Monoclinic
$P2_1/c$
$a = 9.049\,(3)$ Å
$b = 12.898\,(4)$ Å
$c = 9.391\,(2)$ Å
$\beta = 115.65\,(2)°$
$V = 988.0\,(5)$ Å³
$Z = 2$
$D_x = 1.582$ Mg m⁻³
D_m not measured

Cell parameters from 50
reflections
$\theta = 7.0–20.9°$
$\mu = 1.478$ mm⁻¹
$T = 288\,(2)$ K
Spearpoint
$0.63 \times 0.38 \times 0.19$ mm
Orange

Data collection

Siemens $P3$ diffractometer
$\theta/2\theta$ scans
Absorption correction:
  empirical via 8 ψ scans
  in 10° steps (Siemens,
  1991a)
$T_{min} = 0.724$, $T_{max} = 0.755$
2425 measured reflections
1742 independent reflections
1432 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.013$
$\theta_{max} = 25.04°$
$h = -1 \rightarrow 10$
$k = -3 \rightarrow 15$
$l = -11 \rightarrow 10$
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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.896$ e Å⁻³
$\Delta\rho_{min} = -0.296$ e Å⁻³
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Pd—Cl1	2.3001 (10)	N2—C1	1.317 (5)
Pd—Cl2	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)
Cl1—Pd—Cl2	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 (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1⋯Cl1ⁱ	0.96	2.79	3.527 (5)	134
C2—H2⋯Cl1ⁱⁱ	0.96	2.75	3.666 (5)	160
C3—H3⋯Cl2	0.96	2.74	3.664 (5)	162
C6—H6B⋯Cl1ⁱ	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 Å. 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).

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

References

Carlin, R. T., Fuler, J. & Hedenskoog, M. (1994). J. Electrochem. Soc. 141, L21–22.
De Long, H. C., Wilkes, J. S. & Carlin, R. T. (1994). J. Electrochem. Soc. 141, 1000–1005.
Lee, C., Winston, T., Unni, A., Pagni, R. M. & Mamantov, G. (1996). J. Am. Chem. Soc. 118, 4919–4924.
Levasseur, G. & Beauchamp, A. L. (1991). Acta Cryst. C47, 547–549.
Scordilis-Kelly, C. & Carlin, R. T. (1993). J. Electrochem. Soc. 140, 1606–1609.
Sheldrick, G. M. (1990a). Acta Cryst. A46, 467–473.
Sheldrick, G. M. (1990b). SHELXTL/PC. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
Siemens (1991a). P3/P4-PC Diffractometer Program. Version 4.23. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1991b). XDISK. Data Reduction Program. Version 4.20.2PC. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sun, I.-W. & Hussey, C. L. (1989). J. Electroanal. Chem. 274, 325–331.
Valle, G. & Ettorre, R. (1994). Acta Cryst. C50, 1221–1222.
Wavefunction Inc. (1997). PC SPARTAN-Plus. Molecular Modeling for the Desktop. Wavefunction Inc., 18401 Von Karman Avenue, Irvine, CA 92715, USA.

fac-Tricarbonylchlorobis(pyridine-N)-rhenium and fac-Tricarbonylchlorobis(4,4'-bipyridine-N)rhenium

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Abstract
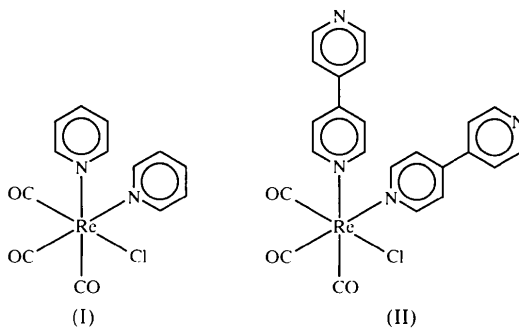
Structural analyses for the title compounds, (OC-6-32)-tricarbonylchlorobis(pyridine-N)rhenium(I), [ReCl-(C₅H₅N)₂(CO)₃], and (OC-6-32)-tricarbonylchlorobis-

(4,4'-bipyridine-N)rhenium(I), [ReCl(C₁₀H₈N₂)₂(CO)₃], show that both complexes have the expected *fac*-octahedral geometry. The bipyridine complex has local C_2 symmetry, with the rotation axis bisecting the N—Re—N' and OC—Re—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 Re^I-containing 'molecular squares' with the general formula [Re(CO)₃(Cl)(*L*)]₄, where *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, [Re(CO)₃(Cl)(py)₂], (I), where py is pyridine, and [Re(CO)₃(Cl)(4,4'-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.

