Asian Journal of Chemistry; Vol. 25, No. 15 (2013), 8759-8761

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15445

Synthesis and Characterization of Nitro Salamo-Type Bisoxime Compounds

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*: 7 March 2013; *Accepted*: 29 August 2013) AJC-14042

A series of nitro salamo-type bisoxime compounds have been synthesized from 2-hydroxy-5-nitrobenzaldehyde and 1,2-*bis*(aminooxy)-ethane, 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane or 1,5-*bis*(aminooxy)pentane in ethanol medium, respectively and characterized by elemental analyses as well as IR, UV-visible and ^{1}H NMR spectroscopy.

Key Words: Salamo-type bisoxime compound, Synthesis, Characterization.

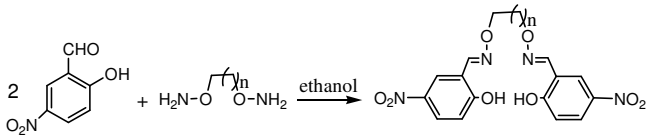
INTRODUCTION

The favourable ligand properties of tetradentate Schiff bases like salen (N,N'-*bis*(salicylidene)-1,2-ethylenediamine), salpr (N,N'-*bis*(salicylidene)-1,3-propanediamine), salbu (N,N'-*bis*(salicylidene)-1,4-butanediamine) and their derivatives have ensured continued interest in their metal complexes for many years[1-5]. Comparing the ligand properties of salen and its oxime-based analogue salamo, the salamo derivatives are at least 10^4 times more stable than salen derivatives and the large 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 complexes[6-9]. Thus, we have recently studied some novel salen-type bisoxime chelating compounds on the basis of O-alkyloxime moiety (-CH=N-O-$(CH_2)_n$-O-N=CH-) instead of the imine (-CH=N-$(CH_2)_n$-N=CH-) group[10]. Here we report the synthesis and characterization of a series of nitro-group substituted salamo-type bisoxime compounds.

EXPERIMENTAL

2-Hydroxy-5-nitrobenzaldehyde (≥ 98 %), 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane and 1,5-dibromopentane 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. ^{1}H 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: Synthetic route to salamo-type bisoxime compounds H_2L^1-H_2L^4 is shown in Fig. 1. 1,2-*Bis*-(aminooxy)ethane, 1,3-*bis*(aminooxy)propane, 1,4-*bis*-(aminooxy)butane and 1,5-*bis*(aminooxy)pentane were synthesized according to an analogous method reported earlier[7,10].



H_2L^1: n = 1; H_2L^2: n = 2; H_2L^3: n = 3; H_2L^4: n = 4

Fig. 1 Synthetic route to salamo-type bisoxime compounds H_2L^1-H_2L^4

Preparation of 4,4'-dinitro-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (5 mL) of 5-nitro-2-hydroxybenzaldehyde (157.1 mg, 1 mmol) was added an ethanol solution (2 mL) of 1,2-*bis*(aminooxy)ethane (45.1 mg, 0.50 mmol). After the solution had been stirred at 58 ºC for 2 h, when cooled to room temperature, the pale-yellow precipitate was filtered and washed successively with ethanol and ether, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to obtain white crystalline salamo compound H_2L^1.

Preparation of 4,4'-dinitro-2,2'-[(propylene-1,3-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^2): To an ethanolic solution (4 mL) of 5-nitro-2-hydroxybenzaldehyde

(157.3 mg, 1 mmol) was added an ethanolic solution (2 mL) of 1,3-*bis*(aminooxy)propane (53.2 mg, 0.50 mmol). The solution had been stirred at 58 ºC 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 white crystalline compound H_2L^2.

Preparation of 4,4'-dinitro-2,2'-[(1,4-butylenediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^3): To an ethanolic solution (4 mL) of 5-nitro-2-hydroxybenzaldehyde (167.4 mg, 1.00 mmol) was added an ethanolic solution (2 mL) of 1,4-*bis*(aminooxy)butane (60.0 mg, 0.50 mmol). After the solution had been stirred at 65 ºC for 5 h, the mixture was filtered, washed successively with ethanol and ether, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to obtain white crystalline compound H_2L^3.

Preparation of 4,4'-dinitro-2,2'-[(1,5-propanediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^4): To an ethanolic solution (4 mL) of 5-nitro-2-hydroxybenzaldehyde (157.6 mg, 1.00 mmol) was added an ethanolic solution (2 mL) of 1,5-*bis*(aminooxy)pentane (68.0 mg, 0.50 mmol). After the solution had been stirred at 55 ºC for 4 h, the mixture was filtered, washed successively with ethanol and ether, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to obtain white crystalline title compound H_2L^4.

RESULTS AND DISCUSSION

A series of salamo-type bisoxime compounds 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 ^{1}H 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 pale yellow or white microcrystalline solid, stable in air and soluble in acetone, chloroform, dichloromethane, tetrahydrofuran, ethyl acetate, acetonitrile, 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 of the salamo-type bisoxime compounds H_2L^1-H_2L^4 are given in Table-2. In the IR spectra of the H_2L^1-H_2L^4, the bands due to characteristic C=N stretching absorption bands appear[11] at 1614-1609 cm^{-1}. The Ar-O stretching frequencies appear within 1233-1245 cm^{-1} as reported for similar bisoxime compounds[12]. 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 *ca*. 3424 cm^{-1} because of the internal hydrogen bond OH···N=C[10] here a strong band at 3439-3429 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 1596-1457 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations.

UV-visible spectra and ^{1}H NMR data: The UV-visible spectra of 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 275 and 320 nm. The former absorption peak at about 275 nm can be assigned to the π-π^* transition of the benzene rings, while the latter can be attributed to the intra-ligand π–π^* transition of the C=N bonds[13].

