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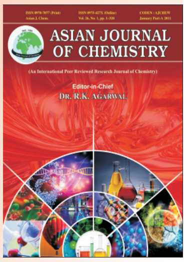

Synthesis and Characterization of Four New Chloro-Group Substituted Salamo-Type Bisoxime Compounds

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A series of chloro-substituted Salamo-type bisoxime compounds 4,4',6,6'-tetrachloro-2.2'-[(1,7-heptanediyldioxy)*bis*(nitrilomethylidyne)] diphenol (H_2L^1), 4,4',6,6'-tetrachloro-2.2'-[(1,8-octanediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^2), 4,4',6,6'-tetrachloro-2.2'-[(1,9-nonanediyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^3) and 4,4',6,6'-tetrachloro-2.2'-[(1,10-decanediyldioxy)bis(nitrilomethylidyne)]diphenol (H_2L^4) have been synthesized and characterized by elemental analyses, IR spectra, UV-visible and ^{1}H NMR spectroscopy. The chloro-group substitutied salamo-type bisoxime compounds H_2L^1-H_2L^4 may be a promising units for the construction of supramolecular complexes.

Keywords: Salamo-type bisoxime compound, Synthesis.

INTRODUCTION

The favourable ligand properties of tetradentate Schiff base Salen (*N*,*N*'-*bis*(salicylidene)-1,2-ethylenediamine) and their derivatives have ensured continued interest in their 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]. Herein, we have recently studied some novel Salen-type bisoxime chelating compounds on the basis of O-alkyloxime moiety (-CH=NO-$(CH_2)_n$-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 chloro-group substituted Salamo-type bisoxime compounds.

EXPERIMENTAL

3,5-Dichlorosalicylaldehyde was 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 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 chloro-group substitutied 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*(aminooxy)nonane and 1,10-*bis*(aminooxy) decane were synthesized according to an analogous method reported earlier[10].

4,4',6,6'-Tetrachloro-2.2'-[(1,7-heptanediyldioxy)*bis*-(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (5 mL) of 1,7-*bis*(aminooxy)heptane (146.7 mg, 1 mmol) was added an ethanolic solution (8 mL) of 3,5-dichloro-2-hydroxybenzaldehyde (382.2 mg, 2 mmol), a pale-yellow precipitation was obtained immediately. 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 ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain 338.4 mg pale-yellow title compound H_2L^1. Yield, 80.20 %. m.p. 100.0-101.0 °C.

4,4',6,6'-Tetrachloro-2.2'-[(1,8-octanediyldioxy)*bis*-(nitrilomethylidyne)]diphenol (H_2L^2): To an ethanolic solution (5 mL) of 1,8-*bis*(aminooxy)octane (161.71 mg, 1 mmol) was added an ethanolic solution (8 mL) of 3,5-dichloro-2-hydroxybenzaldehyde (380.7 mg, 1.99 mmol), a orange mixture was obtained immediately. After the solution had been stirred at 55 °C for 4 h. The formed precipitate was separated by filtration

