$[Cu(H_2dppd)(\eta^1\text{-}OClO_3)]ClO_4$: the first crystallographically characterized phosphine complex of copper(II) {H_2dppd = *N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine}

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The title complex 2, easily obtained by controlled potential oxidation of the copper(I) precursor $[Cu(H_2dppd)]BF_4$ 1, in perchlorate medium, crystallizes as a C_6H_6 monosolvate from dichloroethane–benzene, (2a), or as a CH_2Cl_2 hemisolvate from dichloromethane–toluene (2b), to give dark-red crystals which have been structurally characterized by X-ray crystallography.

We have recently reported on the ability of the ligand H_2dped {*N,N'*-bis[2-(diphenylphosphino)phenyl]ethane-1,2-diamine} to stabilize both Cu^I (ref. 1) and Cu^{II},[2] under carefully controlled experimental conditions and the copper(II)–phosphine complex $[Cu(H_2dped)]^{2+}$ has been characterized mainly on the basis of electrochemical measurements and EPR spectroscopy.[2]

We report here on the single-crystal X-ray diffraction characterization of the closely related complex $[Cu(H_2dppd)(\eta^1\text{-}OClO_3)]ClO_4$ **2**, and we provide preliminary synthetic and electrochemical data which show how the stability of **2** and $[Cu(H_2dped)]^{2+}$, both in the solid state and in solution, is not the result of accidentally favourable kinetic conditions but due to the peculiar properties of the soft–hard (P_2N_2) ligand set.

Complex **2** can be obtained as deep red precipitate upon electrochemical oxidation of the copper(I) precursor $[Cu(H_2dppd)]^+$ in 1,2-dichloroethane containing tetrabutylammonium perchlorate as supporting electrolyte. It crystallizes as a C_6H_6 monosolvate from benzene–dichloroethane (**2a**), or as a CH_2Cl_2 hemisolvate from dichloromethane–toluene (**2b**).†

The structure was solved for both **2a** and **2b**.‡ The molecular structure of the cationic complex $[Cu(H_2dppd)(\eta^1\text{-}OClO_3]^+$ is depicted in Fig. 1. The ligand behaves as a neutral tetradentate chelating agent producing, along with an η^1-$OClO_3$ unit, a square-pyramidal geometry around Cu^{II}. One of the two perchlorate ions is coordinated to Cu^{II} [Cu–O(1) 2.24(2) Å] and the two Cu–P bonds are remarkably longer [Cu–P 2.325(4) Å] in comparison with the value observed by us for the corresponding copper(I) species [Cu–P 2.197(6) Å].[1] Concomitantly, the Cu–N bonds are 2.06(1) *vs.* 2.17(1) Å observed for the copper(I) analogue. A dramatic contraction of the P(1)–Cu–P(2) angle [101.8(1) *vs.* 132.8(1)°] is observed, whereas the N(1)–Cu–N(2) bite angle remains essentially unchanged [86.3(4) *vs.* 85.7(4)°]. The basal plane formed by P_2N_2 atoms is puckered by ±0.06 Å and the Cu–O(1) axis is at 85.6° with respect to the mean P_2CuN_2 plane. The copper atom lies 0.24 Å (0.21 in **2b**) above this plane, towards the apical O(1), with C(7), C(8) and C(9) below by 1.47, 1.58 and 1.29 Å, respectively (the corresponding values in **2b** are 1.48, 1.55 and 1.33 Å). The second perchlorate acts as a counter ion and only in **2a** it is involved in a weak intramolecular hydrogen bond with N(1) [N(1)···O(5) separation of 2.87 Å]. The two five-membered Cu–P–C–C–N chelate rings have an envelope configuration (C_s) with the copper atom out of the plane formed by the remaining four atoms by 0.36 and 0.68 Å (0.28 and 0.63 Å in **2b**) in the two halves of the cation and they make a dihedral angle of 6.3° in **2a** and 18.6° in **2b**. The six-membered CuN(1)C(7)C(8)C(9)N(2) ring has a chair configuration with torsion angles in the range 60.1–71.9°. In view of the relatively strongly bound perchlorate unit, the Cu–O(1) bond [2.24(2) Å] is shorter than the mean of those in 24 other copper(II)–perchlorate complexes (2.51 ± 0.12 Å),[3] but, despite the extra strength of this interaction, both IR and conductivity data reveal that complete ionization occurs in dichloroethane and nitromethane solutions.†

