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Synthesis and Characterization of Salamo-type Bisoximes Based on 3-Ethoxysalicyladehyde and *Bis*(aminooxy)alkane

GANG LI, JIAN-CHUN MA, ZONG-LI REN*, WEI-MIN ZHOU, LI WANG and NA WEN

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

*Corresponding author: E-mail: zlren8@163.com

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A series of ethoxy-substituted Salamo-type bisoximes H_2L^1-H_2L^4 have been synthesized from 3-ethoxysalicyladehyde and 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane, 1,5-*bis*(aminooxy)pentane or 1,6-*bis*(aminooxy)hexane in hot ethanol medium, respectively and characterized by elemental analyses, IR, UV-visible spectra and ^1H NMR spectroscopy. Salamo-type compounds are conducive to coordinate experiments and construct supramolecular complexes.

Keywords: Salamo-type bisoxime, 3-Ethoxysalicyladehyde, *bis*(Aminooxy)alkane.

INTRODUCTION

Salen (N,N'-disalicylideneethylenediamine) and its analogues are most versatile chelate ligands in inorganic and organicmetallic chemistry[1-4]. Simultaneously, as bisoxime (-C=N-OR) ligands, they are usually synthesized by the condensation of aldehydes or ketones with hydroxylamineis. Bisoxime compounds are a kind of good multidentate N_2O_2-donating ligands with large π-conjugating system and often showing a diversity of structure. The chemical characteristics of the oxime compounds have been well known, since they have been widely used in insecticide, anti-virus, especially in medicine, analytical chemistry, metal corrosion and functional material fields[5-10]. There contain two hydroxylamine (-C=N-OR) and more than two hydroxyl (-OH) among each Salamo-type bisoxime ligand, which provide coordination site to combine metal atoms and have advantage to construct supramolecular complexes[11]. So the study on Salamo-type bisoxime compounds has good prospects. Therefore, we have research on synthesis and characterization of those ethoxy-substituted Salamo-type bisoxime compounds, *e.g.*, 6,6'-diethoxy-2,2'-[(propylene-1,3-diyldioxy)-*bis*(nitrilomethylidyne)]-diphenol (H_2L^1), 6,6'-diethoxy-2,2'-[(butylene-1,4-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^2), 6,6'-diethoxy-2,2'-[(propane-1,5-diyldioxy)-*bis*(nitrilomethylidyne)]diphenol (H_2L^3) and 6,6'-diethoxy-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^4), which provided a reference for the further investigation.

EXPERIMENTAL

3-Ethoxysalicyladehyde (≥ 99 %) was purchased and used without further purification. The others reagents used are the same as reported earlier[11]. 1,3-*bis*(Aminooxy)propane, 1,4-*bis*(aminooxy)butane, 1,5-*bis*(aminooxy)penpane and 1,6-*bis*(aminooxy)hexane were synthesized according to an analogous method reported earlier[12-14].

Preparation of 6,6'-diethoxy-2.2'-[(propylene-1,3-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (2 mL) of 1,3-*bis*(aminooxy)propane (53.10 mg, 0.50 mmol) was added an ethanol solution (4 mL) of 3-ethoxy-salicyladehyde (155.2 mg, 1 mmol). The reaction mixture was stirred at 331 K for 4 h, a white precipitation was obtained immediately. The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain white compound H_2L^1 (Fig. 1).

