Asian Journal of Chemistry; Vol. 25, No. 9 (2013), 5039-5041

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14363

Synthesis and Crystal Structure of 6-Ethoxy-4',6'-dibromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol

XIN-WEN LIU[1,*], JUN-JIANG WU[1], YU-JIE ZHANG[2], GANG LI[2], LI WANG[2] and XIU-YAN DONG[1]

[1]School of Biological Science and Chemistry, Tianshui Normal University, Tianshui 741001, P.R. China
[2]School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: liuxwts@126.com

(*Received*: 24 July 2012; *Accepted*: 18 March 2013) AJC-13132

The title compound, 6-ethoxy-4',6'-dibromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol with the molecular formula $C_{18}H_{18}Br_2N_2O_5$, adopts an L-shaped configuration, in which the benzene units are approximately perpendicular, making a dihedral angle of 76.39(3)º. Intramolecular H-bonds are formed between the OH groups and the N atoms. In the crystal structure, each molecule links other molecules into an infinite three-dimensional supramolecular structure by intermolecular C-H···O and C-H···π hydrogen bond interactions.

Key Words: Asymmetric salen-type bisoxime, Synthesis, Crystal structure.

INTRODUCTION

Salen-type compounds constitute an important class of ligands which have been extensively investigated in coordination chemistry[1]. The development of their bisoxime analogues and complexes can provide new topologies for functional materials, in which coordination forms and functionality are significant variables[2]. Mainly due to their facile synthesis and easily tunable steric, electronic and catalytic properties can be used to acquire non-linear optical materials[3], biological systems[4], interesting magnetic properties[5]. They are also useful in constructing supramolecular structures[6]. Thus, new materials can be produced by using these compounds, which seem to be suitable candidates for further chemical modifications[7,8]. Herein, we report on the synthesis and crystal structure of 6-ethoxy-4',6'-dibromo-2,2'-[ethylenedioxy *bis*(nitrilomethylidyne)]diphenol.

EXPERIMENTAL

3,5-Dibromo-2-hydroxybenzaldehyde and 3-ethoxy-2-hydroxy benzaldehyde 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 in the range 4000-400 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. The ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. 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.

General procedure: 6-Ethoxy-4',6'-dibromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol was synthesized according to an analogous method reported earlier[9].

1,2-*Bis*(aminooxy)ethane was synthesized by a reported method[10]. Yield 75.2 %. Anal. calcd. (%) for $C_2H_8N_2O_2$: C, 26.08; H, 8.76; N, 30.42. Found (%): C, 25.99; H, 8.92; N, 30.35.

3-Ethoxysalicylaldehyde O-(1-ethyloxyamide)oxime: A solution of 1,2-*bis*(aminooxy)ethane (368.2 mg, 4 mmol) in ethanol (20 mL) was added to a solution of 3-ethoxy-2-hydroxybenzaldehyde (332.1 mg, 2 mmol) in ethanol (20 mL), the mixture was heated at 328-333 K for 4 h and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, chloroform/ethyl acetate, 50:3) to afford 284.0 mg crystals of the product. Yield 59.2 %. m.p. 336-337 K. Anal. calcd. (%) for $C_{11}H_{16}N_2O_4$: C, 54.99; H, 6.71; N, 11.66. Found (%): C, 54.92; H, 6.75; N, 11.69.

6-Ethoxy-4',6'-dibromo-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol: A solution of 3-ethoxy salicylaldehyde O-(1-ethyloxyamide)oxime (240.3 mg, 1 mmol) in ethanol (20 mL) was added to a solution of 3,5-dibromo-2-hydroxybenzaldehyde (279.2 mg, 1 mmol) in ethanol (20 mL) and the mixture was heated at 328-333 K for 6 h. After cooling to room temperature, white precipitates were collected on a suction filter to give 407.6 mg white powder of the title

compound. Yield: 81.2 %. m.p. 396-398 K. Anal. calcd. (%) for $C_{18}H_{18}N_2O_5Br_2$: C, 43.05; H, 3.61; N, 5.58. Found (%): C, 43.01; H, 2.93; N, 5.61.

