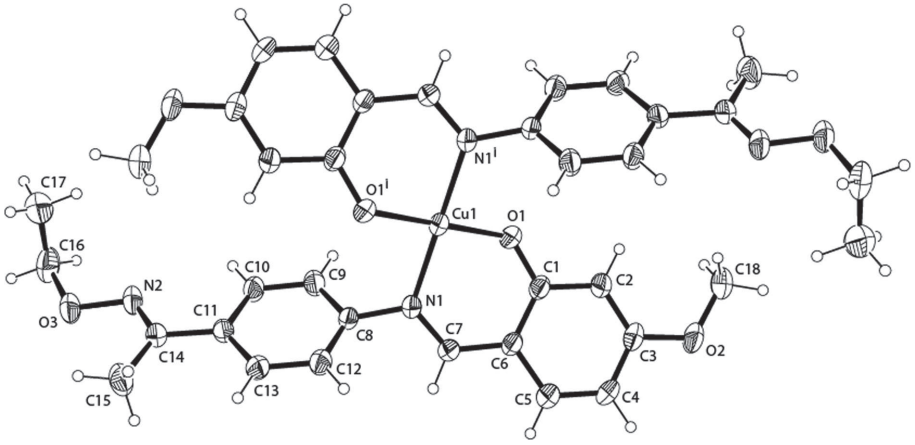
Open Access

Li Zhao*, Qin-Qin An, Ji-Xing Zhao, Peng-Peng Li and Fei Wang

Crystal structure of bis(2-((*E*)-((4-((*E*)-1-(ethoxyimino)ethyl)phenyl)imino)methyl)-5-methoxyphenolato-κ²*O*,*N*)copper(II), $C_{36}H_{38}CuN_4O_6$



DOI 10.1515/ncrs-2016-0358
Received January 2, 2017; accepted May 8, 2017; available online June 5, 2017

Abstract

$C_{36}H_{38}CuN_4O_6$, monoclinic, $P2_1/c$ (no. 14), $a = 10.7510(12)$ Å, $b = 6.4718(7)$ Å, $c = 24.254(2)$ Å, $\beta = 101.99(1)°$, $V = 1650.7(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0525$, $wR_{ref}(F^2) = 0.1621$, $T = 293(2)$ K.

CCDC no.: 1547826

The structure of the title complex is shown in the figure ($i = -x, 1 - y, -z$). Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Dark-brown block
Size:	0.31 × 0.26 × 0.24 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	13.6 cm^{-1}
Diffractometer, scan mode:	SuperNova Dual, ω scans
$2\theta_{max}$, completeness:	140°, 96.8%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5453, 3027, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2429
$N(param)_{refined}$:	217
Programs:	SHELX [1], OLEX^2 [2]

Source of materials

5-Methoxy-2-[methylidynenitrilo(aminoacetophenone-*O*-ethyloxime)]phenol: To an ethanolic solution (8 mL) of 1-(4-aminophenyl)ethan-1-one *O*-ethyl oxime (164.0 mg, 1 mmol) was added an ethanolic solution (5 mL) of 4-methoxysalicylaldehyde (152.3 mg, 2 mmol). After the solution had been stirred at 328 K for 8 h, the mixture was filtered, washed successively with ethanol and ethanol/hexane (1:4), respectively. The isolated compound was dried under reduced pressure and purified by recrystallization from ethanol to

***Corresponding author: Li Zhao,** Lanzhou Jiaotong University, School of Chemical and Biological Engineering, Lanzhou 730070, People's Republic of China, e-mail: zhaol@mail.lzjtu.cn
Qin-Qin An, Ji-Xing Zhao, Peng-Peng Li and Fei Wang: Lanzhou Jiaotong University, School of Chemical and Biological Engineering, Lanzhou 730070, People's Republic of China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.0000	0.5000	0.0000	0.0494(3)
O1	−0.0308(3)	0.5656(4)	0.07171(11)	0.0614(7)
O2	−0.2044(3)	0.3759(5)	0.22894(11)	0.0690(8)
O3	0.6410(3)	0.1509(5)	−0.14046(14)	0.0780(9)
N1	0.1204(3)	0.2788(5)	0.03420(12)	0.0481(7)
N2	0.5554(3)	0.2112(6)	−0.10645(15)	0.0660(9)
C1	−0.0403(3)	0.4292(6)	0.11012(14)	0.0479(8)
C2	−0.1152(3)	0.4796(6)	0.14957(15)	0.0521(9)
H2	−0.1544	0.6082	0.1481	0.062*
C3	−0.1304(3)	0.3397(7)	0.19016(15)	0.0548(9)
C4	−0.0725(4)	0.1469(7)	0.19393(17)	0.0664(11)
H4	−0.0846	0.0532	0.2214	0.080*
C5	0.0023(4)	0.0963(7)	0.15689(17)	0.0655(11)
H5	0.0422	−0.0319	0.1599	0.079*
C6	0.0204(3)	0.2341(6)	0.11399(14)	0.0496(8)
C7	0.1049(3)	0.1774(6)	0.07810(14)	0.0506(9)
H7	0.1527	0.0576	0.0871	0.061*
C8	0.2152(3)	0.2139(6)	0.00416(14)	0.0446(8)
C9	0.2992(4)	0.3610(6)	−0.00781(16)	0.0560(9)
H9	0.2970	0.4945	0.0061	0.067*
C10	0.3860(3)	0.3112(6)	−0.04019(16)	0.0525(9)
H10	0.4426	0.4111	−0.0476	0.063*
C11	0.3901(3)	0.1120(6)	−0.06213(14)	0.0456(8)
C12	0.2206(4)	0.0149(6)	−0.01549(16)	0.0532(9)
H12	0.1666	−0.0864	−0.0067	0.064*
C13	0.3075(4)	−0.0327(6)	−0.04858(16)	0.0540(9)
H13	0.3100	−0.1668	−0.0621	0.065*
C14	0.4813(3)	0.0633(6)	−0.09898(15)	0.0506(8)
C15	0.4829(5)	−0.1467(7)	−0.1241(2)	0.0773(13)
H15A	0.4006	−0.1770	−0.1468	0.116*
H15B	0.5037	−0.2474	−0.0946	0.116*
H15C	0.5454	−0.1510	−0.1472	0.116*
C16	0.7132(5)	0.3313(9)	−0.1508(2)	0.0864(15)
H16A	0.7330	0.4153	−0.1170	0.104*
H16B	0.7927	0.2879	−0.1602	0.104*
C17	0.6406(7)	0.4524(10)	−0.1968(3)	0.121(2)
H17A	0.6203	0.3685	−0.2301	0.181*
H17B	0.6899	0.5694	−0.2038	0.181*
H17C	0.5634	0.4994	−0.1869	0.181*
C18	−0.2666(5)	0.5685(8)	0.2270(2)	0.0824(14)
H18A	−0.3204	0.5873	0.1905	0.124*
H18B	−0.2046	0.6772	0.2340	0.124*
H18C	−0.3173	0.5721	0.2552	0.124*

