Yang Zhang, Yong-Fan Cui, Xiao-Xin An, Peng-Peng Li and Wen-Kui Dong*

Crystal structure of 1-(4-{2,5-dichloro-3-hydroxy-4-[4-(1-methoxyimino-ethyl)-phenylamino]-6-methyl-phenylamino}-phenyl)-ethanone *O*-methyl-oxime, C₂₄H₂₂Cl₂N₄O₄

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Abstract

C₂₄H₂₂Cl₂N₄O₄, triclinic, *P* $\bar{1}$ (no. 2), $a = 9.7533(6)$ Å, $b = 10.2969(8)$ Å, $c = 17.9128(12)$ Å, $\alpha = 104.131(2)^\circ$, $\beta = 99.242(2)^\circ$, $\gamma = 91.106(2)^\circ$, $V = 1718.7(2)$ Å³, $Z = 3$, $R_{\text{gt}}(F) = 0.0502$, $wR_{\text{ref}}(F^2) = 0.1256$, $T = 153(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

1-(4-Aminophenyl)-ethanone *O*-methyl-oxime has been successfully prepared by the one-pot reaction of methoxyamine hydrochloride (183.7 mg, 0.011 mmol), 1-(4-amino-phenyl)-ethanone (270.3 mg, 0.010 mmol) and NaOH (96.0 mg, 0.012 mmol) in ethanol (150 mL) for 10 h in room temperature. 3-Formyl-4-hydroxybenzoic acid (166.13 mg, 0.01 mmol) dissolved in ethanol solution (5 mL) was added to 1-(4-amino-phenyl)ethanone *O*-methyl-oxime (328.4 mg, 0.02 mmol) dissolved in ethanol solution (5 mL). After the solution has been stirred at 338.5 K for 10 h, the mixture was cooled to room temperature. The precipitate was

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.22 × 0.19 × 0.18 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.32 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	12510, 6026, 0.054
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4458
$N(\text{param})_{\text{refined}}$:	466
Programs:	Bruker [1], Olex2 [2], SHELX [3]

filtered and washed with ethanol and hexane. The product was dried under vacuum and we obtained a yellow solid. Block crystals were obtained by slow evaporation from trichloromethane/ethanol (1: 2) at room temperature. Yield: 76%. Elemental analysis – Anal. Calcd. for C₂₄H₂₂Cl₂N₄O₄: C, 57.50%; H, 4.42%; N, 11.18%. Found: C, 57.62%; H, 4.39%; N, 11.04%.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms, with constrained isotropic displacement parameters.

Comment

Oxime-type compounds are considered a very important class of organic ligands in modern coordination chemistry [4–6], and their metal(II/III) complexes generally involve an oxime *N*-metal bonding, which, based on the known geometrical configuration of the ligands, has been accepted as their most stable form [7–9]. So far, a large number of transition metal complexes has been synthesized [10–12], and their supramolecular effects have been studied [13–16].

The current work reports the synthesis of the title compound, which is built up by the C₂₄H₂₂Cl₂N₄O₄ molecules, and all bond lengths are in normal ranges [17]. The asymmetric unit of the title structure consists of 1.5 molecules of the title compound (*cf.* the figure). One molecule is located on a general position, the second molecule is positioned around an inversion center of the triclinic space group. In the molecules, there are strong intramolecular N–H...O hydrogen bonds (O3–H2...N2: $d(\text{N2} \cdots \text{O3}) = 2.577(3)$,

*Corresponding author: Wen-Kui Dong, School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, People's Republic of China, e-mail: dongwk@126.com

Yang Zhang, Yong-Fan Cui, Xiao-Xin An and Peng-Peng Li: Lanzhou Jiaotong University, School of Chemical and Biological Engineering, Lanzhou 730070, P. R. China

