Crystal structure of {4,4',6,6'-tetrabromido-2,2-[ethane-1,4-diyl(nitrilo-methanylylidene)-1-ethylamine-2-methoxyl]diphenolato-κ^5*O,N,N',N'',O'*} zinc(II) — dimethylformamide (2:1), $C_{41}H_{45}Br_8N_7O_7Zn_2$

Liyan Lai[I], Zheng Liu[*, I] and Guo-Cheng Han[II, *]

[I] College of Chemical and Biological Engineering, Guilin University of Technology, Guilin 541004, Guangxi Province, P. R. China
[II] School of Life and Environmental Sciences, Guilin University of Electronic Technology, Guilin 541004, Guangxi Province, P. R. China

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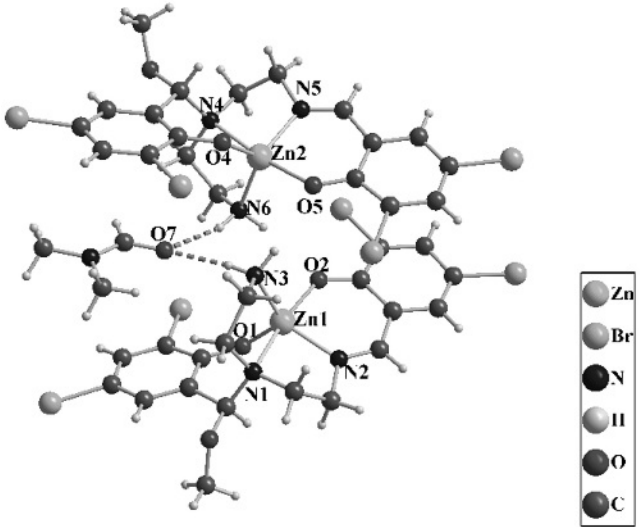

Abstract

$C_{41}H_{45}Br_8N_7O_7Zn_2$, triclinic, $P\bar{1}$ (no. 2), a = 13.7022(5) Å, b = 13.8771(7) Å, c = 14.0928(5) Å, α = 92.665(4)°, β = 98.215(3)°, γ = 109.775(4)°, V = 2482.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.0611, $wR_{ref}(F^2)$ = 0.1491, T = 293 K.

Table 1. Data collection and handling.

Crystal:	light yellow blocks, size 0.28×0.30×0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	74.58 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ and ω
$2\theta_{max}$:	58.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13515, 13515
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6247
$N(param)_{refined}$:	591
Programs:	SHELX [6]

Source of material

The Schiff base ligand H_2L was synthesized according to the following procedure, 3,5-dibromosalicylaldehyde (2.80 g, 10.0 mmol) was dissolved in ethanol(50 mL), diethylenetriamine (0.5 mL) was added dropwise to the mixture with stirring at room temperature. The mixture was refluxed with stirred for 6 h at 60°C until a yellow precipitate was formed. The precipitate was collected by filtration and washed with ethanol. The ligand H_2L (19.2 mg, 0.29 mmol) was dissolved in the mixed solvent of methanol (3.0 mL) and DMF (2.0 mL), then was added to a slender tube. 2.0 mL mixed solvent of dichloromethane (1.0 mL) and methanol (1.0 mL) were added dropwise to the solution. Next 4.0 mL of a methanolic solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.066 mg, 0.3 mmol) was added. Finally the solution divided into three layers. After closing the tube and standing for two weeks at room temperature, light yellow block-shaped crystals were grown with the yield of 45.2% (based on Zn) after filtering.

Experimental details

All hydrogen atoms were identified in difference Fourier synthesis. All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of (C–H = 0.93 Å for aromatic carbon atoms, and C–H = 0.97Å, for the methylene group) with U_{iso} = 1.2U_{eq} (parent atom) and N–H = 0.86 Å with U_{iso} = 1.2U_{eq} (parent atom).

