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# The Synthesis and Ni(II), Co(II), and Cu(II) Complexes of Two New Polymeric *bis*(Oxamidine)aminoglyoximes

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# THE SYNTHESIS AND Ni(II), Co(II), AND Cu(II) COMPLEXES OF TWO NEW POLYMERIC *BIS*(OXAMIDINE)AMINOGLYOXIMES

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## ABSTRACT

In this work, two new polymeric Bis(oxamidine)diaminoglyoximes were synthesized by reacting *anti*-dichloroglyoxime with *sym*-bis(p-aminophenyl)oxamidine and *sym*-bis-4-(4'-aminobiphnyl)oxamidine, and complexes of these *vic*-dioximes with Ni(II), Co(II) and Cu(II) were isolated. All these complexes are insoluble in common solvents; structures are proposed according to elemental analysis, , i.r., and magnetic susceptibility measurements.

## INTRODUCTION

The reaction of aromatic amines with cyanogen {$(CN)_2$} generally yields oxamidines(1). The reaction of aromatic diamines with cyanogen has not been examined in detail; however, p-phenylenediamine reacts with cyanogen to produce *sym*-bis(p-aminophenyl)oxamidine and polymeric substance, whereas 4.4'-diaminobiphnyl yields cyanoformamidine derivative and then an oxamidine(1,2).

Derivatives of polymeric *vic*-dioximes and their complexes with transition metals were reported(3). In our previous paper(4), we have studied the structures of various transition metal complexes of *vic*-dioximes by reacting aromatic oxamidine derivatives with di-cyan-di-N-oxide.

In this article, we reported the synthesis of two novel polymeric *vic*-dioximes substitued with oxamidine and their complexes with Ni(II), Co(II) and Cu(II) ions.

## EXPERIMENTAL

*sym*-Bis(p -aminophenyl)oxamidine(2), *sym*-bis- 4 -(4' -aminobiphenyl)-oxamidine(2) and *anti*-dichloroglyoxime(5-7) were prepared according to the refered procedures. Infrared spectra were obtained on a Pye Unicam SP 1025 spectrophotometer in KBr pellets. The $^1$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 polymeric oxamidineoximes (1 and 2)(General Procedure):

A solution of *anti*-dichloroglyoxime (1.57 g, 10 mmol) in ethanol 50 cm$^3$ was added dropwise over the course 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 $NaHCO_3$ (3 g) in ethanol (50 cm$^3$) under constant stirring at room temperature. After the addition of *anti*-dichloroglyoxime, the solution was stirred for an additional six hours. Water (50 cm$^3$) was then added to the solution to precipitate the red substance. This precipitate was filtered off and dried in vacuo. Yeld of 1 : 87% and 2 : 89%. Melting points of ligands (1 and 2) are above 320 °C.

These compounds were soluble in DMF, pyridine and DMSO. (Found 1 : C, 54.54; H, 4.58; N, 31.80 $(C_{16}H_{16}N_8O_2)_n$ requires : C, 54.69; H, 4.82; N, 31.72. Found 2 : C, 66.65; H, 4.79; N, 22.21 $(C_{28}H_{24}N_8O_2)_n$ requires : C, 66.63; H, 4.61; N, 22.36 %). $^1$H.n.m.r. of 1 : $\delta$ 10.44 (s, 2H, disappears upon deuterim exchange), 7.88 (s, 2H, disappears upon deuterim exchange), 7.55 (s, 4H, disappears upon deuterim exchange), 6.86- 7.42 (m, 8H). $^1$H.n.m.r. of 2 : δ 10.40 (s, 2H, disappears upon deuterim exchange), 7.90 (s, 2H, disappears upon deuterim exchange), 7.56 (s, 4H, disappears upon deuterim exchange), 6.90- 7.37 (m, 16H). I.r. of 1 $\nu_{max.}$ : 3470 (N-H), 3170 (O-H), 3010 (C-H$_{arom}$), 1670 (C=N$_{oxamidine}$), 1640 (C=N $_{oxime}$) and 960 (N-O) cm$^{-1}$; i.r. of 2 $\nu_{max.}$: 3500 (N-H), 3200 (O-H), 3010 (C-H$_{arom}$) 1670 (C=N$_{oxamidine}$), 1635 (C=N $_{oxime}$) and 960 (N-O) cm$^{-1}$.

## The Preparation of Ni(II), Co(II) and Cu(II) Complexes of polymeric oxamidineoximes (Genaral Procedure):

A solution of 0.5 mmol of metal salts of $NiCl_2{\cdot}6H_2O$ (119 mg), $CoCl_2{\cdot}6H_2O$ (119 mg) or $CuCl_2{\cdot}2H_2O$ (170 mg) in 30 cm$^3$ hot ethanol was added to the solution of in 20 cm$^3$ DMSO. The color of the 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 off, washed with hot ethanol and hot water and then dried in vacuo.

