metal-organic compounds

Bis[(R)-3,5-dichloro-N-(1-phenylethyl)salicylideneaminato-κ²N,O]copper(II) and bis[(R)-3-ethoxy-N-(1-phenylethyl)salicylideneaminato-κ²N,O]copper(II)

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The title compounds, $[Cu(C_{15}H_{12}Cl_2NO)_2]$, (I), and $[Cu(C_{17}H_{18}NO_2)_2]$, (II), both adopt a compressed tetrahedral *trans*-$[CuN_2O_2]$ coordination geometry, the molecules having an umbrella conformation overall. These complexes differ from one another with respect to the 1-phenylethylamine moieties, the direction of the benzene rings being either inside [in (I)] or inside and outside [in (II)] of the molecules. The crystals of (I) and (II) have $\Delta(R,R)$ and $\Lambda(R,R)$ absolute configurations, respectively.

Comment

Recent developments in functional switching materials (Sato *et al.*, 2003) have shown that a good way to discover candidate metal complexes is to examine compounds that show any changes between two or more states, such as structural phase transitions, isomerism, mixed valences and spin-crossover. In this respect, bis(*N*-alkylsalicylideneimine)copper(II) complexes are potentially good examples, because some of them exhibit thermally induced structural phase transitions (Yamada, 1999), and structural isomers can be isolated (Chia *et al.*, 1977). In addition, chirality (Barron & Buckingham, 2001) provides several structural and electronic modifications, and absolute asymmetric catalytic reactions (Nozaki *et al.*, 1968) are also often susceptible to external physical influence (Avalos *et al.*, 1998). For example, complexes incorporating 1-phenylethylamine ligands are suitable for studying the correlation between molecular structures and electronic properties (Akitsu *et al.*, 2001, 2003), and optically active bis(*N*-alkylsalicylideneimine) complexes of Cu[II] (Li *et al.*, 1987), Zn[II] (Evans & Luneau, 2002; Sakiyama *et al.*, 1990), Pd[II] (Brunner *et al.*, 2000) and Rh[V] (Kühn *et al.*, 1997) have been investigated in terms of stereochemistry, catalytic applications and second-harmonic generation. In this paper,

we report the crystal structures of the title compounds, (I) and (II), both of which contain 1-phenylethylamine groups.
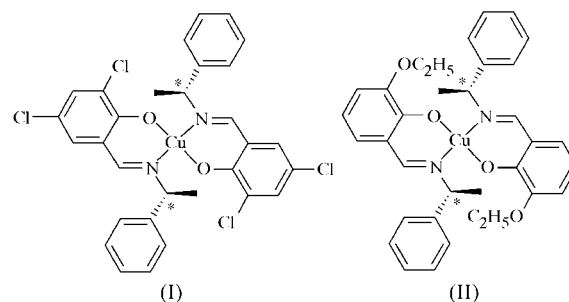
Both (I) (Table 1 and Fig. 1) and (II) (Table 2, and Figs. 2 and 3) adopt a compressed tetrahedral *trans*-$[CuN_2O_2]$ coordination geometry. Both 1-phenylethylamine groups are folded along the molecular axis through the salicylideneaminate moiety, and the molecule of (I) adopts an umbrella conformation. On the other hand, complex (II), which crystallizes in the monoclinic system (space group $P2_1$ with $Z = 4$) contains two crystallographically independent molecules, which we denote molecules 1 (containing atom Cu1) and 2 (Cu2). The overall structure of molecule 1 differs from that of molecule 2. In both molecules of (II), one of the two 1-phenylethylamine groups is folded along the salicylideneaminate moiety, while the other is located towards the outside of the molecule. As the bond angles around the Cu atom show, complex (II) also adopts a tetrahedral *trans*-$[CuN_2O_2]$ coordination geometry, which is closer to an ideal tetrahedron than the geometry of (I). The dihedral angles between the N1/Cu1/O1 and N2/Cu1/O2 planes are 45.0 (1)° for (I), and the dihedral angles between the N1/Cu1/O1 and N2/Cu1/O2 planes and between the N3/Cu2/O5 and N4/Cu2/O6 planes are 39.80 (1) and 45.33 (1)°, respectively, for (II).

