Ji-Xing Zhao*

Synthesis and crystal structure of bis(2-(((4-(1-(ethoxyimino)ethyl)phenyl)imino)methyl)-5-fluorophenolato- $\kappa^2 N,O$)zinc(II) - methanol (1/1), $C_{33}H_{32}F_2N_4O_4Zn$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.21 × 0.19 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.89 mm ⁻¹
Diffractometer, scan mode:	APEX2, φ and ω
$\theta_{\max}$, completeness:	26.8°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24583, 6216, 0.074
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4570
$N(\text{param})_{\text{refined}}$:	412
Programs:	Bruker [1], SHELX [2], Olex2 [3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.0539(3)	0.7570(2)	0.5526(2)	0.0319(7)
C2	1.1295(3)	0.8561(3)	0.5142(2)	0.0355(7)
H2	1.189147	0.860239	0.556235	0.043*
C3	1.1164(3)	0.9455(2)	0.4169(3)	0.0368(7)
C4	1.0323(3)	0.9475(3)	0.3507(3)	0.0431(8)
H4	1.024693	1.012631	0.283910	0.052*
C5	0.9603(3)	0.8515(3)	0.3856(2)	0.0389(7)
H5	0.902731	0.850101	0.340915	0.047*
C6	0.9681(3)	0.7546(2)	0.4853(2)	0.0314(6)
C7	0.8859(3)	0.6613(2)	0.5099(2)	0.0325(7)
H7	0.838534	0.670646	0.455034	0.039*
C8	0.7811(3)	0.4811(2)	0.6082(2)	0.0280(6)
C9	0.7418(3)	0.4800(3)	0.5206(2)	0.0342(7)
H9	0.768963	0.539313	0.449124	0.041*
C10	0.6635(3)	0.3929(3)	0.5376(2)	0.0354(7)
H10	0.636532	0.393778	0.477019	0.042*
C11	0.6221(3)	0.3030(2)	0.6413(2)	0.0302(6)
C12	0.6601(3)	0.3063(2)	0.7286(2)	0.0337(7)
H12	0.631734	0.247674	0.800317	0.040*
C13	0.7385(3)	0.3935(2)	0.7123(2)	0.0333(7)
H13	0.763824	0.393759	0.772893	0.040*
C14	0.5483(3)	0.2055(2)	0.6556(2)	0.0333(7)
C15	0.5461(4)	0.0934(3)	0.7549(3)	0.0441(8)
H15A	0.446953	0.084766	0.801983	0.066*
H15B	0.615659	0.092030	0.795465	0.066*
H15C	0.574373	0.030150	0.732425	0.066*
C16	0.4182(4)	0.1392(3)	0.4880(3)	0.0486(8)
H16A	0.516454	0.131926	0.443691	0.073*
H16B	0.370389	0.215215	0.450480	0.073*
H16C	0.359372	0.079595	0.498448	0.073*

<https://doi.org/10.1515/ncrs-2019-0491>

Received July 12, 2019; accepted September 11, 2019; available online October 9, 2019

Abstract

$C_{33}H_{32}F_2N_4O_5Zn$, triclinic, $P\bar{1}$ (no. 2), $a = 9.5132(5)$ Å, $b = 13.0781(6)$ Å, $c = 14.0448(6)$ Å, $\alpha = 63.0950(10)^\circ$, $\beta = 73.5640(10)^\circ$, $\gamma = 78.870(2)^\circ$, $V = 1490.24(12)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0459$, $wR_{\text{ref}}(F^2) = 0.1004$, $T = 173(2)$ K.

CCDC no.: 1952874

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Synthesis of the ligand: 4-Amino acetophenone methoxy oxime was prepared by a similar method for related compounds reported earlier by us [4–6]. 4-Fluoro-2-hydroxybenzaldehyde (420 mg, 3 mmol) in EtOH (5 mL) was added to 4-amino acetophenone methoxy oxime (492.6, 3 mmol) in

*Corresponding author: Ji-Xing Zhao, Analysis and Testing Center, Shihezi University, Xinjiang 832003, P.R. China, e-mail: zhaojixing_2016@126.com. <https://orcid.org/0000-0002-1322-1860>

