

## Monoclinic

 $P2_1/c$  $a = 9.049 (3) \text{ \AA}$  $b = 12.898 (4) \text{ \AA}$  $c = 9.391 (2) \text{ \AA}$  $\beta = 115.65 (2)^\circ$  $V = 988.0 (5) \text{ \AA}^3$  $Z = 2$  $D_x = 1.582 \text{ Mg m}^{-3}$  $D_m$  not measured

Cell parameters from 50 reflections

 $\theta = 7.0\text{--}20.9^\circ$  $\mu = 1.478 \text{ mm}^{-1}$  $T = 288 (2) \text{ K}$ 

Spearpoint

 $0.63 \times 0.38 \times 0.19 \text{ mm}$ 

Orange

Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXTL/PC* and *SHELXL93*.

We are grateful to Jonathan E. Stevens for help with the quantum calculations.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1431). Services for accessing these data are described at the back of the journal.

## Data collection

Siemens P3 diffractometer

 $\theta/2\theta$  scans

Absorption correction:

empirical via 8  $\psi$  scansin  $10^\circ$  steps (Siemens,

1991a)

 $T_{\min} = 0.724$ ,  $T_{\max} = 0.755$ 

2425 measured reflections

1742 independent reflections

1432 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.013$  $\theta_{\text{max}} = 25.04^\circ$  $h = -1 \rightarrow 10$  $k = -3 \rightarrow 15$  $l = -11 \rightarrow 10$ 

3 standard reflections

every 50 reflections

intensity decay: average

of 0.88% in  $\sigma(I)$ 

## Refinement

Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.030$  $wR(F^2) = 0.078$  $S = 1.081$ 

1738 reflections

98 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2$  $+ 0.2846P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 0.896 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.296 \text{ e \AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

|            |             |          |           |
|------------|-------------|----------|-----------|
| Pd—C11     | 2.3001 (10) | N2—C1    | 1.317 (5) |
| Pd—C12     | 2.3094 (11) | N2—C3    | 1.365 (5) |
| N1—C1      | 1.325 (5)   | N2—C6    | 1.460 (5) |
| N1—C2      | 1.382 (5)   | C2—C3    | 1.325 (6) |
| N1—C4      | 1.469 (5)   | C4—C5    | 1.477 (7) |
| C11—Pd—C12 | 90.49 (4)   | C3—N2—C6 | 125.5 (4) |
| C1—N1—C2   | 107.4 (3)   | N2—C1—N1 | 109.0 (3) |
| C1—N1—C4   | 126.5 (4)   | C3—C2—N1 | 107.4 (4) |
| C2—N1—C4   | 125.8 (3)   | C2—C3—N2 | 107.6 (4) |
| C1—N2—C3   | 108.5 (3)   | N1—C4—C5 | 111.2 (5) |
| C1—N2—C6   | 125.9 (3)   |          |           |

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

| $D\text{---}H\text{---}A$ | $D\text{---}H$ | $H\text{---}A$ | $D\text{---}A$ | $D\text{---}H\text{---}A$ |
|---------------------------|----------------|----------------|----------------|---------------------------|
| C1—H1...C11 <sup>i</sup>  | 0.96           | 2.79           | 3.527 (5)      | 134                       |
| C2—H2...C11 <sup>ii</sup> | 0.96           | 2.75           | 3.666 (5)      | 160                       |
| C3—H3...C12               | 0.96           | 2.74           | 3.664 (5)      | 162                       |
| C6—H6B...C11 <sup>i</sup> | 0.96           | 2.77           | 3.657 (5)      | 153                       |

Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $1 - x, 1 - y, 1 - z$ .H-atom refinement was constrained with C—H distances of 0.96  $\text{\AA}$ . Methyl H atoms were located in a difference map and then idealized.Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991a). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).*Acta Cryst.* (1998). **C54**, 1596–1600**fac-Tricarbonylchlorobis(pyridine-*N*)-rhenium and fac-Tricarbonylchlorobis(4,4'-bipyridine-*N*)rhenium**

