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(4-Bromo-2-formylphenolato)perchlorato(1,10-phenanthroline)copper(II)

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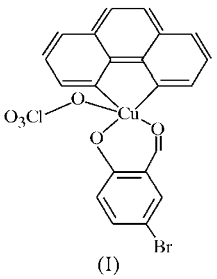
In the title copper(II) compound, $[Cu(C_7H_4BrO_2)(ClO_4)(C_{12}H_8N_2)]$, the Cu atom is five-coordinated in a distorted square-pyramidal geometry by the N- and O-donors of 4-bromo-2-formylphenolate, 1,10-phenanthroline and perchlorate. Pairs of complexes are linked together by Cu$\cdots$O(phenolate) and π–π stacking interactions between 4-bromo-2-formylphenolate and 1,10-phenanthroline. Along the crystallographic *a* axis, the dimers are linked by hydrogen bonds between a perchlorate O atom and a 4-bromo-2-formylphenolate H atom, and by further π–π stacking interactions. Hydrogen bonding between the Br atom and a 1,10-phenanthroline H atom takes place between the stacks of dimers.

Comment

Studies of complexes containing salicylaldehyde and its derivatives have been reported by Janzen *et al.* (2004) and other groups. The five-coordinated Cu^{II} complexes have been extensively investigated and the relationship between their structures and reactivities is of major importance. In the light of conflicting opinions on how best to estimate the geometry of five-coordinated Cu^{II} complexes, Addison *et al.* (1984) introduced a very useful parameter, τ, which provides a measure of the degree of SP (square pyramidal) versus TBP (trigonal–bipyramidal) geometry adopted by five-coordinate Cu^{II} complexes.

We report here the synthesis and structure of the title complex, (I). This is the first reported crystal structure of a complex involving Cu^{2+}, 1,10-phenanthroline (phen), 4-bromo-2-formylphenolate and ClO_4^-. Elemental analysis data for this compound are in good agreement with the experimental crystal pattern. The larger of the basal angles, O2—Cu1—N2, is 176.33 (17)° and the remaining angle, O1—Cu1—N1, is 170.43 (17)°. According to Addison's rule, we calculated the parameter τ to be 0.098. Thus, we can conclude that the complex in this paper will show a square-pyramidal coordination geometry.

In complex (I), the Cu^{II} ion is coordinated by phenolate atom O1, carbonyl atom O2, phen atoms N1 and N2, and atom O3 of the ClO_4^- anion. Atom O3 lies in the axial position and the equatorial positions are occupied by the other four donor atoms. The bond distances for Cu1—N1 and Cu1—N2 of 2.007 (4) and 1.999 (4) Å, respectively, are nearly as long as those found for the similar auxiliary phen ligand (Youngme *et al.*, 2005). The bond lengths for Cu1—O1 and Cu1—O2 are 1.898 (4) and 1.995 (4) Å, respectively, which are in the range of those reported for similar copper(II) complexes [1.953 (2) and 1.952 (2) Å; Yang *et al.*, 2004]. The Cu1—O3 bond distance of 2.423 (11) Å is in the range observed in analogous compounds [2.381 (4) and 2.559 (4) Å; Plieger *et al.*, 2004]. The larger angles around Cu are near 180° (see above), so the ligands form a satisfactory N_2O_2 square, with atom O3 inhabiting the axial position. In this way, a distorted square pyramid is formed (Fig. 1).



(I)

It is interesting that there are weak Cu$\cdots$O interactions, π–π stacking interactions and intermolecular hydrogen bonds in this complex. The CH groups participate in a hydrogen bond with an O atom of the ClO_4^- anion, forming a C—H$\cdots$O hydrogen bond (C—H$\cdots$O = 162°). The Br atom and a H atom of the phen ligand form a weaker hydrogen bond (C—H$\cdots$Br = 136°). Adjacent dimers are then linked by face-to-face π–π stacking interactions between 4-bromo-2-formylphenolate and phen ligands, the shortest centroid–centroid contact being 3.628 Å, which is in the range of average values in π–π stacking interactions (Janiak, 2000). In addition, there is a second, longer, Cu$\cdots$O(phenolate) distance [Cu$\cdots$O1^i = 2.820 (4) Å; symmetry code: (i) $-x, -y+1, -z+1$], which is in the range of values reported previously [2.326 (2)–3.076 (4) Å; Yang *et al.*, 2004]. Dimers based on the above-

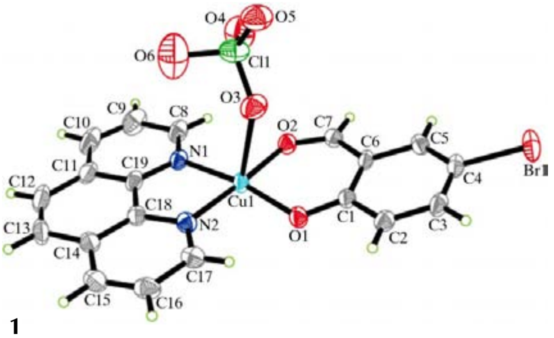


Figure 1
The independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as small spheres of arbitrary radii. Only one of the two disordered orientations of the perchlorate ligand is shown.

