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Synthesis and Structural Characterization of Bromo-Substituted Salamo-Type Bisoximes Based on *Bis*(aminooxy)alkane and 3,5-Dibromosalicylaldehyde

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A series of bromo-substituted Salamo-type bisoximes H_2L^1-H_2L^3 have been synthesized through condensation reactions of 3,5-dibromosalicylaldehyde with 1,2-*bis*(aminooxy)ethane, 1,3-*bis*(aminooxy)propane and 1,4-*bis*(aminooxy)butane in ethanol medium, respectively and characterized by elemental analyses, IR and ^{1}H NMR spectra. In the crystal structure of Salamo-type bisoximes H_2L^1, an infinite 1D supramolecular double chain-like structure is formed by intramolecular hydrogen bonds, π···π stacking interactions and intermolecular Br···Br halogen bondings.

Keywords: Synthesis, Salamo-type bisoxime, Characterization, Crystal structure.

INTRODUCTION

Oxime-type compounds have been widely studied for their prospective application in many fields, such as pharmacological, biological activity reagents, metallurgy, dyes and luminescent materials[1-4]. So, preparing more and more novel oxime-type compounds with different properties and applications are of great importance to the development of coordination chemistry. Especially, bisoxime compounds are being widely concerned because of the new molecular structure, using an *O*-alkyloxime unit [-CH=N-O-$(CH_2)_n$-O-N=CH-] instead of the [-CH=N-$(CH_2)_n$-N=CH-] group and have been used to preparing the neutral complexes with divalent transition metal ions[5]. The complexes not only display fluorescence properties, but can also trace the certain ions as the extracting reagents[6]. The oxygen atoms, in the molecular structure, possess strong electronegativity can lead to different and novel properties and structures of the resulting complexes by affecting strongly the electronic properties of the N_2O_2 coordination sphere[7-9]. Therefore, the researches of novel bisoxime-type complexes with different properties are great significance for the widely applications in scientific research and industrial development in the future[10]. In this article, we report the synthesis and characterization of three Salamo-type bisoximes from 3,5-dibromosalicylaldehyde and 1,2-*bis*(aminooxy)ethane, 1,3-*bis*(aminooxy)propane and 1,4-*bis*(aminooxy)butane molecules, 4,4',6,6'-tetrabromo-2.2'-[(ethylenedioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^1), 4,4',6,6'-tetrabromo-2.2'-[(propylene-1,3-diyldioxy)*bis*(nitrilomethylidyne)]-diphenol (H_2L^2), 4,4',6,6'-tetrabromo-2.2'-[(butylene-1,4-diyldioxy)*bis*(nitrilo-methylidyne)]diphenol (H_2L^3) and the crystal structure of Salamo-type bisoxime H_2L^1 has also been studied.

EXPERIMENTAL

3,5-Dibromosalicylaldehyde (≥ 98 %), 1,2-dibromoethane, 1,3-dibromopropane and 1,4-dibromobutane were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. The physical-chemical measurements are the same as literature early[11].

General procedure: Synthetic route to Salamo-type bisoximes H_2L^1-H_2L^3 are shown in Fig. 1. 1,2-*Bis*(aminooxy)-ethane, 1,3-*bis*(aminooxy)propane and 1,4-*bis*(aminooxy)butane were synthesized according to an analogous method reported earlier[11].

Preparation of 4,4',6,6'-tetrabromo-2.2'-[(ethylenedioxy)-*bis*(nitrilomethylidyne)]diphenol (H_2L^1): To an ethanolic solution (5 mL) of 3,5-dibromosalicylaldehyde (559.9 mg, 2 mmol) was added a ethanol solution (5 mL) of 1,2-*bis*(aminooxy)ethane (92.1 mg, 1 mmol). After the solution had been stirred at 55 °C for 3 h, then cooled to room temperature, 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 white powder H_2L^1. Yield, 78.6 %. m.p. 462-462.5 K.

