

Ta—Cp(centroid) distance is slightly long – 2.095 compared to 2.072 (31) Å – but the Ta—Cp* (centroid) distance is nearly identical to the others cited: 2.124 vs 2.122 (29) Å. In the Cp ring, the C—C distances are somewhat short, averaging 1.359 (50) Å; the compilation of Orpen *et al.* (1989) gives 1.397 (28) Å for this distance (804 examples). The Cp* ring is more nearly normal, with C—C(ring) distances averaging 1.405 (32) Å [1.417 (24) Å, 164 examples] and C—CH₃ distances 1.509 (22) Å [1.512 (25) Å]. In both rings, the average deviation of the interior angles from 108° is 2°.

The triflate anion is also essentially normal, with O atoms showing slightly smaller anisotropic displacement parameters than F atoms; all six terminal atoms are well behaved for this group, however. In the crystal, the triflate anions pack in columns along *a* (see Fig. 2), with one oxygen–methyl group contact less than 3.4 Å and two less than 3.5 Å, indicating some weak interactions. There are similar C—F distances as well: one 3.31 Å, five less than 3.5 Å. No H—O or H—F contact is less than 2.43 Å.

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Structure of μ -Chloro-bis{bis[2-(2-pyridyl)ethylamine-*N,N'*]copper(II)} Trishexafluorophosphate

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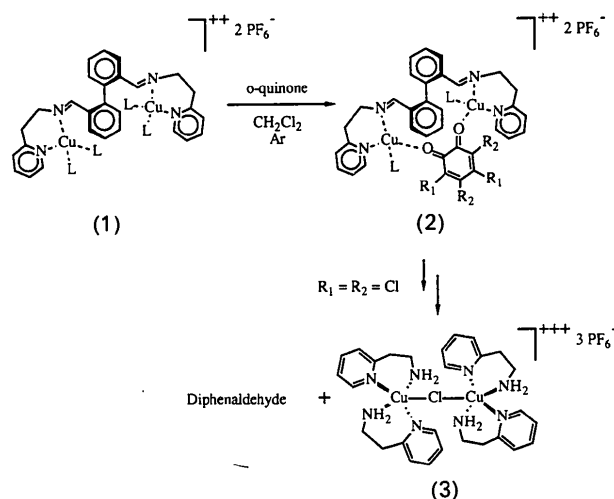
Abstract. $\{[\text{Cu}(\text{C}_7\text{H}_{10}\text{N}_2)_2]_2\text{Cl}\}(\text{PF}_6)_3$, (3), $M_r = 1086.12$, monoclinic, $C2/m$, $a = 16.428$ (4), $b = 12.721$ (3), $c = 12.526$ (6) Å, $\beta = 114.53$ (3)°, $V = 2381.7$ (2) Å³, $Z = 2$, $D_x = 1.51$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 23.04$ cm⁻¹, $F(000) = 1092$, $T = 293$ K, $R = 0.065$ and $wR = 0.095$ for 1425 unique diffractometer data with $I > 3\sigma(I)$. The structure reveals a dimer molecule with a μ -Cl atom linking two Cu^{II} atoms with a linear bridge. The coordination geometry around the Cu atoms is square-based pyramidal.

Introduction. Tyrosinase is a Cu-containing enzyme (type III or binuclear coupled) which catalyzes *ortho*-hydroxylation of phenols into catechols and oxidation of catechols into *ortho*-quinones (Robb, 1984; Latour, 1988; Tyeklar & Karlin, 1989). According to many structural studies, the formation of a μ -peroxo

copper(II) and a catecholate–dicopper(II) species have been postulated during the catalytic process (Wilcox, Porras, Hwang, Lerch, Winkler & Solomon, 1985).

Recently, we have reported (Reglier, Jorand & Waegell, 1990) the synthesis of a binuclear Cu complex (1) which exhibits in the presence of phenols and catechols the same activity as the tyrosinase. With this model, we have shown the occurrence of the catecholate–dicopper(II) species (2), ($R_1 = \text{Bu}$ and $R_2 = \text{H}$). Unfortunately, we have not been able to isolate these complexes which are very sensitive to dioxygen. In order to obtain these species, we treated the Cu complex (2) with 1 equivalent of tetrachloro-*ortho*-benzoquinone which is known to give stable catecholate–copper species (Karlin, Gultneh, Nicholson & Zubieta, 1985). Under argon, a stable catecholate–dicopper species is obtained, but when

the reaction vessel was placed under dioxygen a rapid decomposition occurred giving the Cu complex (3). We report here the structure determination of this Cu complex.



