

Synthesis and Characterization of Tetrahalogen Substituted Salamo-type Bisoximes Possessing More Flexible O-Alkyl Chain

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Four tetrahalogen substituted Salamo-type bisoximes H_2L^1 - H_2L^4 have been synthesized from 3-bromo-5-chloro-2-hydroxybenzaldehyde and 1,7-bis(aminooxy)heptane, 1,8-bis(aminooxy)octane, 1,9-bis(aminooxy)nonane or 1,10-bis(aminooxy)decane in ethanol medium, respectively and characterized by elemental analyses as well as IR, UV-visible and 1H NMR spectroscopy. Salamo-type bisoxime compound is much more useful to assemble supramolecular systems than a Salen moiety.

Keywords: Salamo-type bisoxime, Synthesis, Characterization.

INTRODUCTION

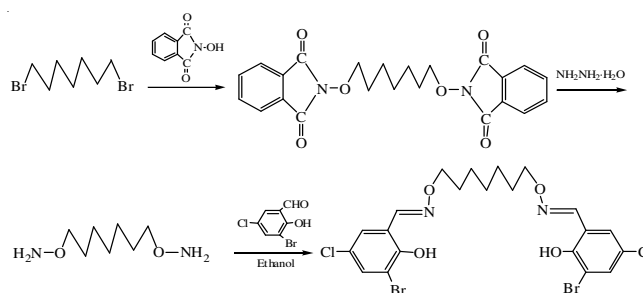
H_2 Salen [N,N-bis(salicylidene)ethylenediamine] derivatives have played a pivotal role in the development of modern coordination chemistry¹⁻⁴. In particular, H_2 Salen-type compounds capable of coordinating to metal ions, are important for the investigation of supramolecular interactions⁵. These substances have also been used for various applications, such as various organic reaction processes as catalysts, models of reaction centers of metalloenzymes and nonlinear optical materials⁶. Numerous researchers have used Schiff-base condensation as the reaction step to synthesize H_2 Salen-type compounds, often in high yield⁷. With the goal of developing H_2 Salen-type compounds that could coordinate to multiple metals and be easily prepared, we identified H_2 Salamo-type compounds as an attractive target. If an O-alkyl oxime moiety ($-CH=N-(CH_2)_n-N=CH-$) is used instead of a Schiff base ($-CH=N-O-(CH_2)_n-O-N=CH-$), the larger electronegativity of oxygen atoms is expected to affect strongly the electronic properties of N_2O_2 coordination sphere, which can lead to different and novel properties and structures of the resulted complexes⁸⁻¹⁰. In this paper, we report the synthesis and spectroscopic properties of a series of multihalogen substituted Salamo-type compounds, which bearing two salicylidene moieties and two O-alkyloxime linkages.

EXPERIMENTAL

3-Bromo-5-chloro-2-hydroxybenzaldehyde, 1,7-dibromoheptane, 1,8-dibromooctane, 1,9-dibromnonane and 1,10-dibromodecane ($\geq 99\%$) 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. 1H 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 Taike Instrument Limited Company and the thermometer was uncorrected.

Preparation of 4,4'-dichloro-6,6'-dibromo-2,2'-[(1,7-heptanedioldioxy)bis(nitrilomethylidene)]diphenol (H_2L^1): Synthetic route to Salamo-type bisoxime H_2L^1 is shown in **Scheme-I**. 1,7-bis(Aminooxy)heptane was synthesized according to an analogous method reported earlier^{10,11}.

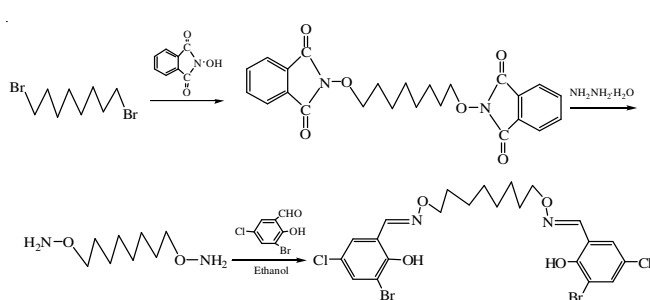


Scheme-I: Synthesis of Salamo-type bisoximes H_2L^1

To an ethanolic solution (8 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (94 mg, 0.40 mmol) was added an

ethanolic solution (3 mL) of 1,7-bis(aminooxy)heptane (32.0 mg, 0.20 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/hexane and hexane, respectively. The product was dried under reduced pressure to obtain white crystalline solid H_2L^1 .

