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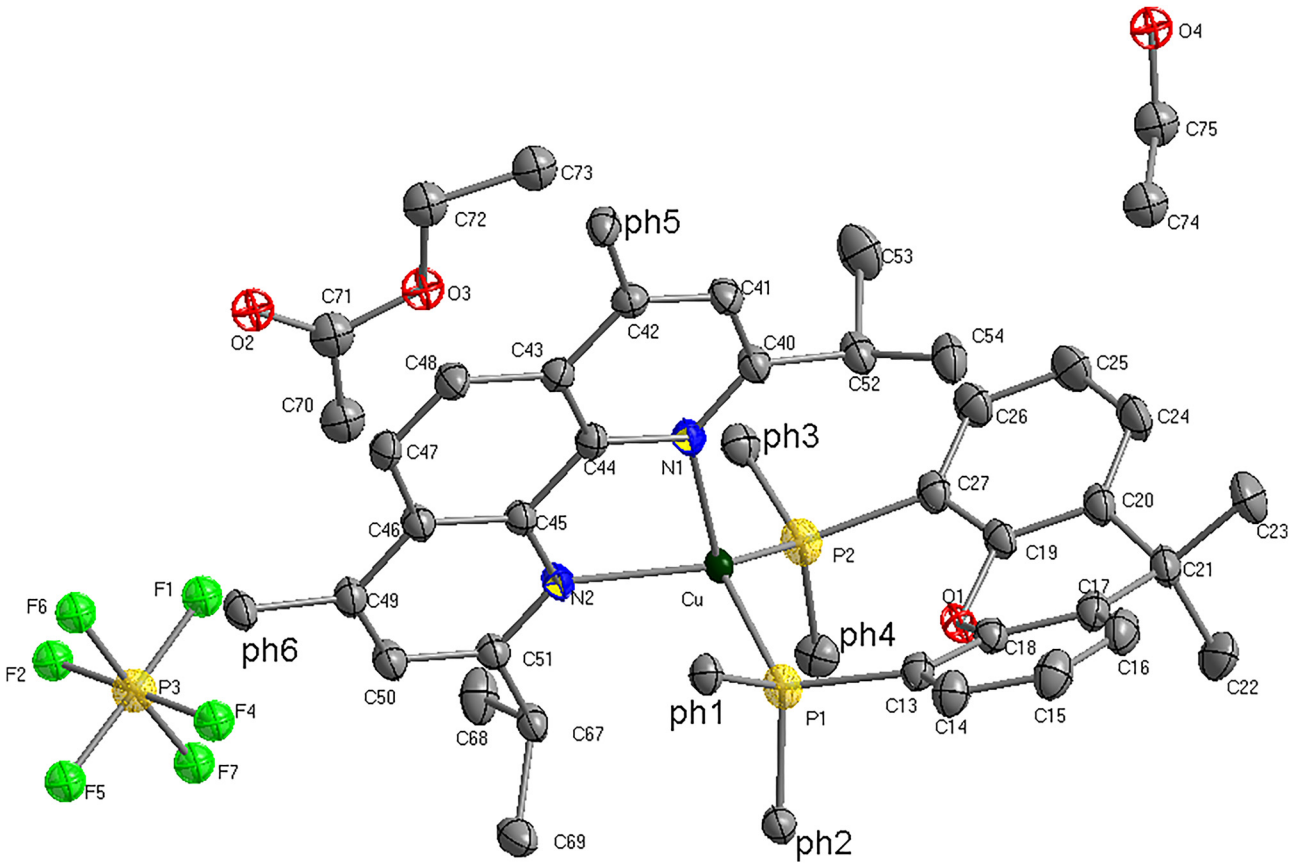
The crystal structure of {Cu(2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline)[4,5-bis(diphenylphosphino)-9,9-dimethylxanthene]}$^{+}$ PF^{6-}·1.5(EtOAC)



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Abstract

$C_{75}H_{725}CuF_6N_2O_4P_3$, monoclinic, $P2_1/n$ (no. 62), 10.9629(7) Å, 33.452(2) Å, 19.7777(13) Å, β = 101.149(2)°, V = 7,116.2(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0623, w$R(F^2)$ = 0.1632, T = 170 K.

