TETRAOXIMES

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### ABSTRACT

In this study, two novel tetraoximes were synthesized by reacting *anti*-chloroglyoxime with *sym*-bis(*p*-aminophenyl)oxamidine and *sym*-bis-4-(4'-aminobiphenyl)oxamidine. Polynuclear complexes with Ni(II), Co(II) and Cu(II) and binuclear complexes with Zn(II) and Cd(II) of these tetraoximes were isolated. All these complexes are insoluble in common solvents; structures are proposed according to elemental analysis, i.r., and magnetic susceptibility measurements.

### INTRODUCTION

Derivatives of polymeric *vic*-dioximes and their complexes with transition metals have been reported<sup>(1)</sup>. In our previous paper<sup>(2)</sup>, we studied the structures of various transition metal complexes of polymeric-dioximes by reacting *sym*-bis(*p*-aminophenyl)-oxamidine and *sym*-bis-4-(4'-amino-biphenyl)oxamidine derivatives with di-cyan-di-N-oxide.

The reaction of aromatic amines with cyanogen  $\{(CN)_2\}$  generally yields oxamidines<sup>(3)</sup>. The reaction of *p*-phenylenediamine reacts with cyanogen to produce *sym*-bis(*p*-aminophenyl)oxamidine and polymeric substance, whereas 4,4'-diaminobiphenyl yields cyanoformamidine derivative and then an oxamidine<sup>(3,4)</sup>.

In this article, we reported the synthesis of two novel tetraoximes substituted with oxamidine and their complexes with Ni(II), Co(II), Cu(II), Zn(II) and Cd(II) ions.

## EXPERIMENTAL

*sym*-Bis(*p*-aminophenyl)oxamidine, *sym*-bis-4-(4'-aminobiphenyl)oxamidine<sup>(4)</sup> and anti-chloroglyoxime<sup>(5,6)</sup> were prepared according to the procedures reported in corresponding literature references. Infrared spectra were recorded on a Pye Unicam SP 1025 spectrophotometer in KBr pellets. The <sup>1</sup>H-n.m.r. spectra were recorded on a Bruker 200 MHz spectrophotometer. The magnetic moments of the complexes were measured according to the Gouy method with a Newport Instruments type D-104 magnet power supply (293 K).

### Preparation of tetra-oximes {N,N'-bis[(4-phenyl)oxamidine]aminoglyoxime (L<sup>1</sup>H<sub>2</sub>) and N,N'-bis[4-(4'-biphenyl)oxamidine]aminoglyoxime (L<sup>2</sup>H<sub>2</sub>)} (General Procedure):

A solution of anti-chloroglyoxime (2.45 g, 20 mmol) in 50 mL ethanol was added dropwise within a period of 2 hours into a solution containing *sym*-bis(*p*-aminophenyl)oxamidine (2.80 g, 10 mmol) or *sym*-bis-4-(4'-aminobiphenyl)oxamidine (4.20 g, 10 mmol) and NaHCO<sub>3</sub> (3 g) in 50 mL ethanol under constant stirring at room temperature. After the addition of anti-chloroglyoxime, the solution was stirred for an additional six hours. 50 mL water was then added to the solution to precipitate a red substance. This precipitate was filtered and dried *in vacuo*. Yield of L<sup>1</sup>H<sub>2</sub> : 75% and L<sup>2</sup>H<sub>2</sub> : 76%. Melting point of ligands are above 255 °C (decomposition).

