metal-organic papers

Bis(5-chloro-*N*-isopropylsalicyldenaminato-$\kappa^2 N,O$)-copper(II)

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The title compound, [Cu(C$_{10}$H$_{11}$ClNO)$_2$], has been structurally characterized in the low-temperature phase (brown form). It adopts a stepped conformation and affords a square-planar *trans*-[CuN$_2$O$_2$] coordination geometry, in which the Cu^{II} ion lies on a center of symmetry. The Cu—N and Cu—O bond distances are 2.032 (3) and 1.891 (2) Å, respectively.

Comment

Recently, the design of optically switchable transition metal complexes has attracted attention in materials science because of the potential applications of these complexes for memory devices (Sato, 2003). In order to search for such switchable compounds, we focus on the candidates that exhibit thermally induced phase transitions of molecular structures, mixed-valences or spin states. It is well known that certain four-coordinated Cu^{II} or Ni^{II} complexes having salicylaldimine Schiff base ligands exhibit planar-tetrahedral distortion isomerism with appropriate substituent groups or solvents of recrystallization (Yamada, 1999). Structural phase transition, that is, transformation from a low-temperature phase (square planar or compressed tetrahedral) to a high-temperature phase (tetrahedral), occurs by heating up to ∼400 K (Arai *et al.*, 1972). Comparative studies of crystal structures have been reported for two isomers (Chia *et al.*, 1977) or specific phases, such as the brown form (Tamura *et al.*, 1977) and the green form (Tamura *et al.*, 1980). The reasons for structural regulation are complicated; tetrahedral distortion may be caused by a less hindered amine moiety (Cheeseman *et al.*, 1965) as well as a bulky one (Fernandez *et al.*, 2000). The chirality of the ligands is also important for applications as homogeneous catalysts (Li *et al.*, 1987). Moreover, electron-withdrawing substituent groups affect not only the molecular structure but also various physical properties concerned with phase transition. We report here the crystal structure of the title compound, (I).

(I)
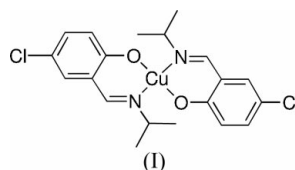
Complex (I) is centrosymmetric, with atom Cu1 located on a center of inversion (Fig. 1 and Table 1). The compound exhibits a square-planar *trans*-[CuN$_2$O$_2$] coordination geometry and adopts a stepped conformation with respect to the arrangement of the ligands; the dihedral angle between the N1/Cu1/O1 plane and the O1/C1/C6/C7/N1 plane is 158.86 (6)°. The structural features are characteristic for (I), because analogous square-planar complexes can also adopt an
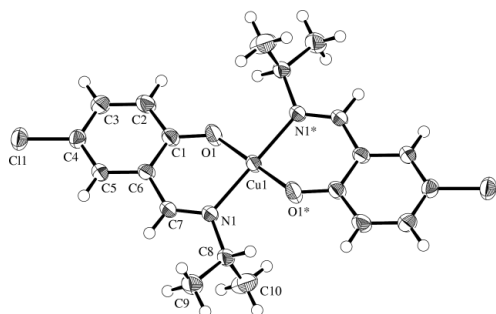
Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms marked with an asterisk (*) are at the symmetry position $(2 - x, -y, 2 - z)$.
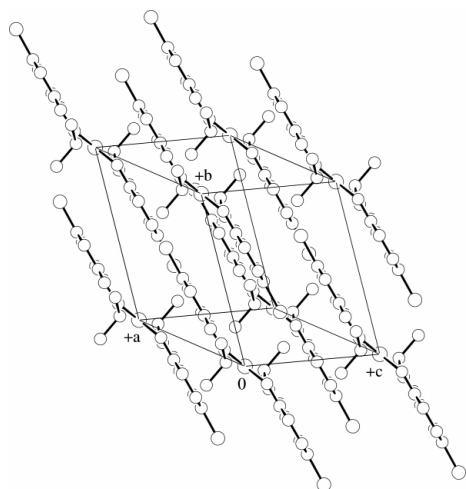

Figure 2
The molecular packing diagram of (I) (perspective view of the stepped conformation).