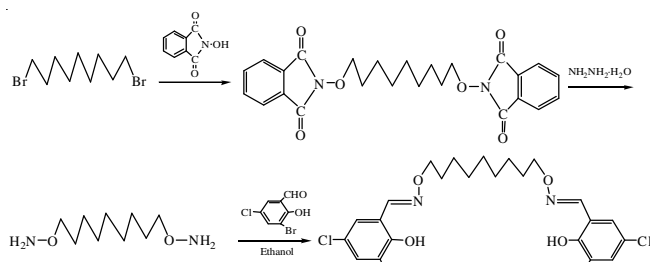
Preparation of 4,4'-dichloro-6,6'-dibromo-2,2'-(1,8-octanediyldioxy)bis(nitrilomethylidyne)diphenol (H_2L^2): Synthetic route to Salamo-type bisoxime H_2L^1 is shown in **Scheme-II**. 1,8-bis(Aminooxy)octane was synthesized according to an analogous method reported earlier^{10,11}.



Scheme-II: Synthesis of Salamo-type bisoximes H_2L^2

To an ethanolic solution (8 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (103.0 mg, 0.44 mmol) was added an ethanolic solution (3 mL) of 1,8-bis(aminooxy)octane (37.0 mg, 0.21 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/hexane and hexane, respectively. The product was dried under reduced pressure to obtain pale-yellow solid H_2L^2 .

Preparation of 4,4'-dichloro-6,6'-dibromo-2,2'-(1,9-nonanediyldioxy)bis(nitrilomethylidyne)diphenol (H_2L^3): Synthetic route to Salamo-type bisoxime H_2L^3 is shown in **Scheme-III**. 1,9-bis(Aminooxy)nonane was synthesized according to an analogous method reported earlier^{10,11}.

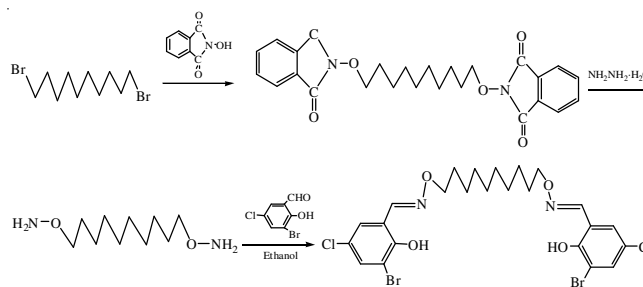


Scheme-III: Synthesis of Salamo-type bisoximes H_2L^3

To an ethanolic solution (8 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (95.0 mg, 0.40 mmol) was added an

ethanol solution (3 mL) of 1,9-bis(aminooxy)nonane (38.1 mg, 0.20 mmol). After the solution had been stirred at 55 °C for 4 h, the mixture was filtered, washed successively with ethanol/hexane and hexane, respectively. The product was dried under reduced pressure to obtain white crystalline solid H_2L^3 .

Preparation of 4,4'-dichloro-6,6'-dibromo-2,2'-(1,10-decanediylldioxy)bis(nitrilomethylidyne)diphenol (H_2L^4): Synthetic route to Salamo-type bisoxime H_2L^1 is shown in **Scheme-IV**. 1,10-bis(Aminooxy)decane was synthesized according to an analogous method reported earlier^{10,11}.



Scheme-IV: Synthesis of Salamo-type bisoximes H_2L^4

To an ethanolic solution (8 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (126.0 mg, 0.54 mmol) was added an ethanolic solution (3 mL) of 1,10-bis(aminooxy)decane (54 mg, 0.26 mmol). After the solution had been stirred at 55 °C for 4 h, the mixture was filtered, washed successively with ethanol/hexane and hexane, respectively. The product was dried under reduced pressure to obtain white crystalline solid H_2L^4 .

RESULTS AND DISCUSSION

A series of multihalogen substituted Salamo-type bisoximes H_2L^1 - H_2L^4 have been synthesized with good yields and the composition 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 microcrystalline solid, stable in air and soluble in hot DMF and DMSO, insoluble in methanol, ethanol, acetone, acetonitrile, chloroform, dichloromethane, tetrahydrofuran, *n*-hexane, ether and water.