The degree of distortion of the *trans*-$[CuN_2O_2]$ coordination environment in (I) and (II) results from both electronic effects of the 3,5-substituents and steric effects of the 1-phenylethylamine groups. However, these effects are complicated. For example, even 2-butylamine (Cheeseman *et al.*, 1965) or 2-propylamine (Orioli & Sacconi, 1966) moieties
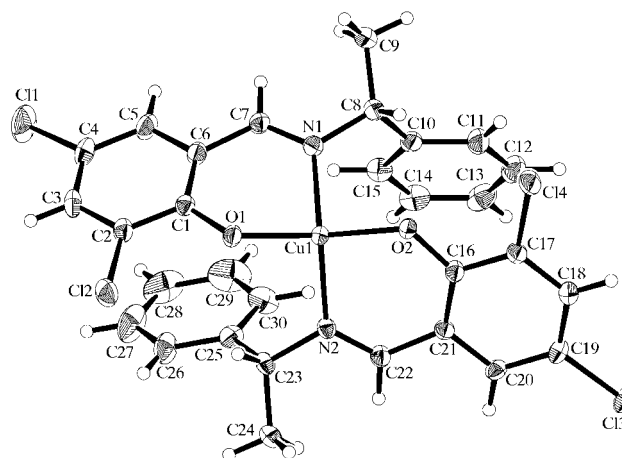

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

can lead to a tetrahedral environment. In contrast, more bulky diphenylethylamine groups result in a planar environment (Fernandez *et al.*, 2000). Most of the geometric parameters for (I) and (II) are comparable to analogous tetrahedral Cu[II] complexes (Yamada, 1999). Nevertheless, only (*R*)-1-phenyl-ethylamine was used for our preparations. The absolute configurations of the crystals of (I) and (II) examined were found to be $\Delta(R,R)$ and $\Lambda(R,R)$, respectively. Both the related Cl-substituted Zn[II] complex (Evans & Luneau, 2001) and the Cu[II] complex without 3-ethoxy substituents (Li *et al.*, 1987) were reported to have $\Lambda(R,R)$ configurations. Intra- and intermolecular hydrogen bonds are not detectable within van der Waals radii (Bondi, 1964) for either (I) or (II), and hence
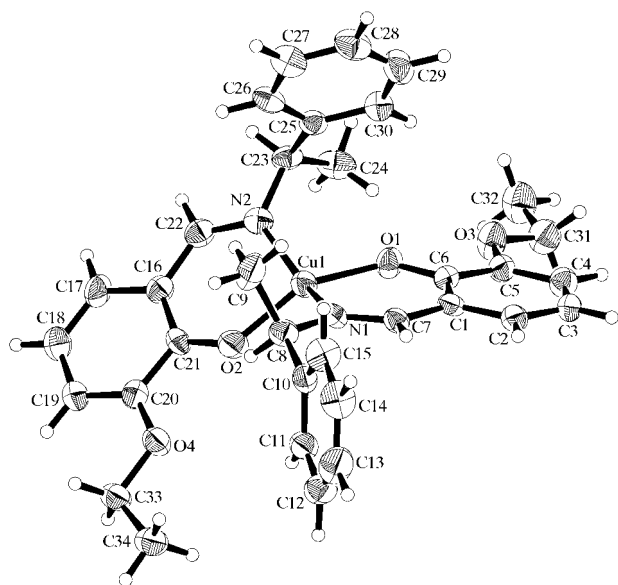
the crystal packing is dominated by weak van der Waals forces. Since no significant intermolecular interactions are found in either crystal, the factors determining the absolute config-uration of the coordination environment are obscure at present.