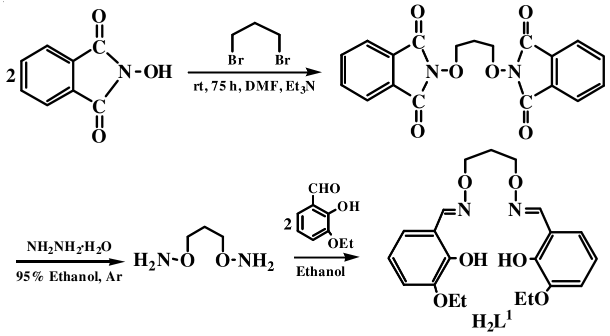
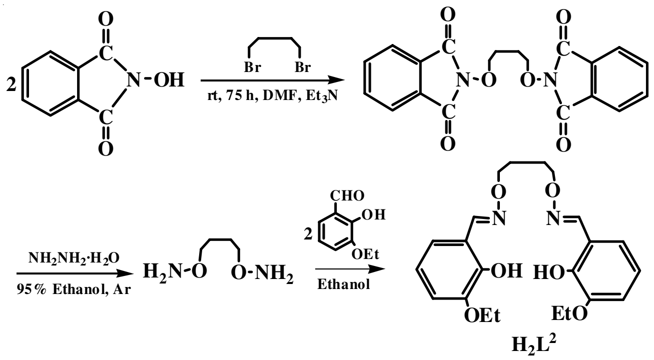


Fig. 1. Synthetic route to the Salamo-type bisoxime H_2L^1

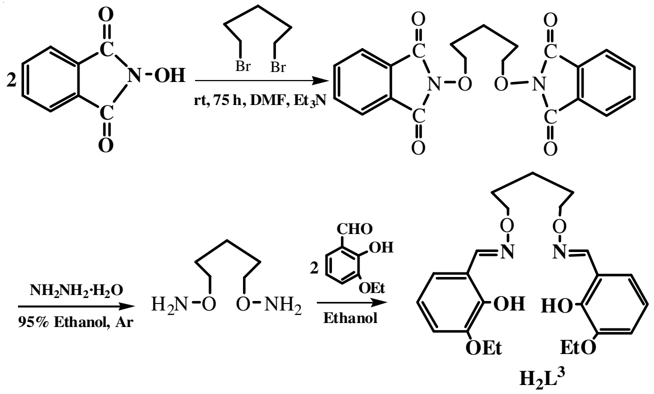
Preparation of 6,6'-diethoxy-2,2'-[(butylene-1,4-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^2): To an ethanol solution (5 mL) of 1,4-*bis*(aminooxy)butane (122.8 mg, 1.02 mmol) was added an ethanolic solution (10 mL) of 3-ethoxysalicyladehyde (362.2 mg, 2.18 mmol). After the solution had been stirred at 328 K for 6 h, a pale-yellow precipitation was obtained immediately. The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain pale-yellow compound H_2L^2 (Fig. 2).



H₂L²

Fig. 2. Synthetic route to the Salamo-type bisoxime H_2L^2

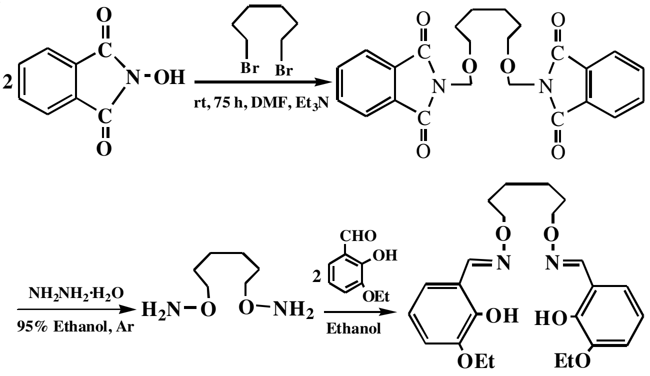
Preparation of 6,6'-diethoxy-2,2'-[(propane-1,5-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^3): To an ethanolic solution (5 mL) of 1,5-*bis*(aminooxy)pentane (133.4 mg, 1 mmol) was added an ethanol solution (8 mL) of 3-ethoxysalicyladehyde (359.2 mg, 2.16 mmol), After the solution had been stirred at 325 K for 3 h, a white precipitation was obtained immediately. The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain white compound H_2L^3 (Fig. 3).