Discussion

The Schiff bases and their derivatives, as a kind of chelating agents, stabilizing agents, catalyst, biological active reagents and so on [1], have been studied and reported by many researchers and are widely applied in chemical industry production and scientific research. In this work, we present the novel Zn(II) complex 2(ZnL)·DMF. The new Schiff base ligand was synthesized by the reaction of 3,5-dibromosalicylal-dehyde and diethylenetriamine. The title structure is built up of two Zn(II) Schiff base units (ZnL) and a DMF molecule through hydrogen bonding interactions (N3–H3A···O7 = 2.065 Å and N6–H6B···O7 = 2.076 Å). The center ion Zn(II) together with two oxygen atoms and three nitrogen atoms of the five dentate Schiff base form a distorted triangular bipyramidal configuration in both cases. Because the coordination environment of two Zn ions is similar, we only describe the coordination mode of Zn1 and the other ion can be described at the same way. The Zn1 is coordinated with three nitrogen atoms of Schiff base ligand L and giving rise to two similar five membered ring [ZnN_3C_2], of which the axial direction is Zn1 and N1, O2 from the ligand while the equatorial plane is constituted of N2, N3 and O1 from the ligand. On the equatorial plane, the bond length between Zn1 and O1 from the ligand is 1.938(5) Å, which is in good agreement with those found in other Zn–O containing coordination complexes [2, 3]; the bond lengths between Zn1 and N2, N3 are 2.026(6) Å and 2.063(6) Å, respectively, and each of them is in the common length range of Zn–N [4, 5]. The N1, O1, O2 atoms from the Schiff base ligand and the central Zn1 ion form three angles, angle O1–Zn–O2 is 100.6(2)°, angle O1–Zn1–N1 is 89.9(2)°, angle O2–Zn1–N1 is 168.4(2)°. It is easy to find that the sum of three angles is 358.9 °, which is close to 360° signifies that ligating atoms N1, O1, O2 are nearly coplanar and Zn ion is also on the plane. Accordingly, the bond lengths and angles of the second complex are as follows: Zn2–O4 = 1.925(6) Å, Zn2–N5 =

* Correspondence author
(e-mail: lisa4.6@163.com and hangc81@guet.edu.cn)

2.034(6) Å, Zn2–N6 = 2.076(6) Å. O4–Zn2–O5 = 98.9(2)°, O4–Zn2–N4 = 89.7(2)°, O5–Zn2–N4=169.5(2)°

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3A)	2*i*	0.6765	0.4052	0.1665	0.046
H(3B)	2*i*	0.6665	0.5064	0.1707	0.046
H(6A)	2*i*	0.1649	0.4893	0.6630	0.044
H(6B)	2*i*	0.2398	0.5934	0.6901	0.044
H(1)	2*i*	0.8815	0.4233	–0.0787	0.040
H(5)	2*i*	0.8895	0.1213	0.1639	0.050
H(7)	2*i*	0.7555	0.1705	–0.0912	0.048
H(8)	2*i*	0.9276	0.7818	0.0018	0.046
H(12)	2*i*	1.0524	0.9222	0.3930	0.053
H(14)	2*i*	0.9979	0.9268	0.1090	0.055
H(15A)	2*i*	0.6930	0.5416	–0.0939	0.049
H(15B)	2*i*	0.7387	0.4909	–0.1702	0.049
H(16A)	2*i*	0.9087	0.5875	–0.1000	0.049
H(16B)	2*i*	0.8471	0.6640	–0.1174	0.049
H(17A)	2*i*	0.6474	0.3087	–0.0034	0.052
H(17B)	2*i*	0.5978	0.3554	–0.0886	0.052
H(18A)	2*i*	0.5945	0.4884	0.0171	0.045
H(18B)	2*i*	0.5370	0.3834	0.0565	0.045
H(19A)	2*i*	0.8826	0.3778	–0.2356	0.091
H(19B)	2*i*	0.7959	0.2761	–0.2873	0.091
H(19C)	2*i*	0.8731	0.2722	–0.1953	0.091
H(20)	2*i*	0.4514	0.6173	0.4401	0.045
H(24)	2*i*	0.6696	0.9081	0.7518	0.058
H(26)	2*i*	0.5026	0.8627	0.4878	0.056
H(27)	2*i*	0.2536	0.2496	0.4371	0.046
H(31)	2*i*	0.2434	0.0805	0.7887	0.053
H(33)	2*i*	0.2061	0.0983	0.5040	0.055
H(34A)	2*i*	0.2712	0.5479	0.3358	0.048
H(34B)	2*i*	0.1837	0.4882	0.3938	0.048
H(35A)	2*i*	0.2553	0.3723	0.3452	0.051
H(35B)	2*i*	0.3703	0.4497	0.3810	0.051
H(36A)	2*i*	0.2103	0.6670	0.4494	0.050
H(36B)	2*i*	0.2869	0.7089	0.5481	0.050
H(37A)	2*i*	0.1194	0.6171	0.5822	0.054
H(37B)	2*i*	0.1126	0.5199	0.5159	0.054
H(38A)	2*i*	0.5336	0.7746	0.3456	0.094
H(38B)	2*i*	0.4406	0.7617	0.2614	0.094
H(38C)	2*i*	0.4664	0.6650	0.2933	0.094
H(39)	2*i*	0.3367	0.8291	0.6913	0.096
H(40A)	2*i*	0.4177	1.0106	0.7288	0.209
H(40B)	2*i*	0.5299	1.0245	0.7845	0.209
H(40C)	2*i*	0.4472	1.0477	0.8393	0.209
H(41A)	2*i*	0.4280	0.8140	0.9161	0.190
H(41B)	2*i*	0.4355	0.9254	0.9516	0.190
H(41C)	2*i*	0.5323	0.9072	0.9173	0.190