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C17	1.1093(3)	0.3376(2)	0.8604(2)	0.0347(7)
C18	1.2247(3)	0.2503(3)	0.8777(3)	0.0438(8)
H18	1.286556	0.237275	0.817446	0.053*
C19	1.2479(3)	0.1847(3)	0.9803(3)	0.0411(8)
C20	1.1650(3)	0.1981(2)	1.0722(3)	0.0365(7)
H20	1.185620	0.151427	1.142438	0.044*
C21	1.0516(3)	0.2819(2)	1.0576(2)	0.0328(7)
H21	0.991680	0.292165	1.119876	0.039*
C22	1.0196(3)	0.3536(2)	0.9540(2)	0.0280(6)
C23	0.8974(3)	0.4369(2)	0.9536(2)	0.0297(6)
H23	0.844867	0.434136	1.023046	0.036*
C24	0.7233(3)	0.5911(2)	0.8841(2)	0.0273(6)
C25	0.6340(4)	0.5788(3)	0.9837(3)	0.0528(10)
H25	0.657425	0.517998	1.048562	0.063*
C26	0.5116(4)	0.6523(3)	0.9917(3)	0.0489(9)
H26	0.453439	0.641926	1.062215	0.059*
C27	0.4708(3)	0.7406(2)	0.9005(2)	0.0306(6)
C28	0.5646(4)	0.7560(3)	0.8007(3)	0.0507(9)
H28	0.543214	0.818533	0.736038	0.061*
C29	0.6890(4)	0.6827(3)	0.7925(3)	0.0485(9)
H29	0.751500	0.695962	0.722635	0.058*
C30	0.3345(3)	0.8165(2)	0.9083(2)	0.0310(6)
C31	0.2685(3)	0.8826(3)	0.8100(3)	0.0417(8)
H31A	0.166048	0.908119	0.833160	0.063*
H31B	0.272139	0.833188	0.773596	0.063*
H31C	0.324190	0.949735	0.758969	0.063*
C32	0.0946(4)	0.8895(3)	1.1075(3)	0.0494(9)
H32A	0.002994	0.938874	1.108362	0.074*
H32B	0.167210	0.917777	1.125513	0.074*
H32C	0.075542	0.810566	1.161698	0.074*
F1	1.3612(2)	0.10248(17)	0.99304(16)	0.0609(6)
F2	1.19074(19)	1.04000(15)	0.38320(15)	0.0494(5)
N1	0.8499(2)	0.51591(19)	0.86919(18)	0.0271(5)
N2	0.2791(3)	0.8177(2)	1.0028(2)	0.0374(6)
N3	0.8678(2)	0.56501(19)	0.59846(18)	0.0286(5)
N4	0.4940(3)	0.2238(2)	0.5740(2)	0.0394(6)
O1	1.0903(2)	0.39835(18)	0.76039(16)	0.0412(5)
O2	0.1500(2)	0.89126(18)	1.00110(17)	0.0445(6)
O3	1.0663(2)	0.67293(17)	0.64792(16)	0.0365(5)
O4	0.4304(2)	0.12574(18)	0.59212(18)	0.0464(6)
Zn1	0.96309(4)	0.53484(3)	0.71929(3)	0.03157(11)
C33	1.3990(4)	0.5684(3)	0.7315(3)	0.0581(10)
H33A	1.440827	0.614686	0.654070	0.087*
H33B	1.370620	0.496012	0.740088	0.087*
H33C	1.472414	0.551816	0.774506	0.087*
O5	1.2736(3)	0.6299(2)	0.7690(2)	0.0574(7)
H5A	1.213601	0.648828	0.728906	0.086*

EtOH (5 mL). The product was filtered and dried under vacuum. A yellow solid was obtained.

Synthesis of the zinc(II) complex: The zinc acetate dihydrate (219.5 mg, 1 mmol) in MeOH (4 mL) and the synthesized ligand (572.6 mg, 2 mmol) in CH₂Cl₂ (4 mL) were

combined forming a light yellow mixture at room temperature. After being stirred for 2 h at room temperature, the filtrate was allowed to stand for 13 days. Several clear light yellow crystals were obtained. Anal. Calcd. for C₃₃H₃₂F₂N₄O₅Zn: C, 59.33%; H, 4.83%; N, 8.39%. Found: C, 59.74%; H, 5.07%; N, 8.11%.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

A wide variety of Schiff base ligands have been proverbially used to prepare transition metal complexes for several decades. Schiff base ligands can be coordinated with transition-metal ions to form mononuclear or multinuclear stable complexes [7–10]. So far, we have designed and synthesized a variety of Schiff base N₂O₂ type complexes [6, 8, 11–14] and others [15, 16].

