Synthesis and Characterization of Five Bisoxime-Type Chelating Ligands Based on *Bis*(aminooxy)alkane and 2-Naphthaldehyde

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Five bisoxime chelating ligands **L**¹-**L**⁵ have been synthesized from 2-naphthaldehyde and 1,2-*bis*(aminooxy)ethane, 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane, 1,5-*bis*(aminooxy)pentane and 1,6-*bis*(aminooxy)hexane in hot ethanolic medium, respectively and characterized by elemental analyses, IR, UV-visible spectra and ¹H NMR spectroscopy. The bisoxime chelating ligands **L**¹-**L**⁵ may be promising units for the construction of supramolecular metal complexes.

Keywords: Bisoxime chelating ligand, Synthesis, Characterization.

INTRODUCTION

In recent year, several workers have produced a large number of oxime-type ligand¹. Oxime, which is a sort of Schiff base ligands, has strong coordination ability and biological activity². Most of the transition metal oxime complexes have bactericidal³, insecticidal⁴ and detoxifying biological functions^{2,5}.

Bisoxime compounds have long been used as organic chelating ligands, because bisoxime complexes offer both high reactivity and selectivity include epoxidation of olefins, asymmetric ring-opening of epoxides, olefin aziridination, olefin cyclopropanation and formation of cyclic, linear polycarbonates⁶ and building blocks for cyclic supramolecular structures⁷. The large electronegativity of oxygen atoms affect strongly the electronic properties of N₂O₂ coordination sphere, which can lead to different and novel properties and structures of the resulted complexes. Thus, we have recently studied some novel bisoxime chelating compounds on the basis of *O*-alkyloxime instead of the imine moiety^{8,9}. Herein, we report on the synthesis and characterization of five bisoximes compounds, 2,2'-[(ethane-1,2-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene, 2,2'-[(propane-1,3-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene, 2,2'-[(butane-1,4-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene, 2,2'-[(pentane-1,5-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene and 2,2'-[(hexane-1,6-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene.

EXPERIMENTAL

2-Naphthaldehyde, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane and 1,6-

dibromohexane were purchased and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. The others are the same as literature^{8,10}.

General procedure: Synthetic route to bisoxime chelating ligands **L**¹-**L**⁵ are shown in Fig. 1. 1,2-*bis*(aminooxy)ethane, 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane, 1,5-*bis*(aminooxy)pentane and 1,6-*bis*(aminooxy)hexane were synthesized according to an analogous method reported earlier¹⁰.

Fig. 1. Synthetic route to bisoxime chelating ligands **L**¹-**L**⁵. **L**¹: n = 1; **L**²: n = 2; **L**³: n = 3; **L**⁴: n = 4; **L**⁵: n = 5

Preparation of 2,2'-[(ethane-1,2-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene (L**¹):** To an ethanolic solution (8 mL) of 2-naphthaldehyde (356.6 mg, 2.28 mmol) was added an ethanolic solution (5 mL) of 1,2-*bis*(aminooxy)ethane (105.7 mg, 1.14 mmol). After the solution had been stirred at 55 °C for 4 h, the white precipitate was filtered, washed successively with ethanol and *n*-hexane, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield white powder-like compound **L**¹.

Preparation of 2,2'-[(propane-1,2-diylldioxy)*bis*(nitrilomethylidyne)]dinaphthalene (L**²):** To a hot ethanolic solution (8 mL) of 2-naphthaldehyde (368.3 mg, 2.40 mmol) was added an ethanolic solution (5 mL) of 1,3-*bis*(aminooxy)propane

(167.8 mg, 1.20 mmol). After the solution had been stirred at 55 °C for 4 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane and dried under vacuum to obtain white powder-like compound **L**².

Preparation of 2,2'-[(butane-1,2-diylldioxy)bis(nitrilomethylidene)]dinaphthalene (L**³):** To a hot ethanolic solution (8 mL) of 2-naphthaldehyde (342.4 mg, 2.20 mmol) was added an ethanolic solution (5 mL) of 1,4-bis(aminoxy)butane (157.6 mg, 1.10 mmol). After the solution had been stirred at 55 °C for 6 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane and dried under vacuum to obtain white powder-like compound **L**³.