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}
Zn(1)	2*i*	0.83315(7)	0.52479(7)	0.10705(6)	0.0333(5)	0.0344(5)	0.0285(5)	0.0119(4)	0.0009(4)	0.0032(4)
Zn(2)	2*i*	0.33174(7)	0.49565(7)	0.60345(6)	0.0365(5)	0.0343(5)	0.0278(5)	0.0138(4)	0.0016(4)	0.0009(4)
Br(1)	2*i*	0.98672(7)	0.32055(7)	0.27551(6)	0.0527(6)	0.0522(6)	0.0325(4)	0.0193(5)	–0.0043(4)	0.0009(4)
Br(2)	2*i*	0.7716(1)	–0.01271(8)	–0.00949(8)	0.0883(8)	0.0366(6)	0.0753(7)	0.0121(6)	–0.0056(6)	–0.0064(5)
Br(3)	2*i*	0.98038(8)	0.70940(7)	0.43184(6)	0.0577(6)	0.0495(6)	0.0427(5)	0.0138(5)	–0.0084(4)	0.0012(4)
Br(4)	2*i*	1.09436(9)	1.08662(8)	0.26588(9)	0.0659(7)	0.0341(6)	0.1032(9)	0.0051(5)	–0.0090(6)	0.0006(6)
Br(5)	2*i*	0.62527(8)	0.70793(8)	0.82257(7)	0.0551(6)	0.0675(7)	0.0415(5)	0.0222(5)	–0.0052(4)	0.0108(5)
Br(6)	2*i*	0.6560(1)	1.04313(8)	0.6052(1)	0.0894(9)	0.0421(6)	0.118(1)	0.0044(6)	–0.0140(8)	0.0213(7)
Br(7)	2*i*	0.33763(7)	0.28685(7)	0.88035(6)	0.0533(6)	0.0479(6)	0.0358(5)	0.0165(5)	0.0002(4)	0.0030(4)
Br(8)	2*i*	0.1570(1)	–0.07190(8)	0.62055(9)	0.133(1)	0.0325(6)	0.0739(8)	–0.0022(7)	0.0162(8)	0.0002(5)
N(1)	2*i*	0.7506(5)	0.4363(5)	–0.0414(4)	0.031(4)	0.052(4)	0.020(3)	0.021(3)	0.000(3)	0.007(3)
N(2)	2*i*	0.8750(5)	0.6401(5)	0.0214(5)	0.040(4)	0.043(4)	0.034(4)	0.016(4)	0.008(3)	0.014(3)
N(3)	2*i*	0.6815(5)	0.4603(5)	0.1337(4)	0.039(4)	0.050(4)	0.029(4)	0.018(4)	0.008(3)	0.001(3)
N(4)	2*i*	0.3112(4)	0.5904(5)	0.4789(4)	0.022(3)	0.045(4)	0.020(3)	0.016(3)	–0.006(2)	–0.003(3)
N(5)	2*i*	0.2977(5)	0.3870(5)	0.4900(4)	0.048(4)	0.038(4)	0.025(3)	0.016(3)	0.007(3)	0.002(3)
N(6)	2*i*	0.2126(5)	0.5423(5)	0.6417(4)	0.037(4)	0.044(4)	0.030(4)	0.015(3)	0.002(3)	0.009(3)
N(7)	2*i*	0.4196(7)	0.9007(7)	0.8103(7)	0.068(6)	0.063(7)	0.078(7)	0.018(5)	0.018(5)	–0.002(6)
O(1)	2*i*	0.9205(4)	0.4402(4)	0.1211(4)	0.041(3)	0.031(3)	0.040(3)	0.015(3)	–0.012(3)	–0.003(3)
O(2)	2*i*	0.8961(4)	0.6244(4)	0.2249(4)	0.046(3)	0.030(3)	0.032(3)	0.007(3)	0.001(3)	–0.001(2)
O(3)	2*i*	0.7624(4)	0.3252(5)	–0.1662(4)	0.038(3)	0.068(4)	0.029(3)	0.032(3)	–0.003(2)	–0.005(3)
O(4)	2*i*	0.4737(4)	0.5897(4)	0.6435(4)	0.034(3)	0.042(4)	0.048(3)	0.011(3)	–0.001(3)	0.012(3)
