



Synthesis and Characterization of Multihalogen Substituted Salamo-Type Bisoximes

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Received: 17 June 2013;

Accepted: 23 July 2013;

Published online: 26 December 2013;

AJC-14525

Four tetrahalogen substituted Salamo-type bisoximes $H_2L^1-H_2L^4$ have been synthesized from 3-bromo-5-chloro-2-hydroxybenzaldehyde and 1,3-bis(aminoxime)propane, 1,4-bis(aminoxime)butane, 1,5-bis(aminoxime)pentane or 1,6-bis(aminoxime)hexane in ethanol solution, respectively and characterized by elemental analyses as well as IR, UV-visible and 1H NMR spectroscopy.

Keywords: Salamo-type bisoxime, Synthesis, Characterization.

INTRODUCTION

Recently, the design and synthesis of multimetallic complexes has been actively investigated because of not only their unique and attractive structures but also their diverse applications such as optical materials¹, magnetic materials^{2,3}, catalysts for organic reactions^{4,5} and multimetalloceptors^{6,7}. Among the various metal clusters, Salen (*N,N'*-bis(salicylidene)-1,2-ethylenediamine) and its analogues have been utilized as ligands to form multimetallic complexes because they are multidentate ligands having an O_2 coordination site besides an N_2O_2 site⁸⁻¹². 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 complexes¹³⁻¹⁶. Thus, we have recently studied some novel Salamo-type chelating compounds on the basis of O-alkyloxime moiety ($-CH=N-O-(CH_2)_n-O-N=CH-$) instead of the imine ($-CH=N-(CH_2)_n-N=CH-$) group¹⁷. Here we report the synthesis and characterization of a series of tetrahalogen substituted Salamo-type compounds.

EXPERIMENTAL

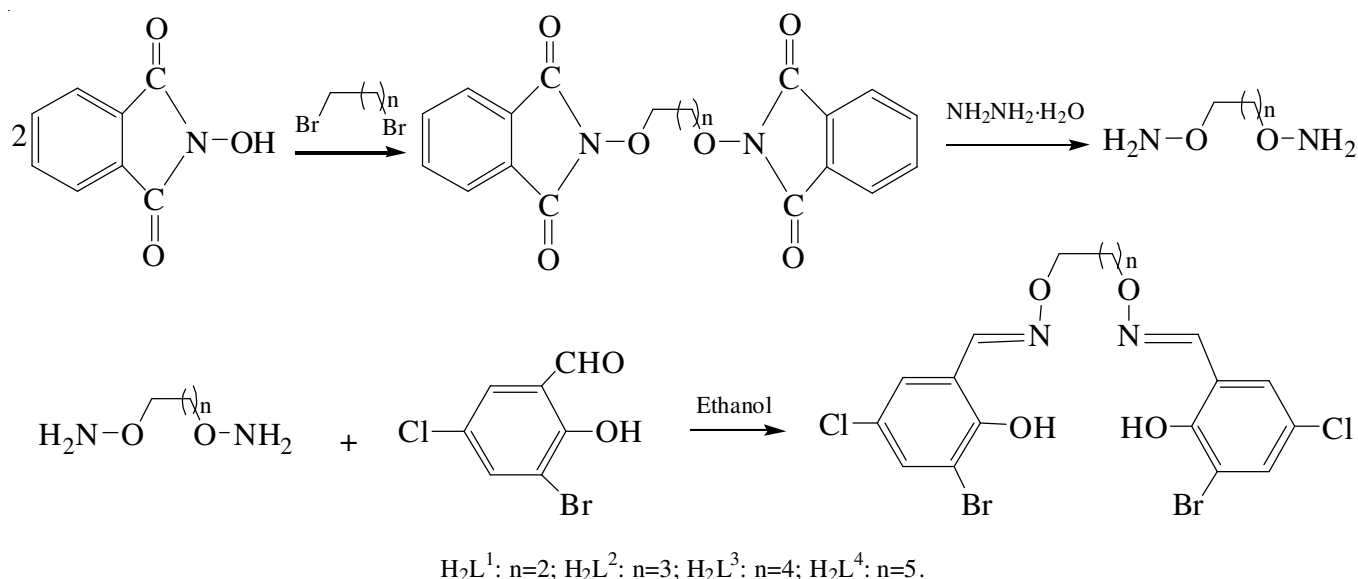
3-Bromo-5-chloro-2-hydroxybenzaldehyde ($\geq 99\%$), 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane and 1,6-dibromohexane were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. 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 Taikhe Instrument Limited Company and the thermometer was uncorrected.