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF SYNTHESIZED BISOXIME COMPOUNDS (H_2L^1-H_2L^4)

Compound	Colour	m.p. (ºC)	Yield(%)	m.f.(m.w.)	Elemental analysis (%):Found (calcd.)		
					C	H	N
H_2L^1	Pale yellow	202-203	83.3	$C_{16}H_{14}N_4O_8$ (390.3)	49.12(49.24)	3.59(3.62)	14.32(14.35)
H_2L^2	White	184.5-185.5	81.6	$C_{17}H_{16}N_4O_8$(404.3)	50.38(50.50)	3.93(3.99)	13.84(13.86)
H_2L^3	White	189.5-190.5	76.6	$C_{18}H_{18}N_4O_8$(418.4)	51.62(51.68)	4.30(4.34)	13.34(13.39)
H_2L^4	White	139.5-140.5	73.2	$C_{19}H_{20}N_4O_8$(432.4)	52.74(52.78)	4.63(4.66)	12.92(12.96)

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

Compound	ν(O-H)	ν(Ar-O)	ν(C=N)	ν(C-C)$_{\text{benzene ring}}$	ν(CH$_{\text{arom}}$)	ν(CH$_2$)
H_2L^1	3435	1236	1613	1573,1521, 1483	3087	2987,2891
H_2L^2	3429	1233	1614	1580,1542, 1471	3093	2941,2880
H_2L^3	3439	1245	1609	1592,1548, 1467	3095	2953,2880
H_2L^4	3433	1241	1609	1596,1543, 1458	3096	2953,2880

TABLE-3
UV-VIS SPECTRA AND ^{1}H NMR DATA OF THE SALAMO-TYPE BISOXIME COMPOUNDS (H_2L^1-H_2L^4)

Compound	π- π* (nm)	^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm)
H_2L^1	275, 318	4.43 (s, 4H), 7.01 (d, *J* = 9.2 Hz, 2H), 8.10 (dd, *J* = 9.2, 2.6 Hz, 2H), 8.34 (d, *J* = 2.6 Hz, 2H), 8.36 (s, 2H), 10.20 (s, 2H)
H_2L^2	275, 318	2.38 (d, *J* = 8.8 Hz, 2H), 4.40 (s, 4H), 6.98 (d, *J* = 9.0 Hz, 2H), 8.08 (dd, *J* = 9.0, 2.8 Hz, 2H), 8.25 (d, *J* = 2.4 Hz, 2H), 8.30 (s, 2H), 9.98 (s, 2H)
H_2L^3	276, 320	2.43 (s, 4H), 4.38 (s, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.89 (dd, *J* = 8.6, 2.4 Hz, 2H), 8.24 (d, *J* = 2.6 Hz, 2H), 8.29 (s, 2H), 9.95 (s, 2H)
H_2L^4	276, 320	2.40 (d, *J* = 7.8 Hz, 2H), 2.48 (s, 4H), 4.26 (s, 4H), 6.90 (d, *J* = 7.6 Hz, 2H), 7.78 (dd, *J* = 8.0, 2.6 Hz, 2H), 8.20 (d, *J* = 2.6 Hz, 2H), 8.24 (s, 2H), 9.90 (s, 2H)

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[14,15].

The ^{1}H NMR spectra of H_2L^1-H_2L^4 in DMSO-d_6 are shown in Table-3. The ^{1}H NMR spectra showed a singlet at *ca.* 8.24-8.36 ppm indicating the the existence of oxime bonds[15].

Conclusion

A new series of 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 1,2-*bis*(aminooxy)ethane, 1,3-*bis*(aminooxy)propane, 1,4-*bis*(aminooxy)butane or 1,5-*bis*(aminooxy)pentane under mild conditions, respectively. The salamo-type compounds may be promising units for the construction of supramolecular complexes.

REFERENCES

1. P.A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, **252**, 1871 (2008).
2. Y. Sui, D.P. Li, C.H. Li, X.H. Zhou, T. Wu and X.Z. You, *Inorg. Chem.*, **49**, 1286 (2010).
3. C. Meermann and K.W. Törnroos, *Inorg. Chem.*, **48**, 2561 (2009).
4. T.K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem.*, **50**, 2720 (2011).
5. R.M. Haak, A. Decortes, E.C. Escudero-Adán, M.M. Belmonte, E. Martin, J. Benet-Buchholz and A.W. Kleij, *Inorg. Chem.*, **50**, 7934 (2011).
6. S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem. Int. Ed.*, **41**, 4670 (2002).
7. S. Akine, W.K. Dong and T. Nabeshima, *Inorg. Chem.*, **45**, 4677 (2006).
8. S. Akine, T. Tadokoro and T. Nabeshima, *Inorg. Chem.*, **51**, 11478 (2012).
9. S. Akine, S. Hotate and T. Nabeshima, *J. Am. Chem. Soc.*, **133**, 13868 (2011); Li Zhao, Y.-J. Zhang, S.-T. Zhang, H.-X. Guo and Q. Cheng, *Asian J. Chem.*, **25**, 4678 (2013).
10. (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, L. Wang, Y.X. Sun, J.F. Tong and J.C. Wu, *Chinese J. Inorg. Chem.*, **27**, 372 (2011); (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); (j) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012); (k) W.K. Dong and Y.J. Ding, *Cryst. Res. Technol.*, **43**, 321 (2008).
11. S. Akine, T. Taniguchi, W.K. Dong and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
12. J.A. Faniran, K.S. Patel and J.C. Bailar Jr., *J. Inorg. Nucl. Chem.*, **36**, 1547 (1974).
13. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
14. H.E. Smith, *Chem. Rev.*, **83**, 359 (1983).
15. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).