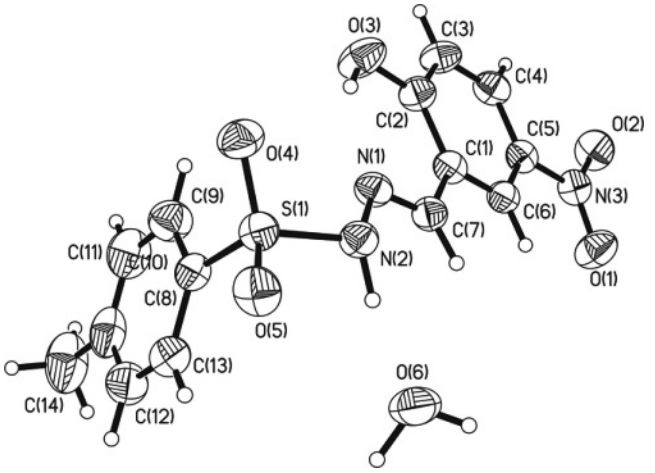
Crystal structure of 5-(nitro)-salicylaldehydebenzenesulfonic-4-methyl-hydrazide, $C_{14}H_{15}N_3O_6S$

Xun Feng*, Rong-Fang Li, Yu Zhang and Wen Yan Ma

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan Province, P. R. China

Received December 14, 2013, accepted March 26, 2014, available online May 05, 2014, CCDC no. 1267/4088



Abstract

$C_{14}H_{15}N_3O_6S$, triclinic, $P\bar{1}$ (no. 2), a = 6.2417(9) Å, b = 9.887(2) Å, c = 14.035(2) Å, α = 76.204(2)°, β = 85.349(2)°, γ = 80.807(2)°, V = 829.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0424, $wR_{ref}(F^2)$ = 0.1136, T = 296 K.

Table 1. Data collection and handling.

Crystal:	red, block, size 0.11×0.18×0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.31 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6365, 3063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2340
$N(param)_{refined}$:	219
Programs:	SHELX [11]

Source of material

The mixture of $Cd(CH_3COO)_2{\cdot}3H_2O$ (0.046 g, 0.2 mmol) was refluxed in anhydrous methanol (15 mL) at 60 °C. After stirring for 2.5 h in air, it is followed by adding a methanol solution (10 mL) containing 5-nitrosalicylaldehyde (0.067 g, 0.4 mmol) and 4-methyl-benzenesulfonic-hydrazide, (0.075 g, 0.4 mmol) at the same time. Then the solution was stirred for 3.5 h, and the pH value was adjusted to 6.0. Afterwards, the mixture was cooled to room temperature and filtered. The filtrate was placed into a clean beaker for aging. A half month later, colourless crystals were obtained. Yield: 0.0217 g (31%) on the basis of 5-nitrosalicylaldehyde. **Elemental Analysis** calcd. for $\mathbf{C}_{14}\mathbf{H}_{15}\mathbf{N}_3\mathbf{O}_6\mathbf{S}$: C, 47.59%; H, 4.28%; N, 11.89%; S, 9.07%; Found: C, 47.42; H, 4.78; S , 9.04; N, 11.54%. **IR** (KBr pellet, cm^{-1}): 3326*s*, 3234*br*, 2905*s*, 2014*m*, 1615*s*, 1398*s*, 792*m*, 817*s*, 725*s*, 572*s*.

* Correspondence author (e-mail: fengqian2004@163.com)