General procedure: 1,3-Bis(aminoxime)propane, 1,4-bis(aminoxime)butane, 1,5-bis(aminoxime)pentane and 1,6-bis(aminoxime)hexane were synthesized according to an analogo method reported earlier^{13,17}. Synthetic route to Salamo-type bisoxime compounds $H_2L^1-H_2L^4$ is shown in **Scheme-I**.

4,4'-Dichloro-6,6'-dibromo-2,2'-[(propylene-1,3-diylidioxo)bis(nitrilomethylidene)]diphenol (H_2L^1): To an ethanolic solution (8 ml) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (235.5 mg, 1 mmol) was added an ethanolic solution (5 mL) of 1,3-bis(aminoxime)propane (53.0 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 2 h, When cooled to room temperature, the pale-yellow precipitate was filtered and washed successively with ethanol/hexane (1:4) and hexane, respectively. The product was dried under reduced pressure and obtained white crystalline compound (H_2L^1).

4,4'-Dichloro-6,6'-dibromo-2,2'-[(butylene-1,4-diylidioxo)bis(nitrilomethylidene)]diphenol (H_2L^2): To an ethanolic solution (6 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (242 mg, 1.03 mmol) was added an ethanolic solution (4 mL) of 1,4-bis(aminoxime)butane (61 mg, 0.51 mmol). After the solution had been stirred at 55 °C for 3 h, the formed precipitate was separated by filtration and washed successively with ethanol/hexane (1:4) and hexane, respectively. The product was dried under reduced pressure to obtain white crystalline compound (H_2L^2).

Scheme-I: Synthetic route to salamo-type bisoximes H_2L^1 - H_2L^4 .

4,4'-Dichloro-6,6'-dibromo-2,2'-[(propane-1,5-diylidioxo)bis(nitrilome-thylidyne)]diphenol (H_2L^3): To an ethanolic solution (5 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (176.6 mg, 0.75 mmol) was added an ethanolic solution (3 mL) of 1,5-bis(aminoxy)pentane (49.0 mg, 0.37 mmol). After the solution had been stirred at 55 °C for 5 h, the mixture was filtered, washed successively with ethanol/hexane and hexane, respectively. The product was dried under reduced pressure and obtained white crystalline compound (H_2L^3).

4,4'-Dichloro-6,6'-dibromo-2,2'-[(hexane-1,6-diylidioxo)bis(nitrilomethylidyne)]diphenol (H_2L^4): To an ethanolic solution (6 mL) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (158 mg, 0.67 mmol) was added an ethanolic solution (2 mL) of 1,6-bis(aminoxy)hexane (49 mg, 0.33 mmol). After the solution had been stirred at 55 °C for 4 h, the mixture was filtered, washed successively with ethanol/hexane (1:4) and hexane, respectively. The product was dried under reduced pressure and obtained white crystalline 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 ^1H NMR data.

The colour, yields, melting points and elemental analytical results of the synthesized compounds H_2L^1 - H_2L^4 are presented in Table-1. Their compositions agree with the formulae. All the compounds are white microcrystalline solid, stable in air

and soluble in DMF and DMSO, insoluble in methanol, ethanol, *n*-hexane, ether and water. In addition, H_2L^1 and H_2L^2 are soluble in hot acetone, acetonitrile, chloroform, dichloromethane and tetrahydrofuran, but H_2L^3 and H_2L^4 are insoluble in hot acetone, acetonitrile, chloroform, dichloromethane and tetrahydrofuran.

