



Synthesis and Dipolymer Structure of Salen-type N₂O₂ Ligand 2,2'-[(Pentane-1,5-diylldioxy-bis)-bis-(nitrilomethylidyne)]dinaphthalene

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The compound, 2,2'-[(pentane-1,5-diylldioxy-bis)-bis-(nitrilomethylidyne)]dinaphthalene has been synthesized by 1,5-bis-(aminoxy)pentane and 2-naphthaldehyde in ethanol solution and characterized structurally by X-ray crystallography. The molecule of the title compound, C₂₇H₂₆N₂O₂, assumes a dipolymer structure through a weak C-H...C hydrogen-bonding interactions. And the single crystal structure of the compound revealed all-conformation of the (-CH=N-O-(CH₂)₅-O-N=CH-) linkage, which resulted in the structure with two nitrilomethylidyne units apart from each other. The compound is sufficiently stable to resist scrambling of the C=N bonds. This may be ascribed to lower reactivity of the C=N-O bonds toward nucleophiles.

Key Words: Salen-type bisoxime compound, Synthesis, Dipolymer, Structure.

INTRODUCTION

Salen-type bisoxime compounds, consisting of two nitrogen and two oxygen donors, are capable of forming stable metal complexes¹ which contain one, two or more metal centers and form homo- and heteronuclear complexes serving as catalysts², models of reaction centers of metalloenzymes³, models of reaction centers of metalloenzymes⁴, nonlinear optical materials and molecular recognition and biological agents⁵. And bisoxime complexes offer both high reactivity and selectivity include epoxidation of olefins, asymmetric ring-opening of epoxides, olefin aziridination, olefin cyclopropan-ation and formation of cyclic, linear polycarbonates⁶ and building blocks for cyclic supramolecular structures⁷. Thus, new materials can be produced by using these compounds, which seem to be suitable candidates for further chemical modifications⁸.

Recently, a preferable class of Salen-type bisoxime ligands have been reported by using an O-alkyloxime unit (-CH=N-O-(CH₂)₂-O-N=CH-) instead of the (-CH=N-(CH₂)₂-N=CH-) group and the large electronegativity of oxygen atoms is expected to affect strongly the electronic properties of N₂O₂ coordination sphere, which can lead to different and novel properties and structures of the resulting complexes⁹⁻¹³. Here, we report on the synthesis and dipolymer structure of Salen-type N₂O₂ compound, 2,2'-[(pentane-1,5-diylldioxybis)bis-(nitrilomethylidyne)]dinaphthalene.

EXPERIMENTAL

2-Naphthaldehyde, *N*-hydroxyphthalimide, 1,5-dibromopentane, triethylamine, hydrazine hydrate and anhydrous magnesium sulfate were purchased 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. X-ray single crystal structure was determined on a Bruker Smart 1000 CCD area detector. 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.

1,5-Bis-(aminoxy)pentane was synthesized according to an analogous method reported earlier¹⁴. Yield: 53.4 %.

2,2'-[(Pentane-1,5-diylldioxy-bis)-bis-(nitrilomethylidyne)]-dinaphthalene was synthesized according to an analogous method reported earlier¹⁵. To an ethanolic solution (8 mL) of 2-naphthaldehyde (203.6 mg, 1.3 mmol) was added an ethanol solution (5 mL) of 1,5-bis-(aminoxy)pentane (121.8 mg, 0.6 mmol). The reaction mixture was stirred at 328-333 K for 4 h. The formed precipitate was separated by filtration and washed successively with ethanol and *n*-hexane. The product was dried under vacuum to yield 124.6 mg of the title compound. Yield, 65.2 %. m.p. 388-389 K. Anal. calcd. for C₂₇H₂₆N₂O₂ (%): C, 79.00; H, 6.38; N, 6.82. Found (%): C, 79.28; H, 6.25; N, 6.70.

After a solution of the title compound (5.0 mg, 0.012 mmol) in ethanol (4 mL) was allowed to stand at room temperature for about 2 weeks, several colourless block-like single crystals suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.40 × 0.37 × 0.11 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. The structure was solved by using the program SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F² using SHELXL-9716. Details of the data collection and refinements of the title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 901641.