Preparation of 2,2'-[(pentane-1,2-diylldioxy)bis(nitrilomethylidene)]dinaphthalene (L**⁴):** To a hot ethanolic solution (8 mL) of 2-naphthaldehyde (203.6 mg, 1.30 mmol) was added an ethanolic solution (5 mL) of 1,5-bis(aminoxy)pentane (121.8 mg, 0.60 mmol). After the solution had been stirred at 55 °C for 4 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane and dried under vacuum to obtain white powder-like compound **L**⁴.

Preparation of 2,2'-[(hexane-1,2-diylldioxy)bis(nitrilomethylidene)]dinaphthalene (L**⁵):** To a hot ethanolic solution (8 mL) of 2-naphthaldehyde (358.2 mg, 2.30 mmol) was added an ethanolic solution (5 mL) of 1,6-bis(aminoxy)hexane (241.8 mg, 1.20 mmol). After the solution had been stirred at 55 °C for 4 h, then cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane and dried under vacuum to obtain white powder-like compound **L**⁵.

RESULTS AND DISCUSSION

Five bisoxime chelating ligands **L**¹-**L**⁵ have been synthesized with good yields and the composition are confirmed by elemental analyses, IR, UV-visible spectra and ¹H NMR spectroscopy.

Physical and chemistry properties: The colour, yields, melting points and elemental analytical results of the synthesized bisoxime chelating ligands **L**¹-**L**⁵ are presented in Table-1.

Their compositions agree with the formulae. All the chelating ligands are stable in air and soluble in chloroform, dichloromethane, DMF and DMSO, insoluble in *n*-hexane. In addition, **L**³, **L**⁴ and **L**⁵ are soluble in methanol, but **L**¹ and **L**² are insoluble in methanol, ethanol. **L**¹, **L**² and **L**³ are soluble in acetone and acetonitrile. But **L**⁴ and **L**⁵ are insoluble in acetone and acetonitrile.

IR spectra: The key IR spectral data for **L**¹-**L**⁵ are given in Table-2. In the IR spectra of the bisoxime chelating ligands **L**¹-**L**⁵, the characteristic C=N stretching bands of the bisoxime chelating ligands **L**¹-**L**⁵ appear at 1616-1610 cm⁻¹, respectively¹⁰. In addition, in the 1488-1472 cm⁻¹ region, the observed bands were attributed to naphthalene ring C=C vibrations.

UV-visible and ¹H NMR spectra: The UV-visible spectra of the bisoxime chelating ligands **L**¹-**L**⁵ in 5 × 10⁻⁵ mol × L⁻¹ dichloromethane solution are presented in Table-3. The bisoxime chelating ligands **L**¹-**L**⁵ exhibit two intense peaks at around 270 and 325 nm. The former absorption peaks at about 270 nm can be assigned to the π-π* transition of the naphthalene rings, while the latter can be attributed to the intra-ligand π-π* transition of the C=N bonds¹¹. It is of note that there was no absorption around 400 nm, which is seen in the corresponding Salen derivatives. The absorption is ascribed to the quinoid form of H₂salen¹¹.

The ¹H NMR spectra of the bisoxime chelating ligands **L**¹-**L**⁵ in DMSO-*d*₆ are shown in Table-3. The ¹H NMR spectra showed a singlet at about 8.28-8.44 ppm indicating the existence of oxime bonds¹¹.

Conclusion

Five new bisoxime chelating ligands **L**¹-**L**⁵ that have two oxime bonds instead of imine bonds have been designed and synthesized by the reaction of 2 equivalents of 2-naphthaldehyde with 1,2-bis(aminoxy)ethane, 1,3-bis(aminoxy)propane, 1,4-bis(aminoxy)butane, 1,5-bis(aminoxy)pentane and 1,6-bis(aminoxy)hexane in hot ethanolic medium, respectively. The characterizations of the bisoxime chelating ligands

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF BISOXIME CHELATING LIGANDS **L**¹-**L**⁵

Compound	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
L ¹	White	153-154	72.1	C ₂₄ H ₂₀ N ₂ O ₂ (368.43)	78.38 (78.24)	5.41 (5.47)	7.68 (7.60)
L ²	White	139-140	69.2	C ₂₅ H ₂₂ N ₂ O ₂ (382.43)	78.59 (78.51)	5.83 (5.80)	7.30 (7.32)
L ³	White	127-128	71.2	C ₂₆ H ₂₄ N ₂ O ₂ (396.41)	78.71 (78.76)	6.07 (6.10)	7.09 (7.07)
L ⁴	White	115-116	65.2	C ₂₇ H ₂₆ N ₂ O ₂ (410.58)	79.08 (79.00)	6.31 (6.38)	6.85 (6.82)
L ⁵	White	102-103	64.5	C ₂₈ H ₂₈ N ₂ O ₂ (424.51)	79.26 (79.22)	6.61 (6.65)	6.68 (6.60)