IR spectra of H_2L^1 - H_2L^4 are given in Figs. 1-4, respectively. In the IR spectra of H_2L^1 - H_2L^4 , the bands due to characteristic C=N stretching absorption bands appear at 1606-1604 cm^{-1} , respectively¹⁸. The Ar-O stretching frequencies appear within 1272-1251 cm^{-1} as reported for similar bisoxime compounds¹⁹. These provide evidence for the formation of the present compounds. The O-H stretching frequency of the bisoxime compounds is expected in the 3800-3300 cm^{-1} region, but this frequency is generally displaced to 3424 cm^{-1} because of the internal hydrogen bond $\text{OH}\cdots\text{N}=\text{C}$ ¹⁷. Here a strong band at 3429 cm^{-1} was observed in H_2L^1 - H_2L^4 and assigned to phenolic alcohol stretching absorption bands. In addition, in the 1481-1433 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations.

The UV-visible spectra of the compounds H_2L^1 - H_2L^4 in 5×10^{-5} DMF solution are presented in Table-2. UV-visible spectra of the compounds H_2L^1 - H_2L^4 exhibit two intense peaks at around 278 and 321 nm. The former absorption peak at about 278 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 bonds²⁰. 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 ^{21,22}.

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

Comp.	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (calcd.)		
					C	H	N
H_2L^1	White	232-234	72.6	$\text{C}_{17}\text{H}_{14}\text{Br}_2\text{Cl}_2\text{N}_2\text{O}_4$ (541.0)	37.92 (37.74)	2.69 (2.61)	5.21 (5.18)
H_2L^2	White	210-212	70.8	$\text{C}_{18}\text{H}_{16}\text{Br}_2\text{Cl}_2\text{N}_2\text{O}_4$ (555.0)	39.71 (39.95)	2.97 (2.91)	5.06 (5.05)
H_2L^3	White	215-216	68.2	$\text{C}_{19}\text{H}_{18}\text{Br}_2\text{Cl}_2\text{N}_2\text{O}_4$ (569.1)	40.04 (40.10)	3.22 (3.19)	4.93 (4.92)
H_2L^4	White	220-221	75.4	$\text{C}_{20}\text{H}_{20}\text{Br}_2\text{Cl}_2\text{N}_2\text{O}_4$ (583.1)	41.35 (41.20)	3.21 (3.46)	4.88 (4.80)

