NOTE

Synthesis and Supramolecular Structure of 4,4',6,6'-Tetrachloro-2,2'-[(decane-1,10-diylldioxy)bis(nitrilomethylidyne)]diphenol

WEN-KUI DONG*, XIANG LI, JUN-JIANG WU, YANG ZHANG and XIAO-LU TANG

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

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

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A new salen-type bisoxime compound, 4,4',6,6'-tetrachloro-2,2'-[(decane-1,10-diylldioxy)bis(nitrilomethylidyne)]diphenol, has been synthesized and characterized structurally. In each molecule, there is a *trans* configuration with respect to the methyldiene unit. The two phenyl rings in each molecule are parallel to each other, with a perpendicular interplanar spacing of *ca.* 6.583(2) Å. In the crystal structure, each molecule links other two molecules into finite 2D supramolecular structure by two pairs of intermolecular C10-H10...Cl2 hydrogen bonds.

Key Words: Salen-type bisoxime, Synthesis, Supramolecular structure.

Salen-type compound and its derivatives have played a significant role in the development of the coordination chemistry as they are one of the most important mixed-donor ligands in the modern coordination chemistry and these compounds have caused growing concern because of their strong coordination capability and important properties, such as diverse biological activities¹⁻³, synthetic and catalytic activities^{4,5}, magnetic properties⁶ and supramolecular architectures⁷. In order to extend our work on supramolecular interactions of salen-type bisoxime compound, we reported the synthesis and crystal structure of the title compound.

3,5-Dichloro-2-hydroxybenzaldehyde was purchased from Alfa Aesar and used without further purification. 1,10-Bis-(aminooxy)decane was synthesized according to an analogous method reported earlier⁸. 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.

4,4',6,6'-Tetrachloro-2,2'-[(decane-1,10-diylldioxy)bis(nitrilomethylidyne)]diphenol was synthesized according to an analogous method reported earlier^{9,10}. To an ethanol solution (5 mL) of 3,5-dichloro-2-hydroxybenzaldehyde (38.2 mg, 0.2 mmol) was added an ethanol solution (5 mL) of 1,10-bis-(aminooxy)decane (20.4 mg, 0.1 mmol). The reaction mixture was stirred at 328 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 32.9 mg of the title compound. Yield, 59.8 %. m.p. 364-365 K. anal. calcd. for C₂₄H₂₈Cl₄N₂O₄: C, 52.38; H, 5.13; N, 5.09; Found: C, 52.71; H, 5.20; N, 4.97.

Colourless block-shaped single crystals suitable for X-ray diffraction studies were obtained after two weeks by slow evaporation from acetone/acetonitrile (1:4) solution of the title compound.

X-Ray structure determination: The single crystal of the title compound, with approximate dimensions of 0.43 × 0.22 × 0.09 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 (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 F² 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: 712163.

X-ray crystallographic analysis revealed the crystal structure of the title compound. And the structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The single crystal structure of the title compound is only built up by the C₂₄H₂₈N₂O₄Cl₄ molecule. In each molecule, there is a *trans* configuration with respect to the methyldiene unit. The two phenyl rings in each molecule are parallel to each other, with C1-O1-N1-C7 torsion angles of -179.2 (8)° and a perpendicular

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

Bond	Lengths	Bond	Lengths	Bond	Lengths
N(1)-C(6)	1.272(12)	C(1)-C(2)	1.498(14)	C(7)-C(12)	1.395(14)
N(1)-O(1)	1.405(10)	C(2)-C(3)	1.471(13)	C(7)-C(8)	1.430(13)
O(1)-C(1)	1.433(11)	C(3)-C(4)	1.513(13)	C(8)-C(9)	1.402(14)
O(2)-C(8)	1.368(11)	C(4)-C(5)	1.495(14)	C(9)-C(10)	1.359(14)
C(11)-C(9)	1.731(10)	C(5)-C(5)	1.495(19)	C(10)-C(11)	1.401(12)
C(12)-C(11)	1.736(9)	C(6)-C(7)	1.449(14)	C(11)-C(12)	1.338(13)
Bond	Angles	Bond	Angles	Bond	Angles
C(6)-N(1)-O(1)	111.3(8)	C(12)-C(7)-C(8)	116.5(9)	C(8)-C(9)-Cl(1)	119.1(8)
N(1)-O(1)-C(1)	109.7(7)	C(12)-C(7)-C(6)	120.9(9)	C(9)-C(10)-C(11)	119.5(9)
O(1)-C(1)-C(2)	107.3(8)	C(8)-C(7)-C(6)	122.6(9)	C(12)-C(11)-C(10)	120.2(9)
C(3)-C(2)-C(1)	116.2(8)	O(2)-C(8)-C(9)	119.6(8)	C(12)-C(11)-Cl(2)	121.2(7)
C(2)-C(3)-C(4)	114.6(8)	O(2)-C(8)-C(7)	120.9(9)	C(10)-C(11)-Cl(2)	118.6(7)
C(5)-C(4)-C(3)	116.1(8)	C(9)-C(8)-C(7)	119.5(9)	C(11)-C(12)-C(7)	123.2(9)
C(4)-C(5)-C(5)	117.2(11)	C(10)-C(9)-C(8)	121.0(9)		
N(1)-C(6)-C(7)	120.1(9)	C(10)-C(9)-Cl(1)	119.9(8)		