These compounds were soluble in DMF, pyridine and DMSO. (Found L<sup>1</sup>H<sub>2</sub> : C, 49.09; H, 4.58; N, 31.80. Calc. for C<sub>18</sub>H<sub>20</sub>N<sub>10</sub>O<sub>4</sub> : C, 48.79; H, 4.73; N, 31.62. Found L<sup>2</sup>H<sub>2</sub> : C, 60.80; H, 4.76; N, 23.64. Calc. for C<sub>30</sub>H<sub>28</sub>N<sub>10</sub>O<sub>4</sub> : C, 60.63; H, 4.61; N, 23.46 %). <sup>1</sup>H-n.m.r. of L<sup>1</sup>H<sub>2</sub>, δ : 12.44 (s, 2H, disappears upon deuterium exchange), 11.44 (s, 2H, disappears upon deuterium exchange), 8.03 (s, C-Haldoxim), 7.88 (s, 2H, disappears upon deuterium exchange), 7.55 (s, 4H, disappears upon deuterium exchange), 6.86-7.42 (m, 8H). <sup>1</sup>H-n.m.r. of L<sup>2</sup>H<sub>2</sub> δ : 12.54 (s, 2H, disappears upon deuterium exchange), 11.47 (s, 2H, disappears upon deuterium exchange), 8.12 (s, C-Haldoxim) 7.90 (s, 2H, disappears upon deuterium exchange), 7.56 (s, 4H, disappears upon deuterium exchange), 6.90-7.37 (m, 16H). IR of L<sup>1</sup>H<sub>2</sub> ν<sub>max</sub> : 3470 (N-H), 3300 (-N-H), 3170 (O-H), 3010 (C-H<sub>arom</sub>), 2980 (C-H<sub>aldoxim</sub>), 1670 (C=N<sub>oxamidine</sub>), 1640 (C=N<sub>oxime</sub>) and 960 (N-O) cm<sup>-1</sup>; IR of L<sup>2</sup>H<sub>2</sub> ν<sub>max</sub> :

3500 (N-H), 3300 (=N-H), 3200 (O-H), 3010 (C-H<sub>arom</sub>), 2980 (C-H<sub>alldoxim</sub>), 1670 (C=N<sub>oxamidine</sub>), 1635 (C=N<sub>oxime</sub>) and 960 (N-O) cm<sup>-1</sup>.

### **The Preparation of Ni(II), Co(II) and Cu(II) Polynuclear complexes of tetraoximes**

#### **(General Procedure):**

A solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.5 mmol, 119 mg), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.5 mmol, 119 mg) or CuCl<sub>2</sub>·2H<sub>2</sub>O (0.5 mmol, 170 mg) in 30 mL hot ethanol was added to the solution of L<sup>1</sup>H<sub>2</sub> (0.5 mmol, 220 mg) or L<sup>2</sup>H<sub>2</sub> (0.5 mmol, 296 mg) in 20 mL DMSO. The color was changed immediately and a sharp decrease in the pH of the solution to 3.5-4.0 was observed. When the pH was increased to 5.0-5.5 with 0.5 % NaOH solution in ethanol, precipitation started. The mixture was further stirred on a water bath at 60 °C for 1 hour in order to complete precipitation. Precipitates were filtered off, washed with hot ethanol and hot water and then dried in vacuo.

### **The Preparation of Zn(II) and Cd(II) Binuclear complexes of tetraoximes**

#### **(General Procedure):**

A solution of ZnCl<sub>2</sub>·2H<sub>2</sub>O (1 mmol, 172 mg) or CdCl<sub>2</sub>·2H<sub>2</sub>O (1 mmol, 219 mg) in 30 mL hot ethanol was added to a solution of L<sup>1</sup>H<sub>2</sub> (0.5 mmol, 220 mg) or L<sup>2</sup>H<sub>2</sub> (0.5 mmol, 296 mg) in 20 mL DMSO. The color changed immediately and a sharp decrease in the pH of the solution to 4.0-4.5 was observed. When the pH was increased to 5.0-5.5 with 0.5 % NaOH solution in ethanol, precipitation started. The mixture was further stirred on a water bath at 60 °C for 1 hour in order to complete precipitation. Precipitates were filtered, washed with hot ethanol and hot water and then dried in vacuo.

The data regarding color, melting point, yield, elemental analyses, IR and magnetic moments of the all the complexes are give in Tables 1 and 2.

## **RESULTS AND DISCUSSION**

In this work, N,N'-bis[(4-phenyl)oxamidine]aminoglyoxime(L<sup>1</sup>H<sub>2</sub>) and N,N'-bis[4-(4'-biphenyl)oxamidine]aminoglyoxime (L<sup>2</sup>H<sub>2</sub>) were synthesized by reacting *anti*-chloroglyoxime with *sym*-bis(4-aminophenyl)oxamidine and *sym*-bis-4-(4'-aminobiphenyl)oxamidine respectively (Schcma 1) and complexes of these *vic*-dioximes with Ni(II), Co(II), Cu(II), Zn(II) and Cd(II) ions were isolated (Fig. 1 and 2).