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## Abstract

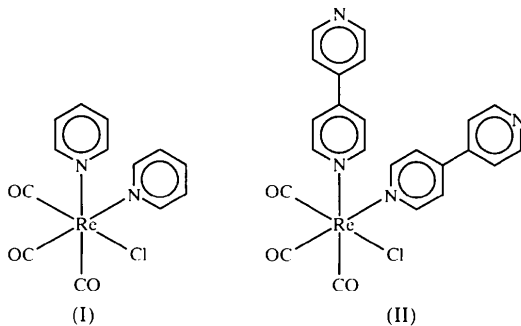
Structural analyses for the title compounds, (*OC*-6-32)-tricarbonylchlorobis(pyridine-*N*)rhenium(I),  $[\text{ReCl}(\text{C}_5\text{H}_5\text{N})_2(\text{CO})_3]$ , and (*OC*-6-32)-tricarbonylchlorobis-

(4,4'-bipyridine-*N*)rhenium(I),  $[\text{ReCl}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{CO})_3]$ , show that both complexes have the expected *fac*-octahedral geometry. The bipyridine complex has local  $\text{C}_2$  symmetry, with the rotation axis bisecting the  $\text{N}-\text{Re}-\text{N}'$  and  $\text{OC}-\text{Re}-\text{CO}$  angles. In contrast with closely related tetrameric assemblies which crystallize as porous channel-containing structures, the title compounds form dense crystals which are packed in a herring-bone fashion.

### Comment

Neutral  $\text{Re}^{\text{I}}$ -containing 'molecular squares' with the general formula  $[\text{Re}(\text{CO})_3(\text{Cl})(\text{L})_2]$ , where  $\text{L}$  is a linear bridging ligand, have been under investigation by our group for some time (Slone *et al.*, 1996, 1998; Slone & Hupp, 1997). The crystal structures of these homometallic rhenium squares (Slone *et al.*, 1996; Bélanger *et al.*, 1998), as well as those of other homometallic and heterometallic squares (Rauter *et al.*, 1994; Stang, Cao *et al.*, 1995; Stang, Chen & Arif, 1995; Whiteford *et al.*, 1997; Slone *et al.*, 1998), have been shown by X-ray diffraction to possess a channel structure in the solid state. Related experiments have shown that thin films of the neutral tetrarhenium squares exhibit exceptional nanometer-scale porosity which can be exploited in electrochemically detected molecular sieving processes and in the recognition and uptake ('chemical sensing') of selected volatile organic species (Slone *et al.*, 1998).

We investigated the crystal structure of two monomers,  $[\text{Re}(\text{CO})_3(\text{Cl})(\text{py})_2]$ , (I), where *py* is pyridine, and  $[\text{Re}(\text{CO})_3(\text{Cl})(4,4'\text{-bpy})_2]$ , (II), where 4,4'-*bpy* is 4,4'-bipyridine, as model compounds for the corners of molecular squares with bridging pyrazine and 4,4'-*bpy* ligands, respectively. Our goal was to determine if porous structures could also be obtained with monomers, and to compare the geometry of the corners with that of the parent squares.



Important bond lengths and angles are given in Tables 1 and 2. Both complexes possess a slightly distorted octahedral geometry around the  $\text{Re}$  atom. Metal-ligand bond lengths are within the expected range for facial tricarbonyl  $\text{Re}^{\text{I}}$  complexes (Civitello *et al.*,

1993; Iha & Ferraudi, 1994; Yang *et al.*, 1994; Catalano *et al.*, 1994; Yam *et al.*, 1995). The  $\text{N}-\text{Re}-\text{N}$  angles are  $84.8(2)$  and  $87.0(2)^\circ$  in (I) and (II), respectively, which compare with the  $82-86^\circ$  range reported for other  $[\text{Re}(\text{CO})_3(\text{Cl})(\text{L})_2]$  complexes [ $\text{L} = \text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2$  (Yang *et al.*, 1994);  $\text{L} = \text{quinoline}$  or *isoquinoline* (Iha & Ferraudi, 1994)] and the  $83-86^\circ$  range usually observed in related homo- and heterometallic molecular squares (Slone *et al.*, 1996, 1998; Bélanger *et al.*, 1998).