Discussion

Schiff bases represent one of the most widely utilized classes of ligands in metal coordination chemistry [1, 2]. The synthesis of new Schiff base complexes becomes widespread due to their potential application in chemistry, biochemistry, medicine and technology [3]. The chelating salicylaldehyde derivatives, ligands containing O and N donor atoms show broad biological activity, especially with one or more sulfonic groups attached to the aromatic ring, shows biological activities like antitumor, antibacterial and anti-fungal activities [4, 5]. In order to develop environmentally friendly methods, there is currently a rapid growth in the use of supported transition metal catalysts [6]. The preparation, characterization and structure of a new Schiff base are reported. The X-ray diffraction analysis reveals that title compound consists of two parts, one Schiff base molecule and one water molecule. The Schiff base is composed by two organic moieties, benzenesulfonic-4-methyl-hydrazide and 5-nitrosalicylaldehyde, being connected by C=N double bonds and the perspective view of the title compound with atom labeling scheme is illustrated in the figure. The Cd(II) cation is not present in the final product, which may be due to the acidic conditions. The Schiff base compound displayed a distorted "V" type configuration, in which the torsion angles of C7–N1–N2–S1 is –156.12(16)°, and the dihedral angles between the two benzene rings within the same compound is 80.0°. This confirmed that the free rotation of the benzene rings at different conformations in the flexible ligand, as the ligands based on the phenyl or the forms of furan-like have been observed in numerous schiff base ligation modes [7]. The first benzene ring of C1-C6 is nearly coplanar with the maximum deviation of 0.006 Å of C4 and –0.04 Å of C7 atom. While, the second benzene ring of C8-C13 is also nearly coplanar with the maximum deviation +0.009 Å of C11 above the mean plane, and 0.121 Å of S1 atom above this aromatic plane. The shortest distance between the N2 atom of hydrazide group and O6 atom from water molecule is just 2.771 Å. The N3 atom of nitro group and O3 atom of hydroxyl are almost coplanar with the benzene ring of C1-C6, and the deviation out of the mean plane defined by the benzene ring is less than 0.025 Å. This implies that the benzene is a fairly rigid ligand and retains its integrity when they were linked by the C=N double bonds. In the molecule, the bond lengths of C1–C2, C11–C14, C8–S1, N2–S1 and C1–C7 are found to be 1.413(3), 1.506(4), 1.754(2), 1.6419(18) and 1.456(3) Å, respectively, which are also nearly equal to each other belonging to typical double bond lengths [8]. While, the bond lengths of O5–S1, O4–S1, C7–N1, C5–C6, C3–C4 are found to be 1.425(2), 1.4273(16), 1.275(3), 1.379(3) and 1.368(3) Å, respectively, which are nearly equal to others belonging to typical double bonds [9]. A closer inspection shows that there exists weak hydrogen bonding interaction between the oxygen atoms of the carboxylate groups and free water molecules,

which are O6–H2W...O4#1 and O6–H1W...O2#2. [O6···O4#1 = 2.919(3) Å, O6–H2W···O4#1 = 161.5°], and, [O6–H1W···O2#2 = 3.032(3) Å, O6–H1W···O2#2 = 161.0°] Symmetry cods: #1 *x*+1, *y*, *z*; #2 –*x*+1, –*y*+2, –*z*+1. These hydrogen bonding interactions between two adjacent fragments connected and extended these units into a binuclear unit [10]. In addition, all the hydrogen atoms from both sulfonic and nitro groups participate in the hydrogen bond, such as, O3–H3A···N1 and N2–H2D···O6, contributing to crystal packing stability.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	2*i*	–0.3256	1.1547	0.2890	0.066
H(4)	2*i*	–0.1804	1.2921	0.3706	0.062
H(6)	2*i*	0.3419	0.9958	0.4283	0.051
H(7)	2*i*	0.3706	0.7731	0.3824	0.053
H(9)	2*i*	0.1177	0.7593	0.0770	0.076
H(10)	2*i*	0.2818	0.8991	–0.0550	0.091
H(12)	2*i*	0.8396	0.6413	–0.0081	0.087
H(13)	2*i*	0.6824	0.4997	0.1249	0.072
H(14A)	2*i*	0.8295	0.8863	–0.1143	0.155
H(14B)	2*i*	0.6017	0.9706	–0.1456	0.155
H(14C)	2*i*	0.6955	0.8379	–0.1867	0.155
H(2D)	2*i*	0.4462	0.5870	0.3210	0.068
H(3A)	2*i*	–0.0973	0.8413	0.2608	0.105
H(1W)	2*i*	0.7651	0.5793	0.4186	0.120
H(2W)	2*i*	0.8546	0.5583	0.3174	0.120

