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# Spectroscopic studies on complexes of magnesium (II) with $C_2$ -chiral *bis*-oxazolines

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#### Abstract

The configurations of chloro, ethyl and *bis*-complexes of magnesium with  $C_2$ -chiral *bis*-oxazolines such as 2,2'-methylenebis[(4S)-4-*iso*-propyl-2-oxazoline] (MBIO), 2,2'-methylenebis[(4S)-4-*tert*-butyl-2-oxazoline] (MBTO) and 2,2'-methylenebis[(4S)-4-*phenyl*-2-oxazoline] (MBPO) have been investigated on the basis of spectroscopic studies. The IR and NMR (<sup>1</sup>H, <sup>13</sup>C) data suggested that the *bis*-oxazoline ligands coordinated magnesium (II) through both the nitrogen atoms. The molecular weight determination in nitrobenzene indicated the dimeric nature of chloro and ethylmagnesium complexes whereas *bis*-magnesium complexes were found to be monomeric. © 1997 Elsevier Science B.V.

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## 1. Introduction

Spectroscopic and structural aspects of metal complexes derived from nitrogen ligands have been the focal points of vigorous research activities. Interesting stereochemical behaviour have been also observed in the metal complexes derived from nitrogen donors [1-3].

The  $C_2$ -chiral metallocenes [4,5] have recently found great application in producing highly stereoregular polymers by controlling the monomer insertion on both the enantiotopic faces specifically. However, studies on  $C_2$ -chiral non-metallocenes are limited [6]. We have synthesized and reported [7-9] several non-chiral non-metallocenes with nitrogen donors. The present investigation is concerned with spectroscopic studies on the complexes of magnesium (II) with  $C_2$ -chiral bis-oxazoline ligands. The following ligands have been used for the synthesis.

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#### 2. Experimental

#### 2.1. Reagents and materials

All chemicals were of analytical grade and solvents were purified and dried by standard methods [10]. Amino alcohols were prepared by the reduction of amino acids with LiAlH<sub>4</sub> [11].  $ClH_2N=(C_2H_5O)CCH_2C(OC_2H_5)=NH_2Cl$  was synthesized [12] by passing dry HCl gas into malononitrile and ethanol (1:2) in 1,4-dioxane.  $C_2$ -chiral *bis*-oxazolines [13], diethylmagnesium [14] and ethylmagnesium chloride [15] were prepared by the literature procedures.

# 2.2. Preparation of $C_2$ -chiral bis-oxazolines [13] and their magnesium (II) complexes

Bis-oxazoline ligands were synthesized by treatment of dichloromethane solution of  $ClH_2N=(C_2H_5O)CCH_2C(OC_2H_5)=NH_2Cl$  with two equivalent amino acids.

For the preparation of chloromagnesium complexes, the stoichiometric amount of ethylmagnesium chloride solution (in THF) was added dropwise to a stirred solution of *bis*-oxazolines (in THF) at 0°C under dry argon atmosphere. The bath temperature was slowly allowed to rise up to room temperature and stirred for 2 h. Removal of THF at reduced pressure gave the colourless solid. The yields of the products were 96%. To get the ethylmagnesium complexes, diethylmagnesium (in THF) was added into the ligand solution (in THF) (1:1 molar ratio) at 0°C. After 3 h reaction, volvent was removed in vacuo. The obtained product was dried at  $20^{\circ}C/0.1 \text{ mm/4}$  h and all handlings were done under argon. The yields of the products were about 95%.

Bis-magnesium complexes were prepared by the slow addition of diethylmagnesium (in THF) into a stirring solution (in THF) of bis-oxazoline ligand at  $-10^{\circ}$ C under argon in 1:2 molar ratio respectively. The bath temperature was slowly allowed to rise to room temperature and stirred for 2 h. Removal of solvent at reduced pressure gave the product which was dried at  $20^{\circ}$ C/0.1 mm/4 h. The yields of the products were about 95%.