O(5)	2*i*	0.3327(4)	0.3899(4)	0.6963(4)	0.056(4)	0.028(3)	0.029(3)	0.015(3)	0.002(3)	0.001(2)
O(6)	2*i*	0.3945(4)	0.7174(5)	0.3824(4)	0.034(3)	0.073(4)	0.042(3)	0.016(3)	0.007(3)	0.022(3)
O(7)	2*i*	0.3313(6)	0.7298(6)	0.7738(6)	0.085(6)	0.043(4)	0.095(6)	0.020(4)	0.017(4)	–0.002(4)
C(1)	2*i*	0.8119(6)	0.3751(6)	–0.0729(5)	0.032(4)	0.040(5)	0.029(4)	0.019(4)	–0.006(3)	0.002(4)
C(2)	2*i*	0.8282(6)	0.3011(7)	–0.0025(6)	0.030(5)	0.053(6)	0.032(4)	0.016(4)	0.007(4)	0.005(4)
C(3)	2*i*	0.8847(6)	0.3421(6)	0.0913(5)	0.025(4)	0.046(5)	0.029(4)	0.018(4)	–0.002(3)	–0.005(4)
C(4)	2*i*	0.9068(6)	0.2701(6)	0.1504(5)	0.029(4)	0.039(5)	0.027(4)	0.010(4)	–0.004(3)	0.002(4)
C(5)	2*i*	0.8737(6)	0.1663(7)	0.1226(6)	0.043(5)	0.041(5)	0.046(5)	0.018(4)	0.012(4)	0.011(4)
C(6)	2*i*	0.8166(7)	0.1313(6)	0.0321(6)	0.039(5)	0.031(5)	0.049(5)	0.010(4)	0.005(4)	–0.008(4)
C(7)	2*i*	0.7941(6)	0.1966(7)	–0.0300(6)	0.035(5)	0.047(6)	0.034(5)	0.012(4)	0.001(4)	–0.003(4)
C(8)	2*i*	0.9167(6)	0.7369(7)	0.0494(6)	0.033(5)	0.040(5)	0.045(5)	0.012(4)	0.010(4)	0.016(4)
C(9)	2*i*	0.9482(6)	0.7823(7)	0.1492(6)	0.035(5)	0.040(5)	0.048(5)	0.012(4)	0.003(4)	–0.003(4)
C(10)	2*i*	0.9375(5)	0.7224(6)	0.2305(6)	0.015(4)	0.035(5)	0.043(5)	0.009(3)	0.004(3)	0.001(4)
C(11)	2*i*	0.9811(6)	0.7816(7)	0.3217(6)	0.026(4)	0.045(5)	0.048(5)	0.015(4)	0.001(4)	–0.006(4)
C(12)	2*i*	1.0261(6)	0.8868(6)	0.3319(7)	0.029(5)	0.034(5)	0.060(6)	0.005(4)	–0.003(4)	–0.009(5)
C(13)	2*i*	1.0322(7)	0.9399(7)	0.2523(8)	0.029(5)	0.033(5)	0.076(7)	0.001(4)	0.004(5)	–0.006(5)
C(14)	2*i*	0.9938(7)	0.8894(7)	0.1623(7)	0.040(5)	0.040(5)	0.057(6)	0.014(4)	0.010(5)	0.017(5)
C(15)	2*i*	0.7504(6)	0.5181(7)	–0.1032(5)	0.045(5)	0.059(6)	0.027(4)	0.030(5)	–0.001(4)	–0.001(4)
C(16)	2*i*	0.8524(7)	0.6076(6)	–0.0814(6)	0.043(5)	0.046(5)	0.039(5)	0.019(4)	0.007(4)	0.014(4)
C(17)	2*i*	0.6452(6)	0.3724(7)	–0.0274(6)	0.033(5)	0.047(5)	0.041(5)	0.006(4)	–0.004(4)	–0.002(4)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(18)	2*i*	0.6043(6)	0.4285(6)	0.0437(5)	0.026(4)	0.046(5)	0.038(5)	0.013(4)	0.004(4)	0.000(4)
C(19)	2*i*	0.8345(8)	0.3117(8)	–0.2261(6)	0.067(7)	0.093(8)	0.044(5)	0.056(6)	0.011(5)	0.002(5)
