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Synthesis and Characterization of Series of Methoxy-Substituted Salamo-Type Compounds Having More Flexible *O*-Alkyl Chain

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Several novel methoxy-substituted Salamo-type compounds have been synthesized by the condensation reactions of 3-methoxy-2-hydroxy-benzaldehyde with 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, IR, UV-visible and ^{1}H NMR spectra.

Keywords: Salamo-type bisoxime ligand, Synthesis, Characterization.

INTRODUCTION

Oxime-type compounds could be of great importance in organic as well as inorganic fields, for the metal complexes which containing these compounds as ligands have been widely used in all kinds of organic reactions as catalyst[1-3]. Even more compelling is that these compounds can be easily synthesized by condensation reaction between ketones or aldehydes with hydroxylamine[4,5]. Furthermore, these compounds can form complexes with transition metal ions easily on the basis of *O*-alkyl oxime moiety and the chemical properties were studied by more and more researchers. In recent years[6], the strongly electronegativity oxygen atoms of N_2O_2 coordination sphere, result in different structures and chemical properties[7]. The bisoxime-type compiounds and their complexes play an important role in the development of coordinating chemistry and preparing new type oxime compounds and complexes are highly desirable[8-10]. Herein, we have synthesized four bisoxime compounds from 3-methoxy-2-hydroxy-benzaldehyde and bis(aminooxy)alkane with different long-chain alkane molecules, 6,6'-dimethoxy-2,2'-[1,7-(heptanediyldioxy)*bis*- (nitrilomethylidyne)]diphenol, 6,6'-dimethoxy-2,2'-[1,8-(octanediyldioxy)*bis*(nitrilomethylidyne)]diphenol, 6,6'-dimethoxy-2,2'-[1,9-(nontanediyldioxy)-*bis*(nitrilomethy-lidyne)]diphenol, 6,6'-dimethoxy-2,2'-[1,10-(decanediyldioxy) *bis*(nitrilomethylidyne)]diphenol and the characterizetions have also been studied in this paper.

EXPERIMENTAL

Material and methods: 3-Methoxy-2-hydroxy-benzaldehyde (≥ 98 %), 1,7-dibromoheptane, 1,8-dibromooctane, 1,9-dibromononane 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. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (400-4000 cm^{-1}) pellets. UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer and the thermometer was uncorrected.

General procedure: Synthetic route to Salamo-type bisoxime compounds **H_2L^1-H_2L^4** are shown in Fig. 1. 1,7-*Bis*-(aminooxy)heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(amino-oxy)nonane and 1,10-*bis*(aminooxy)decane were synthesized according to an analogous method reported earlier[11-13].

Preparation of 6,6'-dimethoxy-2,2'-[1,7-(heptanediyl-dioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (5 mL) of 3-methoxy-2-hydroxy-benzal-dehyde (152.2 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, when cooled to room temperature, the formed white precipitate was separated by filtration and washed successively with a mixture of ethanol and *n*-hexane (v:v = 1:4) and *n*-hexane. The product was dried under vacuum to yield the compound (**H_2L^1**). Yield (%): 39.1; m.p.: 342-343 K.

Preparation of 6,6'-dimethoxy-2,2'-[1,8-(octanediyldioxy) *bis*(nitrilomethylidyne)]diphenol (H_2L^2): To a hot ethanolic