In addition, DSC (differential scanning calorimetry) curves obtained by heating the brown precipitates of (I) and (II) showed endothermic peaks at 419 and 386 K, respectively. By analogy with similar Cu[II] and Ni[II] complexes (Yamada, 1999; Akitsu & Einaga, 2004; Arai *et al.*, 1972), these features are attributed to thermally induced structural phase transitions. The structural change seems to be irreversible for both cases, though there are no intermolecular hydrogen bonds in the crystals. Moreover, whether conversion occurs between $\Lambda(R,R)$ or $\Delta(R,R)$ forms during the phase transition is still unclear.

Figure 2
The molecular structure of (II) (molecule 1), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.
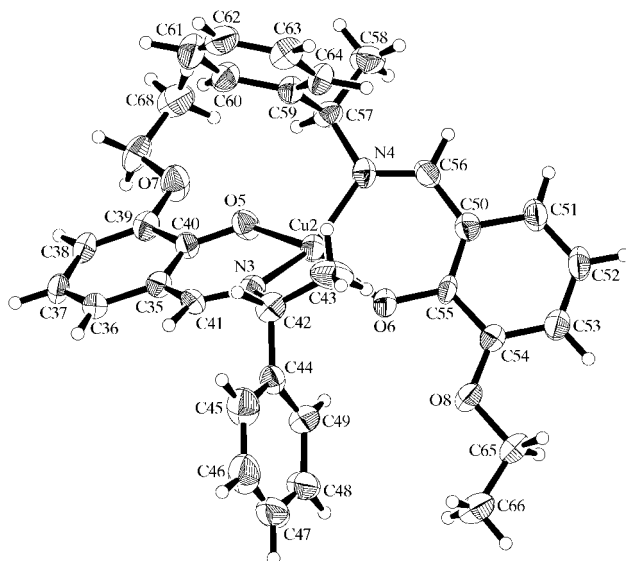

Figure 3
The molecular structure of (II) (molecule 2), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

For the preparation of compound (I), treatment of equimolar quan-tities of copper(II) acetate (0.91 g, 5.00 mmol), (*R*)-1-phenylethyl-amine (1.21 g, 10.0 mmol) and 3,5-dichlorosalicylaldehyde (1.91 g, 10.0 mmol) in methanol (150 ml) at 318 K for 2 h gave rise to a brown precipitate. Plate-like brown crystals were grown by the slow evaporation of a methanol solution at 278 K overnight. Analysis found: C 55.37, H 3.98, N 4.09%; calculated for $C_{30}H_{24}Cl_4CuN_2O_2$: C 55.44, H 3.72, N 4.31%. IR (KBr): 1623 cm^{-1} (C=N); m.p. 556 K (decomposition). The same preparation procedure was used for (II), except that 3-ethoxysalicylaldehyde (1.66 g, 10.0 mmol) was used instead of 3,5-dichlorosalicylaldehyde. Analysis found: C 67.84, H 6.12, N 4.59%; calculated for $C_{34}H_{36}CuN_2O_4$: C 68.04, H 6.05, N 4.67%. IR (KBr): 1636 cm^{-1} (C=N); m.p. 542 K (decomposition).

Compound (I)

Crystal data

$[Cu(C_{15}H_{12}Cl_2NO)_2]$	$D_x = 1.521$ Mg m^{-3}
$M_r = 649.86$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25
$a = 11.166$ (5) Å	reflections
$b = 14.852$ (7) Å	$\theta = 10.2–14.8°$
$c = 8.636$ (4) Å	$\mu = 1.18$ mm^{-1}
$\beta = 97.89$ (4)°	$T = 297$ (1) K
$V = 1418.6$ (11) Å^3	Plate, brown
$Z = 2$	$0.30 \times 0.30 \times 0.20$ mm

Data collection

Rigaku AFC-7*R* diffractometer	$R_{int} = 0.020$
ω–2θ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -5 \rightarrow 14$
(North *et al.*, 1968)	$k = 0 \rightarrow 19$
$T_{min} = 0.709$, $T_{max} = 0.790$	$l = -11 \rightarrow 11$
3771 measured reflections	3 standard reflections
3387 independent reflections	every 150 reflections
2958 reflections with $I > 2\sigma(I)$	intensity decay: 0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.597P]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.002$
2958 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
304 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
	154 Friedel pairs
	Flack parameter = -0.01 (2)