C(20)	2*i*	0.4131(6)	0.6603(6)	0.4613(6)	0.029(5)	0.047(5)	0.038(5)	0.017(4)	0.003(4)	0.006(4)
C(21)	2*i*	0.4822(6)	0.7297(7)	0.5495(6)	0.032(5)	0.047(5)	0.033(5)	0.007(4)	–0.001(4)	0.007(4)
C(22)	2*i*	0.5100(6)	0.6879(6)	0.6326(6)	0.027(4)	0.042(5)	0.038(5)	0.011(4)	0.005(4)	0.010(4)
C(23)	2*i*	0.5829(6)	0.7600(7)	0.7076(5)	0.029(4)	0.055(6)	0.030(4)	0.020(4)	0.002(3)	0.010(4)
C(24)	2*i*	0.6234(7)	0.8639(7)	0.7005(7)	0.034(5)	0.045(6)	0.058(6)	0.010(4)	–0.003(4)	0.000(5)
C(25)	2*i*	0.5951(7)	0.9015(6)	0.6176(7)	0.047(6)	0.030(5)	0.069(6)	0.011(4)	0.002(5)	0.006(5)
C(26)	2*i*	0.5237(7)	0.8359(7)	0.5431(6)	0.044(5)	0.048(6)	0.047(5)	0.016(5)	–0.001(4)	0.014(5)
C(27)	2*i*	0.2706(6)	0.2909(6)	0.4952(6)	0.043(5)	0.035(5)	0.027(4)	0.004(4)	0.004(4)	–0.006(4)
C(28)	2*i*	0.2632(7)	0.2384(6)	0.5814(6)	0.045(5)	0.032(5)	0.039(5)	0.010(4)	0.009(4)	0.008(4)
C(29)	2*i*	0.2953(6)	0.2914(6)	0.6770(6)	0.031(5)	0.038(5)	0.034(5)	0.012(4)	–0.002(4)	–0.003(4)
C(30)	2*i*	0.2868(6)	0.2255(7)	0.7512(6)	0.032(5)	0.046(5)	0.037(5)	0.019(4)	0.003(4)	0.001(4)
C(31)	2*i*	0.2479(7)	0.1201(7)	0.7370(6)	0.041(5)	0.049(6)	0.039(5)	0.010(4)	0.004(4)	0.003(4)
C(32)	2*i*	0.2154(8)	0.0745(7)	0.6426(7)	0.057(6)	0.029(5)	0.061(6)	0.001(4)	0.005(5)	–0.003(5)
C(33)	2*i*	0.2250(7)	0.1310(6)	0.5664(6)	0.060(6)	0.038(5)	0.029(5)	0.006(5)	0.004(4)	–0.003(4)
C(34)	2*i*	0.2590(6)	0.5144(7)	0.3941(5)	0.038(5)	0.062(6)	0.023(4)	0.024(4)	0.000(3)	0.008(4)
C(35)	2*i*	0.2991(7)	0.4267(7)	0.3947(5)	0.053(6)	0.046(5)	0.025(4)	0.016(5)	0.005(4)	–0.005(4)
C(36)	2*i*	0.2441(7)	0.6469(7)	0.5065(6)	0.051(6)	0.054(6)	0.035(5)	0.036(5)	0.010(4)	0.011(4)
C(37)	2*i*	0.1601(7)	0.5784(7)	0.5595(6)	0.041(5)	0.065(6)	0.034(5)	0.021(5)	0.010(4)	0.013(4)
C(38)	2*i*	0.4644(7)	0.7307(8)	0.3153(6)	0.050(6)	0.088(8)	0.044(6)	0.015(6)	0.011(5)	0.023(6)
C(39)	2*i*	0.360(1)	0.819(1)	0.7539(9)	0.090(9)	0.073(9)	0.081(9)	0.041(8)	0.002(7)	–0.006(8)
C(40)	2*i*	0.457(1)	1.0042(9)	0.789(1)	0.18(2)	0.040(8)	0.19(2)	0.04(1)	0.03(1)	0.00(1)
C(41)	2*i*	0.457(1)	0.886(1)	0.907(1)	0.13(1)	0.10(1)	0.12(1)	0.01(1)	0.01(1)	–0.02(1)

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