Crystal structure of bis[2-bromo-4-chloro-6-[(3-nitro-phenyl-imino)methyl]phenol]copper(II), $Cu(C_{13}H_7BrClN_2O_3)_2$

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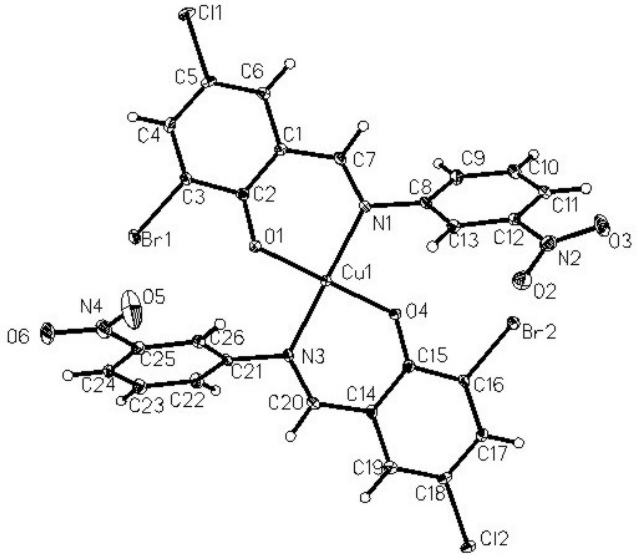

Abstract

$C_{26}H_{14}Br_2Cl_2CuN_4O_6$, triclinic, $P\overline{1}$ (no. 2), a = 7.879(2) Å, b = 12.568(3) Å, c = 14.209(4) Å, α = 72.617(8)°, β = 82.070(9)°, γ = 81.31(1)°, V = 1320.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.072, T = 153 K.

Source of material

3-Bromo-5-chlorosalicylaldehyde (23.5 mg, 0.1 mmol) dissolved in methanol (10 mL) was added to 3-nitroaniline (13.8 mg, 0.1 mmol) in methanol (10 mL). The reaction mixture was stirred for 1 h at room temperature to give a clear orange solution. The product of the title compound was obtained by slowly evaporating the solvent for about five days at ambient temperature. The pro-duct was filtered off, washed with cold methanol, and finally dried (yield 68.6 %).

Discussion

Schiff bases and their metal complex have played an important role in the development of coordination chemistry due to their preparative accessibility, structural variety, catalytic [1] and magnetic [2] as well as biological properties [3,4].

The title crystal structure is built up by units containing Cu(II) ion and two Schiff base ligands, within which all bond lengths and bond angles are in normal ranges.The central Cu(II) atom is four-coordinated by two nitrogen atoms and two oxygen atoms from two Schiff bases in the usual *trans* arrangement, forming a distorted square-planar coordination. The corresponding distances are d(Cu—N1) = 2.000(2) Å, d(Cu—O1) = 1.889(2) Å, d(Cu—O4) = 1.888(2) Å, respectively. These distances are close to the values found in reported copper complexes [5]. Bond angles also show that the coordination around the Cu(II) atom is a slightly distorted square-planar one with the angles ∠O1–Cu–N1 = 92.01(9)°, ∠O4–Cu–N3 = 89.61(9)°, ∠N1–Cu–O4 = 92.35(9)° and ∠O1–Cu–N3 = 89.61(9)°. All these can be interpreted in terms of the phenyl substituent having a bigger steric effect. The C7=N1 and C20=N3 bond lengths of 1.292(3) Å and 1.294(3) Å are conform with double bonds. Two phenyl rings of each Schiff base ligand are non-planar because of coordination effect. To avoid steric conflicts, two phenyl rings are rotated with respect to each other with a dihedral angle of 57.67(1)° and 67.65°, respectively. Cu1···Cl2 (–x+1,–y,–z+2) contacts [d(Cu1—Cl2) = 3.540(2) Å], C18–Cl2···H13 (–x+1,–y,–z+2) and C3–Br1···H9 (–x+1,–y+1,–z+1) intermolecular hydrogen bonds, Br1···Br2 interactions and $\pi\cdots\pi$ (–x+2,–y+1,–z+1) stacking interactions with the center-to-center distances of 3.749 Å and the interplanar distance of 3.5856 Å form a three-dimensional network.

Table 1. Data collection and handling.