RESULTS AND DISCUSSION

X-ray crystallographic analysis revealed the crystal structure of the title compound. The structure is shown in Fig. 1 and packing arrangement of the unit cell of the title compound is given in Fig. 2 and the dipolymer structure of the compound is shown in Fig. 3. Crystal data and structure refinement for the title compound are listed in Table-1. Selected bond distances and angles are listed in Table-2. The single crystal structure of the compound is built up by only the C₂₇H₂₆N₂O₂ molecule, in which all bond lengths are in normal ranges. The title compound is a typical Salen-type bisoxime derivative with normal geometric parameters. The X-ray diffraction analysis revealed all-conformation of the (-CH=N-O-(CH₂)₅-O-N=CH-) linkage, which resulted in the structure with two nitrilomethyl

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

Empirical formula	C ₂₇ H ₂₆ N ₂ O ₂
Formula weight	410.58
Temperature, (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Cell dimensions, (Å°)	a = 10.2673(9), b = 10.3060(11), c = 10.3060(11), $\beta = 96.4800$
Volume, Å ³	4477.8(7)
Z	8
Density (calculated) (mg/m ³)	1.218
Absorption coefficient (mm ⁻¹)	0.077
F(000)	1744
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 8, -50 ≤ l ≤ 50
Reflections collected	10790/7230 [R(int) = 0.0645]
Max. and min. transmission	0.9916 and 0.9699
Data/restraints/parameters	7230/2/559
Goodness of fit indicator	1.051
R [I > 2σ(I)]	R ₁ = 0.1365, wR ₂ = 0.2918
Largest diff. peak and hole, e ² Å ⁻³	0.446 and -0.223

-idyne units apart from each other. The compound is sufficiently stable to resist scrambling of the C=N bonds. This may be ascribed to lower reactivity of the C=N-O bonds toward nucleophiles.

In the crystal structure, packing arrangement of the unit cell of the title compound revealed that each molecule links another neighboring molecule through a weak C-H...C hydrogen-bonding interactions into a dipolymer structure (Fig. 3).

