



## Synthesis and Characterization of Salamo-Type Bisoxime Compounds Bearing Nitro Group

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A series of nitro salamo-type bisoxime compounds have been synthesized from 2-hydroxy-5-nitrobenzaldehyde and 1,6-*bis*(aminoxy)hexane, 1,7-*bis*(aminoxy)heptane, 1,8-*bis*(aminoxy)octane or 1,10-*bis*(aminoxy)decane in ethanolic medium, respectively and characterized by elemental analyses as well as by IR, UV-visible and <sup>1</sup>H NMR spectroscopy. Salamo-type bisoxime compound is much more useful to assemble supramolecular systems than a Salen moiety.

**Key Words:** Salamo-type bisoxime compound, Synthesis and characterization.

### INTRODUCTION

It is well known that H<sub>2</sub>Salen (N,N-*bis*(salicylidene)-ethylenediamine) derivatives have attracted much attention to many organic as well as inorganic chemists<sup>1-5</sup>, because these compounds can easily form complexes with various transition metals and some of them exhibit excellent catalytic activities for epoxidation, aziridination, *etc.*<sup>6</sup>. Highly enantioselective reactions have been also achieved by the use of Salen metal complexes. In addition, these Salen-type units have also been employed to construct supramolecular structures containing transition metal ions<sup>7</sup>. Most of such compounds have two salicylideneamine units, but the linkage was limited to an alkylene (-CH=N-C-X-C-N=CH-) group due to the ease of preparation. Thus modification of a basic Salen skeleton is very interesting and important. If an O-alkyl oxime moiety (-CH=N-O-(CH<sub>2</sub>)<sub>n</sub>-O-N=CH-) is used instead of a Schiff base, the larger electronegativity of oxygen atoms is expected to affect strongly the electronic properties of N<sub>2</sub>O<sub>2</sub> coordination sphere<sup>8-10</sup>, which can lead to different and novel properties and structures of the resulted complexes. In this paper, we report synthesis and spectroscopic properties of a series of nitro Salamo-type bisoxime compounds, which bearing two salicylidene moieties and two O-alkyloxime linkages.

### EXPERIMENTAL

2-Hydroxy-5-nitrobenzaldehyde (≥ 98 %), 1,6-dibromohexane, 1,7-dibromoheptane, 1,8-dibromooctane and 1,10-dibromodecane were purchased from Alfa Aesar and used without further purification. The other reagents and solvents

were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. UV/visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Mercury-400BB spectrometer. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taiké Instrument Limited Company and the thermometer was uncorrected.

**General procedure:** 1,6-*Bis*(aminoxy)hexane, 1,7-*bis*(aminoxy)heptane, 1,8-*bis*(aminoxy)octane and 1,10-*bis*(aminoxy)decane were synthesized according to an analogous method reported earlier<sup>8-11</sup>.

**Preparation of 4,4'-dinitro-2,2'-[(1,6-hexanediyldioxy)bis(nitrilomethylidene)]diphenol (H<sub>2</sub>L<sup>1</sup>):** Synthetic route to Salamo-type bisoxime compounds H<sub>2</sub>L<sup>1</sup> is shown in Fig. 1.

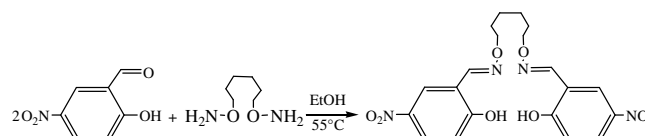


Fig. 1. Synthesis of Salamo-type bisoxime compound H<sub>2</sub>L<sup>1</sup>

To an ethanolic solution (4 mL) of 5-nitro-2-hydroxybenzaldehyde (167.1 mg, 1.00 mmol) was added an ethanolic solution (2 mL) of 1,6-*bis*(aminoxy)hexane (74.6 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 4 h, when cooled to room temperature, the white precipitate was filtered and washed successively with ethanol and ether,

respectively. The product was dried under reduced pressure to obtain white crystalline solid  $H_2L^1$ .

**Preparation of 4,4'-dinitro-2,2'-[(1,7-heptanediyldioxy)bis(nitrilomethylidene)]diphenol ( $H_2L^2$ ):** Synthetic route to Salamo-type bisoxime compounds  $H_2L^2$  is shown in Fig. 2.

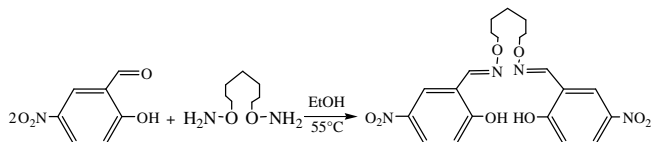


Fig. 2. Synthesis of Salamo-type bisoxime compound  $H_2L^2$

To an ethanolic solution (4 mL) of 5-nitro-2-hydroxybenzaldehyde (167.5 mg, 1 mmol) was added an ethanolic solution (2 mL) of 1,7-bis(aminooxy)heptane (81.1 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 4 h, the formed precipitate was separated by filtration and washed successively with ethanol and ether, respectively. The product was dried under reduced pressure to obtain pale-yellow solid  $H_2L^2$ .

