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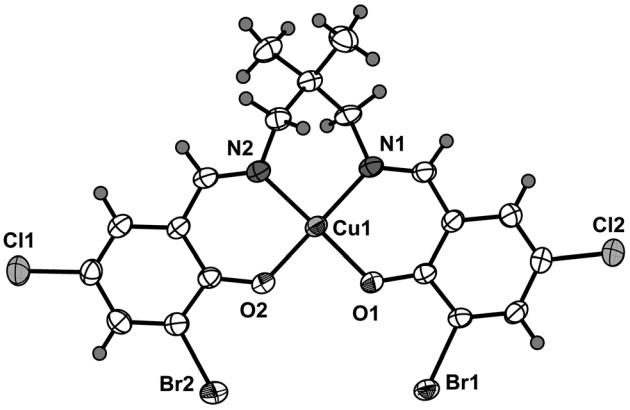
{6,6′-((1*E*,1′*E*)-((2,2-dimethylpropane-1,3-diyl)-bis(azaneylylidene))bis(methaneylylidene))-bis(2-bromo-4-chlorophenolate)-κ^{4}N,N′,O,O′}-copper(II), $C_{19}H_{16}Br_2Cl_2CuN_2O_2$



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Abstract

$C_{19}H_{16}Br_2Cl_2CuN_2O_2$, monoclinic, $P2_1/n$ (no. 14), a = 12.4679(2) Å, b = 8.61760(10) Å, c = 19.7854(3) Å, β = 97.1610(10)°, V = 2109.23(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0325, w$R_{ref}(F^2)$ = 0.0865, T = 170.0 K.

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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

3–Bromosalicylaldehyde (0.100 g, 0.5 mmol) and ethylenediamine (0.030 g, 0.5 mmol) were dissolved in a mixture of 20 mL ethanol. The Schiff base solution was stirred at room temperature for 24 h. After this, copper(II) nitrate (0.75 mmol) was added to the above solution and the obtained black mixture was further stirred for 24 h and filtered. The acquired black filtrate was sealed in a beaker with parafilm and kept undisturbed at room temperature. The black block crystals of the title compound were afforded after one month by slow evaporation.

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.07 × 0.02 × 0.02 mm
Wavelength:	CuKα radiation (1.54184 Å)
μ:	8.39 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	75.9°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13085, 4118, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3541
$N(param)_{refined}$:	255
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Experimental details

X-ray single crystal data was collected on a Bruker SMART APEX II diffractometer with rotating anode source (MoKα radiation, λ = 0.71073 Å). Data reduction was performed using the program SAINT and empirical absorption corrections were made using SADABS [1]. The structure was solved with the Olex2 program [2] as an interface together with the SHELXT and SHELXL programs [3, 4]. All H atoms were placed in geometrically idealized positions and refined using a riding model, with C–H = 0.98 (methylene), 0.95 Å (benzene) and 0.97 Å (methyl); U_{iso}(H) values were set 1.2 times for H atoms on methylene and benzene.

Comment

It is of significance to develop complexes via ligand substitution with different halogen atoms and study the

