*SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *XP* (Siemens, 1996*b*). Software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1216). Services for accessing these data are described at the back of the journal.

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The Chain Polymers (Imidazole)(*N*-salicylideneglycinato)copper(II) and (2-Ethylimidazole)(*N*-salicylideneglycinato)copper(II)

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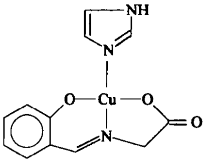
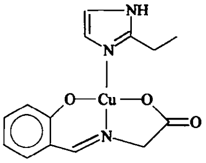
Abstract

The title compounds, (imidazole-N^3)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II), $[Cu(C_9H_7NO_3)(C_3H_4N_2)]$, (I), and (2-ethylimidazole-N^3)(*N*-salicylideneglycinato-*O*,*N*,*O*′)copper(II), $[Cu(C_9H_7NO_3)(C_5H_8N_2)]$, (II), adopt square-pyramidal Cu^{II} coordination with the tridentate *N*-salicylideneglycinato Schiff base dianion and the imidazole ligand bound in the basal plane. In both structures, the apex of the distorted pyramid is occupied by a carboxylic O atom from the neighbouring chelate at an apical distance of 2.563 (2) and 2.683 (2) Å in (I) and (II), respectively, thus building infinite zigzag chains. According to the electron paramagnetic resonance patterns, in compound (I), the Cu^{II} complexes are arranged in two and in compound (II), in four, magnetically inequivalent orientations.

Comment

Copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoalkanoato type (TSB^{2-}) represent a relatively simple model for studies of cooperative bonding effects, which can be investigated by electron paramagnetic resonance (EPR) spectroscopy. In these complexes of the general type $[Cu(TSB)(L)]_n$ (Warda, 1994), three donor atoms (O, N and O) of the Schiff base and a fourth donor atom from the neutral ligand *L* (N, O or S) normally define the base of a square pyramid. For isolated (monomeric) structures, the copper coordination can be square planar or square pyramidal when a neutral donor ligand is located at the apical site (n = 1; Ueki, Ashida, Sasada & Kakudo, 1969; Warda, 1994; Warda, Friebel, Sivý, Plesch & Švajlenová, 1996). Polymeric structures (n = ∞) are achieved when the apical position is occupied by a carboxylic O atom from an adjacent molecule to form infinite chains (Ueki, Ashida, Sasada & Kakudo, 1967; Warda, Friebel, Sivý, Plesch & Bláhová, 1997). In this paper, we report on chain formation in the two different cases of compounds (I) and (II).


(I)


(II)

In both structures, the molecules are characterized by a square-pyramidal Cu^{II} coordination with the tridentate Schiff base *N*-salicylideneglycinato dianion and a monodentate ligand in the basal plane, *i.e.* imidazole in (I) and 2-ethylimidazole in (II). The apical Cu—O3^i distances 2.563 (2) [symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$ in (I)] and 2.683 (2) Å [symmetry code: (i) $\frac{3}{2}-x, \frac{1}{2}+y, z$ in (II)], involving a carboxylic O atom of a neighbouring molecule, are elongated in comparison with the corresponding bond [2.334 (6) Å] in aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki, Ashida, Sasada & Kakudo, 1967). In structure (I), the molecules are connected *via* Cu···O3 bonds leading to an infinite one-

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dimensional chain along the crystallographic x axis. An additional link between N3 and O3 by hydrogen bonding forms a two-dimensional network along [100] and $[01\bar{1}]$. It has been found (Warda, 1994) that EPR patterns display a coupled g tensor indicative of antiferrodistortive ordering, with a tilt angle $2\gamma = 87.6°$, when the distance between the differently oriented paramagnetic centres is shorter than the critical distance of 8.3 Å; these features are found in (I), with a tilt angle of 88.8 (2)° and a Cu···Cu($-x$, $-y$, $-z$) distance of 5.1615 (7) Å.