The colours, melting point, yields, elemental analyses, i.r. and magnetic moments of the all the complexes are give in Tables 1and 2.

## RESULTS AND DISCUSSION

In this work, poly-bis[(4-phenyl)oxamidine]aminoglyoxime and ply-bis[4-(4'-biphenyl)oxamidine]aminoglyoxime were synthesized by reacting *anti*-dichloroglyoxime with *sym*-bis(4,-aminophenyl)oxamidine and *sym*-bis-4-(4'-aminobiphenyl)oxamidine respectively (Fig. 1) and polymeric complexes of these *vic*-dioximes with Ni(II), Co(II) and Cu(II) ions were isolated (Fig. 2).

In the $^1$H-NMR spectra of the ligands in DMSO-d$_6$ the *anti*-isomer of the *vic*-dioxime is indicated by the presence of only one singlet for N-OH protons at the lower field region of the spectrum (δ = 10.44 ppm and δ = 10.40 ppm)(8,9). In addition to this observation, the reddish color of the nickel(II) complex indicates that the *vic*-dioxime is of the *anti*- form.(8-10) The N - H protons were observed at 7.40-7.91 ppm, those of aromatic C-H protons at

**Table 1.** Anallytical,[a] Physical [b] and Magnetic data for the Complexes

| Cpd No | Compound | Color | Yield (%) | Analysis(%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | M | Magnetic Moment (B.M) |
| (1a) | $(C_{32}H_{30}N_{16}O_4Ni)_n$ | Dark red | 94 | 50.48<br>(50.56) | 3.97<br>(3.75) | 29.43<br>(29.31) | 7.71<br>(7.85) | Diamagnetic |
| (1b) | $(C_{32}H_{30}N_{16}O_4Co)_n$ | Dark brown | 87 | 50.46<br>(50.16) | 3.97<br>(3.71) | 29.42<br>(29.20) | 7.74<br>(7.65) | 1.87 |
| (1c) | $(C_{32}H_{30}N_{16}O_4Cu)_n$ | Brown | 84 | 50.16<br>(50.33) | 3.95<br>(3.61) | 29.25<br>(29.30) | 8.29<br>(8.34) | 1.53 |
| (2a) | $(C_{56}H_{46}N_{16}O_4Ni)_n$ | Dark red | 95 | 63.11<br>(63.38) | 4.35<br>(4.29) | 21.03<br>(21.22) | 5.51<br>(5.43) | Diamagnetic |
| (2b) | $(C_{56}H_{46}N_{16}O_4Co)_n$ | Dark brown | 87 | 63.10<br>(63.36) | 4.35<br>(4.32) | 21.02<br>(20.78) | 5.53<br>(5.39) | 1.95 |
| (2c) | $(C_{56}H_{46}N_{16}O_4Cu)_n$ | Brown | 85 | 62.82<br>(62.66) | 4.33<br>(4.32) | 20.92<br>(20.78) | 5.94<br>(5.78) | 1.58 |

[a] Required values are given in parentheses.

[b] Melting points of all the complexes are above 320 °C.

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

| Cpd No | Compound | $\nu$(N-H) | $\nu$(CH) | $\nu$(O-H···O) | $\delta$(O-H···O) | $\nu$(C=N) oxamidine | $\nu$(C=N) oxime | $\nu$(N-O) |
|---|---|---|---|---|---|---|---|---|
| (1a) | $(C_{32}H_{30}N_{16}O_4Ni)_n$ | 3470 | 3015 | 2220 | 1710 | 1670 | 1620 | 960 |
| (1b) | $(C_{32}H_{30}N_{16}O_4Co)_n$ | 3470 | 3010 | 2230 | 1710 | 1670 | 1610 | 960 |
| (1c) | $(C_{32}H_{30}N_{16}O_4Cu)_n$ | 3470 | 3010 | 2260-2360 | 1710 | 1670 | 1610 | 960 |
| (2a) | $(C_{56}H_{46}N_{16}O_4Ni)_n$ | 3500 | 3010 | 2220 | 1710 | 1670 | 1610 | 960 |
| (2b) | $(C_{56}H_{46}N_{16}O_4Co)_n$ | | - | 2220 | 1710 | 1670 | 1610 | 960 |
| (2c) | $(C_{56}H_{46}N_{16}O_4Cu)_n$ | | 3010 | 3260-2360 | 1710 | 1670 | 1605 | 960 |