**Table 1.** Analytical<sup>a</sup> Physical<sup>b</sup> and Magnetic data for the Complexes

Compound	Color	Yield (%)	Magnetic Moment (B.M.)	Analysis (%)				
				C	H	N	M	Cl
$[(L^1H)Ni]_n$ (C <sub>18</sub> H <sub>18</sub> N <sub>10</sub> O <sub>4</sub> Ni) <sub>n</sub>	Dark red	94	Diamagnetic	43.49 (43.56)	3.65 (3.75)	28.18 (28.31)	11.81 (11.79)	-
$[(L^1H)Co]_n$ (C <sub>18</sub> H <sub>18</sub> N <sub>10</sub> O <sub>4</sub> Co) <sub>n</sub>	Dark brown	87	1.99	43.47 (43.16)	3.65 (3.71)	28.16 (28.20)	11.80 (11.66)	-
$[(L^1H)Cu]_n$ (C <sub>18</sub> H <sub>18</sub> N <sub>10</sub> O <sub>4</sub> Cu) <sub>n</sub>	Dark green	84	1.65	43.07 (43.33)	3.61 (3.61)	27.90 (26.11)	12.60 (12.54)	-
$[(L^1H)Cl_2(H_2O)_2Zn]_n$ (C <sub>18</sub> H <sub>22</sub> N <sub>10</sub> O <sub>6</sub> Cl <sub>2</sub> Zn) <sub>n</sub>	Brown	95	Diamagnetic	31.98 (31.58)	3.28 (3.09)	20.72 (20.57)	19.94 (19.85)	10.49 (10.37)
$[(L^1H)Cl_2(H_2O)_2Cd]_n$ (C <sub>18</sub> H <sub>22</sub> N <sub>10</sub> O <sub>6</sub> Cl <sub>2</sub> Cd) <sub>n</sub>	Brown	87	Diamagnetic	28.07 (28.36)	2.88 (3.02)	18.19 (18.08)	20.19 (29.31)	9.21 (9.32)
$[(L^2H)Ni]_n$ (C <sub>30</sub> H <sub>28</sub> N <sub>10</sub> O <sub>4</sub> Ni) <sub>n</sub>	Red	85	Diamagnetic	55.50 (55.66)	4.04 (4.32)	21.57 (21.78)	9.04 (9.23)	-
$[(L^2H)Co]_n$ (C <sub>30</sub> H <sub>28</sub> N <sub>10</sub> O <sub>4</sub> Co) <sub>n</sub>	Dark brown	85	2.06	55.48 (55.66)	4.03 (4.12)	21.56 (21.78)	9.07 (9.18)	-
$[(L^2H)Cu]_n$ (C <sub>30</sub> H <sub>28</sub> N <sub>10</sub> O <sub>4</sub> Cu) <sub>n</sub>	Dark green	85	1.67	55.08 (54.86)	4.01 (4.22)	21.41 (21.48)	9.71 (9.78)	-
$[(L^2H)Cl_2(H_2O)_2Zn]_n$ (C <sub>30</sub> H <sub>30</sub> N <sub>10</sub> O <sub>6</sub> Cl <sub>2</sub> Zn) <sub>n</sub>	Brown	85	Diamagnetic	45.50 (45.66)	3.65 (3.58)	16.91 (16.78)	15.79 (15.58)	8.56 (8.40)
$[(L^2H)Cl_2(H_2O)_2Cd]_n$ (C <sub>30</sub> H <sub>30</sub> N <sub>10</sub> O <sub>6</sub> Cl <sub>2</sub> Cd) <sub>n</sub>	Red	85	Diamagnetic	39.07 (38.79)	2.28 (2.32)	15.91 (15.78)	24.37 (24.18)	7.69 (7.54)

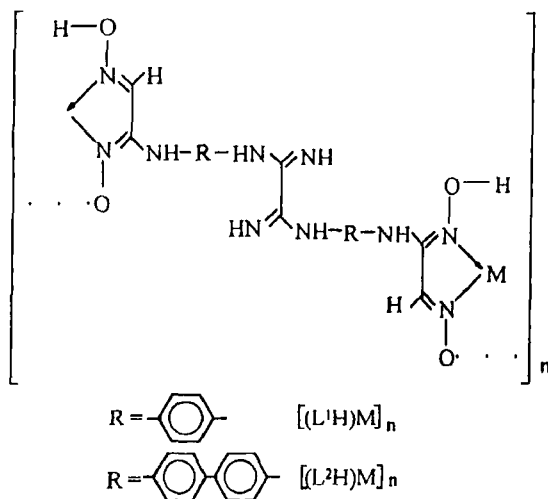
<sup>a</sup>Required values are given in parentheses. <sup>b</sup>Melting points of all the complexes are above 320 °C.