Experimental. Complex (3) was obtained by interaction under argon of complex (1) with 1 equivalent of tetrachloro-*ortho*-benzoquinone in degassed dichloromethane. Elemental analysis: calculated for $\{[\text{Cu}(\text{C}_7\text{H}_{10}\text{N}_2)_2\text{Cl}](\text{PF}_6)_3\}$ C 30.96, H 3.71, N 10.32%; found C 30.87, H 3.73, N 10.29%. A crystal suitable for X-ray diffraction ($0.1 \times 0.4 \times 0.6$ mm) was grown from acetonitrile/ether, sealed in a capillary, and mounted on an Enraf-Nonius CAD-4 diffractometer (graphite monochromator for $\text{Mo K}\alpha$). Unit-cell parameters were refined by least squares on $\sin\theta/\lambda$ values for 25 reflections ($14 < \theta < 16^\circ$). Density was obtained by flotation: $D_m = 1.50$ (1) g cm^{-3} . Intensities were measured using a $\theta/2\theta$ scan $0.91\text{--}10.06^\circ \text{ min}^{-1}$, over a range of $(0.8 + 0.35\tan\theta)^\circ$, $\theta_{\text{max}} = 24^\circ$. Intensities of three standard reflections measured every 10000 s showed a deterioration of 1.7% (without correction). Data were not corrected for absorption effects.

The structure was solved and refined using the SDP software package (Frenz, 1978) via standard heavy-atom procedures and completed by Fourier methods. H atoms were introduced (with $B_{\text{eq}} = 4.0 \text{ \AA}^2$) at idealized positions in the calculation before the last refinement cycle which included anisotropic thermal parameters for all non-H atoms and minimized the function $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2$. Final refinement gave $R = 0.065$ ($wR = 0.095$), $S = 3.296$, $(\Delta/\sigma)_{\text{max}} = 0.15$. A final difference synthesis did not reveal any peak of density $> 0.50 \text{ e \AA}^{-3}$.

Atomic scattering and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No correction for secondary extinction was made.

Table 1. *Positional and equivalent isotropic thermal parameters* (\AA^2)

$$B_{\text{eq}} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$$

	x	y	z	B_{eq}
C(1)	0.3855 (5)	0.2873 (7)	0.2683 (7)	3.7 (2)
C(2)	0.3086 (7)	0.3030 (1)	0.1678 (8)	6.1 (3)
C(3)	0.2343 (7)	0.2320 (1)	0.1460 (1)	7.2 (3)
C(4)	0.2430 (6)	0.1519 (9)	0.2288 (8)	5.2 (3)
C(5)	0.3200 (5)	0.1471 (7)	0.3252 (8)	4.0 (2)
C(6)	0.4681 (6)	0.3540 (8)	0.2957 (8)	4.7 (2)
C(7)	0.5467 (6)	0.2853 (9)	0.3055 (8)	5.5 (3)
Cl	0.500	0.000	0.500	4.1 (1)
Cu	0.500	0.1989 (1)	0.500	2.63 (3)
F(1)	1.0557 (5)	0.000	1.1385 (6)	5.1 (2)
F(2)	0.9091 (5)	0.000	1.0147 (7)	7.5 (3)
F(3)	1.000	-0.1214 (7)	1.000	9.6 (4)
F(7)	0.6693 (5)	0.000	0.402 (1)	7.9 (3)
F(8)	0.7975 (7)	0.000	0.5668 (8)	8.2 (3)
F(9)	0.8764 (5)	0.000	0.4623 (9)	8.9 (3)
F(10)	0.7735 (4)	0.1232 (4)	0.4311 (7)	7.9 (2)
F(11)	0.750	0.000	0.2958 (8)	9.3 (4)
N(1)	0.3896 (4)	0.2114 (5)	0.3457 (6)	3.2 (2)
N(2)	0.5793 (4)	0.2189 (6)	0.4126 (6)	4.2 (2)
P(2)	1.0000	0.000	1.000	3.3 (1)
P(3)	0.7738 (2)	0.000	0.4301 (3)	3.93 (8)

Table 2. *Selected bond distances* (\AA) *and angles* ($^\circ$)