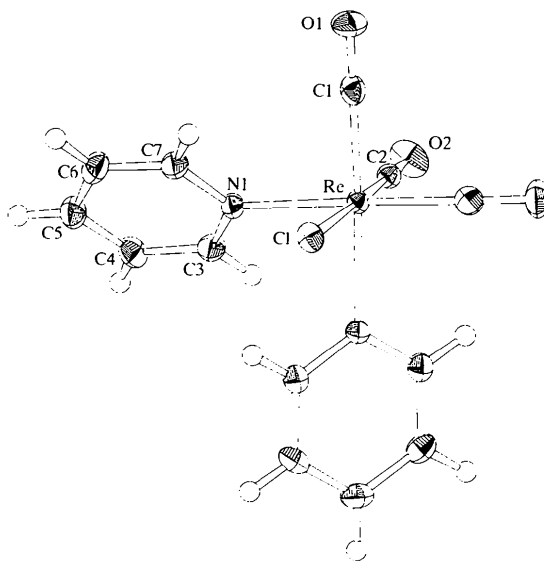


Fig. 1. ORTEP (Johnson, 1965) drawing of (I) showing the numbering scheme, with ellipsoids at the 50% probability level.

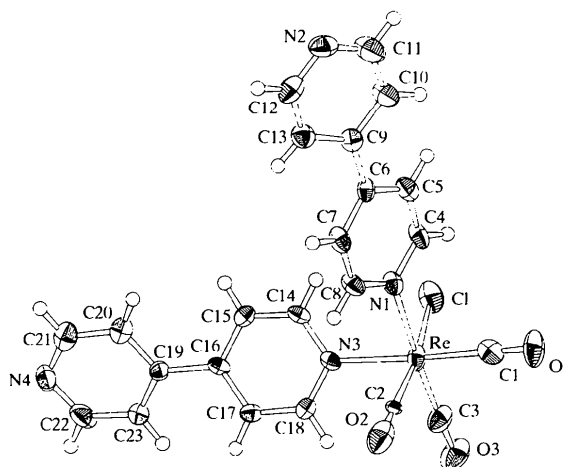


Fig. 2. ORTEP (Johnson, 1965) drawing of (II) showing the numbering scheme, with ellipsoids at the 50% probability level.

The  $\text{Cl}-\text{Re}-\text{N1}-\text{C3}$  torsion angle in (I) is  $49.7(3)^\circ$ , and the analogous  $\text{Cl}-\text{Re}-\text{N1}-\text{C4}$  and  $\text{Cl}-\text{Re}-\text{N3}-\text{C14}$  angles in (II) are  $-37.8(6)$  and  $-55.7(6)^\circ$ , respectively. The dihedral angle between the

planes of the aromatic rings of the 4,4'-bpy ligand in (II) are 15.9(2) and 27.6(2)° for the two crystallographically independent bpy ligands. The two polymorphs of the [Re(CO)<sub>3</sub>(Cl)(4,4'-bpy)]<sub>4</sub> molecular square have dihedral angles of ~25 (Slone *et al.*, 1996) and 37–39° (Bélanger *et al.*, 1998). In molecular squares with bridging 4,4'-bpy and Pt, Pd, Os or mixed Pd/Re corners, this angle is near 35° (Fujita *et al.*, 1996; Stang *et al.*, 1995; Leung *et al.*, 1996; Slone *et al.*, 1998).

Compounds (I) and (II) crystallize in a herringbone fashion (Figs. 3 and 4), resulting in a dense packing in the crystal. This study shows that, under the crystallization conditions used, a porous structure is not obtained with [Re(CO)<sub>3</sub>(Cl)(L)<sub>2</sub>] monomers. These materials are therefore potentially useful as controls for

other experiments (sieving, transport *etc.*) involving the corresponding 'molecular squares'.

## Experimental

The title compounds were prepared as described in the literature (Giordano & Wrighton, 1979). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from acetone/toluene solution, for (I), or from acetone/water solution, for (II).