In the <sup>1</sup>H-NMR spectra, two peaks are present for the OH protons of the oxime groups. These two deuterium exchangeable singlets correspond to two inequivalent OH protons that also indicate the *anti*- configuration of the OH groups relative to each other (Schema 1). When the chemical shift values of the two OH groups are compared in two different ligands, the one at lower field quite closely resemble each other (L<sup>1</sup>H<sub>2</sub>; δ = 12.44 s, 2H and L<sup>2</sup>H<sub>2</sub>; δ = 12.54 s, 2H) while a considerable difference is observed for the one at the higher field (L<sup>1</sup>H<sub>2</sub>; δ = 11.44 s, 2H and L<sup>2</sup>H<sub>2</sub>; δ = 11.47 s, 2H)<sup>(8,9)</sup>. Consequently, the

**Table 2.** Characteristic I.R. Bands ( $\text{cm}^{-1}$ ) of The Complexes (KBr pellets)

Compound	$\nu$ (N-H)	$\nu$ (C-H)	$\nu$ (O-H...O)	$\delta$ (O-H...O)	$\nu$ (C=N) oxamidine	$\nu$ (C=N) oxime	$\nu$ (N-O)
$[(L^1H)Ni]_n$	3470	3015	2220	1710	1670	1620	960
$[(L^1H)Co]_n$	3470	3010	2230	1710	1670	1610	960
$[(L^1H)Cu]_n$	3470	3010	2260-2360	1710	1670	1610	960
$[(L^1H)Cl_2(H_2O)_2Zn_2]$	3500	3010	-	-	1670	1610	960
$[(L^1H)Cl_2(H_2O)_2Cd_2]$	3470	-	-	-	1670	1610	960
$[(L^2H)Ni]_n$	3470	3010	2200-2300	1710	1670	1605	960
$[(L^2H)Co]_n$	3470	3010	3260-2360	1710	1670	1605	960
$[(L^2H)Cu]_n$	3470	3010	3260-2360	1710	1670	1605	960
$[(L^2H)Cl_2(H_2O)_2Zn_2]$	3470	3010	-	-	1670	1605	960
$[(L^2H)Cl_2(H_2O)_2Cd_2]$	3470	3010	-	-	1670	1605	960

Other peaks :  $[(L^1H)Cl_2(H_2O)_2Zn_2]$ ,  $[(L^1H)Cl_2(H_2O)_2Cd_2]$ ,  $[(L^2H)Cl_2(H_2O)_2Zn_2]$ ,  
 $[(L^2H)Cl_2(H_2O)_2Cd_2]$ ;  $\nu(H_2O) = 3350 \text{ cm}^{-1}$ .

**Fig. 1** Polymeric  $[(L^1H)M]_n$  and  $[(L^2H)M]_n$  Complexes  $\{M = Ni(II), Co(II) \text{ or } Cu(II)\}$ .

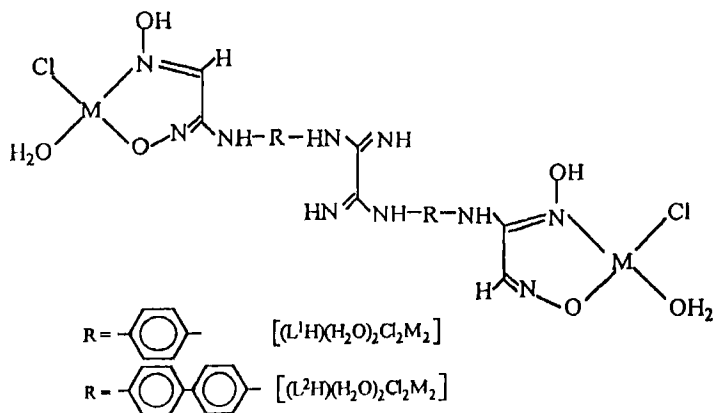
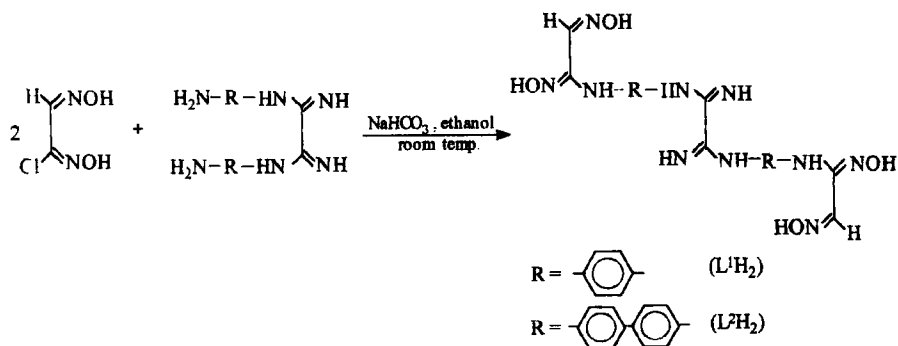


