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Syntheses and spectral studies of zinc(II) complexes with C_2-chiral bis-oxazolines

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Summary — Zinc(II) complexes with C_2-chiral bis-oxazoline ligands of type ClZnL, (PhS)ZnL and $(PhS)_2ZnLH$ (where LH = 2,2′-methylenebis[(4*S*)-4-isopropyl-2-oxazoline] (MBIOH), 2,2′-methylenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] (MBTOH) and 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] (MBPOH)) have been described. Investigations of the complexes by IR, UV and NMR spectra indicated that the ligands act as bidentates coordinating to zinc(II) with both nitrogen atoms. ClZnL and (PhS)ZnL complexes were dimeric whereas $(PhS)_2ZnLH$ complexes were monomeric in benzene as found cryoscopically.

zinc(II) complex / bis-oxazoline / UV spectroscopy / benzenethiol / IR spectroscopy / NMR spectroscopy

Résumé — Synthèses et études spectrales de complexes du zinc(II) avec des bis-oxazolines chirales de symétrie C_2. Les complexes du zinc(II) avec des bis-oxazolines chirales de symétrie C_2, de type ClZnL, (PhS)ZnL et $(PhS)_2ZnLH$ (où LH = 2,2′-methylenebis[(4*S*)-4-isopropyl-2-oxazoline] (MBIOH), 2,2′-methylenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] (MBTOH) et 2,2′-methylenebis[(4*S*)-4-phenyl-2-oxazoline] (MBPOH)) sont décrits. Les études de ces complexes par IR, UV et RMN indiquent que ces ligands agissent comme coordinats bidentés du zinc(II) par les deux atomes d'azote. Les mesures cryoscopiques montrent que les complexes ClZnL et (PhS)ZnL sont des dimères tandis que le complexe $(PhS)_2ZnLH$ est un monomère dans le benzène.

complexe du zinc(II) / bis-oxazoline / spectroscopie UV / benzenethiol / spectroscopie RMN / spectroscopie IR

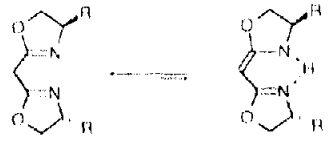
Introduction

Synthetic and structural aspects of metal complexes derived from nitrogen and sulfur ligands have been the focal points of vigorous research activities as evidenced by the appearance of a large number of publications [1-3]. Biological activities [4, 5] and numerous applications [6, 7] of metal nitrogen and sulfur compounds have also aroused interest in them. On the other hand, C_2-chiral metallocenes [8, 9] have recently found 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 [7]. We have synthesized and reported [10-12] several non-chiral non-metallocenes with nitrogen and sulfur donors. The present communication concerns the syntheses and spectral studies of zinc(II) complexes with C_2-chiral bis-oxazoline ligands. The ligands in fig. 1 have been used for the synthesis.

Experimental section

Reagents

All experimental manipulations were performed under strictly anhydrous and dry nitrogen atmosphere. All chemicals used were of AR grade and solvents were purified and dried by standard techniques [13]. Amino alcohols were prepared [14] by the reduction of amino acids with $LiAlH_4$. $CH_2N_2C(C_2H_5O)CH_2C(OC_2H_5)=NH_2Cl$ was synthesized [15] by passing dry HCl gas into malononitrile and ethanol (1:2) in 1,4-dioxane. The bis-oxazoline ligands were prepared according to literature [16] by a reaction of amino alcohol with $CH_2N_2C(C_2H_5O)CH_2C(OC_2H_5)=NH_2Cl$ in 2:1 molar ratio in dichloromethane. Ethylzinc chloride was made by a literature procedure [17].



R = isopropyl = MBIOH
= *tert*-butyl = MBTOH
= phenyl = MBPOH

Fig 1. Structure of the ligands.

Syntheses of complexes

• *ClZnL (L = MBIO, MBTO or MBPO)*

To a stirred toluene (10 mL) solution of 2,2′-methylenebis[(4*S*)-4-isopropyl-2-oxazoline] (MBIOH) (0.917 g,

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(0.0038 mol), and ethylzinc chloride (0.500 g, 0.0038 mol) solution in toluene (25 mL) was added dropwise at 0 °C under dry nitrogen atmosphere. It was an exothermic reaction with evolution of bubbles (ethane gas). The bath temperature was allowed to rise to room temperature and the reaction mixture stirred for 5 h. Solvent was removed at reduced pressure. The obtained product was washed with dry pentane (10 mL) at −10 °C. Drying under vaccuum at room temperature afforded ClZn(MBIO) as a colourless solid. ClZn(MBTO) and ClZn(MBPO) complexes were synthesized by the same procedure.