H₂L³

Fig. 3. Synthetic route to the Salamo-type bisoxime H_2L^3

Preparation of 6,6'-diethoxy-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^4): To an ethanolic solution (5 mL) of 1,6-*bis*(aminooxy)hexane (151.1 mg, 1.02 mmol) was added an ethanolic solution (10 mL) of 3-ethoxysalicyladehyde (347.8 mg, 2.09 mmol). After the solution had been stirred at 328 K for 6 h, a pale-yellow precipitation was obtained. The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain pale-yellow compound H_2L^4.



H₂L⁴

Fig. 4. Synthetic route to the Salamo-type bisoxime H_2L^4

RESULTS AND DISCUSSION

Four ethoxy-substituted Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible spectra and ^{1}H NMR spectroscopy.

The colour, yields, melting points and elemental analytical results of the synthesized Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 are summarized in Table-1.

The bisoxime compounds H_2L^1, H_2L^2, H_2L^3 and H_2L^4 are stable in air and soluble in majority of organic solvents that conclude to coordinated experiments, not soluble in hexane that they can be recrystallized from *n*-hexane. The elemental analytical data and the compositions of the Salamo-type bisoximes show that the elemental analytical data of Salamo-type bisoximes close to the theoretical value which demonstrate the accuracy of the results.

IR spectra: IR spectral data of the Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 exhibit various bands from 4000 to 400 cm^{-1}. The IR spectral details of the Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 are presented in Table-2.

The characteristic C=N stretching bands of the Salamo-type bisoximes H_2L^1-H_2L^4 appear at 1605-1611 cm^{-1}, respectively[15]. And the Ar-O stretching bands occur at 1247, 1252, 1261 and 1256 cm^{-1} for the Salamo-type bisoximes H_2L^1-H_2L^4, respectively indicating that 3-ethoxysalicyladehyde has been condensated with 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane, 1,5-*bis*(aminooxy)pentane and 1,6-*bis*(aminooxy)hexane, respectively and formed new Salamo-type bisoximes[16]. In the 1479-1446 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations. In addition, the O-H stretching bands of the Salamo-type bisoximes at 3600 cm^{-1} region disappear, the strong absorption bands of the Salamo-type bisoximes appear at 3435-3410 cm^{-1} region, which are the evidence for the existence of associating hydroxyl group in the Salamo-type bisoximes. IR spectral results of the Salamo-type bisoximes further confirmed the accuracy of the consequence.

UV-visible and ^{1}H NMR spectra: The UV-visible spectra of the Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 in 5×10^{-5} mol L^{-1} dichloromethane solution are given in Table-3. The Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 exhibit

TABLE-1
COLOUR, YIELDS, MELTING POINTS, ELEMENTARY ANALYTICAL RESULTS AND COMPOSITIONS OF THE BISOXIMES H_2L^1, H_2L^2, H_2L^3 AND H_2L^4

Compound	m.f. (m.w.)	Colour	m.p. (K)	Yield (%)	Elemental analysis (%) Found (Calcd.)		
					C	H	N
H_2L^1	$C_{21}H_{26}N_2O_6$ 402.44	White	462.5-463.5	76.5	62.61 (62.67)	6.40 (6.41)	7.01 (6.95)
H_2L^2	$C_{22}H_{28}N_2O_6$ 416.47	Pale-yellow	413-414	85.8	63.47 (63.45)	6.75 (6.78)	6.66 (6.73)
H_2L^3	$C_{23}H_{30}N_2O_6$ 430.49	White	355.5-356.5	67.7	64.20 (64.17)	7.01 (7.02)	6.48 (6.51)
H_2L^4	$C_{24}H_{32}N_2O_6$ 444.52	Pale-yellow	354.5-355.5	57.2	64.97 (64.85)	7.05 (7.26)	6.12 (6.30)

TABLE-2
IR SPECTRAL DATA FOR THE BISOXIMES H_2L^1, H_2L^2, H_2L^3 AND H_2L^4 (cm^{-1})

