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Synthesis and Characterization of Salamo-Type Bisoxime Compounds Based on 2-Hydroxy-4-methoxybenzaldehyde and *Bis*(aminooxy)alkane

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Three new Salamo-type bisoxime compounds H_2L^1-H_2L^3 have been synthesized from 2-hydroxy-4-methoxybenzaldehyde and 1,5-*bis*(aminooxy)pentane, 1,6-*bis*(aminooxy)hexane or 1,9-*bis*(aminooxy)nonane in hot ethanol medium, respectively and characterized by elemental analysis, IR and ^{1}H NMR spectroscopy.

Keywords: Salamo-type compound, Synthesis, Characterization.

INTRODUCTION

Particular attention has been paid in recent years to the synthesis, characterization and application of Salen-type compounds[1]. The new Salen-type bisoxime compounds have very important value that they are widely used in catalytic domain[2], medical field[3,4], analytical chemistry[5], material world[6,7], *etc*. So we devoted to design and synthesis of a series of new Salamo-type bisoxime compounds which have far-reaching significance. In the present study we have designed and synthesized three new Salamo-type bisoximes, named as 5,5'-dimethoxy-2,2'-[(pentane-1,5-diyldioxy)*bis*-(nitrilo-methylidyne)]diphenol (H_2L^1), 5,5'-dimethoxy-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilo-methylidyne)]diphenol (H_2L^2) and 5,5'-dimethoxy-2,2'-[(nonane-1,9-diyldioxy)*bis*-(nitrilo-methylidyne)]diphenol (H_2L^3).

EXPERIMENTAL

2-Hydroxy-4-methoxybenzaldehyde (≥ 99 %), 1,5-dibromopentane (97 %), 1,6- dibromohexane (97 %) and 1,9-dibromononane (97 %) were purchased and used without further purification. Other reagents were analytical pure grade and purchased from Tianjin Chemical Reagent Factory. The others are the same as literature[8,9].

General procedure: Synthetic route to Salamo-type bisoxime compounds H_2L^1-H_2L^3 are shown in Fig. 1-4. 1,5-*bis*(aminooxy)pentane, 1,6-*bis*(aminooxy)hexane or 1,9-*bis*(aminooxy)nonane were synthesized according to an analogous method reported earlier[7-9].

Preparation of 5,5'-dimethoxy-2,2'-[(pentane-1,5-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (10 mL) of 2-hydroxy-4-methoxybenzaldehyde (304.3 mg, 2 mmol) was added an ethanolic solution (6 mL) of 1,5-*bis*(aminooxy)pentane (134.2 mg, 1 mmol). The reaction mixture was stirred at 328 K for 5 h. The formed precipitate was separated by filtration and washed successively with ethanol/*n*-hexane (1:4). The product was dried under vacuum to obtain white title compound H_2L^1.

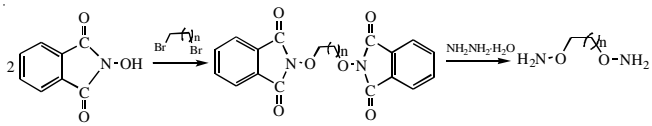

Fig. 1. Synthetic route to *bis*(aminooxy)alkane. H_2L^1: n = 4; H_2L^2: n = 5; H_2L^3: n = 8

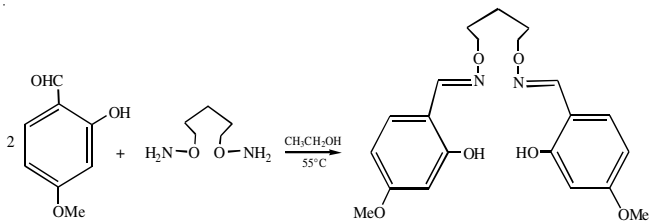

Fig. 2. Synthetic route to the Salamo-type bisoxime compound H_2L^1

Preparation of 5,5'-dimethoxy-2,2'-[(hexane-1,6-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^2): To an ethanolic solution (6 mL) of 2-hydroxy-4-methoxybenzaldehyde (194.5 mg, 1.28 mmol) was added an ethanolic solution (10 mL) of 1,6-*bis*(aminooxy)hexane (81.1 mg, 0.64 mmol). The reaction mixture was stirred at 328-333 K for 6 h. The formed precipitate was separated by filtration and washed

successively with ethanol/*n*-hexane (1:4). The product was dried under vacuum to obtain white title compound H_2L^2.

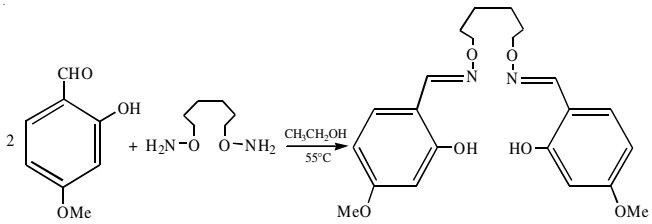

Fig. 3. Synthetic route to the Salamo-type bisoxime compound H_2L^2

Preparation of 5,5'-dimethoxy-2,2'-[(nonane-1,9-diyldi-oxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^3): To an ethanolic solution (5 mL) of 2-hydroxy-4-methoxybenzaldehyde (159.5 mg, 1.05 mmol) was added an ethanolic solution (5 mL) of 1,9-*bis*(aminooxy)nonane (99 mg, 0.52 mmol). The reaction mixture was stirred at 328 K for 8 h. The formed precipitate was separated by filtration under reduced pressure and washed successively with ethanol/*n*-hexane (1:4). The product was dried under vacuum to obtain white powder compound H_2L^3.