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.16560 (2)	0.17648 (4)	0.56144 (2)	0.03300 (10)
Br2	0.24719 (3)	0.30328 (5)	0.29005 (2)	0.04827 (13)
Cu1	0.51776 (3)	0.26844 (5)	0.48725 (2)	0.02739 (12)
Cl1	0.52360 (8)	0.67820 (12)	0.16746 (5)	0.0505 (2)
Cl2	0.37569 (7)	−0.12136 (14)	0.78707 (5)	0.0590 (3)
O1	0.39415 (16)	0.1964 (3)	0.52597 (11)	0.0307 (5)
O2	0.43015 (17)	0.3111 (3)	0.40348 (11)	0.0317 (5)
N1	0.61990 (19)	0.1549 (3)	0.55246 (13)	0.0284 (5)
N2	0.6319 (2)	0.4092 (3)	0.46741 (13)	0.0292 (5)
C1	0.4885 (2)	0.0659 (4)	0.62409 (15)	0.0294 (6)
C2	0.3945 (2)	0.1264 (3)	0.58419 (15)	0.0263 (6)
C3	0.2958 (2)	0.1026 (4)	0.61209 (15)	0.0279 (6)
C4	0.2890 (3)	0.0311 (4)	0.67299 (16)	0.0340 (7)
H4	0.2220	0.0205	0.6897	0.041*
C5	0.3833 (3)	−0.0261 (4)	0.70984 (17)	0.0384 (7)
C6	0.4815 (3)	−0.0101 (4)	0.68603 (17)	0.0361 (7)
H6	0.5442	−0.0503	0.7113	0.043*
C7	0.5949 (2)	0.0759 (4)	0.60271 (16)	0.0302 (6)
H7	0.6505	0.0192	0.6280	0.036*
C8	0.7303 (2)	0.1444 (4)	0.53365 (17)	0.0315 (6)
H8A	0.7262	0.1063	0.4867	0.038*
H8B	0.7708	0.0676	0.5632	0.038*
C9	0.7936 (2)	0.2983 (4)	0.53895 (16)	0.0317 (6)
C10	0.7177 (3)	0.4376 (4)	0.52387 (16)	0.0326 (7)
H10A	0.6845	0.4628	0.5649	0.039*
H10B	0.7602	0.5277	0.5128	0.039*
C11	0.6353 (2)	0.4815 (4)	0.41106 (16)	0.0302 (6)
H11	0.6963	0.5438	0.4078	0.036*
C12	0.5540 (2)	0.4761 (4)	0.35195 (15)	0.0286 (6)
C13	0.4557 (2)	0.3920 (3)	0.35287 (15)	0.0275 (6)
C14	0.3817 (2)	0.4049 (4)	0.29234 (16)	0.0320 (6)
C15	0.4031 (3)	0.4876 (4)	0.23614 (16)	0.0332 (7)
H15	0.3525	0.4899	0.1967	0.040*
C16	0.5003 (3)	0.5679 (4)	0.23806 (16)	0.0340 (7)
C17	0.5742 (2)	0.5634 (4)	0.29518 (16)	0.0319 (7)
H17	0.6391	0.6193	0.2964	0.038*
C18	0.8747 (3)	0.2922 (5)	0.4867 (2)	0.0465 (9)
H18A	0.9179	0.1986	0.4936	0.070*
H18B	0.9215	0.3823	0.4923	0.070*
H18C	0.8358	0.2917	0.4410	0.070*
C19	0.8533 (3)	0.3203 (5)	0.61002 (19)	0.0463 (9)
H19A	0.8025	0.3126	0.6433	0.069*
H19B	0.8872	0.4218	0.6133	0.069*
H19C	0.9082	0.2407	0.6190	0.069*

relationship between structure and properties [5, 6]. Copper based complexes have potential applications in molecular catalysis, biosensors and medicine [7, 8]. The structures of copper complexes can be enriched by connecting copper ions with different halogenated Schiff-base ligands [9, 10]. Herein as a part of our current research on the exploration of the regulating effect of Schiff base metal complexes, we report a new Cu(II) complex.

The asymmetric unit is composed of one title complex (see the figure). The coordination environment of the ion center is defined by two oxygen atoms and two nitrogen atoms.

It should not kept unmentioned that there is an isomorphous structure to the title struture in which the bromo substituents are exchanged by chloro substituents [11] and nickel replaced by copper.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. APEX2 and SAINT; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
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. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Xu X., Tian H., Wang X., Wang M., Wu Q. Crystal structure of 4-bromo-*N*′-[(3-chloro-2-hydroxyphenyl)methylidene] benzohydrazide, $C_{14}H_7Br_2N_2O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 347–348.
6. Liang J., Hui T., Jinrong S., Longduo Z., Qiong W. Crystal structure of rac-*trans*-*N*,*N*′-bis(3,5-dibromosalicylidene)-1,2-cyclohexanediamine, $C_{20}H_{18}Br_4N_2O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2020, *235*, 847–848.
7. Shen Q., Gómez-García C. J., Sun W., Lai X., Pang H., Ma H. Improving the photocatalytic H_2 evolution activity of Keggin polyoxometalates anchoring copper-azole complexes. *Green Chem.* 2021, *23*, 3104–3114.
8. Wu Q., Shi Q., Li Y.-G., Wang E. B. Synthesis, crystal structure and magnetic properties of new MnIII—CuII heterometallic aggregates based on multidentate Schiff-base ligands. *J. Coord. Chem.* 2008, *61*, 3080–3091.
9. Duan R., Man W., Meifen H., Ma X., Wu Q. Crystal structure of 6,6′-((pentane-1,3-diylbis(azaneylylidene))bis(methaneylylidene))

bis(2,4- dibromolphenolato-κ^4N,N',O,O')copper(II), $C_{19}H_{16}Br_4CuN_2O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 67–69.
10. Duan R., Ma X., Huang M., Wang M., Wu Q. Crystal structure of [6,6′-(((2,2-dimethylpropane-1,3-diyl)bis(azanylylidene)) bis(methanylylidene))bis(2-chlorophenolato)-κ^4N,N',O,O'] copper(II). *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 79–80.
11. Kargar H., Kia R., Abbasian S., Tahir M. N. {4,4′,6,6′-Tetrachloro-2,2′- [2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]} nickel(II). *Acta Crystallogr.* 2012, *E68*, m193.