Crystal:	gray block, size 0.13 × 0.17 × 0.17 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	41.06 cm^{-1}
Diffractometer, scan mode:	AFC10/Saturn724+, φ/ω
$2\theta_{max}$:	58.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14824, 7111
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4959
$N(param)_{refined}$:	370
Programs:	SHELXS-97, SHELXL-97 [6]

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

Atom	Site	x	y	z	U_{iso}
H(4)	2*i*	0.7361	0.7296	0.4361	0.023
H(6)	2*i*	0.9029	0.4425	0.3614	0.023
H(7)	2*i*	0.8415	0.2683	0.4656	0.021
H(9)	2*i*	0.6472	0.1307	0.4684	0.024
H(10)	2*i*	0.7143	–0.0535	0.4599	0.024
H(11)	2*i*	0.8696	–0.1870	0.5809	0.023
H(13)	2*i*	0.8842	0.0498	0.7211	0.020
H(17)	2*i*	0.2495	–0.1704	0.9314	0.020
H(19)	2*i*	0.2373	0.0850	1.0513	0.021
H(20)	2*i*	0.3432	0.2523	0.9629	0.019
H(22)	2*i*	0.2210	0.4515	0.8521	0.023
H(23)	2*i*	0.2227	0.6226	0.8834	0.026
H(24)	2*i*	0.4840	0.6785	0.9011	0.023
H(26)	2*i*	0.7406	0.3911	0.8523	0.021

