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

GANG LI*, LI WANG, YU-HUA YANG, MENG-MENG ZHAO and YU-JIE ZHANG

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

*Corresponding author: E-mail: li_gang78@126.com

(Received: 13 March 2013;

Accepted: 29 August 2013)

AJC-14043

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 ¹H 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 H₂Salen (N,N-*bis*(salicylidene)-ethylenediamine) derivatives have attracted much attention to many organic as well as inorganic chemists¹⁻⁵, because these compounds can easily form complexes with various transition metals and some of them exhibit excellent catalytic activities for epoxidation, aziridination, *etc.*⁶. 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 ions⁷. 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-(CH₂)_n-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 N₂O₂ coordination sphere⁸⁻¹⁰, 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. 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.

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 earlier⁸⁻¹¹.

Preparation of 4,4'-dinitro-2,2'-[(1,6-hexanedioldioxy)bis(nitrilomethylidene)]diphenol (H₂L¹): Synthetic route to Salamo-type bisoxime compounds H₂L¹ is shown in Fig. 1.

Fig. 1. Synthesis of Salamo-type bisoxime compound H₂L¹

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-heptanedioxy)bis(nitrilomethylidyne)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-octanedioxy)bis(nitrilomethylidyne)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-decanedioxy)bis(nitrilomethylidyne)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^3

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} , respectively¹². The Ar-O stretching frequencies appear within 1245-1240 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 3800-3300 cm^{-1} region, but this frequency is generally displaced to 3433 cm^{-1} because of the internal hydrogen bond $OH \cdots N=C$ ¹¹. 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 5×10^{-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 bonds¹⁴. 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 ^{8,18}.

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 existence of oxime bonds¹⁵.

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 (H₂L¹-H₂L⁴)

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

TABLE-2
MOST IMPORTANT IR BANDS (cm⁻¹) FOR NITRO SALAMO-TYPE BISOXIME COMPOUNDS (H₂L¹-H₂L⁴)

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

TABLE-3
UV-VIS SPECTRA AND ¹H NMR DATA FOR NITRO SALAMO-TYPE BISOXIME COMPOUNDS (H₂L¹-H₂L⁴)

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

REFERENCES

1. A.M. Castilla, S. Curreli, E.C. Escudero-Adán, M.M. Belmonte, J. Benet-Buchholz and A.W. Kleij, *Org. Lett.*, **11**, 5218 (2009).
2. Z. Li and C. Jablonski, *Inorg. Chem.*, **39**, 2456 (2000).
3. J. Gao, J.H. Reibenspies, R.A. Zingaro, F.R. Woolley, A.E. Martell and A. Clearfield, *Inorg. Chem.*, **44**, 232 (2005).
4. T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammeler, R. Fröhlich, E. Bill and J. Schnack, *Inorg. Chem.*, **48**, 607 (2009).
5. L.C.F. Humphrey, C. Rodolphe, K.P. Annie and B. Sally, *Inorg. Chem.*, **50**, 4232 (2011).
6. (a) E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker and L. Deng, *J. Am. Chem. Soc.*, **113**, 7063 (1991); (b) T. Katsuki, *Coord. Chem. Rev.*, **140**, 189 (1995); (c) P. Zhang, M. Yang and X.P. Lu, *Asian J. Chem.*, **19**, 2083 (2007).
7. T. Mizuno, M. Takeuchi and S. Shinkai, *Tetrahedron*, **55**, 9455 (1999).
8. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).
9. S. Akine, T. Tadokoro and T. Nabeshima, *Inorg. Chem.*, **51**, 11478 (2012).
10. S. Akine, S. Hotate and T. Nabeshima, *J. Am. Chem. Soc.*, **133**, 13868 (2011).
11. (a) W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010); (b) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009); (c) 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); (d) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009); (e) W.K. Dong, C.Y. Zhao, Y.X. Sun, X.L. Tang and X.N. He, *Inorg. Chem. Commun.*, **12**, 234 (2009); (f) W.K. Dong, Y.X. Sun, X.N. He, J.F. Tong and J.C. Wu, *Spectrochim. Acta A*, **76**, 476 (2010); (g) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012); (h) W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012); (i) W.K. Dong, Y.X. Sun, G.H. Liu, L. Li, X.Y. Dong and X.H. Gao, *Z. Anorg. Allg. Chem.*, **638**, 1370 (2012).
12. S. Akine, T. Taniguchi, W.K. Dong and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
13. J.A. Faniran, K.S. Patel and J.C. Bailar Jr., *J. Inorg. Nucl. Chem.*, **36**, 1547 (1974).
14. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
15. H.E. Smith, *Chem. Rev.*, **83**, 359 (1983).