Fig. 2 Binuclear Complexes of  $L^1H_2$  and  $L^2H_2$   $\{M = Zn(II), \text{ or } Cd(II)\}$ .



Scheme 1

first one is assigned to the OH proton on the phenyl side and the latter to OH proton of the amidoxime since the effect of various substituents is expected to be higher on the amidoxime. The N-H protons were observed at 7.40-7.91 ppm and those of aromatic C-H protons at 6.86-7.42 ppm respectively. The IR spectrum of ligands exhibited  $\nu(O-H)$  as a broad absorption at  $3170\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$ . Band due to  $(C=N)$  oxamides<sup>(10)</sup>,  $(C=N)$  oximes and  $(N-O)$  stretches were at  $1670$ ,  $1640-1630$  and  $960-955\text{ cm}^{-1}$ , respectively<sup>(1,2,8-17)</sup>.

Elemental analyses, IR spectroscopy and magnetic susceptibility were employed in order to determine the structural characteristics of the complexes (Table 1 and 2). The reaction of ligands with salts of Ni(II), Co(II) and Cu(II) gave products with metal-ligand ratio of 1:1. In the case of Ni(II), Co(II) and Cu(II) only polynuclear complexes were obtained even when the metal ions were used in excess (Table 1). Since a distinct lowering in the pH of the solution was observed during the complex formation of the ligands with subsequent N,N'-chelation with the *vic*-dioxime groups probably occurs. The usual structure for an *anti*-dioxime complex is based on the formation of two O-H...O bridges for each complex molecule. The weak stretching<sup>(18,19)</sup> and deformation<sup>(1,2,8-17)</sup> bands of these hydrogen bridges were observed at around 2220-2360 cm<sup>-1</sup> and 1710 cm<sup>-1</sup> for all the complexes. The aromatic C-H, C=N and N-O stretching vibrations are very close for ligands as well as the Ni(II), Co(II) and Cu(II) complexes<sup>(1,2,8-17)</sup> (Fig. 2), (Table 2).

L<sup>1</sup>H<sub>2</sub> and L<sup>2</sup>H<sub>2</sub> reacts with Zn(II) and Cd(II) salts to give 2:1 metal-ligand ratio complexes with two of four coordination sites on the per metal are occupied by the N atom of the oxime groups and the O atom of the other. A chloride ion and a water molecule are also coordinated to the metal ion {[L<sup>1</sup>H(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>M<sub>2</sub>], [L<sup>2</sup>H(H<sub>2</sub>O)<sub>2</sub>Cl<sub>2</sub>M<sub>2</sub>]}, (Fig. 2), the physical data and IR spectra are consistent with such a structure<sup>(7,11,15)</sup> (Tables 1 and 2).

The common feature of the complexes of ligands were their insolubility that also hindered spectral investigations. Magnetic susceptibility measurements provide sufficient data to characterize the structures (Table 1). The mononuclear complexes of Ni(II) are diamagnetic as expected for d<sup>8</sup> metal ion in a square-planer field<sup>(1,2,8-17)</sup>. When the magnetic moments of the mononuclear complexes of Co(II) and Cu(II) are about 1.99-2.06 B.M. and 1.65-1.67 B.M., comparable with values reported for slightly distorted square-planer cobalt(II) and copper(II) complexes of *vic*-dioximes<sup>(11,16)</sup>.

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