The title complex presents a symmetric mononuclear structure. In the title complex, Zn1 is four-coordinated by two O atoms and two N atoms from two Schiff base ligands. In the title crystal, there is a strong intermolecular O5–H5A···O3 hydrogen bond between the OH group of methanol molecule and the phenolato oxygen atom O3 (*cf.* the figure) (*d*(O5–H5A) = 0.84, *d*(O3···H5A) = 1.940 and *d*(O5···O3) = 2.775). All geometric parameters are in the typical ranges.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2012).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
4. Zhao, J. X.; Zhao, L.; Li, P. P.; Wang, F.; An, Q. Q.: Crystal structure of (*E*)-1-(4-(((*E*)-5-bromo-2-hydroxybenzylidene)amino)phenyl)ethan-1-one *O*-methyl oxime, C₁₆H₁₅BrN₂O₂. *Z. Kristallogr. NCS* **232** (2017) 731–732.
5. Ma, J. X.; Li, Q. L.; Li, P. P.; Zhao, J. X.; Zhao, L.: Synthesis and crystal structure of (*E*)-1-(4-(((*E*)-5-chloro-2-hydroxybenzylidene)amino)phenyl)ethan-1-one *O*-methyl oxime, C₁₆H₁₅ClN₂O₂. *Z. Kristallogr. NCS* **232** (2018) 463–464.
6. Li, Q. L.; Li, P. P.; Ma, J. X.; Zhao, J. X.; Zhao, L.: Crystal structure of bis{2-(((*E*)-((*E*)-1-(methoxyimino)ethyl)phenyl)imino)methyl}phenolato-κ²N,O}zinc(II), C₃₂H₃₀N₄O₄Zn. *Z. Kristallogr. NCS* **233** (2018) 637–639.
7. Chang, J.; Zhang, H. J.; Jia, H. R.; Sun, Y. X.: Binuclear nickel(II) and zinc(II) complexes based on 2-amino-3-hydroxy-pyridine Schiff base: syntheses, supramolecular structures and spectral properties. *Chin. J. Inorg. Chem.* **34** (2018) 2097–2107.

8. Zhao, J. X.; Zhao, L.; Li, P. P.; Zhu, Z. B.: Crystal structure of bis{5-methoxy-2-((*E*)-((4-((*E*)-1-(methoxyimino)ethyl)phenyl)imino)methyl)phenolato- κ^2N,O }copper(II), $C_{34}H_{34}CuN_4O_6$. Z. Kristallogr. NCS **232** (2017) 863–865.
9. Liu, P. P.; Wang, C. Y.; Zhang, M.; Song, X. Q.: Pentanuclear sandwich-type Zn^{II} - Ln^{III} clusters based on a new Salen-like salicylamide ligand: structure, near-infrared emission and magnetic properties. Polyhedron **129** (2017) 133–140.
10. Dong, Y. J.; Ma, J. C.; Zhu, L. C.; Dong, W. K.; Zhang, Y.: Four 3d-4f heteromultinuclear zinc(II)-lanthanide(III) complexes constructed from a distinct hexadentate N_2O_2 -type ligand: syntheses, structures and luminescence properties. J. Coord. Chem. **70** (2017) 103–115.
11. Zhao, L.; An, Q. Q.; Zhao, J. X.; Li, P. P.; Wang, F.: Crystal structure of bis(2-((*E*)-((4-((*E*)-1-(ethoxyimino)ethyl)phenyl)imino)methyl)-5-methoxyphenolato- κ^2O,N)copper(II), $C_{36}H_{38}CuN_4O_6$. Z. Kristallogr. NCS **232** (2017) 595–597.
12. Li, P. P.; Li, Q. L.; Ma, J. X.; Zhao, J. X.; Zhao, L.: Crystal structure of bis{4-methyl-2-((*E*)-((4-((*E*)-1-(ethoxyimino)ethyl)phenyl)imino)methyl)phenolato- κ^2N,O }copper(II), $C_{36}H_{38}CuN_4O_4$. Z. Kristallogr. NCS **233** (2018) 763–765.
13. Ma, J. X.; Li, Q. L.; Li, P. P.; Zhao, J. X.; Zhao, L.: Crystal structure of bis{5-methoxy-2-((*E*)-((4-((*E*)-1-(methoxyimino)ethyl)phenyl)imino)methyl)phenolato- κ^2N,O }nickel(II), $C_{34}H_{34}NiO_6$. Z. Kristallogr. NCS **233** (2018) 767–769.
14. Li, P. P.; Zhao, L.; Zhao, J. X.; Zhu, Z. B.; Wang, F.; An, Q. Q.: Synthesis and crystal structure of bis{1-(((4-(1-(hydroxyimino)ethyl)phenyl)imino)methyl)naphthalen-2-olato- κ^2O,N }copper(II), $C_{38}H_{30}CuN_4O_4$. Z. Kristallogr. NCS **232** (2017) 889–890.
15. Sun, Y. X.; Zhao, Y. Y.; Li, C. Y.; Yu, B.; Guo, J. Q.; Li, J.: Supramolecular cobalt(II) and copper(II) complexes with Schiff base ligand: syntheses, characterizations and crystal structures. Chin. J. Inorg. Chem. **32** (2016) 913–920.
16. Sun, Y. X.; Lu, R. E.; Li, X. R.; Zhao, Y. Y.; Li, C. Y.: A Schiff base ligand containing oxime group and its Cu(II) complex: syntheses and supramolecular structures. Chin. J. Inorg. Chem. **31** (2015) 1055–1062.