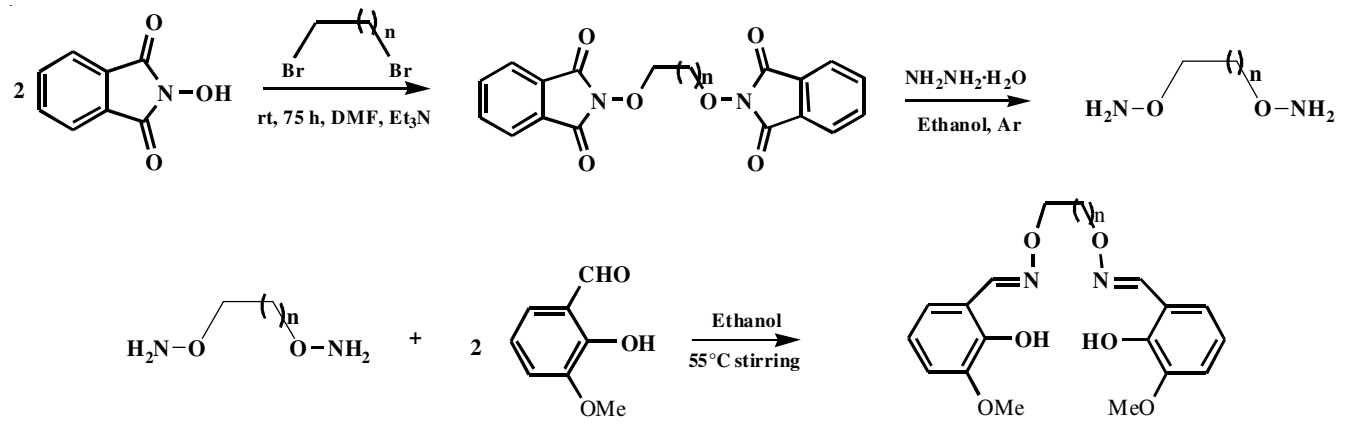

Fig. 1. Synthetic route to salamo-type bisoxime compounds H_2L^1-H_2L^4 (n = 6-9)

solution (5 mL) of 3-methoxy -2-hydroxy-benzaldehyde (152.2 mg, 1 mmol) was added an ethanolic solution (2 mL) of 1,8-*bis*(aminooxy)octane (88.1 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 4 h. On cooling to room temperature, the light yellow precipitate was obtained, which was filtered and washed successively with a mixture of ethanol and *n*-hexane (v:v = 1:4) and *n*-hexane, respectively. The product was dried under vacuum to yield the compound. **H_2L^2**, Yield (%): 75.3; m.p.: 377-379 K.

Preparation of 6,6'-dimethoxy-2,2'-[1,9-(nonanediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^3): To a hot ethanolic solution (5 mL) of 3-methoxy-2-hydroxy-benzaldehyde (152.2 mg, 1 mmol) was added an ethanolic solution (2 mL) of 1,9-*bis*(aminooxy)nonane (95.1 mg, 0.50 mmol). The reaction mixture had been stirred at 55 °C for 4 h. On cooling to room temperature, the light yellow precipitate was obtained, which was filtered and washed successively with a mixture of ethanol and *n*-hexane (v:v = 1:4) and *n*-hexane, respectively. The product was dried under vacuum to yield the compound. **H_2L^3**, Yield (%): 22.60; m.p.: 343-344 K.

Preparation of 6,6'-dimethoxy-2,2'-[1,10-(decanediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^4): To a hot ethanolic solution (5 mL) of 3-methoxy-2-hydroxy-benzaldehyde (152.2 mg, 1 mmol) was added an ethanolic solution (10 mL) of 1,10-*bis*(aminooxy)decane (10.2 mg, 0.50 mmol). The reaction mixture had been stirred at 55 °C for 4 h. On cooling to room temperature, the white precipitate was obtained, which was filtered and washed successively with a mixture of ethanol and *n*-hexane (v:v = 1:4) and *n*-hexane, respectively. The product was dried under vacuum to yield the compound. **H_2L^4**, Yield (%): 72.2; m.p.: 365-366 K.

RESULTS AND DISCUSSION

A series of Salamo-type bisoxime compounds **H_2L^1-H_2L^4** have been synthesized and the composition are confirmed by elemental analyses, IR, UV-visible and ^{1}H NMR spectra.

