C6*B*‡	−0.3814 (6)	−0.0063 (4)	−0.1273 (6)	0.066 (2)
C7*B*‡	−0.3204 (6)	0.1269 (5)	0.0558 (6)	0.078 (3)
C8*B*‡	−0.4777 (8)	0.0858 (4)	−0.0480 (6)	0.084 (3)

† Site occupancy = 0.501 (2). ‡ Site occupancy = 0.499 (2).

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

Cu—N2^i	2.010 (3)	N2—C3	1.135 (4)
Cu—N1	2.064 (3)	N2—Cu^i	2.010 (3)
Cu—P2	2.2412 (13)	C1—C2	1.412 (5)
Cu—P1	2.2735 (13)	C2—C3	1.406 (5)
N1—C1	1.137 (4)		
N2^i—Cu—N1	92.81 (13)	C1—N1—Cu	165.2 (3)
N2^i—Cu—P2	114.64 (10)	C3—N2—Cu^i	166.0 (3)
N1—Cu—P2	110.91 (9)	N1—C1—C2	176.6 (4)
N2^i—Cu—P1	103.67 (10)	C3—C2—C1	114.6 (3)
N1—Cu—P1	102.55 (9)	N2—C3—C2	176.1 (4)
P2—Cu—P1	126.55 (4)		

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

The disordered part of the structure could be described as the rotation around a twofold axis defined through atom C2 and the midpoint of the N3*A* and N3*B* atoms. Because of the disorder overlap, it was not possible to refine the atom sites free of constraints. Each disordered atom was modelled as a pair of separated atoms with the sum of the population constrained to 1.0. The sites were obtained by careful splitting of the atomic positions which were found in a difference map. After this, the structure was refined in two blocks (the disordered and the undisordered part). Displacement parameters were refined anisotropicaly without constraints, but separately from refinement of positional parameters. All H atoms were introduced at calculated positions (C—H 0.93 Å) and refined in the riding mode with isotropic displacement parameters $1.2U_{\rm eq}$ of their carrier atoms.

Data collection: Syntex $P2_1$ software. Cell refinement: Syntex $P2_1$ software. Data reduction: *XP*21 (Pavelčík, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 559–562

Two TEPA–Copper(II) Complexes {TEPA is Tris[2-(2-pyridyl)ethyl]amine}

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Abstract

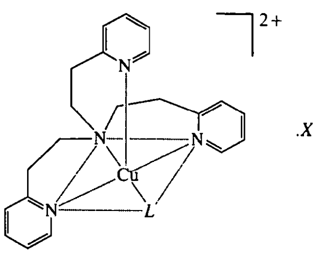
In both the title compounds, aqua{tris[2-(2-pyridyl)-ethyl]amine-*N*,*N*′,*N*″,*N*‴}copper(II) bis(trifluoromethanesulfonate) monohydrate, $[Cu(C_{21}H_{24}N_4)(H_2O)](CF_3SO_3)_2.H_2O$, (1), and (acetato-*O*){tris[2-(2-pyridyl)-ethyl]amine-*N*,*N*′,*N*″,*N*‴}copper(II) hexafluorophosphate, $[Cu(C_2H_3O_2)(C_{21}H_{24}N_4)]PF_6$, (2), the Cu^{II} atom is pentacoordinate and the geometry is described as square-based pyramidal. Three of the atoms in the equatorial plane remain unchanged, *i.e.* N1, N2 and N3 from the tripodal amine and two pyridine groups, respectively, while the fourth ligand is a water molecule in (1) and an acetate group in (2). The axial position is occupied in both cases by the N4 atom of the third pyridine ring.

Comment

Our work on the functional modeling of copper proteins (Réglier, Amadéi, Tadayoni & Waegell, 1989; Réglier, Jorand & Waegell, 1990; Alilou, Giorgi, Pierrot & Réglier, 1992; Amadéi, Alilou, Eydoux, Pierrot, Réglier & Waegell, 1992; Alilou, Amadéi, Pierrot & Réglier, 1993; Réglier, Amadéi, Alilou, Eydoux, Pierrot

& Waegell, 1993) which either interact with or activate dioxygen has led us to study the structure of Cu^{II} complexes with the tripodal tetradentate tris[2-(2-pyridyl)-ethyl]amine ligand (TEPA). Studies on systems like these are of importance in the elucidation of structural, spectroscopic and reactivity correlations in copper–oxygen chemistry.