The chain building in structure (II) follows the same principle. It occurs *via* Cu···O3 bridging with an antiferrodistortive ordering. The ethyl group of the imidazole ring keeps the chains from running parallel to each other in this compound because of steric hindrance. These chains are tilted with respect to each other and therefore four magnetically inequivalent $\mathrm{Cu^{II}}$ positions are created and the crystal system is of higher symmetry. The EPR patterns are in agreement with these results: the very complicated EPR powder spectrum displays this ordering type with two different non-molecular g tensors. Angular-dependent single-crystal measurements were carried out in the planes [001] and [110] using a Q-band EPR spectrometer (35 GHz). Two differently coupled g tensors are observed, describing four inequivalent paramagnetic centers. A strong intra-chain coupling associated with a Cu···Cu($\frac{3}{2}-x$, $-\frac{1}{2}+y$, z) distance of 6.2076 (7) Å between two magnetically inequivalent positions is overlapped by a weak coupling between the chains. In the coincidence points in the ranges −15 to 15, 80 to 90 and −90 to 80°, all the g tensors are coupled together. The inter-chain Cu···Cu($1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$) distance of 8.3379 (8) Å explains the weak coupling between two differently oriented copper(II) polyhedra in the angular ranges mentioned above, where some coupling of the g tensors take place. This distance is close to the maximum $\mathrm{Cu^{II}}\cdots\mathrm{Cu^{II}}$ distance for exchange narrowing. The intra-chain tilt angle from the structure determination is 84.8 (3)° and between the chains is 43.9 (2) and 79.1 (3)°.

In conclusion, the results of the EPR patterns in structure (I) are consistent with that from the structure determination. In structure (II), the ethyl group influences the cooperative ordering very strongly, resulting in four differently oriented copper(II) polyhedra; from the EPR investigations alone many observations cannot be fully

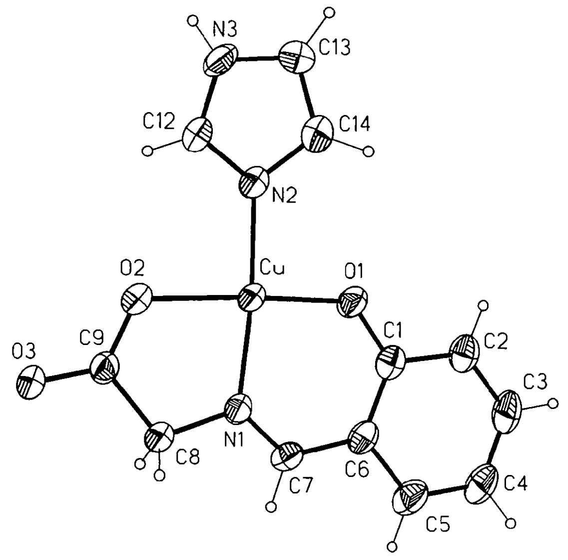

Fig. 1. The asymmetric unit of (I) with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

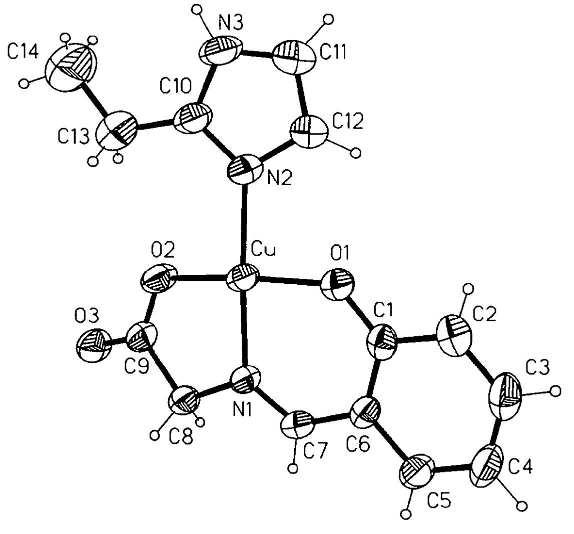

Fig. 2. The asymmetric unit of (II) with the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