Colourless needle-like single crystals suitable for X-ray diffraction studies were obtained after about one month by slow evaporation from a ethanol/acetone (1:1) solution of the title compound.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.32 mm × 0.10 mm × 0.06 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data 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 SHELXS-97 and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97. 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: 891145.

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 is shown in Fig. 2. Selected bond distances and angles are listed in Table-2. The structure of the title compound consists of discrete $C_{18}H_{18}N_2O_5Br_2$ molecule, in which all bond lengths and angles are in normal ranges. The molecule is disposed about an L-shaped configuration, in which the benzene units are approximately perpendicular, making a dihedral angle of 76.39(3)º. There are two weak intramolecular O-H···N hydrogen bonds involving the hydroxyl groups and adjacent N atoms. In the crystal structure, intermolecular C-H···O and C-H···π hydrogen bonds link the molecules, forming an infinite three-dimensional supramolecular structure[11-15].

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

Empirical formula	$C_{18}H_{18}N_2O_5Br_2$
Formula weight	502.16
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Cell dimensions	a = 14.760(1) Å, b = 12.969(1) Å, c = 20.905(2), Å β = 100.871(1)º
Volume	3929.9(6) $Å^3$
Z	8
Density (calculated)	1.697 mg/m^3
Absorption coefficient	4.157 mm^{-1}
$F_{(000)}$	2000
Index ranges	$-17 \le h \le 17$, $-7 \le k \le 15$, $-24 \le l \le 24$
Reflections collected/unique	9261/3460 [$R_{(int)}$ = 0.0781]
Independent reflections	1160
Data/restraints/parameters	3460/0/246
Goodness of fit indicator	1.059
R [I > 2σ(I)]	R_1 = 0.0463, wR_2 = 0.0851
Largest diff. peak and hole	0.809 and -0.873 e $Å^{-3}$

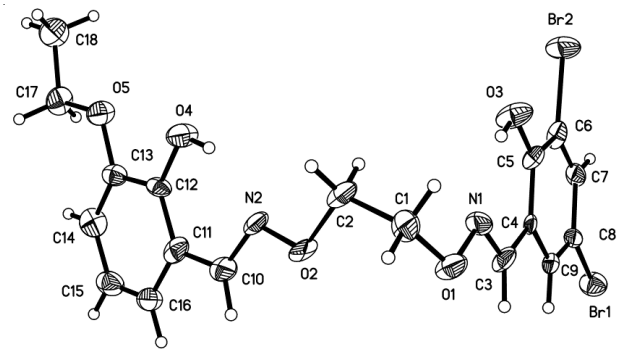

Fig. 1. Molecule structure of the title compound with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Br(1)-C(8)	1.838(13)	O(5)-C(13)	1.365(15)	C(10)-C(11)	1.459(18)
Br(2)-C(6)	1.870(14)	O(5)-C(17)	1.409(14)	C(11)-C(12)	1.358(17)
N(1)-C(3)	1.275(15)	C(1)-C(2)	1.512(16)	C(11)-C(16)	1.441(19)
N(1)-O(1)	1.401(12)	C(3)-C(4)	1.434(16)	C(12)-C(13)	1.374(17)
N(2)-C(10)	1.283(15)	C(4)-C(5)	1.388(16)	C(13)-C(14)	1.381(17)
N(2)-O(2)	1.399(12)	C(4)-C(9)	1.402(16)	C(14)-C(15)	1.381(19)
O(1)-C(1)	1.435(14)	C(5)-C(6)	1.406(16)	C(15)-C(16)	1.317(18)
O(2)-C(2)	1.421(15)	C(6)-C(7)	1.388(17)	C(17)-C(18)	1.499(18)
O(3)-C(5)	1.314(13)	C(7)-C(8)	1.385(16)	–	–
O(4)-C(12)	1.349(14)	C(8)-C(9)	1.385(16)	–	–
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(3)-N(1)-O(1)	110.3(11)	O(3)-C(5)-C(6)	119.8(12)	C(12)-C(11)-C(10)	121.8(14)
C(10)-N(2)-O(2)	112.6(11)	C(4)-C(5)-C(6)	118.3(12)	C(16)-C(11)-C(10)	118.4(14)
N(1)-O(1)-C(1)	109.7(10)	C(7)-C(6)-C(5)	121.2(13)	O(4)-C(12)-C(11)	123.7(14)
N(2)-O(2)-C(2)	109.4(9)	C(7)-C(6)-Br(2)	120.6(9)	O(4)-C(12)-C(13)	116.2(12)
C(13)-O(5)-C(17)	118.0(11)	C(5)-C(6)-Br(2)	118.2(10)	C(11)-C(12)-C(13)	120.1(13)
O(1)-C(1)-C(2)	113.5(11)	C(8)-C(7)-C(6)	120.9(13)	O(5)-C(13)-C(13)	116.6(12)
O(2)-C(2)-C(1)	108.5(10)	C(9)-C(8)-C(7)	117.8(12)	O(5)-C(13)-C(14)	123.7(14)
N(1)-C(3)-C(4)	117.3(13)	C(9)-C(8)-Br(1)	122.7(10)	C(12)-C(13)-C(14)	119.5(13)
C(5)-C(4)-C(9)	119.5(12)	C(7)-C(8)-Br(1)	119.3(11)	C(13)-C(14)-C(15)	120.0(14)
C(5)-C(4)-C(3)	124.7(13)	C(8)-C(9)-C(4)	122.4(12)	C(16)-C(15)-C(14)	121.5(15)
C(9)-C(4)-C(3)	115.8(12)	N(2)-C(10)-C(11)	120.0(13)	C(15)-C(16)-C(11)	119.0(14)
O(3)-C(5)-C(4)	121.9(12)	C(12)-C(11)-C(16)	119.7(14)	O(5)-C(17)-C(18)	106.1(12)