In each of the title structures, the coordination geometry of the Cu^{II} atom is described as a more or less distorted square-based pyramid. The basal plane consists of three N atoms, *i.e.* N1 from the tripodal amine, and N2 and N3 from two of the three pyridine groups. The fourth position is occupied by the O atom from a water molecule in complex (1) and from an acetate ligand in complex (2). The apical position is occupied by the N4 atom of the third pyridine ring. The deviation of the Cu^{II} atom from the mean plane composed of atoms N1, N2, N3 and O1 [r.m.s. deviation is 0.074 and 0.023 Å for (1) and (2), respectively] is 0.234 (1) Å in complex (1) and −0.176 (1) Å in complex (2).



(1) L=H_2O; X=$2CF_3SO_3^-.H_2O$
(2) L=CH_3COO^-; X=PF_6^-

The two structures may be compared with other TEPA-Cu^{II} complexes found in the literature; [Cu^{II}-(TEPA)(X)]$^+$, where X = MeIm (methylimidazole) [(3); Karlin, Hayes, Hutchinson, Hyde & Zubieta, 1982], X = Cl^- [(4); Karlin, Hayes, Juen, Hutchinson & Zubieta, 1982], X = NO_3^- [(5); Karlin, Dahlstrom, Hayes, Simon & Zubieta, 1982] and X = NO_2^- [(6); Feng Jiang, Conry, Bubacco, Tyeklăr, Jacobson, Karlin & Peisach, 1993]. In these complexes, the Cu^{II} atom is pentacoordinate, but the coordination geometry is trigonal bipyramidal in compound (3) and square-based pyramidal in (4), (5) and (6). For the six complexes, the mean values of the distances around the Cu^{II} atom are: Cu—N(tripodal) 2.089 Å, ranging from 2.056 (4) in (1) to 2.102 (13) Å in (5); Cu—N(basal pyridine) 2.036 Å, ranging from 2.015 (4) in (1) to 2.062 (3) Å in (4); Cu—N(axial pyridine) 2.221 Å, ranging from 2.197 (3) in (3) to 2.253 (5) Å in (4); Cu—X (X = N or O) 2.015 Å, ranging from 1.983 (6) in (2) to 2.044 (11) Å in (5) [in (4), Cu—Cl is 2.289 (1) Å].

Both structures (1) and (2) contain extremely short intramolecular contacts of the H···H type for which the distance is shorter than the sum of the van der Waals radii. This is a constant for this kind of compound which is strongly constrained. This feature is particularly enhanced for one H atom linked to the C16 atom of the axial arm and is due to the fact that only two conformations around the tripodal N atom can be adopted by this arm; in this series of complexes, the torsion angles C1—N1—Cu—N2 and C8—N1—Cu—N3 are equal to about 0 or 50°. These conformations are clearly shown on the *ORTEP*II (Johnson, 1976) drawings of compounds (1) and (2) (Figs. 1 and 2, respectively). In the first case, also found in compounds (1) and (6), C1—N1—Cu—N2 is equal to 3.0 (3) and C8—N1—Cu—N3 to 51.5 (3)°, with the N1—C15 bond pointing downwards. The H11 and H2 atoms bonded

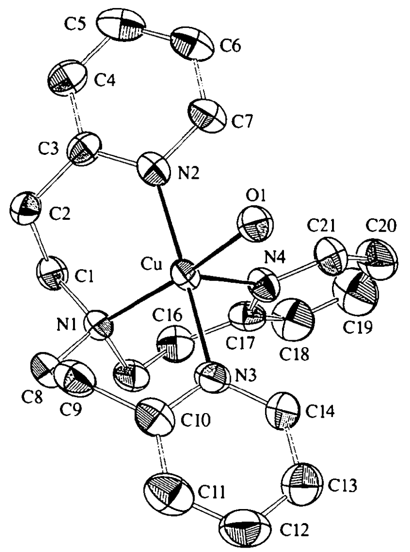


Fig. 1. A perspective *ORTEP*II (Johnson, 1976) view of complex (1) showing 50% probability displacement ellipsoids.

