Synthesis and Characterization of Bromo-Substituted Salamo-Type Bisoxime Compounds Series

LI XU, NA LI, YANG ZHANG, NA WEN, LI-CHUN ZHU and XIU-YAN DONG*

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: dxy568@163.com

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Four novel bromo-substituted Salamo-type bisoxime compounds H_2L^1 - H_2L^4 have been synthesized from 5-bromo-2-hydroxybenzaldehyde and 1,3-bis(aminoxy)propane, 1,4-bis(aminoxy)butane, 1,5-bis(aminoxy)pentane or 1,6-bis(aminoxy)hexane in hot ethanolic medium, respectively and characterized by elemental analyses, IR, UV-visible spectra and 1H NMR spectroscopy.

Keywords: Salamo-type compound, Synthesis, Characterization.

INTRODUCTION

Salamo-type bisoxime compounds have long been used as organic chelating ligands in the synthesis of transition metal complexes, because this compound could be prepared easily from salicylaldehyde and various amines¹⁻⁴. In recent years, these complexes have been found to possess multifarious interesting property. Thus, we have recently studied three novel Salamo-type bisoxime chelating compounds on the basis of *O*-alkyloxime moiety [-CH=N-O-(CH₂)_n-O-N=CH-] group⁵⁻⁷. Herein, we report the synthesis and characterization of four Salamo-type bisoximes compounds, 4,4'-bibromo-2,2'-[(propylene-1,3-diylldioxy)bis(nitrilomethylidyne)]-diphenol, 4,4'-bibromo-2,2'-[(butylene-1,4-diylldioxy)bis(nitrilomethylidyne)]diphenol, 4,4'-bibromo-2,2'-[(propane-1,5-diylldioxy)bis(nitrilomethylidyne)]diphenol and 4,4'-dibromo-2,2'-[(hexane-1,6-diylldioxy)bis(nitrilomethylidyne)]-diphenol.

EXPERIMENTAL

5-Bromo-2-hydroxy-benzaldehyde ($\geq 98\%$), 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane and 1,6-dibromohexane were purchased from Alfa Aesar 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 literature⁸⁻¹⁰.

General procedure: Synthetic route to Salamo-type bisoxime compounds H_2L^1 - H_2L^4 are shown in Fig. 1. 1,3-bis(aminoxy)propane, 1,4-bis(aminoxy)butane, 1,5-bis(aminoxy)pentane and 1,6-bis(aminoxy)hexane were synthesized according to an analogous method reported earlier⁸⁻¹⁰.

Preparation of 4,4'-dibromo-2,2'-[(propylene-1,3-diylldioxy)bis(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (10 mL) of 5-bromo-2-hydroxybenzaldehyde (603.1 mg, 3 mmol) was added an ethanolic solution (10 mL) of 1,3-bis(aminoxy)propane (159.2 mg, 1.50 mmol). After the solution had been stirred at 55 °C for 2 h, the mixture 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 crystalline solid H_2L^1 .

Preparation of 4,4'-dibromo-2,2'-[(butylene-1,4-diylldioxy)bis(nitrilomethylidyne)]diphenol (H_2L^2): To a hot ethanol solution (10 mL) of 5-bromo-2-hydroxybenzaldehyde (603.1 mg, 3 mmol) was added a hot ethanolic solution (5 mL) of 1,5-bis(aminoxy)pentane (201.6 mg, 1.50 mmol). After

Fig. 1. Synthetic route to salamo-type bisoxime compounds H_2L^1 - H_2L^4

the solution had been stirred at 55 °C for 3 h, then cooled to room temperature. The white precipitate was formed, filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain white needle-like compound **H₂L²**.

Preparation of 4,4'-dibromo-2,2'-[(propane-1,5-diylldioxy)bis(nitrilome-thylidyne)]diphenol (H₂L³**):** To a hot ethanolic solution (15 mL) of 5-bromo-2-hydroxy-benzaldehyde (201.3 mg, 1 mmol) was added a hot ethanolic solution (10 mL) of 1,5-bis(aminoxy)pentane (67.1 mg, 0.50 mmol). After the solution had been stirred at 60 °C for 6 h, then cooled to room temperature. The white precipitate which was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain white cotton-like compound **H₂L³**.

