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{2,2′-[(*R*,*R*)-Cyclohexane-1,2-diylbis(nitrilomethylidyne)]bis[6-*tert*-butyl-4-(triphenylphosphoniomethyl)phenolato]-*O*,*N*,*N*′,*O*′}copper(**II**) dichloride hexakis(deuterochloroform) solvate

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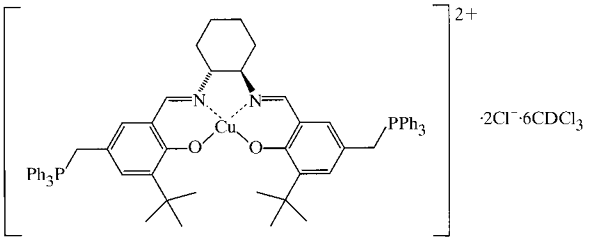
The title compound, $[Cu(C_{66}H_{68}N_2O_2P_2)]Cl_2\cdot 6CDCl_3$, consists of complex cations, chloride ions and deuterochloroform solvate molecules. The complex cation crystallizes in two different conformations. In both cases, Cu^{II} ions lie on twofold axes and the geometry around them is slightly distorted square planar. The dihedral angles between the N/Cu/N and O/Cu/O planes are 5.6 (9) and 3.9 (10)° for molecules *A* and *B*, respectively.

Comment

We have studied the catalytic oxidation of phenolic compounds relevant in lignin biochemistry using hydrogen peroxide and dioxygen as oxidants (Haikarainen, Sipilä & Pietikäinen, 2000; Haikarainen, Sipilä, Pietikäinen, Pajunen & Mutikainen, 2000). During these studies a few copper complexes of the salen-type ligands have been used as models for the laccase enzyme, which has copper ion in its active centre and uses dioxygen as an oxidant (Paice *et al.*, 1997). We have found that all copper complexes studied were inactive when dioxygen was used. However, the bulky title compound, (I),was able to catalyse the oxidation of coniferyl alcohol (lignin precursor) using hydrogen peroxide to the lignin-like material. This unexpected reaction prompted us to determine the crystal structure of this compound in order to get more information of the active site of the complex. The crystallographically independent part consists of two halves of cations (each occupying twofold symmetry axis), and two anions and six deuterochloroform solvent molecules in general positions.



(I)

Experimental

The ligand precursor (200 mg, 0.18 mmol, trihydrate; Haikarainen, Sipilä & Pietikäinen, 2000) was dissolved in absolute ethanol (4 ml) and heated to boiling. Solid copper acetate hydrate (38 mg, 0.19 mmol) was added and the resulting solution was refluxed for 3 h. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (3 ml) and ethyl acetate (3 ml) was added. This solution was allowed to evaporate at room temperature yielding the complex (trihydrate) as a gray–purple solid (180 mg, 1.15 mmol, 85%). Crystals suitable for X-ray structure determination were grown in the NMR tube from a saturated $CDCl_3$ solution at room temperature.

Crystal data

$[Cu(C_{66}H_{68}N_2O_2P_2)]Cl_2\cdot 6CDCl_3$
M_r = 1839.85
Monoclinic, *C*2
a = 19.401 (8) Å
b = 22.383 (9) Å
c = 20.805 (9) Å
β = 107.89 (4)°
V = 8598 (6) Å^3
Z = 4

D_x = 1.421 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 8.02–11.92°
μ = 0.956 mm^{-1}
T = 193 (2) K
Prismatic, red
0.40 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-7*S* diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.680, T_{max} = 0.787
8266 measured reflections
8013 independent reflections
5695 reflections with $I > 2\sigma(I)$

R_{int} = 0.035
θ_{max} = 25.25°
h = 0 → 23
k = 0 → 26
l = −24 → 23
3 standard reflections every 200 reflections intensity decay: 2.0%

Refinement

Refinement on F^2
$R(F)$ = 0.067
$wR(F^2)$ = 0.188
S = 1.046
8013 reflections
893 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.1007P)^2 + 13.8350P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.012
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Absolute structure: Flack (1983), 253 Friedel pairs
Flack parameter = 0.00 (3)

Table 1
Selected geometric parameters (Å, °).

Cu1*A*—O1*A*	1.883 (8)	Cu1*B*—O1*B*	1.902 (7)
Cu1*A*—N1*A*	1.932 (8)	Cu1*B*—N1*B*	1.926 (9)
O1*A*^{i}—Cu1*A*—O1*A*	89.5 (5)	O1*B*—Cu1*B*—O1*B*^{ii}	89.8 (4)
O1*A*—Cu1*A*—N1*A*	93.4 (3)	O1*B*—Cu1*B*—N1*B*	92.9 (3)
N1*A*—Cu1*A*—N1*A*^{i}	84.1 (5)	N1*B*—Cu1*B*—N1*B*^{ii}	84.5 (5)

Symmetry codes: (i) 1 − *x*, *y*, −*z*; (ii) −*x*, *y*, 1 − *z*.

All H (and D) atoms were placed in geometrically calculated positions and their isotropic displacement parameters were set to 1.2 times (1.5 times for CH_3 groups) the equivalent displacement parameter of their parent atoms. The Flack (1983) parameter is consistent with the known absolute stereochemistry of the starting materials.

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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