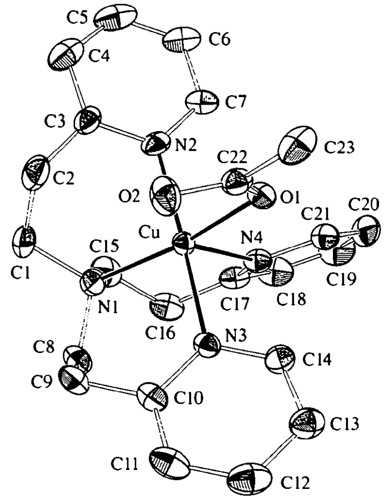


Fig. 2. A perspective *ORTEP*II (Johnson, 1976) view of complex (2) showing 50% probability displacement ellipsoids.

to C16 and C1, respectively, are in close contact (H11···H2 1.88 Å). In the second case, also found in compounds (2), (4) and (5), C8—N1—Cu—N3 is equal to 0.2 (6) and C1—N1—Cu—N2 to 49.5 (8)°, with the N1—C15 bond pointing backwards. The H9 and H19 atoms bonded to C8 and C16, respectively, are 1.89 Å apart.

Another feature common to all these complexes is the opening of the C15—C16—C17 angle which is almost equal to 120° [119.5 (5) in (1) and 118.6 (8)° in (2)]; this is probably due to elongation of the axial Cu—N4 bond which is about 0.2 Å longer than the equatorial Cu—N bonds.

The hydrogen-bond network in compound (1) is shown in Fig. 3, with dimensions given in Table 2. The water molecule linked to the Cu^{II} atom is hydrogen bonded to the second water molecule and to the O3 atom of a SO_3CF_3 group. The second water molecule, not connected to the Cu^{II} atom, is also hydrogen bonded to two trifluoromethanesulfonate ions.

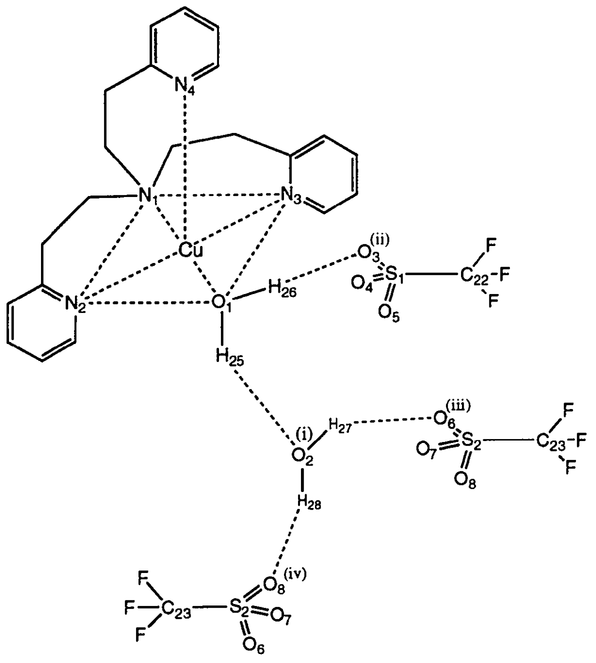


Fig. 3. The intermolecular interactions in complex (1).

Experimental

TEPA was obtained in good yield (75%) by Michael-type addition of (2-pyridyl)ethylamine with vinylpyridine in methanol/acetic acid medium. Complexation with $Cu(CF_3SO_3)_2$ in acetonitrile followed by diethyl ether precipitation led to the copper(II) complex (1). The same reaction, but in the presence of one equivalent of sodium acetate, afforded the copper(II) complex (2). Crystallization in acetonitrile using the diethyl ether diffusion technique afforded suitable crystals.