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1 Source of materials

The title compound was prepared according to the following procedure: In a dried Schlenk tube, $[Cu(MeCN)_4]^+PF^{6-}$ (373 mg, 1 mmol MeCN = acetonitrile) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos, 579 mg, 1 mmol) were

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.15 × 0.09 × 0.06 mm
Wavelength:	Ga *K*α radiation (1.34139 Å)
μ:	2.42 mm^{-1}
Diffractometer, scan mode:	Bruker D8, φ and ω scans
θ_{max}, completeness:	57.0°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	49725, 14517, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 10149
$N(param)_{refined}$:	857
Programs:	SHELX,[5,6] Diamond,[7] Olex2[8]

dissolved in 20 mL of dry DCM at room temperature. The solution was stirred under reflux overnight. After cooling to room temperature, 2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline (phenanthroline, 416 mg, 1 mmol) dissolved in a minimal amount of DCM was added. The mixture was then heated to reflux for another 3 h. After cooling to room temperature, n-hexane was added to precipitate the product, which was filtered and washed with n-hexane. The resulting solid was further purified by recrystallization from a DCM/n-hexane mixture.[1–4]

Then 15 mg of {Cu(2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline)[4,5-bis(diphenylphosphino)-9,9-dimethylxanthene]}$^{+}$ PF^{6-} was added to 5 mL of EtOAc, stirred for 5 min, and filtered. The clear solution was allowed to evaporate slowly at room temperature, yielding crystals after several days.

2 Experimental details

Single-crystal X-ray diffraction measurements were carried out on Bruker D8 Venture with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at low temperature. After absorption correction, the crystal structure was solved using the Olex2 software[5] and the programs SHELXT[6] program and refined with SHELXL[7] and the molecular graphics were drawn by using DIAMOND software.[8] All hydrogens were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement.

There are solvent accessible VOIDS of 69 $Å^3$ in the unit cell and the volume of the void is reasonable. The entire EA molecule is located within a single pore and there are severely disordered solvent molecules which may be EA or water molecules that cannot be crystallographically located residing in the void(s).

3 Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

4 Comment

Photoredox catalysis, driven by visible light, is rapidly developing as an important strategy for organic synthesis and is very attractive as a clean and sustainable technology. However, the most widely used visible light catalysts are mainly based on precious metal complexes such as ruthenium and iridium. Although these precious metal complexes have good stability and catalytic activity, their low abundance and high cost limit large-scale industrial applications.

Cu(I) phthalocyanine derivatives have excellent excited state and redox properties,[9] and the McMillin team has conducted in-depth studies on them, synthesizing $[Cu(dmp)_2]^{+}$(dmp = 2,9-dimethyl-1,10 phthalocyanine),[10] proving that Cu(I) photosensitizers have long excited state lifetimes and excellent photoluminescence performance, which is conducive to constructing efficient photocatalytic systems. With the development of photocatalytic organic reactions, Cu-based photocatalysis gradually replace expensive Ir- and Ru-based photosensitizers in some photocatalytic reactions.[11,12] Although these relatively rare transition metals are the subject of an increasingly large body of work, the potential of copper, an earth-abundant transition metal, to serve as a photocatalyst under visible-light irradiation has been still in its infancy.

The crystal structure reported of the title compound is a novel skeleton copper base of P/N hybrid type photosensitizer, with 1,10-phenanthroline and xantphos as ligand. Cu-based visible-light photoredox catalysis indeed falls across the new phase of fast progress.[13] It is believed that more and more organic reactions catalyzed by Cu-based photosensitizers under visible light will be studied and reported by scientists.

There is one crystallographically independent Cu centre, one 2,9-diisopropyl-4,7-diphenyl-1,10-phenanthroline (phenanthroline), one 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) ligand, 1.5 solvent molecules and one hexafluorophosphate ion in the asymmetric unit. Each copper(II) is four-coordinated and is coordinated by two nitrogen atoms from phenanthroline ligands and two phosphorus atoms from xantphos ligands (Cu(1)–N(1) 2.114(2) Å and Cu(1)–N(2) 2.102(2) Å, Cu(1)–P(1) 2.2992(9) Å, Cu(1)–P(2) 2.2585(9) Å). All Cu centres display distorted tetrahedral coordination geometries with the N–Cu–N

angles ranging 79.50(9)°, the P–Cu–P angles 118.99(3)° and the N–Cu–P angles from 101.59(7) to 126.28(7)°.

Abundant intramolecular hydrogen bonds are found in the compound, three carbon atoms of phenanthroline ligands C62, C50 and C68, respectively donate one hydrogen atom to F4 atom and C62 donates one hydrogen atom to F6 atom. Furthermore, the guest acetones molecules are not in coordination, but are involved in intramolecular hydrogen bonds with guest acetone molecules (C70–H70B···F1 2.795(5) Å). Obviously, the extensive hydrogen bonds make a considerable contribution to stabilization of the crystal structure.

There are three intermolecular C4–H4···F1, C5–H5···F7, C65–H65···F2$^{\#1}$ (symmetry code: #1:x + l, y, z) hydrogen bonding interactions involving the xantphos carbon atoms (C4 and C5), phenanthroline C65 atom and the corresponding fluorine atom in neighboring hexafluorophosphate ion.

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