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR THE TITLE COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
N(1)-C(6)	1.27(2)	C(6)-C(8)	1.45(2)	C(17)-C(19)	1.45(2)
N(1)-O(1)	1.357(16)	C(7)-C(8)	1.36(2)	C(18)-C(19)	1.42(2)
N(2)-C(17)	1.306(17)	C(7)-C(12)	1.44(2)	C(18)-C(23)	1.46(2)
N(2)-O(2)	1.358(15)	C(8)-C(9)	1.39(2)	C(19)-C(20)	1.35(2)
N(3)-O(3)	1.331(16)	C(9)-C(10)	1.35(2)	C(20)-C(21)	1.29(2)
N(4)-O(4)	1.378(16)	C(10)-C(11)	1.344(2)	C(21)-C(22)	1.38(2)
O(1)-C(1)	1.40(2)	C(11)-C(16)	1.374(2)	C(22)-C(23)	1.42(2)
O(2)-C(5)	1.444(19)	C(11)-C(12)	1.399(2)	C(22)-C(27)	1.45(2)
C(1)-C(2)	1.50(2)	C(12)-C(13)	1.36(2)	C(23)-C(24)	1.37(2)
C(2)-C(3)	1.47(2)	C(13)-C(14)	1.33(2)	C(24)-C(25)	1.323(2)
C(3)-C(4)	1.48(2)	C(14)-C(15)	1.41(2)	C(25)-C(26)	1.36(2)
C(4)-C(5)	1.48(2)	C(15)-C(16)	1.349(2)	C(26)-C(27)	1.46(2)
Bond	Angles	Bond	Angles	Bond	Angles
C(6)-N(1)-O(1)	112.5(17)	C(8)-C(7)-C(12)	120.3(17)	C(13)-C(14)-C(15)	115.0(18)
C(17)-N(2)-O(2)	110.5(14)	C(12)-C(7)-H(7)	119.9	C(16)-C(15)-C(14)	120.7(15)
C(33)-N(3)-O(3)	113.7(17)	C(7)-C(8)-C(9)	123.4(15)	C(15)-C(16)-C(11)	120.2(16)
C(44)-N(4)-O(4)	108.9(16)	C(7)-C(8)-C(6)	120(2)	N(2)-C(17)-C(19)	120.1(19)
N(1)-O(1)-C(1)	117.4(16)	C(9)-C(8)-C(6)	116(2)	C(19)-C(18)-C(23)	116.4(17)
N(2)-O(2)-C(5)	107.6(14)	C(10)-C(9)-C(8)	115.5(18)	C(20)-C(19)-C(18)	122.9(18)
N(3)-O(3)-C(28)	118.2(16)	C(11)-C(10)-C(9)	124.2(19)	C(20)-C(19)-C(17)	120(2)
N(4)-O(4)-C(32)	104.2(15)	C(10)-C(11)-C(16)	116(2)	C(18)-C(19)-C(17)	117(2)
O(1)-C(1)-C(2)	113.1(18)	C(10)-C(11)-C(12)	122.1(17)	C(21)-C(20)-C(19)	123(2)
C(3)-C(2)-C(1)	114.2(19)	C(16)-C(11)-C(12)	121.7(16)	C(20)-C(21)-C(22)	117(2)
C(2)-C(3)-C(4)	115.9(19)	C(13)-C(12)-C(11)	113.5(16)	C(21)-C(22)-C(23)	127.0(19)
C(5)-C(4)-C(3)	118.3(19)	C(13)-C(12)-C(7)	132(2)	C(21)-C(22)-C(27)	114.4(19)
O(2)-C(5)-C(4)	110.6(17)	C(11)-C(12)-C(7)	114.5(16)	C(23)-C(22)-C(27)	118.6(16)
N(1)-C(6)-C(8)	124(2)	C(14)-C(13)-C(12)	129(2)	C(24)-C(23)-C(22)	122.4(19)

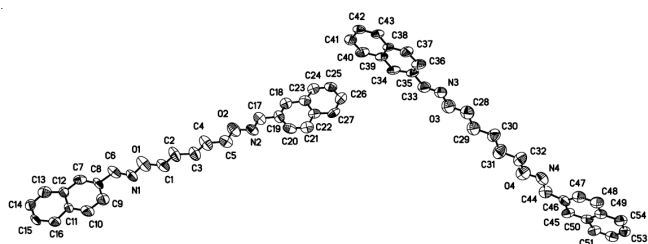


Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30 % probability level

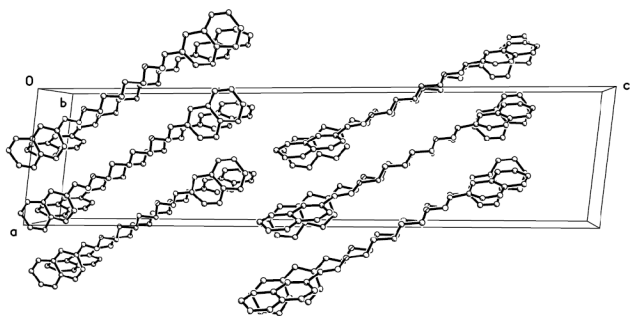


Fig. 2. Packing arrangement of the unit cell of the title compound. H atoms are omitted for clarity

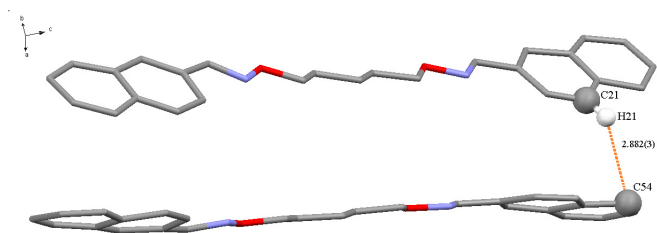


Fig. 3. Dipolymer structure of the compound, hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity

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