Cu—Cl	2.530 (1)	C(1)—C(2)	1.38 (1)
Cu—N(1)	2.030 (5)	C(1)—C(6)	1.51 (1)
Cu—N(2)	2.039 (8)	C(2)—C(3)	1.45 (2)
N(1)—C(1)	1.35 (1)	C(3)—C(4)	1.41 (2)
N(1)—C(5)	1.34 (1)	C(4)—C(5)	1.34 (1)
N(2)—C(7)	1.48 (1)	C(6)—C(7)	1.52 (1)
N(1)—Cu—N(2)	89.8 (3)	C(1)—N(1)—C(5)	121.1 (6)
Cu—Cl—Cu	180.0	N(1)—C(1)—C(6)	117.8 (6)
N(1)—Cu—N(2)	89.1 (3)	N(1)—C(5)—C(4)	123.7 (9)
N(2)—Cu—N(1')	89.1 (3)	C(1)—C(2)—C(3)	117.5 (4)
N(1)—Cu—N(1')	171.1 (3)	N(2)—C(7)—C(6)	111.8 (9)
N(2)—Cu—N(2')	165.7 (3)	C(3)—C(4)—C(5)	117.6 (9)
Cu—N(1)—C(5)	119.1 (6)	C(2)—C(3)—C(4)	119.5 (8)
Cu—N(1)—C(1)	119.7 (5)	C(1)—C(6)—C(7)	110.4 (8)
Cu—N(2)—C(7)	119.2 (6)	N(1)—C(1)—C(2)	120.8 (9)
N(1')—Cu—N(2')	89.8 (3)	C(2)—C(1)—C(6)	121.3 (9)

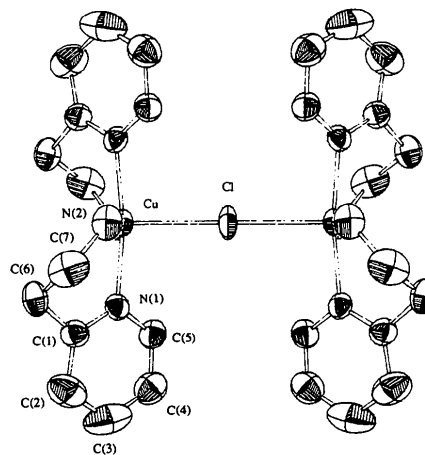


Fig. 1. ORTEP (Johnson, 1965) view of complex (3) showing the atom-numbering scheme.

Discussion. Final positions and thermal parameters for the structure are given in Table 1,* selected bond distances and angles are listed in Table 2. A view of the molecule with the numbering scheme is presented in Fig. 1.

Cu^{II} and Cl atoms are located on special positions: Cu on the twofold axis (site *g*) and Cl on site *d* of 2/*m* symmetry. The structure reveals a dimeric molecule with the two parts of the molecule linked by a bridging μ -Cl atom.

Each Cu^{II} ion is five-coordinated with ligation from pyridines and two primary amine donor groups. The pentacoordination of the Cu atoms is completed by the μ -Cl atom. The geometry around the Cu atoms is described as square-based pyramidal with Cl occupying the axial position. The Cu—Cl bond distances [2.530 (1) Å] are in the range expected for this kind of Cu^{II} complex {2.50 Å found in [Cu₂(tet-b)₂](ClO₄)₃, where tet-b is 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Bauer, Robinson & Margerum, 1973)}. However, the coordination geometry around the Cu^{II} atom is different to that previously found. In [Cu₂(tet-b)₂Cl](ClO₄)₃ it is trigonal bipyramidal with the μ -Cl atom in equatorial position, while in complex (3) we have

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55133 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0275]

found a square-based pyramid with the Cl occupying the axial position. The linearity of the Cu—Cl—Cu bridge is imposed by the symmetry and, as far as we know, is the first example of such a μ -chloro bridge of 180°. In [Cu₂(tet-b)₂Cl](ClO₄)₃ the deviation of the Cu—Cl—Cu bonds from linearity (174.2°) appears to be the result of the disposition of the perchlorate groups situated in special positions along the twofold axis. An O atom of one perchlorate group lies on the twofold axis and is hydrogen bonded to axial N atoms in the coordination polyhedra of both Cu ions.

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3,3,6,9,9-Pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene Hydrogen Trifluoroacetate

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Abstract. C₁₅H₂₅F₃N₂O₂, *M*_r = 322.4, orthorhombic, *Pmmn* (origin at centre of symmetry), *a* = 10.21 (1), *b* = 13.99 (1), *c* = 5.91 (1) Å, *V* = 845.9 Å³, *Z* = 2, *D*_x = 1.28 g cm⁻³, λ(Mo Kα) = 0.71069 Å, μ = 0.69 cm⁻¹, *F*(000) = 344, *T* = 293 K, final *R* = 0.0422 for 807 observed reflections [*F*/σ(*F*) > 5]. The compound is the crystalline TFA salt of a bicyclic amidine formed following treatment of a peptide TFA salt, prepared by solid-phase synthetic methods, with a bicyclic amidine. The N⋯N distance in

the amidine and the O⋯O distance in the carboxyl function of TFA are equivalent and explain the ease of salt formation.

Introduction. The bicyclic amidine 3,3,6,9,9-pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene readily forms salts of carboxylic acids and related proton complexes of bidentate ligands (Heinzer, Soukup & Eschenmoser, 1978; Eschenmoser & Petrilka, 1970), and has been used as a non-nucleophilic base in