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

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.9226(3)	0.6366(4)	−0.09075(16)	0.0334(8)
H1A	0.875191	0.554557	−0.086531	0.050*
H1B	0.948127	0.622338	−0.142743	0.050*
H1C	0.860187	0.710406	−0.082808	0.050*
C2	1.2559(3)	0.7379(4)	0.08372(18)	0.0356(9)
H2A	1.274045	0.669007	0.038511	0.053*
H2B	1.321535	0.732433	0.130245	0.053*
H2C	1.267474	0.826784	0.074071	0.053*
C3	1.1096(3)	0.7154(3)	0.09649(16)	0.0258(7)
C4	1.0764(3)	0.7331(3)	0.17627(16)	0.0223(7)
C5	1.1651(3)	0.8060(3)	0.24277(16)	0.0240(7)
H5	1.251131	0.844564	0.237488	0.029*
C6	1.1305(3)	0.8235(3)	0.31655(16)	0.0231(7)
H6	1.192561	0.873705	0.361123	0.028*
C7	1.0055(3)	0.7679(3)	0.32530(15)	0.0207(7)
C8	0.9141(3)	0.6957(3)	0.25981(15)	0.0235(7)
H8	0.827227	0.659393	0.265471	0.028*
C9	0.9499(3)	0.6768(3)	0.18667(16)	0.0243(7)
H9	0.888271	0.624985	0.142443	0.029*
C10	0.9044(2)	0.7162(3)	0.43643(15)	0.0184(7)
C11	0.8863(3)	0.5807(3)	0.41956(14)	0.0182(7)
C12	0.8189(2)	0.5140(3)	0.46672(14)	0.0177(7)
C13	0.7605(2)	0.6008(3)	0.53560(14)	0.0172(7)
C14	0.7814(3)	0.7362(3)	0.55316(14)	0.0191(7)
C15	0.8520(3)	0.8030(3)	0.50771(15)	0.0187(7)
C16	0.6308(3)	0.5500(3)	0.63828(14)	0.0193(7)
C17	0.5071(3)	0.6132(3)	0.63763(15)	0.0231(7)
H17	0.471161	0.649435	0.595045	0.028*
C18	0.4358(3)	0.6233(3)	0.69979(15)	0.0233(7)
H18	0.351433	0.667883	0.699759	0.028*
C19	0.4860(3)	0.5690(3)	0.76216(15)	0.0191(7)
C20	0.6128(3)	0.5075(3)	0.76189(15)	0.0226(7)
H20	0.650001	0.471965	0.804570	0.027*
C21	0.6839(3)	0.4977(3)	0.70069(15)	0.0226(7)
H21	0.769521	0.455207	0.701076	0.027*
C22	0.4038(3)	0.5686(3)	0.82557(15)	0.0216(7)
C23	0.3003(3)	0.6722(3)	0.84492(17)	0.0293(8)
H23A	0.208682	0.638923	0.813954	0.044*
H23B	0.329767	0.755155	0.832819	0.044*
H23C	0.294967	0.690109	0.900648	0.044*
C24	0.3689(3)	0.3641(4)	0.94853(17)	0.0319(8)
H24A	0.348379	0.283636	0.905129	0.048*
H24B	0.306763	0.362516	0.986234	0.048*
H24C	0.465789	0.366168	0.974293	0.048*
C25	0.3688(3)	1.1147(4)	1.07707(17)	0.0416(10)
H25A	0.448059	1.059969	1.066985	0.062*
H25B	0.347456	1.114122	1.128618	0.062*
H25C	0.392011	1.207064	1.075731	0.062*
C26	0.0439(3)	0.9735(4)	0.90089(17)	0.0357(9)
H26A	0.042953	0.887891	0.915578	0.054*
H26B	−0.021952	0.965820	0.852336	0.054*
H26C	0.016954	1.044115	0.942563	0.054*
C27	0.1868(3)	1.0081(3)	0.88899(16)	0.0227(7)
C28	0.2208(3)	0.9884(3)	0.80905(15)	0.0207(7)
C29	0.3555(3)	1.0190(3)	0.79785(15)	0.0231(7)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H29	0.424280	1.058605	0.841979	0.028*
C30	0.3905(3)	0.9931(3)	0.72431(15)	0.0232(7)
H30	0.483121	1.011943	0.718152	0.028*
C31	0.2891(3)	0.9388(3)	0.65889(15)	0.0188(7)
C32	0.1558(3)	0.9086(3)	0.66880(16)	0.0241(7)
H32	0.086719	0.870894	0.624465	0.029*
C33	0.1221(3)	0.9329(3)	0.74269(16)	0.0250(7)
H33	0.029889	0.911459	0.748493	0.030*
C34	0.4089(2)	0.9628(3)	0.54848(14)	0.0171(6)
C35	0.4628(3)	1.0916(3)	0.56785(14)	0.0180(7)
C36	0.5565(3)	1.1362(3)	0.52339(15)	0.0191(7)
Cl1	0.95924(7)	0.47285(8)	0.34796(4)	0.0248(2)
Cl2	0.73343(7)	0.84068(8)	0.63576(4)	0.0280(2)
Cl3	0.41796(7)	1.21767(8)	0.64184(4)	0.0249(2)
N1	1.0046(2)	0.6831(3)	0.04080(13)	0.0269(6)
N2	0.9699(2)	0.7948(3)	0.40139(12)	0.0210(6)
H2	0.997187	0.881894	0.427734	0.025*
N3	0.6995(2)	0.5220(3)	0.57156(12)	0.0209(6)
H3	0.710238	0.427785	0.550777	0.025*
N4	0.4285(2)	0.4735(3)	0.85967(13)	0.0236(6)
N5	0.2898(2)	1.0499(3)	0.94496(13)	0.0273(6)
N6	0.3218(2)	0.9024(3)	0.58275(12)	0.0202(6)
H6A	0.284303	0.813714	0.551390	0.024*
O1	1.0455(2)	0.6696(2)	−0.03253(11)	0.0325(6)
O2	0.80947(18)	0.3916(2)	0.45660(10)	0.0233(5)
O3	0.87680(19)	0.9247(2)	0.52330(10)	0.0239(5)
O4	0.34815(19)	0.4814(2)	0.91914(10)	0.0266(5)
O5	0.2499(2)	1.0606(2)	1.01833(10)	0.0333(6)
O6	0.6075(2)	1.2503(2)	0.53938(11)	0.0307(5)

d(N2—H2) = 0.917, d(H2...O3) = 2.19; O2—H3...N3: d(N3—H3) = 0.964, d(H3...O2) = 2.04, d(N3...O2) = 2.571(3); O6—H6A...N6: d(N6—H6A) = 0.976, d(N6...O6) = 2.565(3), d(H6A...O6) = 2.06. In addition, there are further intermolecular classical O—H...N and some weak, non-classical C—H...O hydrogen bonds.

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