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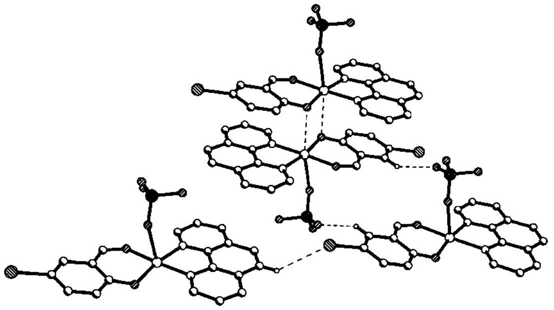

Figure 2
The dimer units of (I), viewed along the a axis, showing the weak Cu$\cdots$O interactions, π–π stacking interactions, and C—H$\cdots$O and C—H$\cdots$Br hydrogen bonds. For the sake of clarity, H atoms have been omitted.

mentioned weak Cu$\cdots$O interactions and π–π stacking interactions are linked along the crystallographic a axis by hydrogen bonding (Fig. 2).

The solid-state IR spectrum of (I) in the region 450–4000 cm^{-1} is in agreement with the X-ray diffraction data with respect to the mode of coordination. The absorption bands in the spectrum of (I) were red-shifted by 10–20 cm^{-1} relative to the bands in the spectrum of the free ligand. The two shortest absorption bands in the UV–vis spectrum of the free ligand, at about 230 nm, characterized by high molecular absorption coeffcients, can be attributed to the π–π* transition of the ligands. The longest wavelength band, at about 650 nm, can be characterized by a d–d transition of the metal ion. This case is very similar to those observed for the structurally well characterized square-bipyramidal geometry (Lever, 1984).

Experimental

For the preparation of the title compound, triethylamine (0.1 mmol) was added to a solution of 5-bromosalicylaldimine (0.0220 g, 0.1 mmol) in methanol (10 ml). After stirring the mixture for 10 min, 1,10-phenanthroline (0.0198 g, 0.1 mmol) was added. To the resulting solution, a methanolic solution (5 ml) of Cu(ClO$_4$)$_2$·6H$_2$O (0.0370 g, 0.1 mmol) was added with stirring at room temperature. The solution was then heated and stirred for 2 h. After about 10 d, green block-shaped crystals of (I) suitable for X-ray analysis appeared. These were collected by filtration, washed with H$_2$O and dried over silica gel (yield 58%). Analysis calculated for $C_{19}H_{12}BrClCuN_2O_6$: C 42.01, H 2.23, N 5.16%; found: C 42.96, H 2.16, N 5.82%.

Crystal data

$[Cu(C_7H_4BrO_2)(ClO_4)(C_{12}H_8N_2)]$
M_r = 543.21
Triclinic, $P\overline{1}$
a = 7.7560 (15) Å
b = 10.336 (2) Å
c = 12.873 (3) Å
α = 83.802 (3)°
β = 75.795 (3)°
γ = 76.010 (3)°
V = 969.5 (3) Å^3
Z = 2
D_x = 1.861 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 3.37 mm^{-1}
T = 294 (2) K
Block, green
0.22 × 0.18 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.763, T_{max} = 1.000
4860 measured reflections
3353 independent reflections
2427 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.138
S = 1.02
3353 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.9337P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.898 (4)	Cu1—N1	2.007 (4)
Cu1—O2	1.955 (4)	Cu1—O3	2.423 (11)
Cu1—N2	1.999 (4)	Cu1—O1^i	2.820 (4)
O1—Cu1—O2	92.72 (16)	N2—Cu1—O3	96.9 (4)
O1—Cu1—N2	90.96 (18)	N1—Cu1—O3	100.8 (3)
O2—Cu1—N2	176.33 (17)	C1—O1—Cu1	125.2 (3)
O1—Cu1—N1	170.43 (17)	C7—O2—Cu1	124.0 (3)
O2—Cu1—N1	93.61 (17)	C8—N1—Cu1	128.2 (4)
N2—Cu1—N1	82.74 (19)	C19—N1—Cu1	111.4 (4)
O1—Cu1—O3	87.0 (3)	C17—N2—Cu1	128.8 (4)
O2—Cu1—O3	83.3 (4)	C18—N2—Cu1	112.4 (4)

Symmetry code: (i) $-x, -y+1, -z+1$

H atoms were included in calculated positions and refined as riding on their parent atoms, with C—H distances in the range 0.93–0.98 Å and with $U_{iso}(H) = 1.2U_{eq}$(C,N). The perchlorate ion is disordered; the occupancies of atoms O3, O4, O5 and O6 are 0.42 (1) and those of atoms O3′, O4′, O5′ and O6′ are 0.58 (1).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3008). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Bruker (1998). *SMART*, *SAINT* and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
Janzen, D. E., Wang, X. L., Carr, P. W. & Mann, K. R. (2004). *Inorg. Chim. Acta*, **357**, 3317–3324.
Lever, A. B. P. (1984). *Inorganic Electronic Spectroscopy*, p. 553. Amsterdam: Elsevier.
Plieger, P. G., Downard, A. J., Moubaraki, B., Murray, K. S. & Booker, S. (2004). *Dalton Trans.* pp. 2157–2165.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Yang, Ch. T., Vetrichelvan, M., Yang, X. D., Moubaraki, B., Murray, K. S. & Vittal, J. J. (2004). *Dalton Trans.* pp. 113–121.
Youngme, S., Phuengphai, P., Pakawatchai, C., van Albada, G. A., Tanase, S., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2005). *Inorg. Chem. Commun.* **8**, 335–338.