### Compound (I)

#### Crystal data

[ReCl(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>(CO)<sub>3</sub>]

$M_r = 463.89$

Monoclinic

$C2/c$

$a = 7.4173(11) \text{ \AA}$

$b = 14.326(2) \text{ \AA}$

$c = 13.077(3) \text{ \AA}$

$\beta = 90.140(13)^\circ$

$V = 1389.6(3) \text{ \AA}^3$

$Z = 4$

$D_x = 2.217 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 11.0\text{--}12.0^\circ$

$\mu = 8.94 \text{ mm}^{-1}$

$T = 153(2) \text{ K}$

Block

$0.28 \times 0.26 \times 0.16 \text{ mm}$

Colorless

#### Data collection

Enraf-Nonius CAD-4

diffractometer

$\omega$ - $\theta$  scans

Absorption correction:

analytical (de Meulenaer

& Tompa, 1965)

$T_{\min} = 0.21$ ,  $T_{\max} = 0.36$

1392 measured reflections

1297 independent reflections

1096 reflections with

$I > 3\sigma(I)$

$R_{\text{int}} = 0.099$

$\theta_{\max} = 25^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 16$

$l = -15 \rightarrow 15$

3 standard reflections

frequency: 90 min

intensity decay: <2.5%

#### Refinement

Refinement on  $F$

$R = 0.015$

$wR = 0.019$

$S = 1.95$

1096 reflections

101 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o)]$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.9 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.4 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1967)

Extinction coefficient:

$9.2(5) \times 10^{-7}$

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I)

|           |          |           |          |
|-----------|----------|-----------|----------|
| Re—C1     | 2.447(4) | Re—C2     | 1.92(1)  |
| Re—N1     | 2.211(3) | O1—C1     | 1.160(5) |
| Re—C1     | 1.913(4) | O2—C2     | 1.18(1)  |
| Cl—Re—N1  | 88.0(1)  | N1—Re—C2  | 88.4(3)  |
| Cl—Re—N1' | 86.4(1)  | N1'—Re—C2 | 92.1(3)  |
| Cl—Re—C1  | 90.1(1)  | Cl—Re—C1' | 88.5(3)  |
| Cl—Re—C1' | 95.3(1)  | Cl—Re—C2  | 91.3(4)  |
| Cl—Re—C2  | 176.2(3) | Cl'—Re—C2 | 88.3(4)  |
| N1—Re—N1' | 84.8(2)  | Re—C1—O1  | 177.4(4) |
| N1—Re—C1  | 93.4(2)  | Re—C2—O2  | 178(1)   |
| N1—Re—C1' | 176.2(2) |           |          |

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

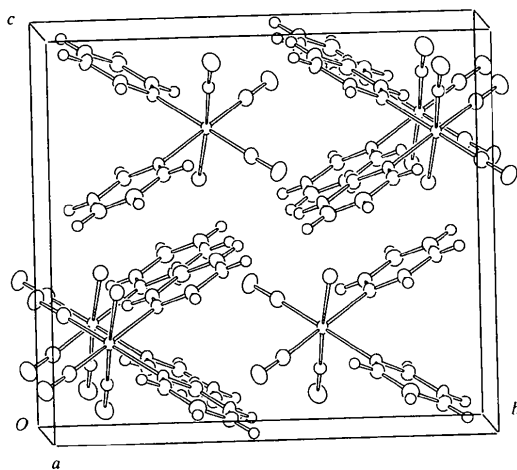


Fig. 3. Packing diagram for (I) in the  $bc$  plane.

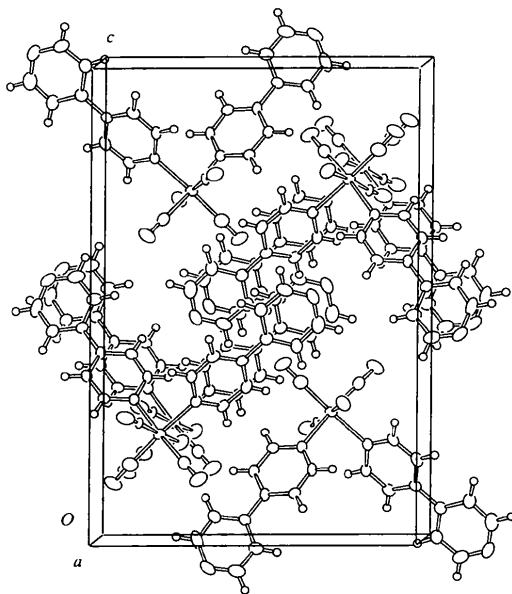


Fig. 4. Packing diagram for (II) in the  $bc$  plane.