1993; Iha & Ferraudi, 1994; Yang *et al.*, 1994; Catalano *et al.*, 1994; Yam *et al.*, 1995). The N—Re—N angles are 84.8 (2) and 87.0 (2)° in (I) and (II), respectively, which compare with the 82–86° range reported for other [Re(CO)₃(Cl)(*L*)₂] complexes [*L* = NH₂CH₂CH=CH₂ (Yang *et al.*, 1994); *L* = quinoline or isoquinoline (Iha & Ferraudi, 1994)] and the 83–86° range usually observed in related homo- and heterometallic molecular squares (Slone *et al.*, 1996, 1998; Bélanger *et al.*, 1998).
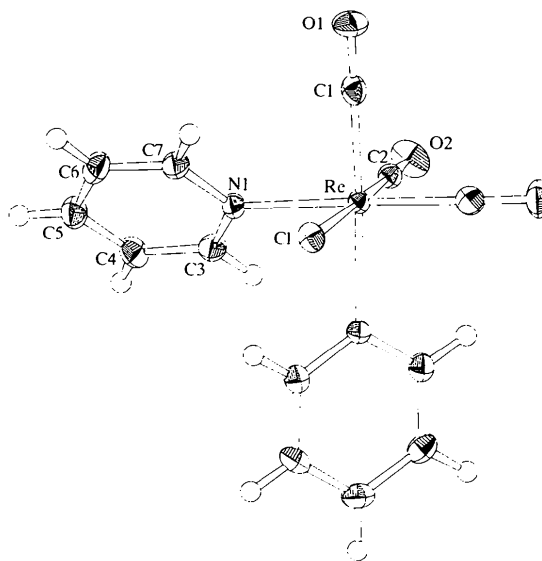

Fig. 1. *ORTEP* (Johnson, 1965) drawing of (I) showing the numbering scheme, with ellipsoids at the 50% probability level.
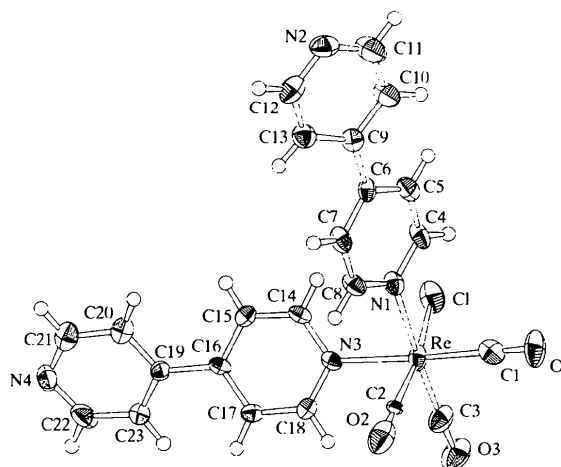

Fig. 2. *ORTEP* (Johnson, 1965) drawing of (II) showing the numbering scheme, with ellipsoids at the 50% probability level.

(I)   (II)

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

The Cl—Re—N1—C3 torsion angle in (I) is 49.7 (3)°, and the analogous Cl—Re—N1—C4 and Cl—Re—N3—C14 angles in (II) are −37.8 (6) and −55.7 (6)°, 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)₃(Cl)(4,4'-bpy)]₄ 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)₃(Cl)(L)₂] 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(C₅H₅N)₂(CO)₃]	Mo $K\alpha$ radiation
$M_r = 463.89$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 7.4173\,(11)$ Å	$\theta = 11.0{-}12.0°$
$b = 14.326\,(2)$ Å	$\mu = 8.94$ mm^{-1}
$c = 13.077\,(3)$ Å	$T = 153\,(2)$ K
$\beta = 90.140\,(13)°$	Block
$V = 1389.6\,(3)$ Å^3	$0.28 \times 0.26 \times 0.16$ mm
$Z = 4$	Colorless
$D_x = 2.217$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1096 reflections with $I > 3\sigma(I)$
ω–θ scans	$R_{int} = 0.099$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$\theta_{max} = 25°$
	$h = 0 \rightarrow 8$
	$k = 0 \rightarrow 16$
$T_{min} = 0.21$, $T_{max} = 0.36$	$l = -15 \rightarrow 15$
1392 measured reflections	3 standard reflections
1297 independent reflections	frequency: 90 min intensity decay: $<2.5\%$