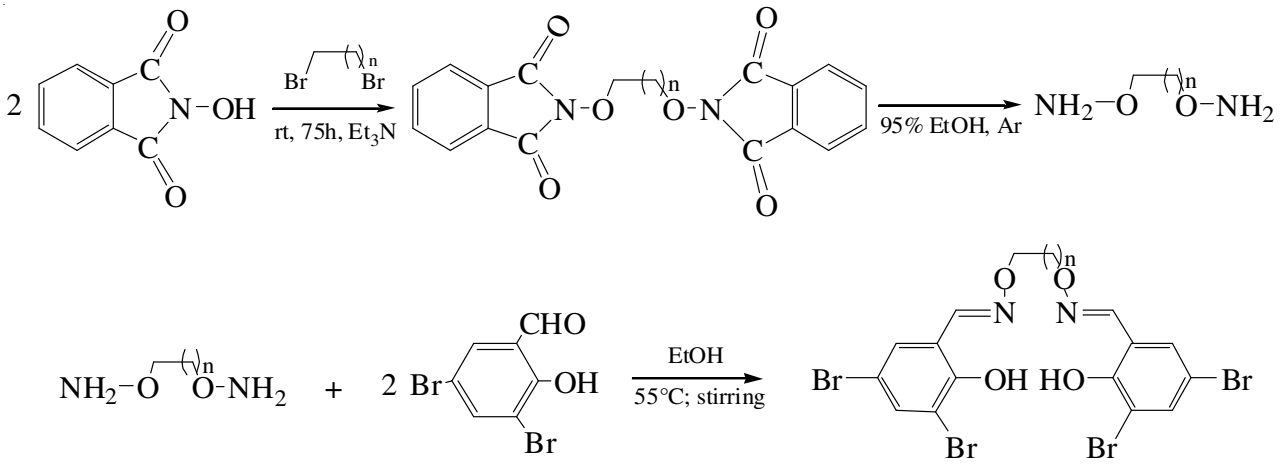

Fig. 1. Synthetic route to Salamo-type bisoxime compounds H_2L^1-H_2L^3 (n = 1-3)

Preparation of 4,4',6,6'-tetrabromo-2.2'-[(propylene-1,3-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^2): To an ethanolic solution (5 mL) of 3,5-dibromosalicylaldehyde (559.9 mg, 2 mmol) was added ethanolic solution (5 mL) of 1,3-*bis*(aminooxy)propane (106.1 mg, 1 mmol). After the solution had been stirred at 55 °C for 3 h, then cooled to room temperature, 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 white powder H_2L^2, Yield, 81.4 %. m.p. 515-516 K.

Preparation of 4,4',6,6'-tetrabromo-2.2'-[(butylene-1,4-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_2L^3): To a ethanol solution (10 mL) of 3,5-dibromosalicylaldehyde (559.9 mg, 2 mmol) was added a ethanol solution (5 mL) of 1,4-*bis*(aminooxy)butane (11.2 mg, 1 mmol). After the solution had been stirred at 55 °C for 3 h, then cooled to room temperature, 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 white powder H_2L^3, Yield, 78.7 %. m.p. 487-488 K.

X-Ray structure determination of Salamo-type bisoximes H_2L^1: The crystal data and structure refinement for the title compound H_2L^1 are given in Table-1.

The single crystal of the title compound H_2L^1 with the approximate dimensions of 0.37 × 0.24 × 0.17 mm was placed on a Bruker Smart 1000 CCD area detector. The reflections were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXL-97 and Fourier difference techniques and refined by the full-matrix least-squares method on F^2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. CCDC: 987936.

RESULTS AND DISCUSSION

A series of new Salamo-type bisoximes H_2L^1-H_2L^3 have been synthesized and the composition are confirmed by elemental analyses, IR, UV-visible and ^{1}H NMR spectra.

Physical and chemistry property of Salamo-type bisoximes H_2L^1-H_2L^3: The colour, yields and elemental analytical results of the synthesized Salamo-type bisoximes H_2L^1-H_2L^3 are presented in Table-2.

Salamo-type bisoxime H_2L^1 is a white solid, stable in air and slightly soluble in chloroform, insoluble in methanol and

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND H_2L^1

Empirical formula	$C_{16}H_{12}Br_4N_2O_4$
Formula weight	615.89
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	a = 9.252(1), b = 9.345(1), c = 11.888(1), α = 110.007(2), β = 92.363(1), γ = 94.727(1)
Volume (Å^3)	959.9(2)
Z	2
Density (calculated) (mg/m^3)	2.134
Absorption coefficient (mm^{-1})	2.415
$F_{(000)}$	596
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14
Reflections collected	6135/3384 [R(int) = 0.0729]
Independent reflections	1724
Data/restraints/parameters	3384/0/236
Goodness of fit indicator	1.024
R [I > 2σ(I)]	R_1 = 0.0361, wR_2 = 0.1012
Largest diff. peak and hole (e Å^{-3})	1.198 and -1.036