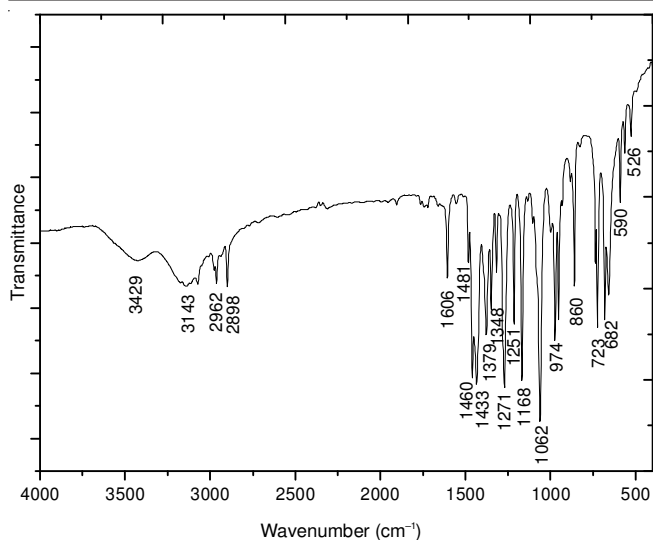
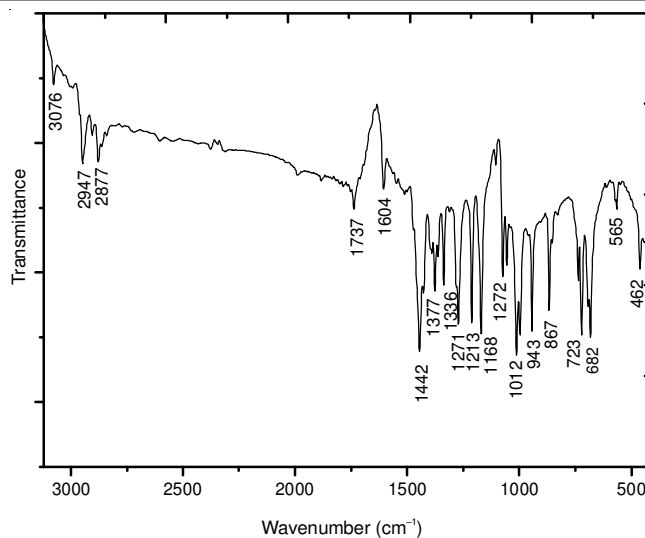
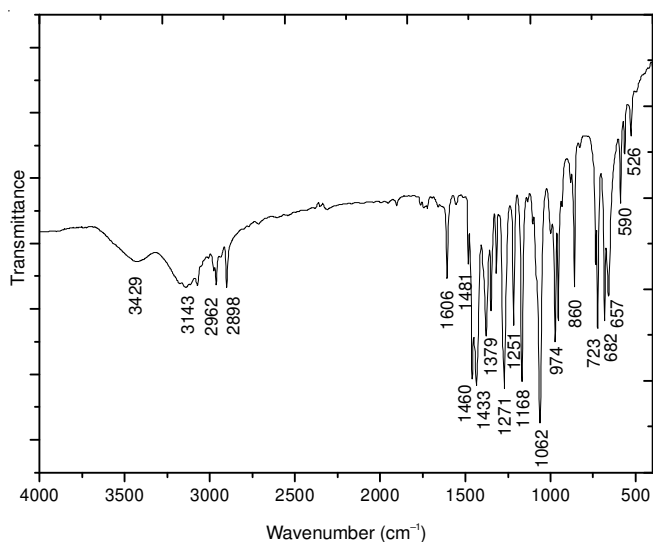
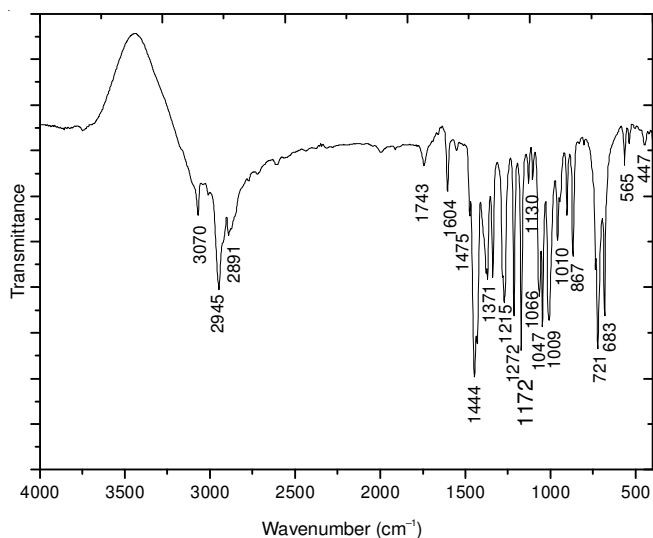
Fig. 1. IR spectrum of H_2L^1 Fig. 4. IR spectrum of H_2L^4 Fig. 2. IR spectrum of H_2L^2 Fig. 3. IR spectrum of H_2L^3