umbrella conformation in which both ligands bend towards the same side. The Cu—N and Cu—O bond distances are 2.032 (3) and 1.891 (2) Å, respectively. The cis–O1—Cu1—N1 and cis–O1—Cu1—N1^i bond angles are 90.70 (7) and 89.30 (7)°, respectively [symmetry code: (i) $2 - x$, y, $2 - z$]. Around the imine groups, the bond distances of the N1=C7 double bond and the C6—C7 bond are 1.282 (3) and 1.446 (3) Å, respectively, and the Cu1—N1—C7 and N1—C7—C6 bond angles are 122.3 (1) and 127.1 (1)°, respectively. For the phenolate group, the O1—C1 bond distance is 1.303 (3) Å, and the Cu1—O1—C1 and O1—C1—C6 bond angles are 128.0 (1) and 123.4 (2)°, respectively. The rest of the geometric parameters in the ligands do not differ significantly from normal values.

In contrast, the derivative without Cl groups adopts a distorted tetrahedral trans-[CuN₂O₂] environment with an umbrella conformation (Orioli & Sacconi, 1966). The averaged Cu—N and Cu—O bond distances are 1.980 and 1.879 Å, and the mean trans-N—Cu—N and trans-O—Cu—O bond angles are 137.7 and 137.1°, respectively. These two complexes indicate that electron-withdrawing Cl groups contribute to reducing the electronic distribution of $d\pi$–$p\pi$-type coordination bonds through the π-conjugated system, causing tetrahedral distortion and long coordination bond distances.

No intermolecular hydrogen bonds or other weak interactions could be observed in (I). Therefore, the crystal packing is controlled by weak van der Waals forces (Fig. 2). Individual molecules are aligned in parallel in the vertices of the triclinic unit cell, which seems to be proper for a cooperative phenomenon such as structural phase transition. In this way, the features of molecular and crystal structures may be favorable for structural phase transition on temperature change, but how the electronic structures of given molecules influence (photo-induced) phase transition is still an open question.

Experimental

Complex (I) was prepared by treatment of copper(II) acetate (0.91 g, 5.00 mmol), 5-chlorosalicylaldehyde (1.57 g, 10.0 mmol) and 2-propylamine (0.59 g, 10.0 mmol) in a methanol solution (100 ml) for 3 h at 318 K. Brown prismatic crystals of (I) were obtained from acetone at 318 K over a period of a few days. By heating, differential scanning calorimetry (DSC) exhibited an endothermic peak of structural phase transition at 444.5 K.

Crystal data

[Cu(C₁₀H₁₁ClNO)₂]	$Z = 1$
$M_r = 456.85$	$D_x = 1.551$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.648$ (4) Å	Cell parameters from 25
$b = 8.994$ (9) Å	reflections
$c = 7.294$ (3) Å	$\theta = 10.1$–13.7°
$\alpha = 97.98$ (5)°	$\mu = 1.41$ mm^{-1}
$\beta = 107.00$ (3)°	$T = 297.2$ K
$\gamma = 64.40$ (5)°	Prism, brown
$V = 489.2$ (6) Å^3	$0.60 \times 0.40 \times 0.30$ mm

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.026$
ω–2θ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -11 \rightarrow 10$
(North et al., 1968)	$k = -11 \rightarrow 4$
$T_{min} = 0.514$, $T_{max} = 0.656$	$l = -9 \rightarrow 9$
2525 measured reflections	3 standard reflections
2251 independent reflections	every 150 reflections
2152 reflections with $I > 2\sigma(I)$	intensity decay: 1.1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.001$
2152 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
124 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.891 (2)	N1—C8	1.493 (3)
Cu1—N1	2.032 (3)	C6—C7	1.446 (3)
Cl1—C4	1.752 (2)	C8—C9	1.517 (2)
O1—C1	1.303 (3)	C8—C10	1.519 (3)
N1—C7	1.282 (3)		
O1—Cu1—N1	90.70 (7)	O1—C1—C2	119.6 (1)
O1—Cu1—N1^i	89.30 (7)	O1—C1—C6	123.4 (2)
Cu1—O1—C1	128.0 (1)	N1—C7—C6	127.1 (1)
Cu1—N1—C7	122.3 (1)	N1—C8—C9	115.6 (2)
Cu1—N1—C8	119.6 (1)	N1—C8—C10	107.8 (2)
C7—N1—C8	118.0 (1)	C9—C8—C10	110.8 (2)

Symmetry code: (i) $2 - x, -y, 2 - z$.

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