- *(PhS)ZnL (L = MBIO, MBTO or MBPO)*

Freshly prepared C_2H_5-Zn(MBIO) (0.332 g, 0.001 mol), by reaction of diethylzinc and 2,2′-methylenebis[(4*S*)-4-isopropyl-2-oxazoline] (MBIOH) in 1:1 molar ratio in toluene, was dissolved in toluene (25 mL) and cooled down to 0 °C under dry nitrogen. To the above stirred solution, benzenethiol (0.111 g, 0.001 mol) was added dropwise. The bath was allowed to rise to room temperature and the reaction mixture was stirred for 18 h. Removal of the solvent at reduced pressure gave (PhS)Zn(MBIO) as a colourless solid which was washed with dry pentane (10 mL) at −10 °C. (PhS)Zn(MBTO) and (PhS)Zn(MBPO) complexes were also prepared by the same method.

- *$(PhS)_2$ZnLH (LH = MBIOH, MBTOH or MBPOH)*

To a toluene (50 mL) solution of freshly prepared C_2H_5-Zn(MBIO) (0.332 g, 0.001 mol), benzenethiol (0.222 g, 0.002 mol) was added dropwise at room temperature. The reaction mixture was stirred for 24 h at room temperature. Solvent was removed at reduced pressure. The obtained solid was washed with pentane (10 mL) at −10 °C. Removal of the solvent under vacuum at room temperature gave $(PhS)_2$Zn(MBIOH) as a colourless solid. $(PhS)_2$Zn(MBTOH) and $(PhS)_2$Zn(MBPOH) complexes were also prepared by the above procedure.

Measurements

Carbon, hydrogen and nitrogen were estimated microanalytically. Zinc, sulfur and chlorine were estimated by literature methods.[18] Infrared spectra were recorded on a Perkin-Elmer 621 instrument as nujol mulls using a CsI disc. Electronic spectra were measured on a Carry-23 spectrophotometer. NMR spectra were recorded on a JEOL FX 90 Q spectrometer in C_6D_6 using TMS as an internal standard. Molecular weights of the complexes were determined cryoscopically in benzene by the following procedure. A Beckmann thermometer fitted with a B-19 standard glass cone and an inner jacket fitted with a B-39 standard glass socket were used to avoid moisture from the atmosphere. 0.2–0.4 g of the compound was added to benzene (15 g) and the depression at the freezing point was recorded. The following formula was used to calculate the molecular weight:

$$M = \frac{1000 \times K \times w}{W \times T}$$

where M = molecular weight of the compound, K = constant (0.085 for benzene), w = weight of the compound, W = weight of benzene, T = depression at the freezing point of benzene.

Results and discussion

Complexes of zinc(II) with bis-oxazolines have been synthesized by the following reaction routes

$$C_2H_5ZnCl + LH \longrightarrow ClZnL + C_2H_6$$

$$(C_2H_5)_2Zn + LH \longrightarrow C_2H_5ZnL + C_2H_6$$

$$PhSH \longrightarrow (PhS)ZnL + C_2H_6$$

$$C_2H_5ZnL + 2PhSH \longrightarrow (PhS)_2ZnLH + C_2H_6$$

(LH = MBIOH, MBTOH, MBPOH)

All the complexes of zinc(II) with bis-oxazolines are colourless solids and soluble in common organic solvents. The isolated ClZnL and (PhS)ZnL complexes are moisture-sensitive and all handlings were done under dry nitrogen atmosphere. The complexes of composition $(PhS)_2$ZnLH were found to be fairly stable in air and moisture. Spectroscopic

Table I. Analytical data of zinc(II) complexes with bis-oxazolines.