**Preparation of 4,4'-dinitro-2,2'-[(1,8-octanediyldioxy)bis(nitrilomethylidene)]diphenol ( $H_2L^3$ ):** Synthetic route to Salamo-type bisoxime compounds  $H_2L^3$  is shown in Fig. 3.

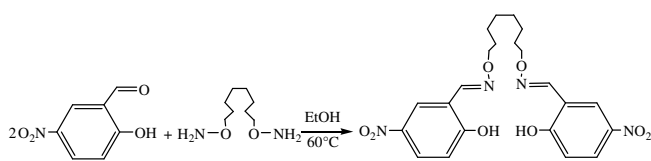


Fig. 3. Synthesis of Salamo-type bisoxime compound  $H_2L^3$

To an ethanolic solution (5 mL) of 5-nitro-2-hydroxybenzaldehyde (167.2 mg, 1.00 mmol) was added an ethanolic solution (2 mL) of 1,8-bis(aminooxy)octane (88.7 mg, 0.50 mmol). After the solution had been stirred at 60 °C for 3 h, the mixture was filtered, washed successively with ethanol and ether, respectively. The product was dried under reduced pressure to obtain white crystalline solid  $H_2L^3$ .

**Preparation of 4,4'-dinitro-2,2'-[(1,10-decanediyl-dioxy)bis(nitrilomethylidene)]diphenol ( $H_2L^4$ ):** Synthetic route to Salamo-type bisoxime compounds  $H_2L^4$  is shown in Fig. 4.

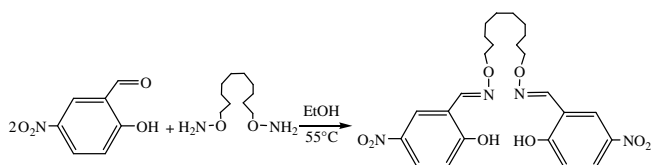


Fig. 4. Synthesis of Salamo-type bisoxime compound  $H_2L^4$

To an ethanolic solution (4 mL) of 5-nitro-2-hydroxybenzaldehyde (167.5 mg, 1 mmol) was added an ethanolic solution (2 mL) of 1,10-bis(aminooxy)decane (102.1 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 4 h, the mixture was filtered, washed successively with ethanol and ether, respectively. The product was dried under reduced pressure to obtain white crystalline solid  $H_2L^4$ .

## RESULTS AND DISCUSSION

A series of nitro Salamo-type bisoxime compounds  $H_2L^1$ - $H_2L^4$  have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible spectra and  $^1H$  NMR data.

The colour, yields, melting points and elemental analytical results of the synthesized Salamo-type bisoxime compounds  $H_2L^1$ - $H_2L^4$  are presented in Table-1. Their compositions agree with the formulae. All the compounds are white or pale-yellow microcrystalline solid, stable in air and soluble in acetone, chloroform, dichloromethane, tetrahydrofuran, ethyl acetate, DMF and DMSO, insoluble in water, ether and *n*-hexane. In addition,  $H_2L^1$  and  $H_2L^2$  are soluble in hot ethanol and methanol, but  $H_2L^3$  and  $H_2L^4$  are insoluble in hot ethanol and methanol.

**IR Spectra:** IR spectra data of nitro Salamo-type bisoxime compounds  $H_2L^1$ - $H_2L^4$  are given in Table-2.

In the IR spectra of  $H_2L^1$ - $H_2L^4$ , the bands due to characteristic C=N stretching absorption bands appear at 1610-1608  $cm^{-1}$ , respectively<sup>12</sup>. The Ar-O stretching frequencies appear within 1245-1240  $cm^{-1}$  as reported for similar bisoxime compounds<sup>13</sup>. These provide evidence for the formation of the title compounds. The O-H stretching frequency of the bisoxime compound is expected in the 3800-3300  $cm^{-1}$  region, but this frequency is generally displaced to 3433  $cm^{-1}$  because of the internal hydrogen bond  $OH \cdots N=C$ <sup>11</sup>. Here a strong band at 3433-3419  $cm^{-1}$  was observed in the title compounds  $H_2L^1$ - $H_2L^4$  and assigned to phenolic alcohol stretching absorption bands. In addition, in the 1599-1477  $cm^{-1}$  region, the observed bands were attributed to aromatic C=C vibrations.

**UV-visible spectra and  $^1H$  NMR data:** The UV-VIS spectra of the title compounds  $H_2L^1$ - $H_2L^4$  in  $5 \times 10^{-5}$  mol/L chloroform solution are presented in Table-3. UV-visible spectra of  $H_2L^1$ - $H_2L^4$  exhibit two intense peaks at around 270 and 326 nm. The former absorption peak at 270 nm can be assigned to the  $\pi-\pi^*$  transition of the benzene rings, while the latter can be attributed to the intra-ligand  $\pi-\pi^*$  transition of the C=N bonds<sup>14</sup>. 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  $H_2salen$ <sup>8,18</sup>.