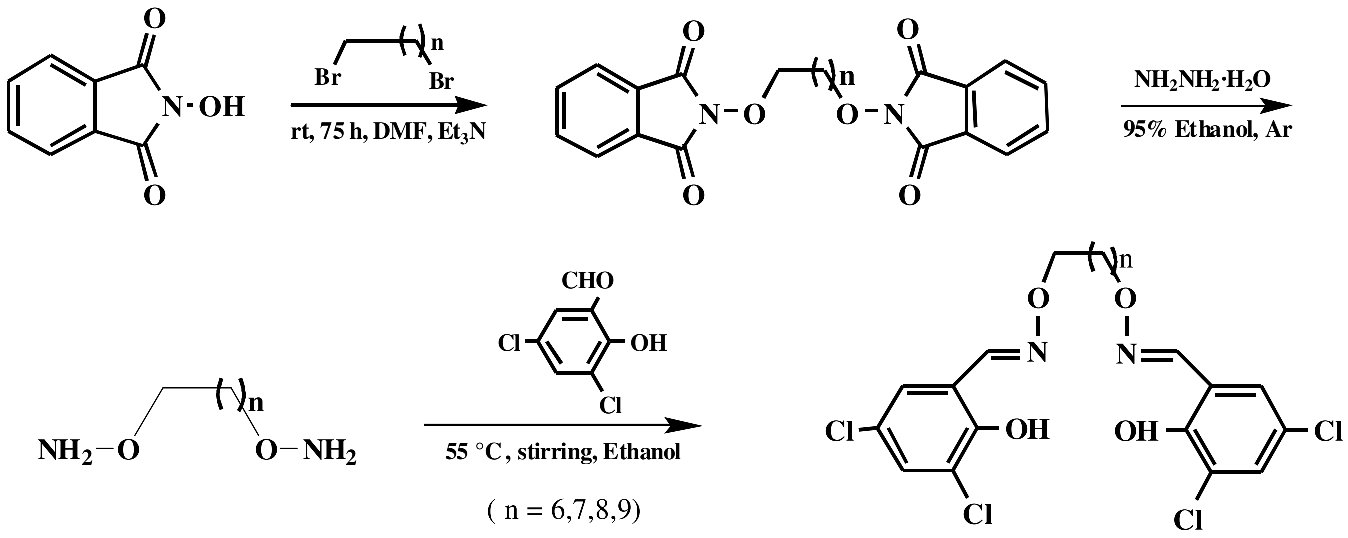

Fig. 1. Synthetic route to chloro-group substituted salamo-type bisoxime compounds (H_2L^1-H_2L^4)

and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain 371.8 mg yellow title compound H_2L^2. Yield, 71.50 %. m.p. 110.0-111.0 °C.

4,4',6,6'-Tetrachloro-2.2'-[(1,9-nonanediyldioxy)*bis* (nitrilomethylidyne)]diphenol (H_2L^3): To an ethanolic solution (5 mL) of 1,9-*bis*(aminooxy)nonane (51.9 mg, 0.27 mmol) was added an ethanolic solution (8 mL) of 3,5-dichloro-2-hydroxybenzaldehyde (104.2 mg, 0.55 mmol). After the pale-purple solution had been stirred at 55 °C for 4 h, precipitation was obtained and stirred for 6 h. The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain 105 mg white title compound H_2L^3. Yield, 72.80 %. m.p. 66.5-68.0 °C.

4,4',6,6'-Tetrachloro-2.2'-[(1,10-decanediyldioxy)*bis* (nitrilomethylidyne)]diphenol (H_2L^4): To an ethanolic solution (5 mL) of 1,10-*bis*(aminooxy)decane (203.8 mg, 0.99 mmol) was added an ethanolic solution (8 mL) of 3,5-dichloro-2-hydroxybenzaldehyde (382.6 mg, 2 mmol). The color of the mixing solution immediately turned pale-yellow and a white precipitation was obtained. After the solution had been stirred at 55 °C for 6 h, The formed precipitate was separated by filtration and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure to obtain 435.2 mg pale-yellow title compound H_2L^4. Yield, 80.20 %. m.p. 91.0-91.5 °C.

RESULTS AND DISCUSSION

A series of chloro-group Salamo-type bisoxime compounds H_2L^1, H_2L^2, H_2L^3 and H_2L^4 have been synthesized with high yields and the compositions 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 white microcrystalline solid, stable in air and soluble in hot DMF and DMSO, insoluble in methanol, ethanol, acetone, acetonitrile, chloroform, dichloromethane, tetrahydrofuran, *n*-hexane, ether and water.

IR spectra: IR spectra of the ligands H_2L^1, H_2L^2, H_2L^3 and H_2L^4 exhibit various bands from 4000 to 400 cm^{-1}. The IR spectral details of the ligand H_2L^1, H_2L^2, H_2L^3 and H_2L^4 are given in Table-2.

TABLE-2
IR SPECTRAL DATA (cm^{-1}) FOR H_2L^1, H_2L^2, H_2L^3 AND H_2L^4

Comp.	ν(C=N)	ν (Ar-O)	ν (O-H)	ν (C=C) benzene ring skeleton
H_2L^1	1607	1215	3431	1586, 1464, 1452
H_2L^2	1605	1209	3431	1582, 1447, 1452
H_2L^3	1607	1215	3433	1587, 1466, 1448
H_2L^4	1609	1209	3432	1585, 1463, 1445

The Ar-O stretching bands occur at 1215, 1209, 1215 and 1209 cm^{-1} for the ligands H_2L^1-H_2L^4, respectively[11]. And the characteristic C=N stretching bands of H_2L^1-H_2L^4 appear at 1609-1605 cm^{-1}, indicating that 3,5-dichloro-2-hydroxybenzaldehyde has been condensated with 1,7-*bis*(aminooxy)heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane and 1,10-*bis*(aminooxy)decane, respectively and formed new Salamo-type compounds[12]. In the 1587-1445 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations. In addition,