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—O1	1.890 (3)	Cu1—N2	1.984 (4)
Cu1—O2	1.878 (3)	N1—C7	1.275 (6)
Cu1—N1	1.995 (4)	N2—C22	1.280 (5)
O1—Cu1—O2	150.9 (1)	O2—Cu1—N1	94.6 (1)
O1—Cu1—N1	91.9 (1)	O2—Cu1—N2	93.6 (1)
O1—Cu1—N2	97.3 (1)	N1—Cu1—N2	144.7 (2)
C7—N1—C8—C10	−104.1 (4)	C22—N2—C23—C25	−108.0 (4)

Compound (II)

Crystal data

[Cu(C$_{17}$H$_{18}$NO$_2$)$_2$]	$D_x = 1.306$ Mg m^{-3}
$M_r = 600.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25
$a = 9.227$ (4) Å	reflections
$b = 42.38$ (1) Å	$\theta = 10.5–12.0°$
$c = 8.035$ (3) Å	$\mu = 0.76$ mm^{-1}
$\beta = 103.67$ (3)°	$T = 298$ (1) K
$V = 3053.0$ (19) Å^3	Plate, brown
$Z = 4$	$0.40 \times 0.30 \times 0.20$ mm

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.161$
ω–2θ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -4 \rightarrow 11$
(North et al., 1968)	$k = 0 \rightarrow 55$
$T_{min} = 0.762$, $T_{max} = 0.860$	$l = -10 \rightarrow 10$
7924 measured reflections	3 standard reflections
7100 independent reflections	every 150 reflections
3976 reflections with $I > 2\sigma(I)$	intensity decay: 0.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1162P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.066$	$+ 4.3366P]$
$wR(F^2) = 0.242$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
3976 reflections	$\Delta\rho_{max} = 0.69$ e Å^{-3}
644 parameters	$\Delta\rho_{min} = -0.77$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
	157 Friedel pairs
	Flack parameter = −0.04 (3)

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1—O1	1.895 (9)	Cu2—N3	1.98 (1)
Cu1—O2	1.90 (1)	Cu2—N4	1.97 (1)
Cu1—N1	1.98 (1)	N1—C7	1.30 (1)
Cu1—N2	1.980 (10)	N2—C22	1.32 (2)
Cu2—O5	1.899 (9)	N3—C41	1.30 (1)
Cu2—O6	1.891 (8)	N4—C56	1.31 (2)
O1—Cu1—O2	148.9 (3)	O5—Cu2—O6	144.0 (3)
O1—Cu1—N1	94.0 (4)	O5—Cu2—N3	93.5 (4)
O1—Cu1—N2	95.2 (4)	O5—Cu2—N4	90.6 (4)
O2—Cu1—N1	90.5 (4)	O6—Cu2—N3	99.2 (4)
O2—Cu1—N2	94.4 (4)	O6—Cu2—N4	94.8 (4)
N1—Cu1—N2	153.4 (4)	N3—Cu2—N4	150.0 (4)
C7—N1—C8—C10	−22 (1)	C41—N3—C42—C44	69 (1)

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 [U_{iso}(H) = 1.2U_{eq}(parent atom)]. The C atoms of the phenyl groups, namely C1–C6, C10–C15, C16–C21 and C25–C30 for (I), and C1–C6, C10–C15, C16–C21, C25–C30, C35–C40, C44–C49, C50–C55 and C59–C64 for (II), were treated as rigid groups of anisotropic atoms. Because of the remarkable plate-like shape and relatively poor quality of the crystals of (II), we employed the present data as the best result. Since we do not have another good single crystal, we could not recollect the data.

For both compounds, data collection and cell refinement: *WinAFC Diffractometer Control Software* (Rigaku, 1999); data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); 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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