**Compound (II)***Crystal data*[ReCl(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(CO)<sub>3</sub>] $M_r = 618.06$ 

Monoclinic

 $P2_1/n$  $a = 7.126 (2) \text{ \AA}$  $b = 14.658 (3) \text{ \AA}$  $c = 21.517 (6) \text{ \AA}$  $\beta = 98.63 (2)^\circ$  $V = 2222.0 (10) \text{ \AA}^3$  $Z = 4$  $D_x = 1.847 \text{ Mg m}^{-3}$  $D_m$  not measuredMo  $K\alpha$  radiation $\lambda = 0.7107 \text{ \AA}$ 

Cell parameters from 25 reflections

 $\theta = 10.0\text{--}11.0^\circ$  $\mu = 5.62 \text{ mm}^{-1}$  $T = 153 (2) \text{ K}$ 

Needle

 $0.41 \times 0.07 \times 0.05 \text{ mm}$ 

Yellow

*Data collection*

Enraf–Nonius CAD-4

diffractometer

 $\omega$ – $\theta$  scans

Absorption correction:

analytical (de Meulenaer &amp; Tompa, 1965)

 $T_{\min} = 0.65$ ,  $T_{\max} = 0.76$ 

3956 measured reflections

3853 independent reflections

2481 reflections with

 $I > 3\sigma(I)$  $R_{\text{int}} = 0.041$  $\theta_{\max} = 24.5^\circ$  $h = -8 \rightarrow 8$  $k = -16 \rightarrow 0$  $l = -25 \rightarrow 0$ 

3 standard reflections

every 0 reflections

intensity decay: &lt;1%

*Refinement*Refinement on  $F$  $R = 0.033$  $wR = 0.028$  $S = 1.49$ 

2481 reflections

289 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o)]$  $(\Delta/\sigma)_{\max} = 0.002$  $\Delta\rho_{\max} = 1.3 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.8 \text{ e \AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II)

|          |           |          |            |
|----------|-----------|----------|------------|
| Re—Cl    | 2.450 (2) | Re—C3    | 1.914 (10) |
| Re—N1    | 2.218 (6) | O1—C1    | 1.144 (9)  |
| Re—N3    | 2.200 (6) | O2—C2    | 1.033 (8)  |
| Re—C1    | 1.939 (9) | O3—C3    | 1.152 (9)  |
| Re—C2    | 1.980 (8) |          |            |
| Cl—Re—N1 | 86.8 (2)  | N3—Re—C1 | 174.9 (3)  |
| Cl—Re—N3 | 84.5 (2)  | N3—Re—C2 | 87.3 (3)   |
| Cl—Re—C1 | 97.3 (2)  | N3—Re—C3 | 94.1 (3)   |
| Cl—Re—C2 | 171.8 (2) | C1—Re—C2 | 90.8 (3)   |
| Cl—Re—C3 | 89.4 (3)  | C1—Re—C3 | 90.8 (3)   |
| N1—Re—N3 | 87.0 (2)  | C2—Re—C3 | 91.2 (4)   |
| N1—Re—C1 | 88.3 (3)  | Re—C1—O1 | 178.3 (7)  |
| N1—Re—C2 | 92.8 (3)  | Re—C2—O2 | 172.2 (8)  |
| N1—Re—C3 | 176.0 (3) | Re—C3—O3 | 177.5 (8)  |

Statistics on the reflections obtained for (I) indicated the non-centrosymmetric space group  $Cc$ . Refinement was initially carried out in this space group, but several of the atoms could only be refined with isotropic displacement parameters, and large correlations were present in the refinement. For these reasons, the coordinates were transferred to the centrosymmetric space group  $C2/c$  where the presence of a twofold rotation angle introduced disorder on the chloride and carbonyl ligands *trans* to one another, but refinement was improved. The disordered CO/Cl ligands were assigned occupancy factors of 0.5.