TABLE-1
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA FOR H_2L^1, H_2L^2, H_2L^3 AND H_2L^4

Comp.	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
H_2L^1	Pale-yellow	100-101	80.20	$C_{21}H_{22}N_2O_4Cl_4$ (508.22)	49.67 (49.63)	4.42 (4.36)	5.39 (5.51)
H_2L^2	Yellow	110-111	71.50	$C_{22}H_{24}N_2O_4Cl_4$ (522.25)	50.52 (50.60)	4.74 (4.63)	5.31 (5.36)
H_2L^3	White	66.5-68.0	72.80	$C_{23}H_{26}N_2O_4Cl_4$ (536.27)	51.49 (51.51)	4.95 (4.89)	5.17 (5.22)
H_2L^4	White	91.0-91.5	80.20	$C_{24}H_{28}N_2O_4Cl_4$ (550.30)	52.45 (52.38)	5.28 (5.31)	5.00 (5.09)

TABLE-4
^{1}H NMR DATA FOR H_2L^1, H_2L^2, H_2L^3 AND H_2L^4

Comp.	^{1}H NMR (400 MHz, DMSO-d_6, δppm)
H_2L^1	2.42-.50 (m, 10H), 4.45 (s, 4H), 7.55 (d, J = 2.0 Hz, 2H), 7.71 (d, J = 2.2 Hz, 2H), 8.45 (s, 2H), 9.95 (s, 2H)
H_2L^2	2.43-.51 (m, 12H), 4.45 (s, 4H), 7.52 (d, J = 2.0 Hz, 2H), 7.72 (d, J = 2.2 Hz, 2H), 8.46 (s, 2H), 9.85 (s, 2H)
H_2L^3	2.43-.53 (m, 14H), 4.43 (s, 4H), 7.52 (d, J = 2.0 Hz, 2H), 7.68 (d, J = 2.2 Hz, 2H), 8.41 (s, 2H), 9.76 (s, 2H)
H_2L^4	2.40-.54 (m, 16H), 4.43 (s, 4H), 7.50 (d, J = 2.0 Hz, 2H), 7.72 (d, J = 2.2 Hz, 2H), 8.43 (s, 2H), 9.77 (s, 2H)

the O-H stretching bands of the ligands at 3600-3200 cm^{-1} region disappear in the ligands and the strong absorption bands of the ligands appear at about 3431 cm^{-1}, which are the evidence for the existence of hydroxyl group in ligands[13]. IR spectral results of the ligands further confirmed the correctness of the target ligands.

UV-Vis spectra: The UV-visible spectra of the title compounds H_2L^1-H_2L^4 in 5 × 10^{-5} chloroform solution are shown in Table-3.

TABLE-3
UV-VISIBLE SPECTRA DATA FOR H_2L^1, H_2L^2, H_2L^3 AND H_2L^4

Comp.	C (×10^{-5} mol L^{-1})	First band λ_{max1} (nm)	Second band λ_{max2} (nm)
H_2L^1	5.02	275	313
H_2L^2	5.01	276	315
H_2L^3	5.03	278	318
H_2L^4	5.08	280	321

The absorption spectra of H_2L^1-H_2L^4 have small difference. Each ligand exhibits two intense peaks at 275 and 313 nm. The former absorption peaks can be assigned to the π-π* transition of the benzene rings, while the latters one can be attributed to the intra-ligand π-π* transition of the C=N bonds[13]. It is of note that there was no absorption at 400 nm, which is seen in the corresponding salen derivatives. The absorption is ascribed to the quinoid form of H_2 salen[14,15].

^{1}H NMR data: 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 8.41-8.46 ppm indicating the the existence of oxime bonds[14].

Conclusion

A new series of Salamo-type compounds H_2L^1-H_2L^4 possessing two oxime bonds instead of imine bonds have been designed and synthesized by the reaction of 2 equivalents of 3,5-dichloro-2-hydroxybenzaldehyde with 1,7-*bis*(aminooxy)-heptane, 1,8-*bis*(aminooxy)octane, 1,9-*bis*(aminooxy)nonane or 1,10-*bis*(aminooxy)decane under mild conditions, respectively. The Salamo-type compounds may be a promising units for the construction of supramolecular complexes.

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