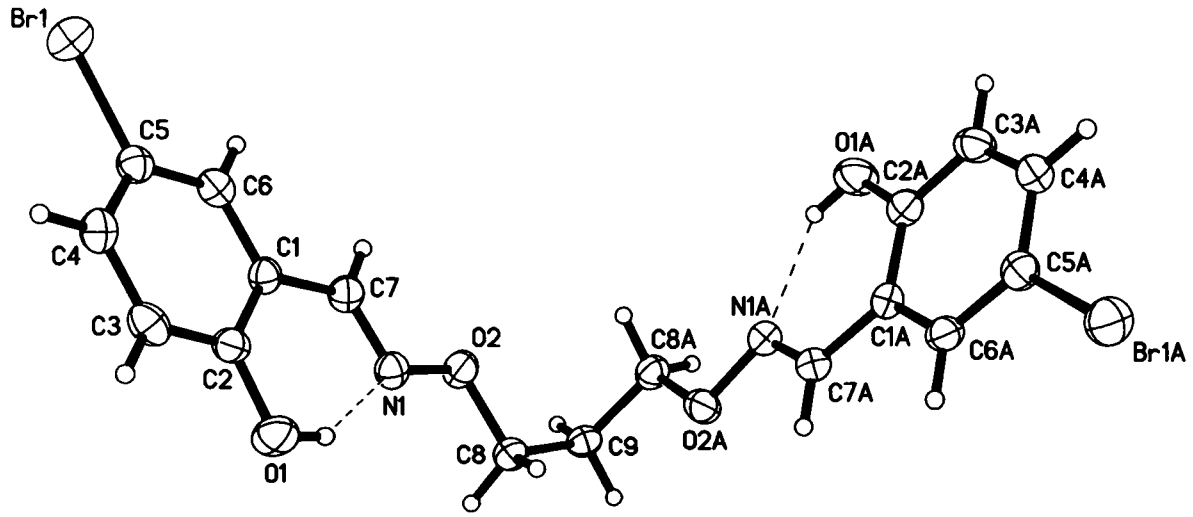
Z. Kristallogr. NCS 221 (2006) 447-448 / DOI 10.1524/ncrs.2006.0149

Crystal structure of 4,4′-dibromo-2,2′-((1,3-propylene)dioxybis(nitrilomethylidyne))diphenol, $C_{17}H_{16}Br_2N_2O_4$

W.-K. Dong*, J.-H. Feng and X.-Q. Yang

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

Received August 8, 2006, accepted and available on-line November 13, 2006; CCDC no. 1267/1866



Abstract

$C_{17}H_{16}Br_2N_2O_4$, orthorhombic, *Pnn*2 (no. 34), a = 6.2054(8) Å, b = 28.788(4) Å, c = 5.0063(6) Å, V = 894.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.068, T = 293 K.

Source of material

To an ethanol solution (10 ml) of 5-bromo-2-hydroxybenzaldehyde (201.0 mg, 1.00 mmol) was added an ethanol solution (5 ml) of 1,3-bis(aminooxy)propane (53.1 mg, 0.50 mmol). After the solution had been stirred at 55 °C for 2 h, the mixture was filtered, washed successively with ethanol and hexane, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 139.30 mg of colorless crystalline solid (yield 59 %, m.p. 163-164 °C). The single crystals were obtained by slow evaporation from an acetone solution after several weeks.

Elemental analysis – found: C, 43.85 %; H, 3.44 %; N, 5.69 %; calc. for $C_{17}H_{16}Br_2N_2O_4$: C, 43.25 %; H, 3.42 %; N, 5.93 %. ^{1}H NMR data are available in the CIF.

Discussion

Salen and its derivatives are extensively studied because they are not only fascinating and versatile chelating ligands in inorganic and organometallic chemistry, but are also used as catalysts for various organic reactions, models of reaction centers of metalloenzymes [1], have interesting magnetic properties and are nonlinear optical materials [2]. Although most of the metal complexes containing salen ligands are stable in solution and in the solid state, C=N bonds often suffer on exchange reaction as well as hydrolysis. In some cases, macrocyclic imine is formed via C=N bond recombination of an acyclic diamine [3]. To tune or improve such functions, chemical modifications of the ligand, e.g., introduction of some functional groups or substitution of some parts with appropriate ones, are effective and inevitable. Rate constants of oxime formation are smaller than those of imine formation and the equilibrium constants are larger by several orders. Hence, the oxime-type ligands should be stable enough to resist the metathesis of the C=N bonds. Thus, we planned synthesis of a new series salen-type chelating ligands on the basis of *O*-alkyloxime instead of the imine moiety [4,5]. We have recently reported an *O*-alkyloxime derivative of salen, 4,4′-dibromo-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol [6].

The crystal structure of the title compound is only built up by the $C_{17}H_{16}Br_2N_2O_4$ molecules, in which all bond lengths are in normal ranges. The molecule adopts a *trans* configuration in which two salicylaldoxime moieties adopts an extended form, where the bromo and hydroxyl groups lie in *trans* positions relative to the C9 atom in the N-O-CH_2-CH_2-CH_2-O-N linkage. There is a crystallographic twofold rotation axis passing through the middle point of the C—C—C unit. The angle of the C8–C9–C8A in the N-O-CH_2-CH_2-CH_2-O-N linkage is 113.3(5)°. All the torsion angles around the C—C, C—O, and O—N bonds are there about 120 °. The intramolecular hydrogen bonds are found between the hydroxyl groups and the oxime nitrogens. The O···N distances between the hydroxyl groups and the oxime nitrogen atoms are about 2.641 Å, indicating strong hydrogen bonds. The results strongly indicate that the oxime-OH form is more favorable in the crystalline state for the ligand 4,4′-dibromo-2,2′-[(1,3-propylene)-dioxybis(nitrilomethylidyne)]diphenol (d(O1—H1) = 0.82 Å, d(H1···N1) = 1.92 Å, d(O1···N1) = 2.641(5) Å, ∠O1–H1···N1 = 145°).