Physico-chemical properties: 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 formula. Compounds **H_2L^1** and **H_2L^4** are white microcrystalline solid, **H_2L^2** and **H_2L^3** are light-yellow powder. All the compounds are stable in air and soluble in acetone, chloroform, dichloromethane, tetrahydrofuran, ether, acetonitrile, ethyl acetate, DMF and DMSO, insoluble in water, methanol, ethanol and *n*-hexane.

IR spectra: The most important IR spectra date for **H_2L^1-H_2L^4** are given in Table-2.

TABLE-2
KEY IR BANDS (cm^{-1}) FOR THE BROMO SALAMO-TYPE BISOXIME COMPOUNDS **H_2L^1-H_2L^4**

Compound	ν(O-H)	ν (CH_2)	ν (C=N)	ν (C-C)	ν (Ar-O)
H_2L^1	3432	2945, 2886	1605	1471	1262
H_2L^2	3438	2950, 2870	1608	1476	1257
H_2L^3	3442	2941, 2881	1607	1472	1260
H_2L^4	3435	2946, 2875	1604	1473	1268

In the IR spectra of the compounds **H_2L^1-H_2L^4**, the characteristic C=N stretching bands of the compound **H_2L^1-H_2L^4** appear at 1608-1605 cm^{-1}, respectively[14]. The Ar-O stretching bands occur at 1268-1257 cm^{-1} as reported for similar bisoxime compounds[15]. The O-H stretching band of the title compounds

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF BROMO SALAMO-TYPE BISOXIME COMPOUNDS **H_2L^1-H_2L^4**

Compound	Colour	m.p. (K)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (calcd.)		
					C	H	N
H_2L^1	White	342-343	39.1	$C_{23}H_{30}N_2O_6$ (430.2)	64.12 (64.17)	6.99 (7.02)	6.47 (6.51)
H_2L^2	Light yellow	377-379	75.3	$C_{24}H_{32}N_2O_6$ (444.5)	64.88 (64.85)	7.23 (7.26)	6.35 (6.30)
H_2L^3	Light yellow	343-344	22.6	$C_{25}H_{34}N_2O_6$ (458.5)	65.45 (65.48)	7.50 (7.47)	6.08 (6.11)
H_2L^4	White	365-366	72.2	$C_{26}H_{36}N_2O_6$ (472.5)	66.05 (66.08)	7.70 (7.68)	5.91 (5.93)

appears at 3442-3432 cm^{-1} region, but this frequency is generally displaced to about 3424 cm^{-1} because of the internal hydrogen bond OH···N=C[16].

UV-visible spectra: The absorption spectra of **H_2L^1-H_2L^4** (Table-3), in diluted dichloromethane solution show that the spectra of **H_2L^1-H_2L^4**, are similar to each other. The compounds **H_2L^1-H_2L^4** exhibit two intense peaks at around 280 and 328 nm. The former absorption peaks at about 280 nm can be assigned to the π-π^* transition of the benzene 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 are seen in the corresponding Salen derivatives. The absorption is ascribed to the quinoid form of H_2 salen[18].

TABLE-3
UV-VIS SPECTRAL DATA FOR THE SALAMO-TYPE BISOXIME COMPOUNDS **H_2L^1-H_2L^4**

Compound	C ($\times10^{-5}$ mol L^{-1})	First band	Second band
		λ_{max1} (nm)	λ_{max2} (nm)
H_2L^1	5.00	280	320
H_2L^2	5.00	280	322
H_2L^3	5.00	282	325
H_2L^4	5.00	282	328

^{1}H NMR Spectra: The ^{1}H NMR spectra of the title compounds **H_2L^1-H_2L^4** in DMSO-d_6 are shown in Table-4. The ^{1}H NMR spectra showed a singlet at about 8.26-8.29 ppm indicating the existence of oxime bonds[18].

