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Bis[(*S*)-*N*-(2-butyl)-3,5-dichlorosalicylideneaminato-κ^2N,O]copper(II)

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The title compound, [Cu($C_{11}H_{12}Cl_2NO$)$_2$], has a compressed tetrahedral *trans*-[CuN_2O_2] coordination environment. The absolute configuration is found to be Δ(*S*,*S*) for the crystal examined. The Cu—N bond distances are 1.969 (4) and 1.971 (4) Å, while the Cu—O bond distances are 1.886 (3) and 1.892 (3) Å. The ligands, containing optically active (*S*)-2-butylamine moieties and electron-withdrawing Cl substituents, lead to an umbrella conformation of the overall molecule. On heating to 387 K, a structural phase transition is observed, probably involving a change in coordination geometry.

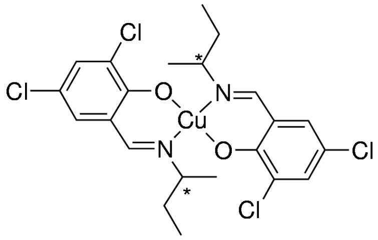
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.008 Å
R factor = 0.047
wR factor = 0.107
Data-to-parameter ratio = 9.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In recent years, there has been great interest in developing functional switching materials whose properties or structures can be controlled by several types of external perturbation (Sato *et al.*, 2003; Sato, 2003). In order to realise optical switching in the solid state, structural changes should be small to induce relaxation by tunnelling. In this respect, compounds which exhibit a structural phase transition in multiple steps with small energy barriers may be good candidates for these materials. It is well known that four-coordinate Cu^{II} complexes with bidendate Schiff base ligands, such as salicylaldimines, can vary from a square-planar (Manríquez *et al.*, 1990) to a distorted tetrahedral (Orioli & Sacconi, 1966; Cheeseman *et al.*, 1965) environment. Additionally, their overall molecular shape can also vary, to have flat (Chia *et al.*, 1977), umbrella (Fernandez-G. *et al.*, 2000) or stepped (Akitsu & Einaga, 2004) conformations. Furthermore, the introduction of chirality, commonly used in catalysis (Li *et al.*, 1987; Avalos *et al.*, 1998), will result in additional degrees of freedom in the structure, as well as a theoretical time-reversal symmetry of spins (Barron & Buckingham, 2001). This modification may lead to smaller energy barriers for structural phase transitions, if individual steps can be trapped successfully. Here, we report the crystal structure of the title compound, (I), which has chiral ligands and exhibits a structural phase transition upon heating.



(I)

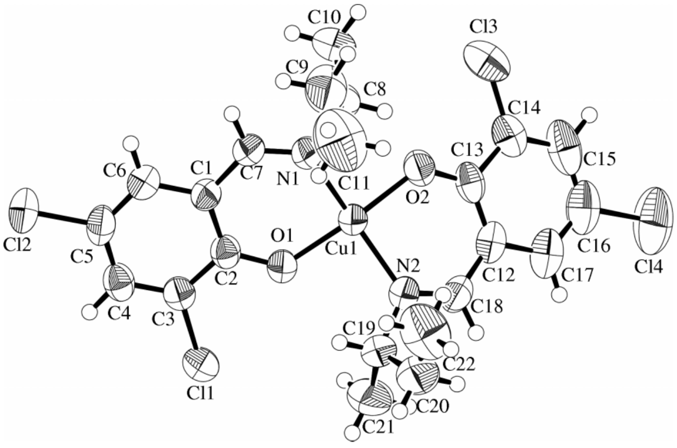


Figure 1
The molecular structure of (I), viewed from above the mean coordination plane, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitray radii.

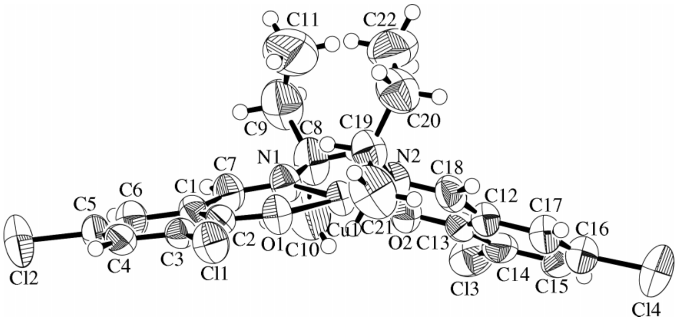


Figure 2
The molecular structure of (I), viewed from the side, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitray radii.

Complex (I) has a compressed tetrahedral *trans*-[CuN_2O_2] coordination geometry and adopts an umbrella conformation (Figs. 1 and 2; Table 1). The absolute configuration of (I) was found to be $\Delta(S,S)$ for the chiral atoms C8 and C19. The Cu1—N1 and Cu1—N2 bond distances are 1.969 (4) and 1.971 (4) Å, respectively, whereas the Cu1—O1 and Cu1—O2 bond distances are 1.886 (3) and 1.892 (3) Å, respectively. These values are in the normal ranges for analogous tetrahedrally distorted complexes, which are significantly influenced by $d\pi$–$p\pi$ interaction of coordination bonds.