#### 2.3. Physical measurements

The IR spectra were recorded on Perkin–Elmer 621 spectrometer as Nujol mull in the range of 4000–200 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL FX 90Q spectrometer in  $C_6D_6$  or CDCl<sub>3</sub> using TMS as an internal standard. Molecular weights of the complexes were determined cryscopically in nitrobenzene.

### 3. Results and discussion

All the complexes of magnesium with *bis*-oxazolines are colourless solid and soluble in common organic solvents. They are sensitive to moisture. The sensitivity of the complexes to-



Fig. 1. PMR spectrum of MBIO in C<sub>6</sub>D<sub>6</sub> showing the tautomeric forms.

wards moisture increases in the order *bis*-magnesium < chloromagnesium < ethylmagnesium complexes. Chloro and ethylmagnesium complexes are dimeric whereas bis-magnesium complexes are monomeric as found cryscopically in nitrobenzene. Infrared spectra of *bis*-oxazolines were examined in Nujol mull which showed a band at about 3300 cm<sup>-1</sup> due to v(NH) vibration. Infrared spectra also exhibited two bands in the region 1670–1585 cm<sup>-1</sup> attributed to v(C=N) and v(C=C) vibration respec-

Table 1					
Assignment of important	bands $(cm^{-1})$ in the IR	spectra of $C_2$ -chiral	bis-oxazolines an	nd their Mg	(II) complexes

Compounds	v(NH)	v(C=N)	v(C=C)	v(Mg-C)	v(Mg-N)	v(Mg-Cl)
MBIO	3300 b	1669 s	1590 s			
мвто	3300 b	1668 s	1590 s		<u> </u>	
MBPO	3300 b	1669 s	1589 s			
ClMg(MBIO)		1600 s	1542 s		355 m	380 m
CIMg(MBTO)		1600 s	1542 s		354 m	381 m
CIMg(MBPO)		1601 s	1540 s	<i></i>	355 m	380 m
C-H-Mg(MBIO)		1602 s	1541 s	820 m	352 m	
C <sub>1</sub> H <sub>2</sub> Mg(MBTO)		1602 s	1540 s	821 m	352 m	e. 154
Mg(MBIO) <sub>2</sub>		1600 s	1540 s		355 m	
Mg(MBTO)	and app on	1600 s	1541 s	_	356 m	
Mg(MBPO)		1600 s	1541 s		356 m	

b, broad; s, strong; m, medium.



Fig. 2. Structure of complexes (a) X MgL; (b)  $ML_2$  (X =  $C_2H_5$ , Cl; L = *bis*-oxazoline ligand).

tively. PMR spectra of the ligands were examined in non-polar solvent such as  $C_6D_6$ . Both the above IR and PMR observations revealed that the *bis*-oxazolines exists in two tautomeric forms (Fig. 1) where the contribution of NH form of the ligand is observed to be smaller.

Inspection of the IR spectral data (Table 1) of ethyl, chloro and *bis*-magnesium complexes shows that *bis*-oxazolines act as bidentate donors towards magnesium (II). This is consistent with the acceptor properties of magnesium (II) as well as with chelating behaviour of *bis*-oxazolines. The IR spectra of the ligands showed a broad band at about 3300 cm  $^{-1}$  due to v(NH) vibration and two intense band at about 1669 and 1590 cm<sup>-1</sup> due to v(C=N) and v(C=C) vibrations respectively [16]. In all the complexes the absence of absorption due to v(NH) vibration in the IR spectra, suggested the deprotonation of the ligand has taken place. Presence of absorptions due to r(C=N) and v(C=C) at lower frequencies in the region 1602 -1542 cm<sup>-1</sup> in the complexes (in comparison to the free ligands) indicated bidentely chelated ligand pattern. The far infrared region contains the contributions from v(Mg-C) [17] at about 820  $cm^{-1}$ , v(Mg-N) [18] at about 355 cm<sup>-1</sup> and v(Mg-Cl) [19] at about 280 cm<sup>-1</sup> vibrations respectively. All the above IR observations are consistent with the complexes having structure shown in Fig. 2.