Refinement

Refinement on F	$\Delta\rho_{max} = 0.9$ e Å^{-3}
$R = 0.015$	$\Delta\rho_{min} = -0.4$ e Å^{-3}
$wR = 0.019$	Extinction correction:
$S = 1.95$	Zachariasen (1967)
1096 reflections	Extinction coefficient:
101 parameters	$9.2\,(5) \times 10^{-7}$
H atoms not refined	Scattering factors from
$w = 1/[\sigma^2(F_o)]$	*International Tables for*
$(\Delta/\sigma)_{max} < 0.001$	*Crystallography* (Vol. C)

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

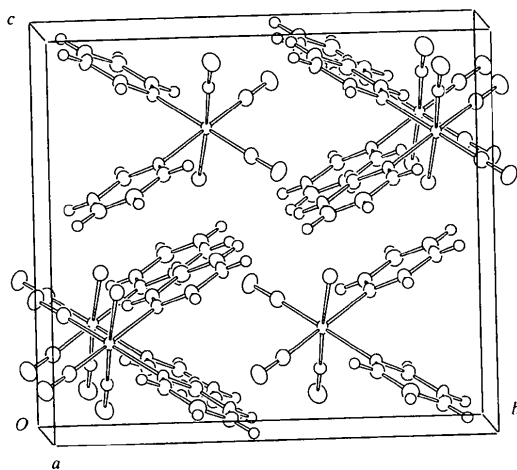|			
Re—Cl	2.447 (4)	Re—C2	1.92 (1)
Re—N1	2.211 (3)	O1—C1	1.160 (5)
Re—C1	1.913 (4)	O2—C2	1.18 (1)
Cl—Re—N1	88.0 (1)	N1—Re—C2	88.4 (3)
Cl—Re—N1ⁱ	86.4 (1)	N1ⁱ—Re—C2	92.1 (3)
Cl—Re—C1	90.1 (1)	C1—Re—Clⁱ	88.5 (3)
Cl—Re—C1ⁱ	95.3 (1)	C1—Re—C2	91.3 (4)
Cl—Re—C2	176.2 (3)	Clⁱ—Re—C2	88.3 (4)
N1—Re—N1ⁱ	84.8 (2)	Re—Cl—O1	177.4 (4)
N1—Re—Cl	93.4 (2)	Re—C2—O2	178 (1)
N1—Re—C1ⁱ	176.2 (2)		

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

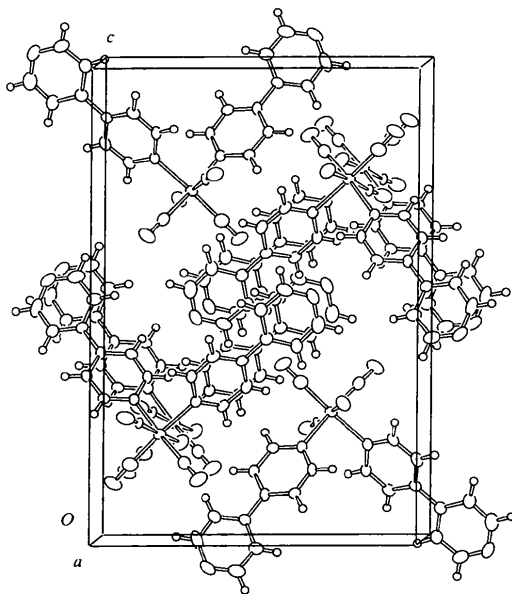Fig. 3. Packing diagram for (I) in the *bc* plane.