Complexes	*Mp (°C)*	*Yield (%)*	*Analyses found (calc) (%)*						*Mol weight[a] found (calc)*
			C	*H*	*N*	*Cl*	*S*	*Zn*	
ClZn(MBIO)	143	90	45.88	6.15	8.01	10.32		19.50	665
			(46.12)	(6.20)	(8.27)	(10.48)		(19.32)	(338.2)
ClZn(MBTO)	151	89	49.01	6.78	7.56	9.60		17.91	726
			(49.15)	(6.82)	(7.64)	(9.68)		(17.85)	(366.2)
ClZn(MBPO)	147	90	55.06	8.10	6.81	8.63		15.91	804
			(56.13)	(8.18)	(6.89)	(8.72)		(16.09)	(406.2)
(PhS)ZnMBIO)	189	88	61.41	7.00	5.43		6.30	12.65	1014
			(61.53)	(7.07)	(5.46)		(6.25)	(12.78)	(511.9)
(PhS)ZnMBTO)	175	89	57.11	6.90	6.26		7.31	11.71	871
			(57.28)	(6.81)	(6.36)		(7.27)	(11.85)	(439.9)
(PhS)ZnMBPO)	196	87	62.41	7.51	5.78		6.52	13.71	943
			(62.51)	(7.58)	(5.83)		(6.66)	(13.62)	(479.9)
$(PhS)_2$ZnMBIOH)	185	89	57.52	6.02	5.32		12.18	12.58	513
			(57.45)	(6.12)	(5.36)		(12.25)	(12.52)	(522.1)
$(PhS)_2$Zn(MBTOH)	181	90	58.78	6.61	5.00		11.59	11.80	545
			(58.89)	(6.51)	(5.08)		(11.63)	(11.88)	(550.1)
$(PhS)_2$Zn(MBPOH)	173	89	62.88	4.67	4.70		10.74	11.92	598
			(63.01)	(4.74)	(4.74)		(10.84)	(11.07)	(590.1)

[a] Molecular weights were determined cryoscopically in benzene.

Table II. IR and electronic spectral data of bis-oxazolines and their zinc(II) complexes. b = broad, s = strong, m = medium.

Compounds	*ν(NH)*	*ν(C=N)*	*ν(C=C)*	*ν(Zn N)*	*ν(Zn S)*	*ν(Zn Cl)*	*UV-visible* λ_{max} *(nm) in methanol*
MBIOH	3 300 b	1 669 s	1 590 s				340
MBTOH	3 300 b	1 668 s	1 590 s	-	-		348
MBPOH	3 300 b	1 669 s	1 589 s	490 m			345, 230
ClZn(MBIO)		1 600 s	1 541 s	487 m	-	270 m	360
ClZn(MBTO)	-	1 600 s	1 541 s	485 m	-	271 m	355
ClZn(MBPO)		1 602 s	1 542 s	480 m	-	270 m	354, 232
(PhS)Zn(MBIO)		1 601 s	1 540 s	490 m	375 m		362
(PhS)Zn(MBTO)	-	1 601 s	1 542 s	485 m	379 m		360
(PhS)Zn(MBPO)	-	1 602 s	1 540 s	491 m	380 m		351, 231
$(PhS)_2$Zn(MBIOH)	3 200 b	1 660 s	1 580 m	488 m	376 m		350
$(PhS)_2$Zn(MBTOH)	3 200 b	1 661 s	1 580 m	485 m	375 m		352
$(PhS)_2$Zn(MBPOH)	3 200 b	1 660 s	1 581 m	479 m	378 m		350, 232

and elemental analysis data suggested that ClZnL, (PhS)ZnL complexes (under dry nitrogen atmosphere) and $(PhS)_2$ZnLH (in open atmosphere) are completely free from coordinated water. Cryoscopic molecular weight determination in benzene suggested that ClZnL and (PhS)ZnL complexes are dimeric whereas $(PhS)_2$ZnLH complexes are monomeric.

Infrared and electronic spectra

IR and electronic spectra of ligands and complexes are given in table II. Inspection of the infrared spectral data of zinc(II) complexes with bis-oxazolines shows that bis-oxazolines are coordinated to zinc(II) as bidentate with both nitrogen atoms. This is consistent with the chelating behaviour of bis-oxazoline ligands. The infrared spectra of the ligands showed a broad band at about 3300 cm^{-1} due to ν(NH) vibration and two bands at about 1669 and 1590 cm^{-1} due to ν(C=N) and ν(C=C) vibration respectively [19]. In the infrared spectra of the complexes of type ClZnL and (PhS)ZnL, the absence of absorption due to ν(NH) vibration suggests that deprotonation of the ligand has taken place. Absorption due to ν(C=N) and ν(C=C) at lower frequencies in the region 1602–1542 cm^{-1} (in comparison to the free ligands) indicates a bidently chelated ligand pattern. On the other hand, the infrared spectra of $(PhS)_2$ZnLH complexes showed a band at 3200 cm^{-1} due to coordinated ν(NH) and bands at about 1660–1550 cm^{-1} due to ν(C=N) and ν(C=C) vibrations. The far infrared region contained contributions from ν(Zn N) [20] at about 485–470 cm^{-1}, ν(Zn S) [12] at about 388–355 cm^{-1} and ν(Zn Cl) [21] at about 280–260 cm^{-1}. In the electronic spectra of all the complexes, the bands in the higher region in comparison to the ligand have been observed which supports the chelation of the ligands to zinc(II). All the above IR and electronic observations are consistent with the complexes having the structure depicted in figure 2.

