Synthesis and Crystal Structure of 6-Ethoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol

W.-K. DONG*, L. XU, X.-Y. DONG, G. LI, M.-M. ZHAO and J.-J. WU

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P. R. China

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

(Received: 7 June 2013;

Accepted: 30 October 2013)

AJC-14319

The molecule of 6-ethoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol with the molecular formula $C_{18}H_{19}N_2O_5Cl$, adopts a V-shaped configuration, in which the benzene units are approximately perpendicular, making a dihedral angle of $78.97(3)^\circ$. Intramolecular H-bonds are formed between the OH groups and the oxime N atoms. In the crystal structure, each molecule links other neighbouring molecules by intermolecular $C-H\cdots O$ and $C-H\cdots\pi$ hydrogen-bonding interactions into an infinite 1D supramolecular chain and the corresponding rectangular pore canal along a-axis.

Key Words: Asymmetric Salamo-type compound, Synthesis, Crystal Structure.

INTRODUCTION

Salen-type compounds constitute an important class of ligands which have been extensively investigated in modern coordination chemistry¹. The development of their bisoxime analogues and their metal complexes can provide new topologies for functional materials, in which coordination forms and functionality are significant variables². Due to their facile synthesis and easily tunable steric, electronic and catalytic properties can be used to acquire non-linear optical materials³, biological systems⁴, interesting magnetic properties⁵. They are also useful in constructing supramolecular structures⁶. Thus, new materials can be produced by using these compounds, which seem to be suitable candidates for further chemical modifications^{7,8}. Herein, we reported on the synthesis and crystal structure of 6-ethoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol.

EXPERIMENTAL

5-Chlorosalicylaldehyde and 3-ethoxy-2-hydroxy benzaldehyde were purchased from Alfa Aesar and used without further purification. The others are the same as reported in literature⁹.

General procedure: The major reaction steps involved in the synthesis of the title compound are given in **Scheme-I**. 6-Ethoxy-4'-chloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol was synthesized according to an analogous method reported earlier^{9,10}. Yield: 72.6 %. m.p. 400-402 K. Anal. calcd. for $C_{18}H_{19}N_2O_5Cl$ (%): C, 57.07; H, 5.06; N, 7.40. Found: C, 56.91; H, 5.01; N, 7.49.

Pale-green needle-like single crystals suitable for X-ray diffraction studies were obtained after one month by slow evaporation from a methanol/acetone (3:4) solution of the title compound.

Scheme-I: Synthetic route to the asymmetrical Salamo-type compound

X-Ray structure determination: The X-Ray structure determination of the title compound is the same as reported early⁹. Details of the data collection and refinements of the title compound are listed in Table-1.

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

Empirical formula	C ₁₈ H ₁₉ N ₂ O ₅ Cl
Formula weight	378.80
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Cell dimensions, (Å, deg)	a = 8.9873(8), b = 9.678(1), c = 11.966(1) α = 70.817(1), β = 94.962(2), γ = 72.429(1)
Volume (Å ³)	937.0(2)
Z	2
Density (calculated) (mg/m ³)	1.343
Absorption coefficient (mm ⁻¹)	0.234
F ₍₀₀₀₎	396
Crystal size	0.45 × 0.35 × 0.32
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 1, -13 ≤ l ≤ 14
Reflections collected	5416/3294 [R(int) = 0.0246]
Independent reflections	1219
Data/restraints/parameters	3294/0/236
Goodness of fit indicator	1.042
R [I > 2σ(I)]	R ₁ = 0.0459, wR ₂ = 0.0945
Largest diff. peak and hole (e Å ⁻³)	0.153 and -0.193

RESULTS AND DISCUSSION

X-ray crystallographic analysis reveals the crystal structure of the title compound. The structure is shown in Fig. 1. Selected

bond distances and angles are listed in Table-2. Hydrogen bonds for the title compound are listed in Table-3. The structure of the title compound consists of discrete C₁₈H₁₉N₂O₅Cl molecule, in which all bond lengths and angles are in normal ranges. The molecule is disposed about an V-shaped configuration, in which the two benzene ring units are approximately perpendicular each other, making a dihedral angle of 78.97(3)°.

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

In the crystal structure, there are two weak intramolecular O-H...N hydrogen bonds involving the hydroxyl groups and adjacent oxime N atoms forming a six-membered ring with a graph motif S(6). In addition, a pair of intermolecular C7-H7... $\pi_{\text{centroid}}(\text{C13-C18})$ hydrogen-bonding interactions link the neighboring two V-shaped molecules, forming a rectangular macrocycle (Fig. 2). Furthermore, these rectangular macrocycles are further linked by a pair of intermolecular C12-H12...O3 hydrogen-bonding interactions into an infinite 1D chain and the corresponding rectangular pore canal along a axis (Fig. 3)¹¹⁻¹⁵.