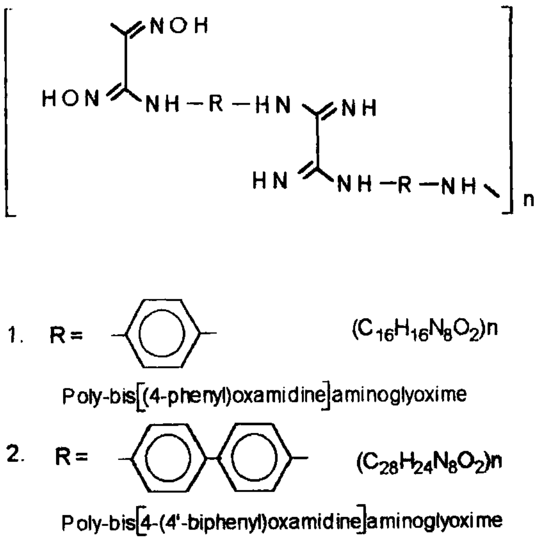

**Fig.1. Polymeric Bis(oxamidine)aminoglyoximes.**

6.86-7.42 ppm respectively. The i.r. spectrum of ligands exhibits ν(O-H) as a broad absorption at 3170 $cm^{-1}$ and 3200 $cm^{-1}$ . Bands due to C=N oxamidines(4), C=N oximes and N-O stretches are at 1670, 1640-1630 and 960-955 $cm^{-1}$ respctively.(3,4,8,9,11-19)

Elemental analyses, i.r. spectroscopy and magnetic susceptibility were employed in order to determine the structural characteristies of the complexes (Table I and III). The reaction of ligands with salts of Ni(II), Co(II) and Cu(II) gives products with metal-ligand ratios of 1:2. In the case of Ni(II), Co(II) and Cu(II) only mononuclear 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, deportation of the ligand 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 2 O-H···O bridges for each complex molecule. The weak stretching(20-22) and deformation(3,4,8,9,11-19) bands of these hdrogen bridges were observed at

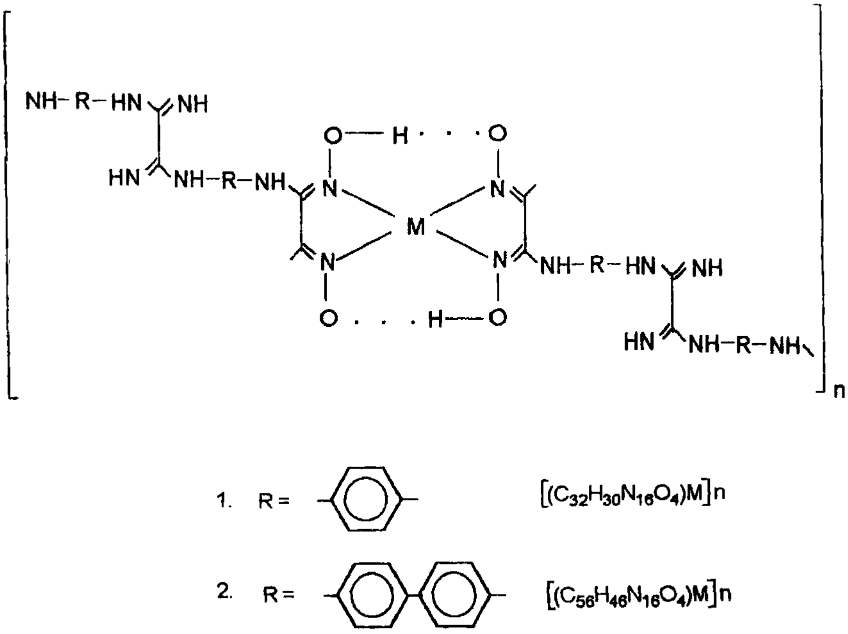

**Fig.2.** Polynuclearcomplexes of Poly- Bis(oxamidine)aminoglyoximes {M = Ni(II), Co(II) or Cu(II)}.

around 2220-2360 cm$^{-1}$ and 1710 cm$^{-1}$ for all the complexes. The aromatic C-H , C=N and N-O strectching vibrations are very close for ligands as well as the Ni(II), Co(II) and Cu(II) complexes(3,4,8,9,11-19) (Fig. 2), (Table 2).

The common feature of the complexes of ligands are their insolubility which also hindered spectral investigations on their solutions. Magnetic susceptibility measurements provide sufficient data to characterize the structures (Table 1). The mononuclear complexes of Ni(II) are diamagnetic as expected for d$^8$ metal ion in a square-planer field(15-19) When the magnetic moments of the mononuclear complexes of Co(II) and Cu(II) are abaut 1.87-1.95 B.M. and 1.53-1.58 B.M., compareble with values reported for slightly distorted square-planer cobalt(II) and copper(II) complexes of *vic*-dioximes.(14,17)

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