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}
C(1)	2*i*	0.1207(3)	0.9414(2)	0.3523(2)	0.042(1)	0.038(1)	0.042(1)	–0.0026(9)	0.0011(9)	–0.0044(9)
C(2)	2*i*	–0.0825(4)	0.9914(2)	0.3095(2)	0.047(1)	0.044(1)	0.054(1)	–0.004(1)	–0.006(1)	–0.010(1)
C(3)	2*i*	–0.1916(4)	1.1224(2)	0.3171(2)	0.043(1)	0.046(1)	0.071(2)	0.003(1)	–0.012(1)	–0.009(1)
C(4)	2*i*	–0.1054(4)	1.2048(2)	0.3652(2)	0.050(1)	0.039(1)	0.060(1)	0.002(1)	0.002(1)	–0.009(1)
C(5)	2*i*	0.0951(3)	1.1563(2)	0.4058(2)	0.047(1)	0.037(1)	0.042(1)	–0.0061(9)	0.001(1)	–0.0052(9)
C(6)	2*i*	0.2077(3)	1.0264(2)	0.4001(2)	0.041(1)	0.041(1)	0.041(1)	–0.0028(9)	–0.0003(9)	–0.0043(9)
C(7)	2*i*	0.2418(3)	0.8035(2)	0.3497(2)	0.043(1)	0.042(1)	0.045(1)	–0.0014(9)	–0.0029(9)	–0.009(1)
C(8)	2*i*	0.3856(3)	0.6168(2)	0.1145(2)	0.046(1)	0.052(1)	0.047(1)	–0.009(1)	–0.005(1)	–0.016(1)
C(9)	2*i*	0.2639(4)	0.7359(3)	0.0604(2)	0.060(2)	0.062(2)	0.063(2)	–0.003(1)	–0.004(1)	–0.006(1)
C(10)	2*i*	0.3630(5)	0.8191(3)	–0.0186(2)	0.095(2)	0.065(2)	0.061(2)	–0.015(2)	–0.009(2)	0.002(1)
C(11)	2*i*	0.5791(5)	0.7866(3)	–0.0448(2)	0.092(2)	0.080(2)	0.050(2)	–0.041(2)	–0.002(2)	–0.017(1)
C(12)	2*i*	0.6943(4)	0.6658(3)	0.0095(2)	0.058(2)	0.103(2)	0.066(2)	–0.030(2)	0.009(1)	–0.028(2)
C(13)	2*i*	0.6013(4)	0.5803(3)	0.0891(2)	0.054(2)	0.071(2)	0.057(2)	–0.009(1)	–0.005(1)	–0.016(1)
C(14)	2*i*	0.6861(6)	0.8787(4)	–0.1306(2)	0.139(3)	0.119(3)	0.062(2)	–0.071(2)	0.012(2)	–0.013(2)
N(1)	2*i*	0.1737(3)	0.7238(2)	0.3031(1)	0.041(1)	0.038(1)	0.049(1)	0.0011(8)	–0.0016(8)	–0.0089(8)
N(2)	2*i*	0.2924(3)	0.5900(2)	0.3109(1)	0.044(1)	0.041(1)	0.050(1)	0.0006(8)	–0.0050(8)	–0.0126(8)
N(3)	2*i*	0.1892(3)	1.2408(2)	0.4589(1)	0.058(1)	0.041(1)	0.051(1)	–0.0059(9)	–0.0009(9)	–0.0096(9)
O(1)	2*i*	0.3730(3)	1.2015(2)	0.4875(1)	0.068(1)	0.066(1)	0.090(1)	0.0012(9)	–0.026(1)	–0.031(1)
O(2)	2*i*	0.0787(3)	1.3489(2)	0.4735(1)	0.079(1)	0.0480(9)	0.079(1)	0.0039(9)	–0.0087(9)	–0.0270(9)
O(3)	2*i*	–0.1764(3)	0.9159(2)	0.2611(2)	0.062(1)	0.054(1)	0.099(1)	0.0063(8)	–0.033(1)	–0.028(1)
O(4)	2*i*	0.0421(2)	0.5263(2)	0.2069(1)	0.0467(9)	0.068(1)	0.070(1)	–0.0165(8)	–0.0059(8)	–0.0181(9)
O(5)	2*i*	0.3990(3)	0.3814(2)	0.2468(1)	0.073(1)	0.0375(8)	0.067(1)	0.0032(8)	–0.0038(8)	–0.0129(7)
O(6)	2*i*	0.7171(3)	0.5745(2)	0.3614(2)	0.050(1)	0.094(1)	0.107(2)	0.0036(9)	–0.017(1)	–0.050(1)
S(1)	2*i*	0.26897(9)	0.51571(6)	0.22011(4)	0.0467(3)	0.0415(3)	0.0518(3)	–0.0059(2)	–0.0041(2)	–0.0129(2)