It is well known that coordination geometry is dominated by both electronic effects and steric effects of the ligands, which readily leads to structural isomerism or phase transitions in analogous complexes (Yamada, 1999). Because of the steric hindrance of the 2-butylamine moieties, the degree of tetrahedral distortion in (I) is in the middle of the range found in analogous complexes: the *trans*-N1—Cu1—N2 and *trans*-O1—Cu1—O2 bond angles are 158.4 (2) and 158.7 (1)°, respectively, and the dihedral angle between the N1/Cu1/O1 and N2/Cu1/O2 planes is 29.85 (1)°. The imine C═N bond lengths are C7═N1 1.284 (6) and C18═N2 1.279 (6) Å, while the phenolate C—O bond distances are O1—C2 1.292 (5) and O2—C13 1.298 (6) Å, due to the electronic states of the π-conjugated ligands. With regard to the chiral ligands, the torsion angles around the (*S*)-2-butylamine moieties are C7—N1—C8—C9 56.4 (7), C7—N1—C8—C10 −69.1 (6), C18—N2—C19—C20 63.0 (7) and C18—N2—C19—C21 −63.0 (6)°.

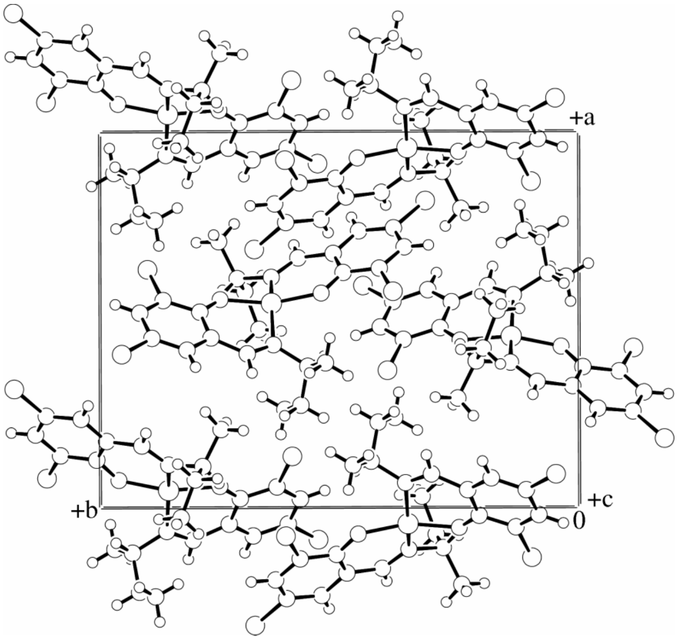


Figure 3
A molecular packing diagram for (I), viewed down the crystallographic *b* axis.

Since no remarkable hydrogen bonds within the van der Waals radii (Bondi, 1964) are observed for (I) (Fig. 3), molecular recognition for the chiral molecules could not be carried out using hydrogen bonding. An endothermic peak at 387 K in the differential scanning calorimetry curve reveals the occurrence of a thermally induced structural phase transition, from a square-planar to a tetrahedral coordination environment, as seen in related complexes (Yamada, 1999).

Experimental

Treatment of copper(II) acetate (0.453 g, 2.50 mmol), 3,5-dichlororosalicylaldehyde (0.956 g, 5.00 mmol) and (*S*)-2-butylamine (0.366 g, 5.00 mmol) in methanol (100 ml) at 313 K for 4 h gave rise to brown prismatic crystals of (I) [yield 76.8%; m.p. 566 K (decomposition)]. Analysis, found: C 47.69, H 4.38, N 5.27%; calculated for $C_{22}H_{24}Cl_4CuN_2O_2$: C 47.71, H 4.37, N 5.06%; IR (KBr) 1618 cm^{-1} (imine stretching band); absorption electron spectra (at 298 K) 26 400 cm^{-1} in $CHCl_3$, 26 800 cm^{-1} in methanol and 26 600 cm^{-1} in acetone (π–π*).

Crystal data

[$Cu(C_{11}H_{12}Cl_2NO)_2$]
M_r = 553.78
Orthorhombic, $P2_12_12_1$
a = 13.825 (3) Å
b = 17.563 (5) Å
c = 10.499 (1) Å
V = 2549.3 (9) Å^3
Z = 4
D_x = 1.443 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.1–12.5°
μ = 1.30 mm^{-1}
T = 297 (1) K
Prism, brown
0.40 × 0.40 × 0.30 mm

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.601$, $T_{\max} = 0.678$
4081 measured reflections
3289 independent reflections
2757 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 27.5°$
$h = -7 \rightarrow 17$
$k = -22 \rightarrow 9$
$l = -5 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.107$
$S = 1.02$
2757 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 1.0606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}
Absolute structure: Flack (1983), with 260 Friedel pairs
Flack parameter = −0.01 (2)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.886 (3)	Cl3—C14	1.727 (5)
Cu1—O2	1.892 (3)	Cl4—C16	1.722 (7)
Cu1—N1	1.969 (4)	O1—C2	1.292 (5)
Cu1—N2	1.971 (4)	O2—C13	1.298 (6)
Cl1—C3	1.744 (5)	N1—C7	1.284 (6)
Cl2—C5	1.735 (5)	N2—C18	1.279 (6)
O1—Cu1—O2	158.7 (1)	Cu1—O1—C2	129.4 (3)
O1—Cu1—N1	92.9 (2)	Cu1—O2—C13	127.5 (3)
O1—Cu1—N2	90.8 (2)	Cu1—N1—C7	123.9 (3)
O2—Cu1—N1	92.1 (2)	Cu1—N1—C8	118.3 (3)
O2—Cu1—N2	92.2 (2)	Cu1—N2—C18	124.0 (3)
N1—Cu1—N2	158.4 (2)	Cu1—N2—C19	117.8 (3)

H atoms were placed in calculated positions, with C—H = 0.95 Å, and were included in the final cycles of refinement using a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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