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

Compound (II)

Crystal data

[ReCl(C$_{10}$H$_8$N$_2$)$_2$(CO)$_3$]
M_r = 618.06
Monoclinic
$P2_1/n$
a = 7.126 (2) Å
b = 14.658 (3) Å
c = 21.517 (6) Å
β = 98.63 (2)°
V = 2222.0 (10) Å^3
Z = 4
D_x = 1.847 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25
    reflections
θ = 10.0–11.0°
μ = 5.62 mm^{-1}
T = 153 (2) K
Needle
0.41 × 0.07 × 0.05 mm
Yellow

Data collection

Enraf–Nonius CAD-4
    diffractometer
ω–θ scans
Absorption correction:
    analytical (de Meulenaer
    & Tompa, 1965)
    T_{min} = 0.65, T_{max} = 0.76
3956 measured reflections
3853 independent reflections

2481 reflections with
    $I > 3\sigma(I)$
R_{int} = 0.041
θ_{max} = 24.5°
h = −8 → 8
k = −16 → 0
l = −25 → 0
3 standard reflections
    every 0 reflections
    intensity decay: <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 e Å^{-3}
$\Delta\rho_{min}$ = −0.8 e Å^{-3}
Extinction correction: none
Scattering factors from
    *International Tables for
    Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) 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*.

References

Bélanger, S., Hupp, J. T., Stern, C. L., Slone, R. V., Watson, D. F. & Carrell, T. M. (1998). *J. Am. Chem. Soc.* Submitted.
Catalano, V. J., Larson, W. E., Olmstead, M. M. & Gray, H. B. (1994). *Inorg. Chem.* **33**, 4502–4509.
Civitello, E. R., Dragovich, P. S., Karpishin, T. B., Novick, S. G., Bierach, G., O'Connell, J. F. & Westmoreland, T. D. (1993). *Inorg. Chem.* **32**, 237–241.
Fujita, M., Sasaki, O., Mitsuhashi, T., Fujita, T., Yazaki, J., Yamaguchi, K. & Ogura, K. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1535–1536.
Giordano, P. J. & Wrighton, M. S. (1979). *J. Am. Chem. Soc.* **101**, 2888–2897.
Iha, N. M. & Ferraudi, G. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2565–2571.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Leung, W.-H., Cheng, J. Y. K., Hun, T. S. M., Che, C.-M., Wong, W.-T. & Cheung, K.-K. (1996). *Organometallics*, **15**, 1497–1501.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Rauter, H., Hillgeris, E. C., Erxleben, A. & Lippert, B. (1994). *J. Am. Chem. Soc.* **116**, 616–624.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
Slone, R. V., Benkstein, K. D., Bélanger, S., Hupp, J. T., Guzei, I. A. & Rheingold, A. L. (1998). *Coord. Chem. Rev.* **171**, 221–243.
Slone, R. V. & Hupp, J. T. (1997). *Inorg. Chem.* **36**, 5422–5423.

Slone, R. V., Hupp, J. T., Stern, C. L. & Albrecht-Schmitt, T. E. (1996). *Inorg. Chem.* **35**, 4096–4097.

Stang, P. J., Cao, D. H., Saito, S. & Arif, A. M. (1995). *J. Am. Chem. Soc.* **117**, 6273–6283.

Stang, P. J., Chen, K. & Arif, A. M. (1995). *J. Am. Chem. Soc.* **117**, 8793–8797.

Whiteford, J. A., Lu, C. V. & Stang, P. J. (1997). *J. Am. Chem. Soc.* **119**, 2524–2533.

Yam, V. W.-W., Lau, V. C.-Y. & Cheung, K.-K. (1995). *Organometallics*, **14**, 2749–2753.

Yang, Y.-L., Chen, J.-D., Lin, Y.-C., Cheng, M.-C. & Wang, Y. (1994). *J. Organomet. Chem.* **467**, C6–8.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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-pentanediylbis(nitrilomethylidyne)]diphenolato}copper(II)–ethanol (2/1), 2[Cu(C₁₉H₂₀N₂O₂)].C₂H₆O, the Cu atom is coordinated by an N₂O₂ 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[II] 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).
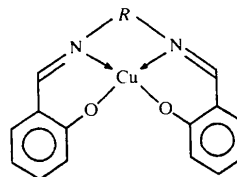
(I) R = CH₂-CH₂
(II) R = C₆H₄-C₆H₄
(III) R = CH₂-CH₂-CH₂-CH₂
(IV) R = CH₂-CH₂-CHCH₂CH₃

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(C₁₉H₂₀N₂O₂)] 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)