Compound (1)

Crystal data

$[Cu(C_{21}H_{24}N_4)(H_2O)](CF_3SO_3)_2.H_2O$
$M_r = 730.16$
Triclinic
$P\bar{1}$
$a = 12.736\,(5)$ Å
$b = 12.911\,(2)$ Å
$c = 9.805\,(2)$ Å
$\alpha = 102.62\,(1)°$
$\beta = 100.02\,(2)°$
$\gamma = 71.58\,(2)°$
$V = 1483\,(1)$ Å^3
$Z = 2$
$D_x = 1.635$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10$–$14°$
$\mu = 0.959$ mm^{-1}
$T = 294$ K
Prismatic
0.45 × 0.30 × 0.25 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4640 measured reflections
4635 independent reflections
3378 reflections with $I > \sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 24°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 11$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.050$
$wR = 0.050$
$S = 1.319$
3378 reflections
397 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$

$(\Delta/\sigma)_{max} = 0.037$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cu—O1	2.032 (3)	Cu—N3	2.015 (4)
Cu—N1	2.056 (4)	Cu—N4	2.212 (3)
Cu—N2	2.033 (4)		
O1—Cu—N1	162.4 (1)	N1—Cu—N3	88.5 (2)
O1—Cu—N2	86.6 (1)	N1—Cu—N4	97.7 (1)
O1—Cu—N3	87.0 (1)	N2—Cu—N3	169.6 (1)
O1—Cu—N4	99.7 (1)	N2—Cu—N4	94.6 (1)
N1—Cu—N2	95.2 (2)	N3—Cu—N4	94.6 (1)

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H25···O2^{i}	0.958	1.703	2.648 (6)	168.7
O1—H26···O3^{ii}	1.094	1.668	2.707 (4)	156.5
O2—H27···O6^{iii}	0.813	2.018	2.768 (5)	153.3
O2—H28···O8^{iv}	1.080	1.868	2.775 (5)	139.0

Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 - x, 1 - y, 2 - z$; (iii) $x - 1, y, z$; (iv) $1 - x, -y, -z$.

Compound (2)

Crystal data

$[Cu(C_2H_3O_2)(C_{21}H_{24}N_4)]PF_6$
$M_r = 600.00$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
$a = 18.168$ (2) Å
$b = 7.867$ (2) Å
$c = 21.908$ (3) Å
$\beta = 125.58$ (4)°
$V = 2546$ (2) Å^3
$Z = 4$
$D_x = 1.56$ (5) Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.991$ mm^{-1}
$T = 294$ K
Prismatic
0.35 × 0.30 × 0.20 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4467 measured reflections
2862 independent reflections
2607 reflections with $I > 3\sigma(I)$

$R_{\rm int} = 0.055$
$\theta_{\rm max} = 24°$
$h = -20 \rightarrow 19$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 21$
2 standard reflections
frequency: 60 min
intensity decay: 0.79%

Refinement

Refinement on F
$R = 0.075$
$wR = 0.098$
$S = 3.208$
2607 reflections
334 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o{}^4]$

$(\Delta/\sigma)_{\rm max} = 0.025$
$\Delta\rho_{\rm max} = 0.90$ e Å^{-3}
$\Delta\rho_{\rm min} = 0.56$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Cu—O1	1.983 (6)	Cu—N3	2.059 (5)
Cu—N1	2.089 (8)	Cu—N4	2.234 (7)
Cu—N2	2.021 (5)		
O1—Cu—N1	168.6 (3)	N1—Cu—N3	94.3 (3)
O1—Cu—N2	88.8 (2)	N1—Cu—N4	96.3 (3)
O1—Cu—N3	87.3 (2)	N2—Cu—N3	170.8 (3)
O1—Cu—N4	94.7 (2)	N2—Cu—N4	93.4 (2)
N1—Cu—N2	87.9 (3)	N3—Cu—N4	95.2 (2)

In compound (1), the H atoms of the O1 and O2 water molecules were located by difference Fourier synthesis and the remaining H atoms of both structures were introduced at idealized positions. In complex (2), the F atoms of the PF_6^- anion are disordered, but it was not possible to resolve them into several sites. The displacement parameters of these atoms are therefore high and not significant. Correction for absorption was considered unnecessary on the basis of ψ scans which did not show significant variation.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *BEGIN* in *SDP* (Frenz, 1985); program(s) used to solve structures: *MULTAN*80 (Main *et al.*, 1980); program(s) used to refine structures: *LSFM* in *SDP*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Arene–Arene Stacking in *cis*-Bis[2-(2-thienyl-*C*^{3})pyridine-*N*]platinum(II)

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Abstract

In the crystal structure of the title complex, $[Pt(C_9H_6NS)_2]$, although the aromatic ligands are coordinated to a central heavy metal atom, T-shaped and shifted

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