Preparation of 4,4'-bibromo-2,2'-[(hexane-1,6-diylldioxy)bis(nitrilomethylidyne)]diphenol (H₂L⁴**):** To a hot ethanolic solution (15 mL) of 5-bromo-2-hydroxy-benzaldehyde (201.3 mg, 1 mmol) was added a hot ethanolic solution (10 mL) of 1,6-bis(aminoxy)hexane (74.1 mg, 0.50 mmol). After the solution had been stirred at 60 °C for 6 h, then cooled to room temperature. The white precipitate which was filtered and washed successively with ethanol and *n*-hexane, respectively. The product was purified with recrystallization from ethanol/*n*-hexane (1/4) and dried under vacuum to obtain white cotton-like compound **H₂L⁴**.

RESULTS AND DISCUSSION

Four Salamo-type bisoxime compounds **H₂L¹-H₂L⁴** have been synthesized with good yields and the composition are confirmed by elemental analyses, IR, UV-visible spectra and ¹H NMR spectroscopy.

Physico-chemical properties: The colour, yields, melting points and elemental analytical results of the synthesized Salamo-type bisoxime compounds **H₂L¹-H₂L⁴** are presented in Table-1. Their compositions agree with the proposed molecular formula. All the compounds are stable in air and soluble in chloroform, dichloromethane, tetrahydrofuran, benzene, acetone, DMF and DMSO, insoluble in *n*-hexane, ether and

water. In addition, **H₂L¹** and **H₂L²** are soluble in hot methanol, ethanol and acetonitrile, but **H₂L³** and **H₂L⁴** are insoluble in hot methanol, ethanol and acetonitrile.

IR spectra: The most important IR spectra data for **H₂L¹-H₂L⁴** are given in Table-2. In the IR spectra of the compounds **H₂L¹-H₂L⁴**, the characteristic C=N stretching bands of the compound **H₂L¹-H₂L⁴** appear at 1614-1611 cm⁻¹, respectively¹¹. The Ar-O stretching bands occur at 1265-1255 cm⁻¹ as reported for similar bisoxime compounds¹². Meanwhile, the O-H stretching bands of phenolic alcohol in the title compounds **H₂L¹-H₂L⁴** appear at 3441-3424 cm⁻¹ region, but this frequency is generally displaced to ca. 3424 cm⁻¹ because of the internal hydrogen bond OH...N=C¹⁰. In addition, in the 1481-1479 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations.

UV-visible and ¹H NMR spectra: The UV-visible spectra of the compounds **H₂L¹-H₂L⁴** in 5 × 10⁻⁵ mol L⁻¹ dichloromethane solution are presented in Table-3. The compounds **H₂L¹-H₂L⁴** exhibit two intense peaks at around 277 and 315 nm. The former absorption peaks at about 277 nm can be assigned to the π-π* transition of the benzene rings, while the latter can be attributed to the intra-ligand π-π* transition of the C=N bonds¹³. 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 H₂ salen^{14,15}.

The ¹H NMR spectra of the title compounds **H₂L¹-H₂L⁴** in DMSO-*d*₆ are shown in Table-3. The ¹H NMR spectra showed a singlet at about 8.25-8.45 ppm indicating the existence of oxime bonds¹⁴.

Conclusion

Four novel Salamo-type compounds **H₂L¹-H₂L⁴** that have two oxime bonds instead of imine bonds have been designed and synthesized by the reaction of 2 equivalents of 5-bromo-2-hydroxy-benzaldehyde with 1,3-bis(aminoxy)propane, 1,4-bis(aminoxy)butane, 1,5-bis(aminoxy)pentane or 1,6-bis(aminoxy)hexane in hot ethanol medium, respectively. And the structures of the title compounds **H₂L¹-H₂L⁴** have been analyzed by elemental analysis, IR, UV-visible spectra and ¹H NMR spectroscopy. The Salamo-type compounds may be promising units for the construction of supramolecular metal complexes.