TABLE-4
UV-VISIBLE SPECTRAL DATA AND ^{1}H NMR DATA FOR THE BROMO-SUBSTITUTED SALAMO-TYPE BISOXIMES **H_2L^1-H_2L^4**

Compound	^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm)
H_2L^1	2.45-2.56 (m, 10H, CH_2), 3.90 (s, 6H, CH_3), 4.49 (s, 4H, CH_2-O), 6.84 (dd, *J* = 7.8, 1.8 Hz, 2H, PhH), 6.87 (t, *J* = 7.6 Hz, 2H, PhH), 6.93 (dd, *J* = 7.6, 1.8 Hz, 2H, PhH), 8.26 (s, 2H, N=CH), 9.74 (s, 2H, OH)
H_2L^2	2.46-2.57 (m, 12H, CH_2), 3.92 (s, 6H, CH_3), 4.50 (s, 4H, CH_2-O), 6.84 (dd, *J* = 7.8, 1.9 Hz, 2H, PhH), 6.87 (t, *J* = 7.7 Hz, 2H, PhH), 6.95 (dd, *J* = 7.8, 1.8 Hz, 2H, PhH), 8.27 (s, 2H, N=CH), 9.76 (s, 2H, OH)
H_2L^3	2.48-2.57 (m, 14H, CH_2), 3.92 (s, 6H, CH_3), 4.51 (s, 4H, CH_2-O), 6.83 (dd, *J* = 7.9, 1.8 Hz, 2H, PhH), 6.87 (t, *J* = 8.0 Hz, 2H, PhH), 6.90 (dd, *J* = 7.8, 1.6 Hz, 2H, PhH), 8.26 (s, 2H, N=CH), 9.78 (s, 2H, OH)
H_2L^4	2.50-2.59 (m, 16H, CH_2), 3.93 (s, 6H, CH_3), 4.52 (s, 4H, CH_2-O), 6.85 (dd, *J* = 7.7, 1.9 Hz, 2H, PhH), 6.88 (t, *J* = 8.2 Hz, 2H, PhH), 6.91 (dd, *J* = 7.5, 1.9 Hz, 2H, PhH), 8.29 (s, 2H, N=CH), 9.77 (s, 2H, OH)

Conclusion

In this work, a series of methoxy-substituted 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 3-methoxy-2-hydroxy-benzaldehyde with 1,7-*bis*(aminooxy)heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane or 1,10-*bis*(aminooxy)decane under hot ethanol medium, respectively. It is shown that a bisoxime moiety is much more useful to assemble supramolecular systems than a Schiff base moiety.

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REFERENCES

1. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
2. T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill and J. Schnack, *Inorg. Chem.*, **48**, 607 (2009).
3. M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohba and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 259 (2000).
4. N.S. Venkataramanan, G. Kuppuraj and S. Rajagopal, *Coord. Chem. Rev.*, **249**, 1249 (2005).
5. S.S. Sun, C.L. Stern, S.T. Nguyen and J.T. Hupp, *J. Am. Chem. Soc.*, **126**, 6314 (2004).
6. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).
7. J.C.G. Bünzli and C. Piguet, *Chem. Rev.*, **102**, 1897 (2002).
8. S. Akine, W.K. Dong and T. Nabeshima, *Inorg. Chem.*, **45**, 4677 (2006).
9. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).
10. P.G. Lacroix, *Eur. J. Inorg. Chem.*, 339 (2001).
11. S. Akine, Y. Morita, F. Utsuno and T. Nabeshima, *Inorg. Chem.*, **48**, 10670 (2009).
12. W.K. Dong, L. Li, C.F. Li, L. Xu and J.G. Duan, *Spectrochim. Acta A*, **71**, 650 (2008).
13. W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao and X.L. Tang, *Polyhedron*, **28**, 1419 (2009).
14. W.K. Dong, S.S. Gong, J.F. Tong, Y.X. Sun and J.C. Wu, *Chinese J. Inorg. Chem.*, **26**, 1868 (2010).
15. W.K. Dong, J. Yao, and Y.X. Sun, *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.*, **41**, 177 (2011).
16. W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010).
17. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
18. H.E. Smith, *Chem. Rev.*, **83**, 359 (1983).