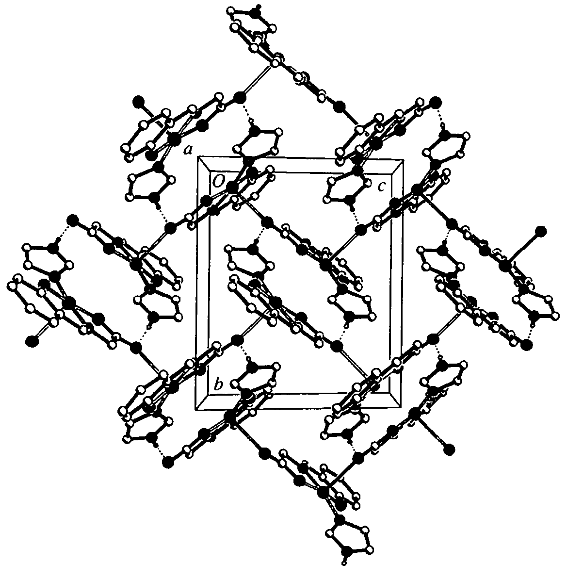

Fig. 3. The polymeric association of compound (I).

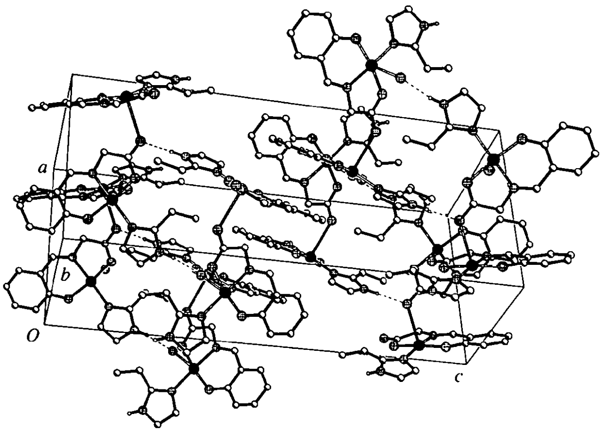

Fig. 4. The polymeric association of compound (II) displaying the four different orientations of Cu^{II} polyhedra.

explained. Only with the structural information can the coupling be completely understood, the Q band (35 GHz) displaying, in this case, the maximal resolution. The distance of 8.3 Å is a very important value in copper(II) chemistry. Only at shorter distances will there be an observable coupling between differently oriented copper(II) polyhedra. In all of these substances, there is only one exception to this rule until now (Warda *et al.*, 1996).

Experimental

The title compounds were synthesized from aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Ueki, Ashida, Sasada & Kakudo, 1967; Warda, 1994) and imidazole in compound (I) or 2-ethylimidazole in compound (II).

Compound (I)

Crystal data

$[Cu(C_9H_7NO_3)(C_3H_4N_2)]$
$M_r = 308.78$
Monoclinic
$P2_1/c$
$a = 11.0647\ (5)$ Å
$b = 11.5200\ (4)$ Å
$c = 9.6867\ (4)$ Å
$\beta = 103.199\ (4)°$
$V = 1202.10\ (8)$ Å^3
$Z = 4$
$D_x = 1.706$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 17.24–19.63°$
$\mu = 2.658$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.24 \times 0.18 \times 0.12$ mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical with ψ scans (Siemens, 1996*a*)
$T_{\min} = 0.572$, $T_{\max} = 0.727$
1883 measured reflections
1783 independent reflections

1614 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\max} = 59.95°$
$h = -12 \rightarrow 0$
$k = -12 \rightarrow 0$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.119$
$S = 1.053$
1783 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0834P)^2 + 1.0679P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.538$ e Å^{-3}
$\Delta\rho_{\min} = -1.008$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0029 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—O1	1.917 (2)	Cu—O2	1.993 (2)
Cu—N1	1.930 (3)	Cu—O3$^{\rm i}$	2.563 (2)
Cu—N2	1.957 (3)		
O1—Cu—N1	92.71 (10)	N2—Cu—O2	92.25 (10)
O1—Cu—N2	90.81 (10)	O1—Cu—O3$^{\rm i}$	97.61 (9)
N1—Cu—N2	172.68 (11)	N1—Cu—O3$^{\rm i}$	95.79 (9)
O1—Cu—O2	171.59 (10)	N2—Cu—O3$^{\rm i}$	90.10 (10)
N1—Cu—O2	83.41 (9)	O2—Cu—O3$^{\rm i}$	90.22 (8)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H31$\cdots$O3$^{\rm i}$	0.86	1.91	2.763 (4)	172