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

Empirical formula	C ₂₄ H ₂₈ N ₂ O ₄ Cl ₄
Formula weight	550.28
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P -1
Cell dimensions, (Å, deg)	a = 4.5804(6), b = 7.9141(11), c = 17.9692(18), α = 84.2770(10), β = 86.437(2), γ = 80.8340(10)
Volume, Å ³	639.15(14)
Z	1
Density (calculated), mg/m ³	1.430
Absorption coefficient, mm ⁻¹	0.497
F(000)	286
Index ranges	-5 ≤ h ≤ 5, -9 ≤ k ≤ 7, -16 ≤ l ≤ 21
Reflections collected	2889/2079 [R(int) = 0.0529]
Independent reflections	930
Data/restraints/parameters	2079/0/155
Goodness of fit indicator	1.041
R [I > 2σ(I)]	R ₁ = 0.0529, wR ₂ = 0.1214
Largest diff. peak and hole, e-Å ⁻³	0.803 and -0.583

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

interplanar spacing of *ca.* 6.583(2) Å. There are two intramolecular O2-H2...N1 hydrogen bonds between the hydroxyl groups and the oxime N atoms in each molecule (Table-3). In the crystal structure, each molecule links other two molecules into finite 2D supramolecular structure by two pairs of intermolecular C10-H10...Cl2 hydrogen bonds (Fig. 2).

TABLE-3
HYDROGEN BOND (Å, °) FOR THE TITLE COMPOUND

D-H...A	d(D-H)	d(H...A)	∠DHA	d(D...A)
O2-H2...N1	0.82	1.89	146	2.609(3)
C10-H10...Cl2	0.93	2.88	166	3.794(3)

Fig. 2. A perspective view of the intramolecular and intermolecular hydrogen-bond interactions

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REFERENCES

1. S. Koizumi, M. Nihei, M. Nakano and H. Oshio, *Inorg. Chem.*, **44**, 1208 (2005).
2. C. Boskovic, R. Bircher, P.L.W. Tregenna-Piggott, H.U. Güdel, C. Paulsen, W. Wernsdorfer, A.L. Barra, E. Khatsko, A. Neels and H. Stoeckli-Evans, *J. Am. Chem. Soc.*, **125**, 14046 (2003).
3. H. Oshio, M. Nihei, S. Koizumi, T. Shiga, H. Nohiri, M. Nakano, N. Shirakawa and M. Akatsu, *J. Am. Chem. Soc.*, **127**, 4568 (2005).
4. S.A. Mohand, A. Levina and J. Muzart, *J. Chem. Res. (S)*, **25**, 2051 (1995).
5. J.E. Campbell, H. Zhou and T.S. Nguyen, *Org. Lett.*, **3**, 2391 (2001).
6. J. Nishijo, C. Okabe, O. Oishi and N. Nishi, *Carbon*, **44**, 2943 (2006).
7. S. Akine, T. Taniguchi, W.K. Dong, S. Masubuchi and T. Nabeshima, *J. Org. Chem.*, **70**, 1704 (2005).
8. W.K. Dong, G. Wang, S.S. Gong, J.F. Tong, Y.X. Sun and X.H. Gao, *Transition Met. Chem.*, **37**, 271 (2012).
9. W.K. Dong, J.Y. Shi, J.K. Zhong, Y.Q. Tian and J.G. Duan, *Chinese J. Inorg. Chem.*, **24**, 10 (2008).
10. W.K. Dong, J.Y. Shi, J.K. Zhong, Y.X. Sun and J.G. Duan, *Struct. Chem.*, **19**, 95 (2008).