TABLE-2

 1H NMR DATA FOR THE SALAMO-TYPE BISOXIMES H_2L^1 - H_2L^4

Comp.	π - π^* (nm)	1H NMR (400 MHz, DMSO- d_6 , δ /ppm)
H_2L^1	278, 321	2.38 (d, $J = 8.8$ Hz, 2H), 4.48 (s, 4H), 7.56 (d, $J = 2.4$ Hz, 2H), 7.74 (d, $J = 2.4$ Hz, 2H), 8.26 (s, 2H), 10.39 (s, 2H).
H_2L^2	278, 321	2.36 (d, $J = 8.6$ Hz, 4H), 4.46 (s, 4H), 7.55 (d, $J = 2.2$ Hz, 2H), 7.72 (d, $J = 2.2$ Hz, 2H), 8.25 (s, 2H), 10.20 (s, 2H).
H_2L^3	279, 323	2.33 (s, 2H), 2.36 (d, $J = 8.7$ Hz, 4H), 4.45 (s, 4H), 7.54 (d, $J = 2.0$ Hz, 2H), 7.71 (d, $J = 2.2$ Hz, 2H), 8.24 (s, 2H), 10.12 (s, 2H).
H_2L^4	279, 325	2.32 (s, 4H), 2.35 (d, $J = 8.0$ Hz, 4H), 4.44 (s, 4H), 7.54 (d, $J = 2.0$ Hz, 2H), 7.70 (d, $J = 2.2$ Hz, 2H), 8.24 (s, 2H), 10.02 (s, 2H).

The 1H NMR spectra of the compounds H_2L^1 - H_2L^4 in DMSO- d_6 are shown in Table-2. The 1H NMR spectra showed a singlet at about 8.24-8.26 ppm indicating the existence of oxime bonds¹⁵.

Conclusion

Four new 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-bromo-5-chloro-2-hydroxybenzaldehyde with 1,3-bis(aminoxy)propane, 1,4-bis(aminoxy)butane, 1,5-bis(aminoxy)pentane or 1,6-bis(aminoxy)hexane under mild conditions, respectively. The synthesized Salamo-type compounds may be promising units for the construction of supramolecular complexes.

REFERENCES

- V. Balzani and S. Campagna, Photochemistry and Photophysics of Coordination Compounds II, Springer: Berlin (2007).
- R. Bagai and G. Christou, *Chem. Soc. Rev.*, **38**, 1011 (2009).
- D. Gatteschi and R. Sessoli, *Angew. Chem. Int. Ed.*, **42**, 268 (2003).
- M. Shibasaki and Y. Yamamoto, *Multimetallic Catalysts in Organic Synthesis*, Wiley-VCH: Weinheim, Germany (2004).
- E.N. Jacobsen, in ed.: I. Ojima, In *Catalytic Asymmetric Synthesis*; VCH: New York (1993).
- A. Robertson and S. Shinkai, *Coord. Chem. Rev.* **205**, 157 (2000).
- P.D. Beer and E.J. Hayes, *Coord. Chem. Rev.* **240**, 167 (2003).
- S.J. Wezenberg and A.W. Kleij, *Angew. Chem. Int. Ed.*, **47**, 2354 (2008).
- A.W. Kleij, *Chem.-Eur. J.*, **14**, 10520 (2008).
- H.L.C. Feltham and S. Brooker, *Coord. Chem. Rev.* **253**, 1458 (2009).
- A.W. Kleij, *Dalton Trans.*, 4635 (2009).

12. S. Akine and T. Nabeshima, *Dalton Trans.*, 10395 (2009).
13. S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem. Int. Ed.*, **41**, 4670 (2002).
14. S. Akine, W.K. Dong and T. Nabeshima, *Inorg. Chem.*, **45**, 4677 (2006).
15. S. Akine, T. Tadokoro and T. Nabeshima, *Inorg. Chem.*, **51**, 11478 (2012).
16. S. Akine, S. Hotate and T. Nabeshima, *J. Am. Chem. Soc.*, **133**, 13868 (2011).
17. (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).
18. S. Akine, T. Taniguchi, W.K. Dong and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
19. J.A. Faniran, K.S. Patel and J.C. Bailar Jr., *J. Inorg. Nucl. Chem.*, **36**, 1547 (1974).
20. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
21. H.E. Smith, *Chem. Rev.*, **83**, 359 (1983).
22. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).