<sup>1</sup>H-NMR data summarized in Table 2 are very helpful in assigning the stereochemistry in the magnesium complexes. The most significant difference in the <sup>1</sup>H-NMR spectra of the complexes in comparison to the free ligand (Table 2) is the change of C-CH<sub>2</sub>-C of the ligand into C-CH-C in the complexes due to deprotonation. The CH<sub>2</sub> in the ligands appeared at about 3.3 $\delta$  (Table 2) was found to be shifted in the complexes at about 4.7 $\delta$  in the CH form. In <sup>13</sup>C NMR spectra (Table 3) the CH<sub>2</sub> carbon of C-CH<sub>2</sub>-C appeared at about 28.4 ppm has found to be shifted at about 55 ppm due to change of CH<sub>2</sub> into CH. Also the carbon resonance due to C=N which appeared in

Table 2 Important <sup>1</sup>H-NMR chemical shift ( $\delta$ ) of C<sub>2</sub>-chiral *bis*-oxazolines and their magnesium complexes

Compounds	CH <sub>3</sub> (Et)	$CH_2$ (Et)	$CH_3$ ( <i>i</i> -Pr)	$CH_3 (t-Bu)$	CH (i-Pr)	$C \cdot CH_2$	C-CH	Ph
						-C	-C	
MBIO			0.78 d, 0.95 d		1.53 m	3.31 s		
MBTO			_	0.88 s		3.35 s		s
MBPO						3.57 s		7.2–7.3 m
ClMg(MBIO)	_		0.90 d, 0.95 d		1.85 m		4.72 s	
ClMg(MBTO)				0.90 s			4.70 s	· ~-
ClMg(MBPO)							4.74 s	7.3–7.5 m
$C_2H_5Mg(MBIO)$	1.80 t	0.82 q	0.85 d, 0.90 d		1.82 m	_	4.72 s	
$C_2H_5Mg(MBTO)$	1.78 t	0.70 q		0.91 s			4.72 s	
$Mg(MBIO)_2$			0.86 d, 0.92 d		1.85 m		4.68 s	
Mg(MBTO),	e-			0.90 s			4.70 s	

s, singlet; d, doublet; t. triplet; q, quarter; m, multiplet.

MBIO	MBTO	ClMg(MBIO)	ClMg(MBTO)	$C_2H_5Mg(MBIO)$	Mg(MBIO) <sub>2</sub>	Mg(MBTO) <sub>2</sub>	Assignments
161.6	161.5	172.5	172.4	172.4	172.6	172.2	C=N
72.2	75.8	72.0	74.8	69.9	69.5	74.2	N-C-C chiral
70.5	69.1	68.8	69.0	68.6	68.4	69.2	O-CH C ring
		55.4	55.5	55.1	55.2	55.6	C -CH- C
32.5		33.1	_	33.0	33.2		i-Pr-CH
	33.7		34.0			34.5	t-Bu · C
28.5	28,4						CCH,C
	25.7		26.0	_	_	26.2	t-BuCH <sub>3</sub>
18.6	÷ •	20.1		20.0	20.1		<i>i-</i> Pr-CH
18.0		19.5		19.2	19.3		
				12.2			CH <sub>3</sub> (Et)
				5.3			$CH_2(Et)$

Table 3  $^{13}$ C-NMR data (ppm) of *bis*-oxazolines and their magnesium complexes

the ligand at about 161 ppm (Table 3) has shifted at about 172 ppm. These shifts in <sup>1</sup>H and <sup>13</sup>C NMR spectra are suggested a strong chelation of the *bis*-oxazoline to magnesium (II) as bidentate and supporting the proposed structure in Fig. 2. Repeated efforts to grow suitable single crystal of the complexes by using various solvent combinations have been unsuccessful.

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