TABLE-2
COLOUR, YIELDS, MELTING POINTS AND ANALYTICAL DATA OF SALAMO-TYPE BISOXIMES H_2L^1-$_2L^3$

Comp.	Colour	m.p. (K)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
					C	H	N
H_2L^1	White	462-462.5	78.6	$C_{16}H_{12}N_2O_4Br_4$ (615.9)	31.18 (31.20)	1.93 (1.96)	4.57 (4.55)
H_2L^2	White	515-516	81.4	$C_{17}H_{14}N_2O_4Br_4$ (629.9)	32.44 (32.41)	2.23 (2.24)	4.43 (4.45)
H_2L^3	White	487-488	78.7	$C_{18}H_{16}N_2O_4Br_4$ (643.9)	33.53 (33.57)	2.48 (2.50)	4.39 (4.35)

ethanol. Salamo-type bisoxime H_2L^2 is a white solid, stable in air and soluble in THF, DMF and DMSO, slightly soluble in chloroform, insoluble in methanol, ethanol, acetone and acetonitrile. Salamo-type bisoxime H_2L^3 is a white solid, stable in air and soluble in DMF, DMSO and THF, insoluble in methanol, ethanol, acetone and acetonitrile. The elemental analysis data and the composition of the ligands show that the elemental analysis data of Salamo-type bisoximes H_2L^1-H_2L^3 close to the theoretical value, prove their compositions agree with the given formulae.

IR spectra of Salamo-type bisoximes H_2L^1-H_2L^3: The most important IR spectra data for Salamo-type bisoximes H_2L^1-H_2L^3 are given in Table-3.

In the IR spectra of Salamo-type bisoximes H_2L^1-H_2L^3, an O-H stretching band appears at 3438-3431 cm^{-1}, which is the evidence for the existence of associating hydroxyl group in Salamo-type bisoximes H_2L^1-H_2L^3 [11]. In the 1559-1425 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations. In addition, a characteristic C=N stretching band of Salamo-type bisoximes H_2L^1-H_2L^3 appears at 1608-1605 cm^{-1}, respectively[11]. And a strong Ar-O stretching band in Salamo-type bisoximes H_2L^1-H_2L^3 occurs at 1269, 1273 and 1271 cm^{-1}, respectively, indicating that 3,5-dibromosalicylaldehyde has been condensated with 1,2-*bis*(aminooxy)ethane 1,3-*bis*(aminooxy)propane and 1,4-*bis*(aminooxy)butane, respectively and formed new Salamo-type bisoximes[11]. IR spectral results of Salamo-type bisoximes H_2L^1-H_2L^3 further confirmed the correctness of the target compounds.

^{1}H NMR spectra of Salamo-type bisoximes H_2L^1-H_2L^3: The ^{1}H NMR spectra of Salamo-type bisoximes H_2L^1-H_2L^3 in DMSO-d_6 are shown in Table-4. The ^{1}H NMR spectra shows a singlet at about 8.44-8.47 ppm indicating the existence of oxime bonds[12].

Crystal structure of Salamo-type bisoxime H_2L^1: ORTEP representation of Salamo-type bisoxime H_2L^1 is shown in Fig. 2. Selected bond lengths and angles are listed in Table-5.

In the crystal structure, two intramolecular O3-H3···N1 and O4-H4···N2 hydrogen bonds involving the hydroxyl groups and oxime N atoms generate S(6) ring motifs in each molecule (Table-6). Moreover, a pair of intermolecular Br···Br halogen bondings link two neighbouring molecules into a 1D chain, in which the Br-Br distance is 3.643(2) Å. In addition,

TABLE-3
KEY IR SPECTRAL BANDS (cm^{-1}) FOR SALAMO-TYPE BISOXIMES H_2L^1-H_2L^3

Compound	ν (O-H)	ν (CH_2)	ν (C=N)	ν (C-C)	ν (Ar-O)
H_2L^1	3431	2955, 2893	1605	1552, 1479, 1458	1269
H_2L^2	3438	2955, 2889	1603	1555, 1458, 1425	1273
H_2L^3	3437	2945, 2885	1604	1559, 1474, 1445	1271

TABLE-4
^{1}H NMR DATA FOR SALAMO-TYPE BISOXIMES H_2L^1-H_2L^3

Compound	^{1}H NMR (400 MHz, DMSO-d_6, δ/ppm)
H_2L^1	4.49 (s, 4H, CH_2-O), 7.68 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.82 (d, *J* = 2.4 Hz, 2H, Ar-H), 8.47 (s, 2H, N=CH), 10.43 (s, 2H, OH)
H_2L^2	2.45-2.51 (m, 2H, CH_2), 4.48 (s, 4H, CH_2-O), 7.66 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.80 (d, *J* = 2.4 Hz, 2H, Ar-H), 8.45 (s, 2H, N=CH), 10.40 (s, 2H, OH)
H_2L^3	2.46-2.56 (m, 4H, CH_2), 4.50 (s, 4H, CH_2-O), 7.67 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.81 (d, *J* = 2.4 Hz, 2H, Ar-H), 8.44 (s, 2H, N=CH), 10.41 (s, 2H, OH)