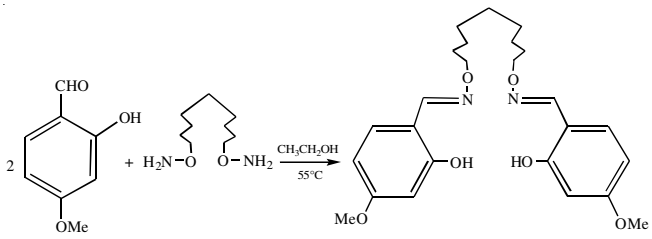

Fig. 4. Synthetic route to the Salamo-type bisoxime compound H_2L^3

RESULTS AND DISCUSSION

Three Salamo-type bisoxime compounds H_2L^1-H_2L^3 have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible and ^{1}H NMR spectroscopy.

Physico-chemical property: The colour, yields, melting points and elemental analytical results of the synthesized Salamo-type bisoxime compounds H_2L^1-H_2L^3 are presented in Table-1. Their compositions agree with the formulae. All the compounds are stable in air and soluble in chloroform, tetrahydrofuran, acetone, DMF, DMSO and hot methanol or ethanol, insoluble in *n*-hexane. In addition, H_2L^1 are soluble in dichloromethane and acetonitrile, but H_2L^3 are insoluble in dichloromethane and just soluble in hot acetonitrile. H_2L^1 and H_2L^3 are easy to be dissolved in ethyl ether and acetic ether, but H_2L^2 are difficult to be dissolved in ethyl ether, simultaneously, it can't be dissolved in acetic ether.

IR spectra: The most important IR spectral data for Salamo-type bisoxime compounds H_2L^1-H_2L^3 are given in Table-2. In the IR spectrum of Salamo-type bisoxime compound H_2L^1, 2950 and 2879 cm^{-1} are the weak absorption peaks for both antisymmetric and symmetric stretching vibration absorption of C-H bond of methylene. In the IR Spectrum of Salamo-type bisoxime compound H_2L^2, it contains $\nu_{O\text{-}H}$ bond, but no corresponding peaks were observed near 3600 cm^{-1}, while at 3169 and 3072 cm^{-1}, there exists strong broad absorption peaks, indicating that Salamo-type bisoxime compound H_2L^2 may have freedom intramolecular hydrogen bond (OH···N and OH···O) and at 2945 and 2879 cm^{-1}, the weak absorption peak can be attributed to the antisymmetric and symmetric stretching vibration absorption of C-H bond from methylene. Similarly, infrared spectrum of Salamo-type bisoxime compound H_2L^3 contains broad absorption peak at 3431 and 3161 cm^{-1} also shows that the Salamo-type bisoxime compound H_2L^3 may contain an intramolecular hydrogen bond (OH···N). The anti-symmetric and symmetric methyl stretching vibration absorption peak of C-H bond presented at 2989 and 2852 cm^{-1} which was very weak.

Meanwhile, the characteristic C=N stretching bands of the Salamo-type bisoximes H_2L^1-H_2L^3 appear at 1609-1606 cm^{-1}, respectively[10]. And the Ar-O stretching bands occur at 1225, 1223 and 1211 cm^{-1} for the Salamo-type bisoximes H_2L^1-H_2L^3, indicating that 2-hydroxy-4-methoxybenzaldehyde has been condensated with 1,5-*bis*(aminooxy)penpane, 1,6-*bis*(aminooxy)hexane or 1,9-*bis*(aminooxy)nonane, respectively and formed new Salamo-type bisoximes[11]. In the 1572-1441 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations. IR spectral results of the Salamo-type bisoximes further confirmed the accuracy of the consequence. So in this research we have successfully synthesized the target compounds, H_2L^1, H_2L^2 and H_2L^3.