Compound	ν(O-H)	ν (CH_2)	ν (C=N)	ν (Ar-O)	ν $(C-C)_{\text{benzene ring}}$
H_2L^1	3410	2970, 2885	1605	1247	1446
H_2L^2	3427	2977, 2882	1607	1252	1475
H_2L^3	3441	2941, 2880	1611	1261	1481
H_2L^4	3435	2975, 2879	1608	1256	1479

TABLE-3
UV-VISIBLE SPECTRA AND ^1H NMR DATA FOR THE SYNTHESIZED BISOXIMES H_2L^1, H_2L^2, H_2L^3 AND H_2L^4

Compound	π-π* (nm)	^1H NMR (400 MHz, DMSO-d_6, δ/ppm)
H_2L^1	272, 310	2.18 (m, *J* = 6.5 Hz, 2H, CH_2), 3.92 (s, 6H, CH_3), 4.17 (m, *J* = 7.2 Hz, 4H, CH_2-O), 4.36 (m, *J* = 6.2, 1.4 Hz, 4H, CH_2-O), 6.78 (s, 2H, PhH), 6.85 (m, 2H, PhH), 6.92 (dd, *J* = 7.6, 2.2 Hz, 2H, PhH), 8.25 (s, 2H, N=CH), 9.89 (s, 2H, OH).
H_2L^2	274, 315	2.22 (m, *J* = 6.2 Hz, 4H, CH_2), 3.90 (s, 6H, CH_3), 4.16 (m, *J* = 7.0 Hz, 4H, CH_2-O), 4.37 (m, *J* = 6.0, 1.4 Hz, 4H, CH_2-O), 6.78 (s, 2H, PhH), 6.85 (m, 2H, PhH), 6.92 (dd, *J* = 7.2, 2.3 Hz, 2H, PhH), 8.23 (s, 2H, N=CH), 9.87 (s, 2H, OH).
H_2L^3	272, 312	2.19 (m, *J* = 6.2 Hz, 6H, CH_2), 3.91 (s, 6H, CH_3), 4.18 (m, *J* = 7.4 Hz, 4H, CH_2-O), 4.35 (m, *J* = 6.3, 1.4 Hz, 4H, CH_2-O), 6.78 (s, 2H, PhH), 6.85 (m, 2H, PhH), 6.92 (dd, *J* = 7.4, 2.2 Hz, 2H, PhH), 8.26 (s, 2H, N=CH), 9.88 (s, 2H, OH).
H_2L^4	273, 321	2.20 (m, *J* = 6.0 Hz, 8H, CH_2), 3.93 (s, 6H, CH_3), 4.18 (m, *J* = 7.0 Hz, 4H, CH_2-O), 4.35 (m, *J* = 6.4, 1.4 Hz, 4H, CH_2-O), 6.78 (s, 2H, PhH), 6.85 (m, 2H, PhH), 6.92 (dd, *J* = 7.5, 2.0 Hz, 2H, PhH), 8.21 (s, 2H, N=CH), 9.86 (s, 2H, OH).

two intense peaks at around 272 and 310 nm. The former absorption peaks at about 270 nm can be assigned to the π-π* transition of the naphthalene rings, while the latters can be attributed to the intra-ligand π-π* transition of the C=N bonds[17]. 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[17].

The ^1H NMR spectra of the Salamo-type bisoximes H_2L^1, H_2L^2, H_2L^3 and H_2L^4 in DMSO-d_6 are shown in Table-3. The ^1H NMR spectra showed a singlet at about 8.21-8.26 ppm indicating the existence of oxime bonds[17,18].

Conclusion

Four Salamo-type bisoximes H_2L^1-H_2L^4 have been designed and successfully synthesized by the reaction of 2 equivalents of 3-ethoxysalicyladehyde with 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane, 1,5-*bis*(aminooxy)pentane or 1,6-*bis*(aminooxy)hexane under comfortable conditions, respectively.

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