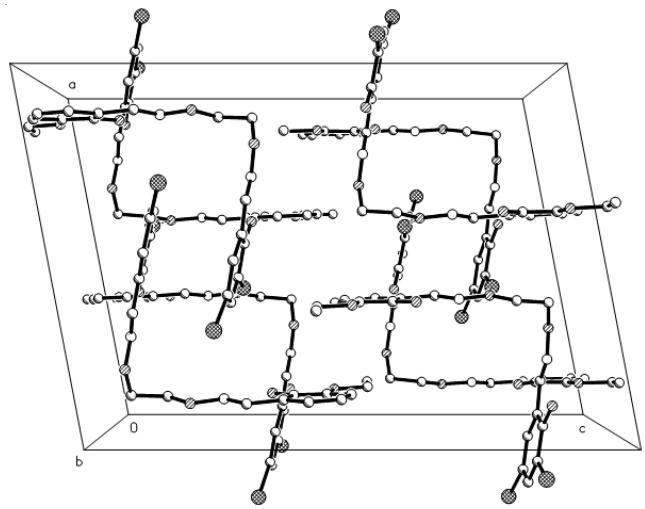

Fig. 2. Packing arrangement of the unit cell of the title compound. H atoms are omitted for clarity

REFERENCES

1. P.G. Cozzi, *Chem. Soc. Rev*., **33**, 410 (2004).
2. R. Ziessel, *Coord. Chem. Rev*., **216**, 195 (2001).
3. H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo and C. Floriani, *J. Am. Chem. Soc*., **118**, 981 (1996).
4. P.G. Lacroix, *Eur. J. Inorg. Chem*., 339 (2001).
5. T.K. Ronson, H. Adams and M.D. Ward, *Inorg. Chim. Acta*, **358**, 1943 (2005).
6. A.K. Sharma, F. Lloret and R. Mukherjee, *Inorg. Chem*., **46**, 5128 (2007).
7. C. Policar, F. Lambert, M. Cesario and I. Morgenstern-Badarau, *Eur. J. Inorg. Chem*., **12**, 2201 (1999).
8. D.A. Atwood and M.J. Harvey, *Chem. Rev*., **101**, 37 (2001).
9. W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch*., **67b**, 197 (2012).
10. W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009).
11. W.K. Dong and J.G. Duan, *J. Coord. Chem*., **61**, 781 (2007).
12. W.K. Dong, X.N. He, Y.X. Sun, L. Xu and Y.H. Guan, *Acta Cryst*., **E64**, 1917 (2008).
13. 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).
14. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and Y. Bai, *Z. Naturforsch*., **66b**, 1049 (2011).
15. W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).