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL
DATA OF SYNTHESIZED SALAMO-TYPE BISOXIME COMPOUNDS **H₂L¹-H₂L⁴**

Compound	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
H₂L¹	White	163-164	59.0	C ₁₇ H ₁₆ N ₂ O ₄ Br ₂ (472.13)	43.85 (43.25)	3.44 (3.42)	5.69 (5.93)
H₂L²	White	143-144	60.1	C ₁₈ H ₁₈ N ₂ O ₄ Br ₂ (486.15)	44.56 (44.47)	3.96 (3.73)	5.68 (5.76)
H₂L³	White	121-122	76.3	C ₁₉ H ₂₀ N ₂ O ₄ Br ₂ (500.18)	45.62 (45.31)	4.03 (4.10)	5.60 (5.62)
H₂L⁴	White	134-135	63.2	C ₂₀ H ₂₂ N ₂ O ₄ Br ₂ (514.21)	46.72 (46.65)	4.31 (4.36)	5.45 (5.51)

TABLE-2
KEY IR BANDS FOR THE SALAMO-TYPE BISOXIME COMPOUNDS **H₂L¹-H₂L⁴** (cm⁻¹)

Compound	ν(O-H)	ν(CH _{arom})	ν(CH ₂)	ν(C=N)	ν(C-C) _{benzene ring}	ν(Ar-O)
H₂L¹	3424	3042	2946, 2889	1612	1481	1255
H₂L²	3427	3045	2937, 2883	1613	1480	1264
H₂L³	3441	3057	2941, 2880	1611	1481	1261
H₂L⁴	3433	3053	2941, 2882	1614	1479	1265

TABLE-3
THE UV-VISIBLE SPECTRA AND ^1H NMR DATA FOR THE SALAMO-TYPE BISOXIME COMPOUNDS H_2L^1 - H_2L^4

Compound	π - π^* (nm)	^1H NMR (400 MHz, DMSO- d_6 , δ /ppm)
H_2L^1	270, 324	2.14 (t, J = 6.0 Hz, 2H, CH_2), 4.31 (t, J = 6.0 Hz, 4H, CH_2 -O), 6.85 (d, J = 8.0 Hz, 2H, PhH), 7.25 (s, 2H, PhH), 7.33 (d, J = 8.0 Hz, 2H, PhH), 8.09 (s, 2H, N=CH), 9.80 (s, 2H, OH)
H_2L^2	269, 323	2.04 (t, J = 4.0 Hz, 4H, CH_2), 4.23 (t, J = 4.0 Hz, 4H, CH_2 -O), 6.85 (d, J = 4.0 Hz, 2H, PhH), 7.24 (s, 2H, PhH), 7.34 (d, J = 4.0 Hz, 2H, PhH), 8.08 (s, 2H, N=CH), 9.89 (s, 2H, OH)
H_2L^3	277, 315	2.34 (s, 2H, CH_2), 2.37 (d, J = 8.7 Hz, 4H, CH_2), 4.46 (s, 4H, CH_2 -O), 7.40 (d, J = 2.0 Hz, 2H, PhH), 7.55 (d, J = 2.0 Hz, 2H, PhH), 7.72 (d, J = 2.2 Hz, 2H), 8.25 (s, 2H, N=CH), 10.14 (s, 2H, OH)
H_2L^4	276,322	2.33 (s, 4H, CH_2), 2.36 (d, J = 8.0 Hz, 4H, CH_2), 4.45 (s, 4H, CH_2 -O), 7.41 (d, J = 2.0 Hz, 2H, PhH), 7.55 (d, J = 2.0 Hz, 2H, PhH), 7.71 (d, J = 2.2 Hz, 2H), 8.25 (s, 2H, N=CH), 10.05 (s, 2H, OH)

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