* Correspondence author (e-mail: dongwk@mail.lzjtu.cn)

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.05 × 0.13 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	45.56 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.48°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4609, 1485
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1219
$N(param)_{refined}$:	115
Programs:	SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(3)	4c	−0.3010	0.3784	0.3860	0.061
H(4)	4c	−0.1658	0.3154	0.1523	0.057
H(6)	4c	0.3746	0.3209	0.5860	0.052
H(7)	4c	0.4326	0.3798	0.9246	0.052
H(8A)	4c	0.1936	0.4749	1.4600	0.054
H(8B)	4c	0.2685	0.5066	1.2209	0.054
H(9)	4c	0.4502	0.5250	1.6249	0.053
H(1)	4c	−0.0435	0.4350	0.8593	0.093

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	4c	0.23226(7)	0.26070(1)	0.1604(2)	0.0723(3)	0.0571(3)	0.0543(3)	0.0056(2)	−0.0038(4)	−0.0078(4)
C(1)	4c	0.1609(6)	0.3706(1)	0.687(1)	0.042(2)	0.034(2)	0.044(3)	−0.003(2)	−0.001(3)	0.003(3)
C(2)	4c	−0.0456(6)	0.3870(1)	0.628(1)	0.040(2)	0.041(2)	0.046(3)	0.003(2)	0.006(2)	0.003(2)
C(3)	4c	−0.1653(7)	0.3668(2)	0.427(1)	0.037(2)	0.060(3)	0.056(3)	0.001(2)	−0.005(2)	0.011(3)
C(4)	4c	−0.0849(7)	0.3292(1)	0.2872(9)	0.048(3)	0.046(3)	0.050(3)	−0.006(2)	−0.008(2)	0.002(2)
C(5)	4c	0.1167(6)	0.3124(1)	0.3502(9)	0.044(3)	0.044(2)	0.040(3)	−0.003(2)	0.002(2)	0.004(2)
C(6)	4c	0.2387(6)	0.3327(2)	0.5469(9)	0.039(2)	0.043(2)	0.049(3)	0.002(2)	−0.001(2)	0.010(2)
C(7)	4c	0.2966(6)	0.3921(2)	0.8915(9)	0.041(3)	0.039(2)	0.050(3)	0.002(2)	−0.005(2)	0.003(2)
C(8)	4c	0.3145(6)	0.4828(1)	1.346(1)	0.044(2)	0.039(2)	0.052(3)	0.003(2)	0.002(2)	0.001(2)
C(9)	2a	½	½	1.511(1)	0.045(3)	0.039(3)	0.047(4)	0.007(3)	0	0
N(1)	4c	0.2341(5)	0.4269(1)	1.0241(8)	0.044(2)	0.040(2)	0.047(2)	−0.001(2)	−0.003(2)	0.004(2)
O(1)	4c	−0.1340(5)	0.4235(1)	0.7602(7)	0.051(2)	0.061(2)	0.074(3)	0.016(2)	−0.011(2)	−0.011(2)
O(2)	4c	0.3907(4)	0.44214(9)	1.2044(7)	0.044(2)	0.045(2)	0.064(2)	0.005(1)	−0.012(2)	−0.008(2)

Acknowledgment. This work was supported by the 'Qing Lan' Talent Engineering Funds of Lanzhou Jiaotong University which is gratefully acknowledged.

References

1. Katsuki, T.: Catalytic asymmetric oxidations using optically active (salen) manganese(III) complexes as catalysts. Coord. Chem. Rev. **140** (1995) 189-214.
2. Costes, J.-P.; Dahan, F.; Dupuis, A.: Influence of anionic ligands (X) on the nature and magnetic properties of dinuclear LCuGdX_3nH$_2$O complexes (LH$_2$ standing for tetradentate Schiff Base ligands deriving from 2-Hydroxy-3-methoxybenzaldehyde and X being Cl, N_3C_2, and CF_3COO). Inorg. Chem. **39** (2000) 165-168.
3. Houjou, H.; Nagawa, Y.; Hiratani, K.: Spontaneous macrocyclization via recombination of a Schiff-base linkage. Tetrahedron Lett. **42** (2001) 3861-3863.
4. Akine, S.; Dong, W. K.; Nabeshima, T.: Octanuclear Zinc(II) and Cobalt(II) clusters produced by cooperative tetrameric assembling of oxime chelate ligands. Inorg. Chem. **45** (2006) 4677-4684.
5. Akine, S.; Takanori, T.; Dong, W. K.; Nabeshima, T.: Oxime-Based Salen-Type Tetradentate Ligands with High Stability against Imine Metathesis Reaction. J. Org. Chem. **70** (2005) 1704-1711.
6. Dong, W. K.; Feng, J. H.: 4,4′-Dibromo-2,2′-[ethylenedioxybis (nitrilomethylidyne)]diphenol. Acta Crystallogr. E**62** (2006) o3577-o3578.
7. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
8. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.