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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}
Cu(1)	2*i*	0.57940(5)	0.26441(3)	0.71019(3)	0.0189(2)	0.0124(2)	0.0141(2)	–0.0038(1)	0.0031(1)	–0.0047(1)
Br(1)	2*i*	0.55464(4)	0.66341(2)	0.63364(2)	0.0381(2)	0.0142(2)	0.0179(2)	–0.0013(1)	–0.0002(1)	–0.0061(1)
Br(2)	2*i*	0.42723(4)	–0.09833(2)	0.73263(2)	0.0372(2)	0.0191(2)	0.0181(2)	–0.0096(1)	0.0053(1)	–0.0090(1)
Cl(1)	2*i*	0.9302(1)	0.67263(6)	0.27384(6)	0.0360(5)	0.0257(4)	0.0198(4)	–0.0132(3)	0.0077(3)	0.0000(3)
Cl(2)	2*i*	0.1241(1)	–0.12949(6)	1.11275(5)	0.0256(4)	0.0206(4)	0.0159(3)	–0.0076(3)	0.0028(3)	–0.0008(3)
O(1)	2*i*	0.6049(3)	0.4183(2)	0.6546(2)	0.032(1)	0.013(1)	0.015(1)	–0.0041(9)	0.0053(9)	–0.0038(8)
O(2)	2*i*	1.0005(3)	–0.1398(2)	0.8118(2)	0.036(1)	0.030(1)	0.021(1)	–0.004(1)	–0.008(1)	–0.006(1)
O(3)	2*i*	1.0551(3)	–0.2493(2)	0.7157(2)	0.044(2)	0.023(1)	0.031(1)	0.016(1)	–0.009(1)	–0.011(1)
O(4)	2*i*	0.4919(3)	0.1245(2)	0.7456(2)	0.028(1)	0.017(1)	0.015(1)	–0.0098(9)	0.0076(9)	–0.0063(8)
O(5)	2*i*	0.9262(3)	0.5110(2)	0.8844(3)	0.020(2)	0.068(2)	0.152(4)	–0.003(1)	–0.003(2)	–0.076(2)
O(6)	2*i*	0.7932(3)	0.6678(2)	0.9014(2)	0.046(2)	0.036(1)	0.051(2)	–0.026(1)	0.011(1)	–0.028(1)
N(1)	2*i*	0.7274(3)	0.2241(2)	0.5969(2)	0.018(1)	0.013(1)	0.013(1)	–0.002(1)	0.001(1)	–0.0064(9)
N(2)	2*i*	0.9884(3)	–0.1620(2)	0.7348(2)	0.025(2)	0.021(1)	0.021(1)	–0.002(1)	–0.001(1)	–0.000(1)
N(3)	2*i*	0.4759(3)	0.2952(2)	0.8367(2)	0.018(1)	0.012(1)	0.017(1)	–0.003(1)	0.001(1)	–0.007(1)
N(4)	2*i*	0.7957(4)	0.5752(2)	0.8883(2)	0.029(2)	0.035(2)	0.038(2)	–0.016(1)	0.008(1)	–0.022(1)
C(1)	2*i*	0.7659(4)	0.4171(2)	0.4993(2)	0.017(2)	0.015(1)	0.015(1)	–0.004(1)	0.001(1)	–0.004(1)
C(2)	2*i*	0.6775(4)	0.4695(2)	0.5695(2)	0.015(2)	0.017(1)	0.016(1)	–0.003(1)	–0.001(1)	–0.005(1)
C(3)	2*i*	0.6703(4)	0.5899(2)	0.5413(2)	0.017(2)	0.016(1)	0.016(1)	–0.003(1)	–0.001(1)	–0.007(1)
C(4)	2*i*	0.7449(4)	0.6501(2)	0.4523(2)	0.024(2)	0.013(1)	0.021(2)	–0.004(1)	–0.005(1)	–0.003(1)
C(5)	2*i*	0.8333(4)	0.5948(2)	0.3855(2)	0.018(2)	0.021(2)	0.017(2)	–0.008(1)	0.004(1)	–0.001(1)
C(6)	2*i*	0.8436(4)	0.4798(2)	0.4077(2)	0.022(2)	0.021(2)	0.016(2)	–0.005(1)	0.003(1)	–0.008(1)
C(7)	2*i*	0.7830(4)	0.2970(2)	0.5176(2)	0.016(2)	0.017(1)	0.020(2)	–0.001(1)	0.002(1)	–0.010(1)
C(8)	2*i*	0.7621(4)	0.1091(2)	0.5935(2)	0.016(2)	0.015(1)	0.019(2)	–0.002(1)	0.004(1)	–0.009(1)
C(9)	2*i*	0.7104(4)	0.0770(2)	0.5175(2)	0.026(2)	0.016(1)	0.019(2)	–0.002(1)	–0.004(1)	–0.005(1)
C(10)	2*i*	0.7499(4)	–0.0326(2)	0.5125(2)	0.025(2)	0.020(2)	0.018(2)	–0.004(1)	–0.002(1)	–0.010(1)
C(11)	2*i*	0.8410(4)	–0.1118(2)	0.5838(2)	0.021(2)	0.016(1)	0.019(2)	–0.002(1)	0.005(1)	–0.007(1)
C(12)	2*i*	0.8889(4)	–0.0784(2)	0.6588(2)	0.016(2)	0.014(1)	0.017(2)	–0.002(1)	0.003(1)	–0.004(1)
C(13)	2*i*	0.8509(4)	0.0302(2)	0.6672(2)	0.018(2)	0.018(1)	0.015(1)	–0.004(1)	0.001(1)	–0.006(1)
C(14)	2*i*	0.3578(4)	0.1168(2)	0.9100(2)	0.016(2)	0.013(1)	0.019(2)	–0.003(1)	–0.001(1)	–0.006(1)
C(15)	2*i*	0.4095(4)	0.0726(2)	0.8280(2)	0.015(2)	0.015(1)	0.017(1)	–0.001(1)	–0.002(1)	–0.005(1)
C(16)	2*i*	0.3645(4)	–0.0366(2)	0.8403(2)	0.017(2)	0.014(1)	0.014(1)	–0.001(1)	–0.001(1)	–0.007(1)
C(17)	2*i*	0.2779(4)	–0.0979(2)	0.9262(2)	0.018(2)	0.013(1)	0.019(2)	–0.003(1)	–0.003(1)	–0.004(1)
C(18)	2*i*	0.2331(4)	–0.0511(2)	1.0049(2)	0.013(2)	0.017(1)	0.014(1)	–0.003(1)	–0.000(1)	0.001(1)
C(19)	2*i*	0.2706(4)	0.0540(2)	0.9972(2)	0.017(2)	0.020(2)	0.015(1)	–0.001(1)	–0.001(1)	–0.006(1)
C(20)	2*i*	0.3900(4)	0.2268(2)	0.9071(2)	0.014(2)	0.019(1)	0.015(1)	0.001(1)	–0.001(1)	–0.008(1)
C(21)	2*i*	0.4799(4)	0.4036(2)	0.8528(2)	0.020(2)	0.013(1)	0.013(1)	–0.000(1)	–0.000(1)	–0.007(1)
C(22)	2*i*	0.3269(4)	0.4739(2)	0.8598(2)	0.015(2)	0.020(2)	0.025(2)	0.000(1)	–0.002(1)	–0.009(1)
C(23)	2*i*	0.3278(4)	0.5756(2)	0.8779(2)	0.024(2)	0.018(2)	0.021(2)	0.004(1)	–0.004(1)	–0.006(1)
C(24)	2*i*	0.4817(4)	0.6089(2)	0.8879(2)	0.031(2)	0.011(1)	0.015(2)	–0.002(1)	0.001(1)	–0.004(1)
C(25)	2*i*	0.6320(4)	0.5394(2)	0.8785(2)	0.019(2)	0.020(2)	0.018(2)	–0.008(1)	0.001(1)	–0.007(1)
C(26)	2*i*	0.6349(4)	0.4369(2)	0.8599(2)	0.017(2)	0.018(1)	0.018(2)	–0.002(1)	0.002(1)	–0.006(1)

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