Acknowledgments. This work was supported by Foundation of the Program for Backbone Teachers in Universities of Henan Province, China (No. 2012GGJS158), and the tackle key problem of science and technology Project of Henan Province (No 142102310483), the Key Foundation of Education Committee of Henan Province, China (No 14B150033).

References

1. Raman, N.; Raja, S. J.; Sakthivel, A.: Transition metal complexes with Schiff-base ligands: 4-aminoantipyrine based derivatives - a review. J. Coord. Chem. **62** (2009) 691-709.
2. Feng, X.; Zhao, J. S.; Wang, L.Y.; Shi, X.-G.: A novel Potassium Complex Based on the Taurine-Salicylaldehyde Schiff Base, Synthesis, Crystal Structure and Spectroscopy. Chin. J. Struct. Chem. **5** (2010) 706-711.
3. Kursunlu, A. N.; Guler, E.; Sevgi, F.; Ozkalp, B.: Synthesis, spectroscopic characterization and antimicrobial studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff bases derived from 5-bromo-salicylaldehyde. J. Mol. Struct. **1048** (2013) 476-481.
4. Naeimi, H.; Safari, J.; Heidarnezhad, A.: Synthesis of Schiff base ligands derived from condensation of salicylaldehyde derivatives and synthetic diamine. Dyes and Pigments. 73 (2007) 251-253.
5. Feng, W.-X.; Hui, Y.; Shi, G. X.; Zou, D.; Li, X. Q.; Song, J-R.; Fan, D.-D.; Wong, W.-K.; Jones, R. A.: Synthesis, structure and near-infrared (NIR) luminescence of series of Zn_2Ln (Ln=Nd, Yb or Er) complexes based on the Salen-type Schiff-base ligand with the flexible linker. Inorg. Chem. Commun. **20** (2012) 33-36.
6. Golcu, A.; Tumer, M.; Demirelli, H.; Wheatley, R. A.: Cd(II) and Cu(II) complexes of polydentate Schiff base ligands: synthesis, characterization, properties and biological activity. Inorg. Chim. Acta **358** (2005) 1785-1797.
7. Halli, M. B.; Sumathi, R. B.: Synthesis, spectroscopic, antimicrobial and DNA cleavage studies of new Co(II), Ni(II), Cu(II), Cd(II), Zn(II) and Hg(II) complexes with naphthofuran-2-carbohydrazide Schiff base. J. Mol. Struct. **1022** (2012) 130-138.
8. Zhao, H. R.; Sun, J.-S.; Sui, Y.-X.; Ren, X.-M.; Yao, B.-Q.; Shen, L.-J.; Meng, Q.-J.: Observation of steric hindrance effect controlling crystal packing structures and physical properties in three new isomeric nitronyl nitroxide radicals. J. Mol. Struct. **930** (2009) 167-175.
9. Jiang, D. W.; He, Y.; Budow, S.; Kazimierczuk, Z.; Eickmeier, H.; Reuter, H.; Seela, F.: 7-Amino-1-(2-deoxy-beta-erythro-pentofuranosyl)-1*H*-1,2,3-triazolo[4,5-*d*] pyrimidine: an 8-azaadenine nucleoside with the nucleobase in a *syn* conformation. Acta Crystallogr. **C66** (2010) o561-o564.
10. Feng, X.; Ling, X. L.; Liu, L.; Song, H.-L.; Wang, L.-Y.; Ng, S.W.; Su, B.-Y.: A series of 3D lanthanide frameworks constructed from aromatic multi-carboxylate ligand: Structural diversity, luminescence and magnetic propertieses. Dalton Trans. **14** (2013) 10292-10303.
11. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.