yield 248.9 mg of red crystalline solid (yield 78.7%, m.p. 436–440 K).

A solution of copper(II) acetate monohydrate (1.5 mg, 7.5 mmol) in ethanol (4 mL) was added dropwise to a solution of (2-((4-(1-(ethoxyimino)ethyl)phenyl)imino)methyl)-5-methoxyphenol (3.0 mg, 5.0 mmol) in ethanol (3 mL) at room temperature. The colour of the solution turned to blue and then the mixture was stirred for 1 h at room temperature. The mixture was filtered and the filtrate was allowed to stand at room temperature for six weeks. The solvent partially evaporated and obtained dark brown block single crystals suitable for X-ray crystallographic analysis. **Elemental analysis** – Anal. calcd for $C_{36}H_{38}CuN_4O_6$: C, 63.01%; H, 5.58%; N, 8.16%; Found: C, 62.98%; H, 5.55%; N, 8.13%.

Experimental details

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

Comment

Oxime-type compounds are often synthesized by aldehydes or ketones with hydroxylamine or its derivatives through condensation reaction, with a general formula of $R^1R^2C=N-OR^3$ [3–5]. As chelating agents, these compounds have excellent coordination abilities with metal ions [6–8]. Particular attention has been paid to the synthesis and application of oxime-type metal complexes [9–11].

The crystal structure of the title compound is built up by copper(II) complexes which are located at an inversion center. All bond lengths and angles are in normal ranges. Each Cu(II) atom is tetra-coordinated by two N and two O atoms from two crystallographically related bidentate ligands. The coordination around Cu(II) atom is best described as distorted square planar (*cf.* the figure). The title complex has at least a weak intermolecular C7—H7···O3 hydrogen bond involving the C7 atom (d(C7—H7) = 0.93 Å, d(H7···O3) = 2.687 Å, d(C7···O3) = 3.542(4) Å, the angle of C7—H7···O3 = 153.06(3)°).

References

1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
2. 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. Cryst. **42** (2009) 339–341.
3. Dong, W. K.; He, X. N.; Dong, C. M.; Wang, L.; Zhong, J. K.; Chen, X.; Yu, T. Z.: Crystal structure of 2,2′-((1,4-butylene)dioxybis(nitriloethylidyne) diphenol, $C_{20}H_{24}N_2O_4$. Z. Kristallogr. – NCS **222** (2007) 289–290.
4. Dong, W. K.; Feng, J. H.; Yang, X. Q.: Crystal structure of 4,4′-dibromo-2,2′-((1,3-propylene)dioxybis (nitrilomethylidyne))diphenol, $C_{17}H_{16}Br_2N_2O_4$. Z. Kristallogr. – NCS **221** (2006) 447–448.
5. 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.
6. Dong, W. K.; Duan, J. G.; Guan, Y. H.; Shi, J. Y.; Zhao, C. Y.: Synthesis, crystal structure and spectroscopic behaviors of

Co(II) and Cu(II) complexes with Salen-type bisoxime ligands. Inorg. Chim. Acta **362** (2009) 1129–1134.
7. Li, X. B.; Li, X. J.; Meng, W. S.; Zhang, Y. J.; Li, G.: Bis[2,4-dibromo-6-(*N*-{4-[(*E*)-1-(benzyloxyimino)ethyl]phenyl}carboximidoyl) phenolato]copper(II). Acta Crystallogr. **E69** (2013) m267.
8. Dong, W. K.; Sun, Y. X.; He, X. N.; Tong, J. F.; Wu, J. C.: Trinuclear and mononuclear copper(II) complexes incorporating tetradentate 2,2′-[1,1′-(ethylenedioxydinitrilo)diethylidyne]diphenol ligand: Syntheses, crystal structures, spectral and thermal behaviors. Spectrochim. Acta **A76** (2010) 476–483.
9. Zhao, L.; Wang, L.; Sun, Y. X.; Dong, W. K.; Tang, L.; Gao, X. H.: A supramolecular copper(II) complex bearing Salen-type bisoxime ligand: Synthesis, structural characterization, and thermal property. Synth. React. Inorg., Met.-Org., Nano-Met. Chem. **42** (2012) 1303–1308.
10. 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.
11. Sun, Y. X.; Gao, X. H.: Synthesis, characterization, and crystal structure of a new Cu^{II} complex with Salen-type ligand. Synth. React. Inorg. Met.-Org. Nano-Met. Chem. **41** (2011) 973–978.