Anisotropic refinement was possible for all non-H atoms, except for the C atom of the disordered carbonyl. CO/Cl disorder of the type observed in (I) is not uncommon, and unresolved disorder could be responsible for the abnormal displacement parameters associated with the carbonyl ligand *trans* to the Cl atom. Attempts to obtain a reasonable model for the disorder were not successful, but the presence of unresolved disorder is not unlikely.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

The authors thank Kurt D. Benkstein and Robert V. Slone for preparing the complexes. Acknowledgement is made to Donors to the Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Naval Research, for support of this work. SB thanks the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (Québec) for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1384). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 1600–1602

## An Ethanol-Solvated Copper(II) Complex of 1,3-Bis(2-hydroxybenzylimino)pentane

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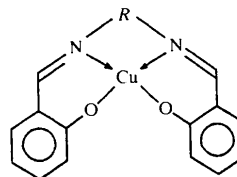
### Abstract

In the title compound, {2,2'-[1,3-pentanediylo-bis(nitrilomethylidene)]diphenolato}copper(II)-ethanol (2/1), 2[Cu(C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>)]·C<sub>2</sub>H<sub>6</sub>O, the Cu atom is coordinated by an N<sub>2</sub>O<sub>2</sub> donor set from the imine-phenol ligand in a distorted tetrahedral coordination geometry, with the two phenol O atoms being deprotonated. There are two 'unsolvated' copper complexes and two ethanol-solvated copper complexes in the triclinic unit cell. The Cu—O and Cu—N distances are 1.891 (4)–1.897 (4) and 1.943 (5)–1.978 (5) Å, respectively. The angle between the two coordination planes defined by the ligating atoms of one complex (O11, O12, N11 and N12) and those of the other independent complex (O21, O22, N21 and N22) is 49.4 (2)°.

### Comment

Radioactive copper-labelled compounds have been studied extensively because of their diagnostic and/or therapeutic potential. Thus, we have been interested in the development of suitable ligands that can form stable complexes with this metal. The chemistry of Schiff base ligands has aroused considerable attention, mainly because of preparative accessibility, diversity and struc-

tural variability. Although tetradentate imine-phenol ligands can readily form complexes with copper (John *et al.*, 1994), very few have been characterized. The solid-state structures of monomeric Cu<sup>II</sup> imine-phenol complexes have been determined so far for the complexes shown schematically below: (I) (Baker *et al.*, 1970), (II) (Cheeseman *et al.*, 1966) and (III) (Yao *et al.*, 1997). We report here the synthesis and characterization of the title compound, (IV).



- (I) R = CH<sub>2</sub>-CH<sub>2</sub>  
 (II) R = C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>  
 (III) R = CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>  
 (IV) R = CH<sub>2</sub>-CH<sub>2</sub>-CH(CH<sub>2</sub>)CH<sub>3</sub>

In the title compound, the coordination about the Cu atom forms a 6–6–6 chelate ring structure and a distorted tetrahedron with two imine N atoms and two phenol O atoms. There are two 'unsolvated' copper [Cu(C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>)] complex molecules, *A*, and two ethanol-solvated molecules, *B*, in the centrosymmetric unit cell. The ethanol solvate is hydrogen bonded to a phenolate O atom [O50···O11 = 2.851 (8) Å] of *B*. The angle between the two coordination planes, defined by atoms O11, O12, N11 and N12, and atoms O21, O22, N21 and N22, is 49.4 (2)°.

The N—Cu1—N and O—Cu1—O angles in *B* are 92.2 (2) and 89.6 (2)°, respectively. The distortion of the coordination geometry in *A* is evident in the expansion of the N—Cu2—N angle [94.4 (2)°] and in the compression of the O—Cu2—O angle [82.4 (2)°] from 90°. Inversely, the two *trans*-O—Cu—N angles in *B*, O11—Cu1—N12 and O12—Cu1—N11, are 155.9 (2) and 156.1 (2)°, respectively, while the O—Cu—N angles in *A*, O21—Cu2—N22 and O22—Cu2—N21, are 170.1 (2) and 172.6 (2)°, respectively. As a result, the dihedral angle between the two chelate rings defined by Cu1, O11 and N11, and Cu1, O12 and N12, in *B* is 33.0 (2)°, which is much larger than the corresponding angle in *A* [8.8 (2)°].

Steric interactions of the propyl, butyl and biphenyl backbones affect the copper coordination geometry significantly in many respects (see Table 1). In the five-membered-ring system with a two-C-atom backbone [complex (I)], the Cu—N distances are short (average 1.916 Å), and the N—Cu—N angle (82.7°) and the dihedral angle (5.3°) are small. Adding a third C atom to the backbone to make a six-membered chelate ring (*A* and *B*) results in increased Cu—N lengths, N—Cu—N angles and dihedral angles. Further increasing the backbone size to give a seven-membered ring [complexes (II)