^{1}H NMR spectra: The ^{1}H NMR spectral data of the Salamo-type bisoxime compounds H_2L^1-H_2L^3 in the solvent of $CDCl_3$ are shown in Table-3. The ^{1}H NMR analytical results are

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF SYNTHESIZED SALAMO-TYPE BISOXIME COMPOUNDS H_2L^1-H_2L^3

Compound	Colour	m.p. (K)	Yield (%)	m.f.	m.w.	Elemental analysis (%): Found (Calcd.)		
						C	H	N
H_2L^1	White	349-350	51.8	$C_{21}H_{26}N_2O_6$	402.44	62.79 (62.67)	6.68 (6.51)	6.83 (6.96)
H_2L^2	White	349-350	46.5	$C_{22}H_{28}N_2O_6$	416.47	63.78 (63.45)	6.91 (6.78)	6.68 (6.73)
H_2L^3	White	465-467	32.3	$C_{25}H_{34}N_2O_6$	458.55	65.63 (65.48)	7.79 (7.47)	6.07 (6.11)

TABLE-2
KEY IR BANDS (cm^{-1}) FOR THE SALAMO-TYPE BISOXIME COMPOUNDS H_2L^1-H_2L^3

Compound	ν(O-H)	ν(CH_2)	ν(C=N)	ν(C=C)$_{benzene\ ring}$	ν(Ar-O)
H_2L^1	3435	2950, 2879	1606	1568, 1506, 1467	1225
H_2L^2	3443	2945, 2879	1626	1572, 1505, 1464	1223
H_2L^3	3431	2989, 2852	1609	1568, 1505, 1441	1211

TABLE-3
THE ^{1}H NMR DATA FOR THE SALAMO-TYPE BISOXIME COMPOUNDS H_2L^1-H_2L^3

Compound	^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm)
H_2L^1	2.79 (s, 6H, CH_2), 4.41 (s, 10H, CH_2-O, CH_3-O), 6.46 (d, *J* = 2.8 Hz, 2H, PhH), 6.47 (dd, *J* = 8.4 Hz, 2.6 Hz, 2H, PhH), 7.04 (d, *J* = 8.8 Hz, 2H, PhH), 8.17 (s, 2H, N=CH), 9.94 (s, 2H, OH)
H_2L^2	2.13 (t, *J* = 6.6 Hz, 2H, CH_2), 3.64 (s, 6H, CH_2), 4.26 (t, *J* = 6.20 Hz, 10H, CH_2-O, CH_3-O), 6.46 (d, *J* = 2.4 Hz, 2H, PhH), 6.50 (s, *J* = 2.4 Hz, 2H, PhH), 7.06 (S, 2H, PhH), 8.09 (s, 2H, N=CH), 10.02 (s, 2H, OH)
H_2L^3	2.02 (t, *J* = 6.6 Hz 2H, CH_2), 3.81 (s, 18H, CH_2, CH_3-O), 4.26 (t, *J* = 6.20 Hz, 4H, CH_2-O), 6.57 (d, *J* = 2.8 Hz, 2H, PhH), 6.58 (d, *J* = 2.62 Hz, 2H, PhH), 6.98 (s, 2H PhH), 8.09 (s, 2H, N=CH), 12.12 (s, 2H, OH)

consistent with the elemental analytical results and the synthesized Salamo-type bisoxime compounds H_2L^1-H_2L^3 is the target compounds. The ^{1}H NMR spectra showed a singlet at about 8.09-8.17 ppm indicating the existence of oxime bonds[12].

Conclusion

Three new Salamo-type compounds H_2L^1-H_2L^3 that have two oxime bonds instead of imine bonds have been designed and synthesized by the reaction of 2 equivalents of 2-hydroxy-4-methoxybenzaldehyde with 1,5-*bis*(aminooxy)pentane, 1,6-*bis*(aminooxy)hexane or 1,9-*bis*(aminooxy)nonane in hot ethanol medium, respectively. The structures of the Salamo-type bisoxime compounds H_2L^1-H_2L^3 have been analyzed by EA, IR spectra and ^{1}H NMR spectroscopy. The Salamo-type bisoxime compounds may be promising units for the construction of supramolecular metal complexes and have reference for the further investigation.

REFERENCES

1. H.L. Wang, D.P. Zhang, Z.H. Ni, X.Y. Li, L.J. Tian and J.Z. Jiang, *Inorg. Chem.*, **48**, 5946 (2009).
2. J.K. Karjalainen, O.E.O. Hormi and D.C. Sherrington, *Tetrahedron Asymm.*, **9**, 3895 (1998).
3. H. Chen and J. Rhodes, *J. Mol. Med.*, **74**, 497 (1996).
4. A. Iqbal, H.L. Siddiqui, CM. Ashraf, M.H. Bukhari and C.M. Akram, *Chem. Pharm. Bull. (Tokyo)*, **55**, 1070 (2007).
5. S.T. Girousi, E.E. Golia, A.N. Voulgaropoulos and A.J. Maroulis, *Fresenius J. Anal. Chem.*, **358**, 667 (1997).
6. M.N. Desal, P.O. Chauhan and N. Shan, *Eur. Symp. Corrision Inhibitors*, **27**, 891 (1995).
7. S. Akine, T. Tadokoro and T. Nabeshima, *Inorg. Chem.*, **51**, 11478 (2012).
8. 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).
9. W.K. Dong, C.Y. Zhao, Y.X. Sun, X.L. Tang and X.N. He, *Inorg. Chem. Commun.*, **12**, 234 (2009).
10. S. Akine, T. Taniguchi, W. Dong, S. Masubuchi and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
11. J.A. Faniran, K.S. Patel and J.C. Bailar Jr., *J. Inorg. Nucl. Chem.*, **36**, 1547 (1974).
12. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).