TABLE-2
KEY IR BANDS (cm⁻¹) FOR THE SYNTHESIZED BISOXIME CHELATING LIGANDS **L**¹-**L**⁵

Compound	ν(CH _{arom})	ν(CH ₂)	ν(C=N)	ν(C=C) _{naphthalene ring}
L ¹	3045	2944, 2888	1616	1488
L ²	3049	2933, 2887	1612	1483
L ³	3050	2948, 2882	1613	1484
L ⁴	3058	2945, 2889	1615	1476
L ⁵	3056	2940, 2880	1610	1472

TABLE-3
 UV-VISIBLE SPECTRA AND ^1H NMR DATA OF THE BISOXIME CHELATING LIGANDS $\text{L}^1\text{-L}^5$

Compound	$\pi-\pi^*$ (nm)	^1H NMR (400 MHz, DMSO- d_6 , δ /ppm)
L^1	270, 325	4.23 (t, $J = 5.0$ Hz, 4H, $\text{CH}_2\text{-O}$), 6.79 (d, $J = 8.0$ Hz, 2H, PhH), 6.92 (dd, $J = 7.8, 1.8$ Hz, 4H, PhH), 7.07 (s, 2H, PhH), 7.12 (s, 2H, PhH), 7.25 (s, 2H, PhH), 7.33 (d, $J = 8.0$ Hz, 2H, PhH), 8.44 (s, 2H, N=CH).
L^2	269, 323	2.08 (t, $J = 4.2$ Hz, 2H, CH_2), 4.20 (t, $J = 4.6$ Hz, 4H, $\text{CH}_2\text{-O}$), 6.80 (d, $J = 8.2$ Hz, 2H, PhH), 6.93 (d, $J = 7.6, 1.4$ Hz, 4H, PhH), 7.05 (s, 2H, PhH), 7.13 (s, 2H, PhH), 7.22 (s, 2H, PhH), 7.33 (d, $J = 8.0$ Hz, 2H, PhH), 8.38 (s, 2H, N=CH).
L^3	271, 323	2.30 (d, $J = 8.0$ Hz, 4H, CH_2), 4.41 (s, 4H, $\text{CH}_2\text{-O}$), 6.81 (d, $J = 8.0$ Hz, 2H, PhH), 6.96 (d, $J = 8.2, 2.4$ Hz, 4H, PhH), 7.05 (s, 2H, PhH), 7.10 (s, 2H, PhH), 7.18 (s, 2H, PhH), 7.38 (d, $J = 7.0$ Hz, 2H, PhH), 8.28 (s, 2H, N=CH).
L^4	272, 326	2.32 (d, $J = 7.6$ Hz, 6H, CH_2), 4.42 (s, 4H, $\text{CH}_2\text{-O}$), 6.80 (d, $J = 8.0$ Hz, 2H, PhH), 6.97 (d, $J = 7.8, 1.8$ Hz, 4H, PhH), 7.08 (s, 2H, PhH), 7.18 (s, 2H, PhH), 7.29 (s, 2H, PhH), 7.37 (d, $J = 7.0$ Hz, 2H, PhH), 8.31 (s, 2H, N=CH).
L^5	274, 325	2.26 (d, $J = 7.4$ Hz, 8H, CH_2), 4.46 (s, 4H, $\text{CH}_2\text{-O}$), 6.83 (d, $J = 6.8$ Hz, 2H, PhH), 6.98 (d, $J = 7.0, 2.2$ Hz, 4H, PhH), 7.09 (s, 2H, PhH), 7.17 (s, 2H, PhH), 7.28 (s, 2H, PhH), 7.39 (d, $J = 7.4$ Hz, 2H, PhH), 8.30 (s, 2H, N=CH).

$\text{L}^1\text{-L}^5$ have been made by elemental analysis, IR, UV-visible spectra and ^1H NMR spectroscopy. The bisoxime chelating ligands may be promising units for the construction of supra-molecular metal complexes.

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