IR spectra of multihalogen substituted Salamo-type bisoxime compounds H_2L^1 - H_2L^4 are given in Table-2. In the IR spectra of the title compounds H_2L^1 - H_2L^4 , the bands due to characteristic C=N stretching absorption bands appear at 1604-1602 cm^{-1} , respectively^{11,12}. The Ar-O stretching frequencies

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF
TETRAHALOGEN SUBSTITUTED SALAMO-TYPE BISOXIMES H_2L^1 - H_2L^4

Comp.	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
H_2L^1	White	205-206	65.2	$C_{21}H_{22}N_2O_4Br_2Cl_2$ (597.1)	42.14 (42.24)	3.73 (3.71)	4.69 (4.69)
H_2L^2	White	211-212	70.1	$C_{22}H_{24}N_2O_4Br_2Cl_2$ (611.2)	43.13 (43.24)	4.10 (3.96)	4.57 (4.58)
H_2L^3	White	213-215	68.7	$C_{23}H_{26}N_2O_4Br_2Cl_2$ (625.2)	44.17 (44.19)	4.08 (4.19)	4.63 (4.48)
H_2L^4	White	221-222	78.1	$C_{24}H_{28}N_2O_4Br_2Cl_2$ (639.2)	44.84 (45.10)	4.26 (4.42)	4.47 (4.38)

TABLE-2
 KEY IR BANDS (cm⁻¹) FOR THE TETRAHALOGEN SUBSTITUTED SALAMO-TYPE BISOXIMES H₂L¹-H₂L⁴

Compound	$\nu(\text{O-H})$	$\nu(\text{Ar-O})$	$\nu(\text{C=N})$	$\nu(\text{C-C})_{\text{benzene ring}}$	$\nu(\text{CH}_{\text{arom}})$	$\nu(\text{CH}_2)$
H ₂ L ¹	3744	1215	1604	1554, 1450, 1446	3070	2931, 2858
H ₂ L ²	3747	1209	1602	1555, 1481, 1440	3074	2941, 2858
H ₂ L ³	3743	1215	1604	1553, 1512, 1461	3074	2933, 2850
H ₂ L ⁴	3664	1242	1604	1475, 1460, 1442	3078	2925, 2846

 TABLE-3
¹H NMR DATA FOR THE TETRAHALOGEN SUBSTITUTED SALAMO-TYPE BISOXIMES H₂L¹-H₂L⁴

Compound	$\pi-\pi^*(\text{nm})$	¹ H NMR (400 MHz, DMSO-d ₆ , δ/ppm)
H ₂ L ¹	274, 327	2.45-2.53 (m, 10H), 4.44 (s, 4H), 7.54 (d, $J = 2.0$ Hz, 2H), 7.70 (d, $J = 2.2$ Hz, 2H), 8.44 (s, 2H), 9.92 (s, 2H).
H ₂ L ²	274, 326	2.43-2.52 (m, 12H), 4.43 (s, 4H), 7.53 (d, $J = 2.0$ Hz, 2H), 7.71 (d, $J = 2.2$ Hz, 2H), 8.45 (s, 2H), 9.83.02 (s, 2H).
H ₂ L ³	276, 328	2.43-2.50 (m, 14H), 4.42 (s, 4H), 7.52 (d, $J = 2.0$ Hz, 2H), 7.69 (d, $J = 2.2$ Hz, 2H), 8.40 (s, 2H), 9.75 (s, 2H).
H ₂ L ⁴	277, 328	2.42-2.52 (m, 16H), 4.42 (s, 4H), 7.50 (d, $J = 2.0$ Hz, 2H), 7.70 (d, $J = 2.2$ Hz, 2H), 8.42 (s, 2H), 9.76 (s, 2H).

appear within 1242-1209 cm⁻¹ as reported for similar bisoxime compounds¹³. These provide evidence for the formation of the title compounds. The O-H stretching frequency of the bisoxime compound is expected in the 3300-3800 cm⁻¹ region¹¹, here a strong band at 3747-3664 cm⁻¹ was observed in the title compounds H₂L¹-H₂L⁴ and assigned to phenolic alcohol stretching absorption bands. In addition, in the 1555-1440 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations.

UV-visible spectra and ¹H NMR data: The UV-visible spectra of the title compounds H₂L¹-H₂L⁴ in 5 × 10⁻⁵ DMF solution are presented in Table-3. UV-visible spectra of the title compounds H₂L¹-H₂L⁴ exhibit two intense peaks at around 274 and 327 nm. The former absorption peak at about 277 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^{11,14}. 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 H₂Salen¹⁵.

The ¹H NMR spectra of the title compounds H₂L¹-H₂L⁴ in DMSO-d₆ are shown in Table-3. The ¹H NMR spectra showed a singlet at about 8.40-8.44 ppm indicating the the existence of oxime bonds¹⁵.

Conclusion

In this paper, a series of variational tetrahalogen substituted 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 3-bromo-5-chloro-2-hydroxybenzaldehyde with 1,7-bis(aminoxoy)heptane, 1,8-bis(aminoxoy)octane, 1,9-bis(aminoxoy)nonane or 1,10-bis(aminoxoy)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 tetrahalogen substituted Salamo-type complexes with transition

metal ions such as copper, manganese, iron, cobalt, nickel and zinc is now in progress.

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