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
Cl1-C17	1.736(3)	O4-C10	1.440(3)	C8-C9	1.365(4)
N1-C3	1.271(3)	O5-C14	1.352(3)	C10-C11	1.492(3)
N1-O1	1.410(2)	C1-C2	1.489(3)	C12-C13	1.455(3)
N2-C12	1.273(3)	C3-C4	1.451(3)	C13-C18	1.389(3)
N2-O2	1.399(2)	C4-C5	1.395(3)	C13-C14	1.402(3)
O1-C1	1.427(3)	C4-C9	1.401(3)	C14-C15	1.383(4)
O2-C2	1.432(2)	C5-C6	1.398(3)	C15-C16	1.374(4)
O3-C5	1.359(2)	C6-C7	1.380(3)	C16-C17	1.383(4)
O4-C6	1.367(2)	C7-C8	1.383(3)	C17-C18	1.373(3)
Bond	Angles	Bond	Angles	Bond	Angles
C3-N1-O1	112.8(2)	O3-C5-C6	117.1(2)	C14-C13-C12	122.3(2)
C12-N2-O2	111.5(2)	C4-C5-C6	120.4(2)	O5-C14-C15	117.8(2)
N1-O1-C1	108.4(2)	O4-C6-C7	125.6(2)	O5-C14-C13	122.3(2)
N2-O2-C2	109.2(2)	O4-C6-C5	115.2(2)	C15-C14-C13	119.9(2)
C6-O4-C10	117.8(2)	C7-C6-C5	119.3(2)	C16-C15-C14	120.7(3)
O1-C1-C2	113.5(2)	C6-C7-C8	120.5(3)	C15-C16-C17	119.6(3)
O2-C2-C1	106.8(2)	C9-C8-C7	120.4(2)	C18-C17-C16	120.3(2)
N1-C3-C4	120.9(2)	C8-C9-C4	120.6(2)	C18-C17-Cl1	119.8(2)
C5-C4-C9	118.7(2)	O4-C10-C11	107.3(2)	C16-C17-Cl1	119.9(2)
C5-C4-C3	121.7(2)	N2-C12-C13	120.7(2)	C17-C18-C13	120.9(2)
C9-C4-C3	119.6(2)	C18-C13-C14	118.5(2)	—	—
O3-C5-C4	122.5(2)	C18-C13-C12	119.2(2)	—	—

TABLE-3
HYDROGEN BONDS [$\text{\AA}$, $^\circ$] FOR THE TITLE COMPOUND

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle\text{D-H}\cdots\text{A}$	Symmetry code
O3-H3...N1	0.82	1.89	2.607(3)	146	x, y, z
O5-H5...N2	0.82	1.91	2.625(3)	146	x, y, z
C12-H12...O3	0.93	2.39	3.253(3)	154	1-x, 1-y, 1-z
C7-H7...Cg1 ^a	0.930	2.85	3.672(3)	148	-1+x, y, z

^a Cg1 is the centroid of the ring C13-C18

Fig. 3 View of the 1D chain linked by C12-H12...O3 hydrogen bonds and the corresponding rectangular pore canal (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Fig. 2 View of rectangular macrocycle connected by C7-H7... $\pi_{\text{centroid}}(\text{C13-C18})$ hydrogen bonding interactions (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

ACKNOWLEDGEMENTS

This work was supported by the Foundation of Preparative Research of Jin-Chuan Corporation (No. 209125-1102, 1103), the Fundamental Research Funds for the Gansu Province Universities (212086) and the Science and Technology support funds of Lanzhou Jiaotong University (ZC2012003), which are gratefully acknowledged.

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. (a) W.K. Dong, K.Q. Li, Y. Zhang, L. Xu, L. Wang and X.Y. Dong, *Asian J. Chem.*, **25**, 4398 (2013). (b) 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). (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, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010). (e) W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012). (f) 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). (g) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012).
10. S. Akine, T. Taniguchi, W.K. Dong, S. Masubuchi and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
11. S. Akine, T. Matsumoto, S. Sairenjia and T. Nabeshima, *Supramol. Chem.*, **23**, 106 (2011).
12. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and Y. Bai, *Z. Naturforsch.*, **66b**, 1049 (2011).
13. H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu and K.T. Wang, *Eur. J. Med. Chem.*, **45**, 5324 (2010).
14. H.L. Wu, K. Li, T. Sun, F. Kou, F. Jia, J.K. Yuan, B. Liu and B.L. Qi, *Transition Met. Chem.*, **36**, 21 (2011).
15. H.L. Wu, F. Jia, F. Kou, B. Liu, J.K. Yuan and Y. Bai, *Transition Met. Chem.*, **36**, 847 (2011).