TABLE-5
SELECTED BOND LENGTHS (Å) AND ANGLES (º) FOR SALAMO-TYPE BISOXIME H_2L^1

Bond	Lengths	Bond	Lengths	Bond	Lengths
Br1-C6	1.89(2)	Br2-C8	1.89(2)	Br3-C13	1.90(2)
Br4-C15	1.90(2)	N1-C3	1.27(2)	N1-O1	1.38(2)
N2-C10	1.28(2)	N2-O2	1.41(2)	O1-C1	1.43(3)
O2-C2	1.43(3)	O3-C5	1.35(2)	O4-C12	1.34(3)
C1-C2	1.54(2)	C3-C4	1.45(2)	C4-C5	1.41(2)
C4-C9	1.42(2)	C5-C6	1.38(2)	C6-C7	1.39(2)
C7-C8	1.36(2)	C8-C9	1.39(2)	C10-C11	1.43(2)
C11-C16	1.41(2)	C11-C12	1.45(2)	C12-C13	1.36(2)
C13-C14	1.37(2)	C14-C15	1.40(2)	C15-C16	1.35(2)
Bond	Angles	Bond	Angles	Bond	Angles
C3-N1-O1	112.4(3)	C10-N2-O2	109.7(3)	N1-O1-C1	109.2(3)
N2-O2-C2	109.9(3)	O1-C1-C2	110.1(3)	O2-C2-C1	112.4(3)
N1-C3-C4	122.0(3)	C5-C4-C9	119.7(3)	C5-C4-C3	121.1(3)
C9-C4-C3	119.2(3)	O3-C5-C6	119.0(3)	O3-C5-C4	122.7(3)
C6-C5-C4	118.3(3)	C5-C6-C7	122.1(3)	C5-C6-Br1	118.5(3)
C7-C6-Br1	119.2(3)	C8-C7-C6	119.0(3)	C7-C8-C9	122.3(3)
C7-C8-Br2	118.6(3)	C9-C8-Br2	119.1(3)	C8-C9-C4	118.4(3)
N2-C10-C11	121.2(3)	C16-C11-C10	119.2(3)	C16-C11-C12	116.7(3)
C10-C11-C12	124.0(3)	O4-C12-C13	122.5(3)	O4-C12-C11	119.2(3)
C13-C12-C11	118.2(3)	C12-C13-C14	124.1(3)	C12-C13-Br3	116.8(3)
C14-C13-Br3	119.1(3)	C13-C14-C15	117.7(3)	C16-C15-C14	121.1(3)
C16-C15-Br4	119.0(3)	C14-C15-Br4	119.9(3)	C15-C16-C11	121.9(3)

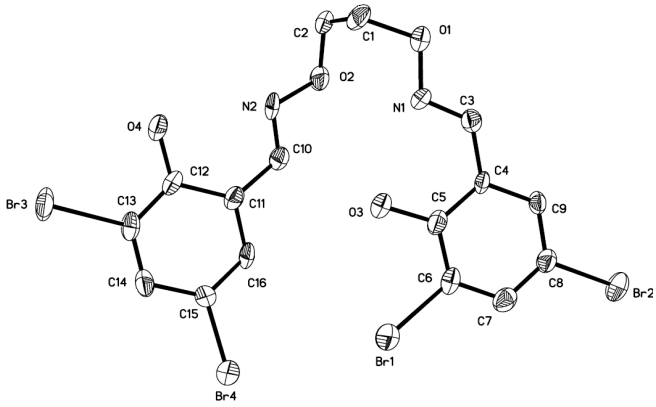

Fig. 2. ORTEP-style drawing of Salamo-type bisoxime H_2L^1

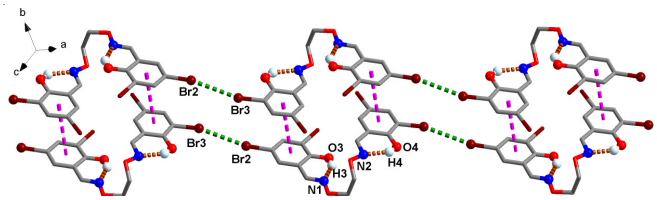

Fig. 3. View of an infinite 1D supramolecular double chain-like structure formed by intramolecular hydrogen bonds, π···π stacking interactions and intermolecular Br···Br halogen bondings

two formed 1D chains are held together to form an infinite 1D supramolecular double chain-like structure (Fig. 3) by intermolecular π···π stacking interactions of the two aromatic ring of the adjacent molecules with the centroid-centroid distance 3.911(7) Å.

TABLE-6
DATA FOR HYDROGEN-BONDING INTERACTIONS (Å, º)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
O(3) -H(3) ···N(1)	0.82	1.91	2.63(3)	146
O(4) -H(4) ···N(2)	0.82	1.93	2.66(3)	148

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