^1H NMR spectra

^1H NMR data of zinc(II) complexes with bis-oxazolines are summarized in table III and are helpful in assigning the stereochemistry of the complexes. The most significant difference in ^1H NMR spectra of ClZnL and

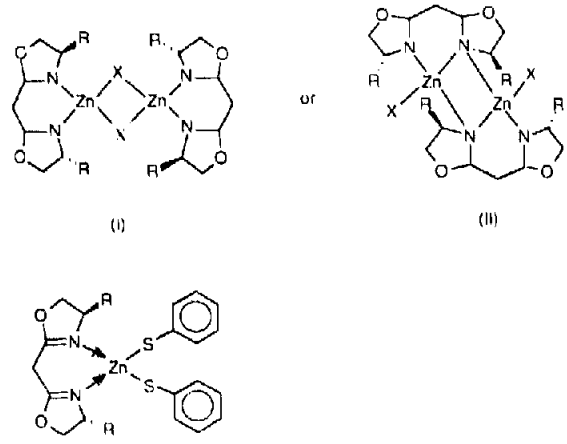

Fig 2. Structure of zinc(II) complexes (I) and (II) XZnL (X = Cl, PhS; L = deprotonated bis-oxazoline) (II) $(PhS)_2$ZnLH (LH = bis-oxazoline).

(PhS)ZnL complexes in comparison to the free ligand is the change of C CH_2 C of the bis-oxazoline into C CH C in the complexes due to deprotonation. The CH_2 protons in the bis-oxazolines appearing at about 3.3 δ were found to be shifted in the complexes at about 4.7 δ in the CH form. On the other hand, the CH_2 shift in the complexes of type $(PhS)_2$ZnLH are small due to coordination of the ligand in the protonated form. Other protons of the ligand were also found to be shifted in ^1H NMR spectra of all the complexes.

^{13}C NMR spectra

^{13}C NMR spectra of complexes were also examined and the results are summarized in table IV. In ^{13}C NMR spectra of the complexes of type ClZnL and (PhS)ZnL, the CH_2 carbon of C CH_2 C appeared at about 55 ppm while in the free ligand at about 28.4 ppm. This shifting indicates the change of CH_2 to the

Table III. Important ^1H NMR chemical shifts (δ) of bis-oxazolines and their zinc(II) complexes. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Compounds	CH_3 (i-Pr)	CH (t-Bu)	CH (i-Pr)	$C-CH_2-C$	C-CH-C	Ph
MBIOH	0.78 d, 0.95 d		1.53 m	3.31 s		
MBTOH		0.88 s		3.35 s		
MBPOH				3.57 s		7.2–7.33 m
ClZn(MBIO)	0.92 d, 0.96 d		1.82 m		4.72 s	–
ClZn(MBTO)		0.95 s			4.71 s	
ClZn(MBPO)					4.75 s	7.3–7.6 m
(PhS)Zn(MBIO)	0.86 d, 0.92 d		1.83 m		4.71 s	7.3–7.7
(PhS)Zn(MBTO)		0.92 s			4.70 s	7.3–7.7
$(PhS)_2Zn(MBIOH)$	0.70 d, 0.78 d		2.24 m	3.51 s	–	7.3–7.7
$(PhS)_2Zn(MBTOH)$		0.85 s		3.50 s		7.3–7.7

Table IV. Important ^{13}C NMR chemical shifts (ppm) of bis-oxazolines and their zinc(II) complexes.

MBIOH	MBTOH	ClZn(MBIO)	ClZn(MBTO)	(PhS)Zn(MBIO)	$(PhS)_2Zn(MBIOH)$	$(PhS)_2Zn(MBTOH)$	Assignments
161.6	161.5	172.1	172.6	172.5	166.3	166.1	C=N
		55.2	55.3	55.2			C-CH-C
28.5	28.1				26.31	26.5	$C-CH_2-C$
	25.7		26.2			26.4	t-Bu CH_3
18.6		20.3		20.1	20.0		i-Pr CH_3
18.0		19.2		19.2	19.2		

CH form. Also the carbon resonances due to C=N appearing in the free bis-oxazolines at about 161 ppm have shifted to about 172 ppm. On the other hand, in ^{13}C NMR spectra the CH_2 carbon of $C-CH_2-C$ in (PHS)ZnLH showed little shifting due to coordination of the ligand in the protonated form. Shifts in all carbon resonances have also been observed in these complexes. These shifts in ^1H and ^{13}C NMR spectra strongly suggest a bidentate coordination of the ligands and structure proposed in figure 2. For the complexes of type XZnL (X = Cl, PhS) a dimeric bridging structure via Cl or PhS is more likely, based on the literature [3].

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