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

Compound (II)

Crystal data

$[Cu(C_9H_7NO_3)(C_5H_8N_2)]$
$M_r = 336.83$
Orthorhombic
$Pbca$
$a = 11.2152\ (5)$ Å
$b = 9.3864\ (5)$ Å
$c = 26.2788\ (9)$ Å
$V = 2766.4\ (2)$ Å^3
$Z = 8$
$D_x = 1.617$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 17.22–19.57°$
$\mu = 2.362$ mm^{-1}
$T = 293\ (2)$ K
Plate
$0.30 \times 0.15 \times 0.04$ mm
Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical with ψ scans (Siemens, 1996*a*)
$T_{\min} = 0.794$, $T_{\max} = 0.910$
2054 measured reflections
2054 independent reflections

1715 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 59.93°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 29$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.107$
$S = 1.031$
2054 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 2.7991P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.412$ e Å^{-3}
$\Delta\rho_{\min} = -0.522$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Cu—O1	1.919 (2)	Cu—N2	1.989 (3)
Cu—N1	1.945 (2)	Cu—O3^{i}	2.683 (2)
Cu—O2	1.975 (2)		
O1—Cu—N1	91.36 (9)	O2—Cu—N2	95.65 (11)
O1—Cu—O2	171.05 (10)	O1—Cu—O3^{i}	98.94 (8)
N1—Cu—O2	82.97 (9)	N1—Cu—O3^{i}	91.16 (9)
O1—Cu—N2	89.20 (11)	O2—Cu—O3^{i}	88.14 (9)
N1—Cu—N2	173.38 (11)	N2—Cu—O3^{i}	95.27 (10)

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, z$.

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···O3^{i}	0.86	1.974	2.824 (4)	170

Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

For both compounds, data collection: *CAD*-4 *Express* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *Express*; data reduction: *XCAD*-4 (Harms, 1997); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*96 (Sheldrick, 1996); molecular graphics: *XP* (Siemens, 1996*b*); software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1215). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1593–1596

{1,2-Bis[*N*-(4-methylphenyl)imino-*N*]-acenaphthene}(η^2-maleic anhydride)-palladium(0)

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(*Received 29 November 1996; accepted 27 May 1997*)

Abstract

The title compound, $[Pd(C_{26}H_{20}N_2)(C_4H_2O_3)]$, displays trigonal coordination of palladium by both N atoms and the double bond of maleic anhydride. The spatial arrangement of the *N*-aryl groups in the title compound, compared with a more sterically congested analogue, explains satisfactorily its enhanced reactivity towards organic substrates. The crystal packing involves weak C—H···O and C—H···π interactions.

Comment

Bidentate nitrogen ligands are useful ancillary ligands in palladium-catalyzed processes such as C—C coupling reactions (Süstmann, Lau & Zipp, 1986; van Asselt & Elsevier, 1992, 1994*a*). Among these, the rigid bidentate nitrogen compound bis[(*N*-aryl)imino]acenaphthene (Ar–BIAN) has been used as the spectator ligand in reaction sequences modeling the copolymerization of CO and alkenes (van Asselt, Gielens, Rülke, Vrieze & Elsevier, 1994; Markies *et al.*, 1995), as well as in propene polymerization (Johnson, Killian & Brookhart, 1995). For these selective reactions, evaluation of the spatial disposition of the *N*-aryl groups in *M*(Ar–BIAN) relative to the coordination plane appears to be important (Johnson, Killian & Brookhart, 1995; van Asselt & Elsevier, 1994*b*). We have studied previously the structure and dynamics of low valent Pd(Ar–BIAN) compounds and obtained the X-ray structure of {bis[*N*-(2,6-diisopropylphenyl)imino]acenaphthene}(maleic anhydride)-palladium(0), (1) (van Asselt, Elsevier, Smeets & Spek, 1994). In order to explain the enhanced reactivity of the title compound, (2) (the *N*-*p*-tolyl analogue, which lacks the bulky *ortho*-substituents on the *N*-aryl moiety), in C—C coupling and oxidative addition reactions (van Asselt & Elsevier, 1992, 1994*a*,*b*), a single crystal X-ray study was performed for the title compound which may