The  $^1H$  NMR spectra of the title compounds  $H_2L^1$ - $H_2L^4$  in  $DMSO-d_6$  are shown in Table-3. The  $^1H$  NMR spectra showed a singlet at *ca.* 8.25-8.34 ppm indicating the the existence of oxime bonds<sup>15</sup>.

## Conclusion

A series of nitro Salamo-type compounds  $H_2L^1$ - $H_2L^4$  that have two oxime bonds instead of imine bonds have been designed and synthesized by the reaction of 2 equivalents of 2-hydroxy-5-nitrobenzaldehyde with 1,6-bis(aminooxy)hexane, 1,7-bis(aminooxy)heptane, 1,8-bis(aminooxy)octane or 1,10-bis(aminooxy)decane under mild conditions, respectively. It is shown that an O-alkyl oxime moiety is much more useful to assemble supramolecular systems than a Schiff base moiety. Further investigation on the synthesis and structures of nitro Salamo-type metal complexes with transition metal ions such as copper, manganese, iron, cobalt, nickel and zinc is now in progress.

TABLE-1  
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF NITRO SALAMO-TYPE BISOXIME COMPOUNDS (H<sub>2</sub>L<sup>1</sup>-H<sub>2</sub>L<sup>4</sup>)

Compound	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (calcd.)		
					C	H	N
H <sub>2</sub> L <sup>1</sup>	White	103-105	79.6	C <sub>20</sub> H <sub>22</sub> N <sub>4</sub> O <sub>8</sub> (446.4)	53.97 (53.81)	4.78 (4.97)	12.30 (12.55)
H <sub>2</sub> L <sup>2</sup>	Pale-yellow	118-120	75.5	C <sub>21</sub> H <sub>24</sub> N <sub>4</sub> O <sub>8</sub> (460.4)	54.92(54.78)	5.36(5.25)	12.02(12.17)
H <sub>2</sub> L <sup>3</sup>	Pale-yellow	141-143	61.7	C <sub>22</sub> H <sub>26</sub> N <sub>4</sub> O <sub>8</sub> (474.5)	55.83(55.69)	5.40(5.52)	11.56 (11.81)
H <sub>2</sub> L <sup>4</sup>	White	168-170	60.8	C <sub>24</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> (502.5)	57.32 (57.36)	6.00 (6.02)	11.07 (11.15)

TABLE-2  
MOST IMPORTANT IR BANDS (cm<sup>-1</sup>) FOR NITRO SALAMO-TYPE BISOXIME COMPOUNDS (H<sub>2</sub>L<sup>1</sup>-H<sub>2</sub>L<sup>4</sup>)

Compound	ν(O-H)	ν(Ar-O)	ν(C=N)	ν(C-C) <sub>benzene ring</sub>	ν(CH <sub>atom</sub> )	ν(CH <sub>2</sub> )
H <sub>2</sub> L <sup>1</sup>	3433	1241	1609	1588,1529, 1477	3096	2953,2880
H <sub>2</sub> L <sup>2</sup>	3419	1240	1608	1592,1540, 1483	3097	2943, 2878
H <sub>2</sub> L <sup>3</sup>	3433	1243	1610	1595,1542, 1485	3082	2922, 2890
H <sub>2</sub> L <sup>4</sup>	3429	1245	1608	1599,1536, 1483	3097	2945,2878

TABLE-3  
UV-VIS SPECTRA AND <sup>1</sup>H NMR DATA FOR NITRO SALAMO-TYPE BISOXIME COMPOUNDS (H<sub>2</sub>L<sup>1</sup>-H<sub>2</sub>L<sup>4</sup>)

Compound	π-π*(nm)	<sup>1</sup> H NMR(400 MHz,DMSO-d <sub>6</sub> , δ/ppm)
H <sub>2</sub> L <sup>1</sup>	270, 319	2.43~2.49 (m, 12H), 4.27 (s, 4H), 6.91 (d, J=7.8 Hz, 2H), 7.82 (dd, J=8.2, 2.4 Hz, 2H), 8.18 (d, J= 2.4 Hz, 2H), 8.25 (s, 2H), 9.94 (s, 2H)
H <sub>2</sub> L <sup>2</sup>	270, 320	2.41~2.50 (m, 14H), 4.28 (s, 4H), 6.92 (d, J=8.2 Hz, 2H), 7.80 (dd, J=8.0, 2.2 Hz, 2H), 8.21 (d, J= 2.6 Hz, 2H), 8.27 (s, 2H), 9.95 (s, 2H)
H <sub>2</sub> L <sup>3</sup>	272, 326	2.40~2.51 (m, 18H), 4.29 (s, 4H), 6.90 (d, J=8.0 Hz, 2H), 7.81 (dd, J=8.4, 2.2 Hz, 2H), 8.20 (d, J= 2.2 Hz, 2H), 8.26 (s, 2H), 9.94 (s, 2H)
H <sub>2</sub> L <sup>4</sup>	272, 326	2.43~2.54 (m, 20H), 4.27 (s, 4H), 6.91 (d, J=8.4 Hz, 2H), 7.82 (dd, J=8.2, 2.4 Hz, 2H), 8.26 (d, J= 2.4 Hz, 2H), 8.34 (s, 2H), 9.97 (s, 2H)

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