We have tested the bonding ability towards Cu^{II} of three further bidentate (PN) and two tetradentate $[P_2N(CH_2)_nN]$ ligands, all closely related to H_2dppd. In four cases we could isolate and/or voltammetrically detect copper(II)–phosphine adducts, the stabilities of which are strongly dependent on the geometric features of the tetradentate ligands, in particular on the number, *n*, of methylenes bridging the two nitrogen atoms, and on the degree of *N*-alkyl substitution in the case of the bidentate ones. For example, in dichloroethane the $E_{1/2}$ of the Cu^I–Cu^{II} redox couple, expressed as the mean value of the potentials for the anodic ($E_p{}^a$) and cathodic ($E_p{}^c$) peak currents, moves anodically from 0.08_0 to 0.14_5 and 0.31_5 V (*vs.* ferrocenium–ferrocene) on going from $n = 2$ to $n = 3$ and finally to $n = 5$ in the case of the tetradentate ligands, with a

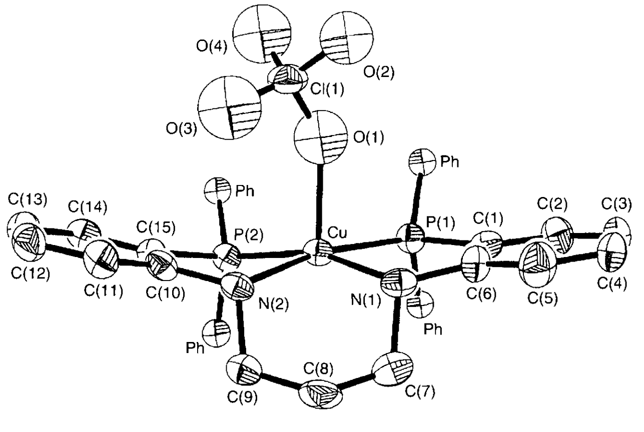

Fig. 1 ORTEP representation of the complex cation $[Cu(H_2dppd)(\eta^1\text{-}OClO_3)]^+$. Selected bond lengths (Å) and angles (°), as mean values from **2a** and **2b**: Cu–P 2.325(4), Cu–N 2.06(1), Cu–O(1) 2.24(2), P(1)–C(1) 1.81(1), P(2)–C(15) 1.80(1), N(1)–C(6) 1.49(2), N(1)–C(7) 1.52(2), N(2)–C(10) 1.44(2), N(2)–C(9) 1.48(2), C(7)–C(8) 1.50(2), C(8)–C(9) 1.55(2), P(1)–Cu–P(2) 101.8(1), N(1)–Cu–N(2) 86.3(4), P(1)–Cu–N(1) 85.9(3), P(2)–Cu–N(2) 83.8(3), Cu–P(1)–C(1) 98.7(5), Cu–P(2)–C(15) 98.5(5), Cu–N(1)–C(6) 116(1), Cu–N(2)–C(10) 114(1). Perchlorate counteranion and solvent molecules have been omitted for clarity, and phenyl rings are designated as Ph.

concomitant marked decrease of the reversible character of the $Cu^I \rightleftharpoons Cu^{II}$ interconversion reaction ($E_p{}^a - E_p{}^c$ = 132, 170 and 400 mV, respectively). Thus, longer alkylene tethers appear to stabilize Cu^I *vs.* Cu^{II} as well as to make the electron-transfer reaction slower. This observation is the likely consequence of an increasing reluctance of the tetrahedral (P_2N_2) coordination sphere around Cu^I (ref. 1) to convert to the square-planar environment required for Cu^{II}.

Footnotes

† A slurry of **1** (0.500 g, 0.671 mmol) in dichloroethane (25 ml) containing 0.2 mol dm^{-3} tetrabutylammonium perchlorate, was exhaustively (1 F mol^{-1}) oxidized at a platinum gauze electrode at +0.900 V *vs.* SCE. During the electrolysis a deep red solid began to precipitate. Upon completion, toluene (25 ml) was added to induce precipitation, and the mixture was cooled to 0 °C. The product was isolated by filtration, rinsed with two 5 ml portions of cold dichloroethane–toluene, and dried *in vacuo*; yield 0.40 g (70%) (Found: C, 55.05; H, 4.30; N, 3.20. Calc. for $C_{39}H_{36}Cl_2CuN_2O_8P_2$: C, 54.65; H, 4.23; N, 3.27). IR (Nujol): $\nu_{(Cl-O)}$ 1125, 1095, 1080, 1034 cm^{-1}; single band at 1095 cm^{-1} in dichloroethane solution Λ_M ($MeNO_2$) = 140 Ω^{-1} cm^2 mol^{-1}.

Single crystals of **2a** were grown by layering benzene onto a dichloroethane solution of **2**. Suitable crystals of **2b** were obtained by layering toluene onto a dichloromethane solution of **2**.

‡ *Crystallography*: *T* = 294 K; Siemens Nicolet R3m/V four-circle diffractometer, Mo-Kα radiation (λ = 71073 Å), graphite monocromator, θ–2θ scan mode, no crystal decay; full-matrix least-squares refinement with heavy atoms and C(1)–(15) anisotropic; $w^{-1} = \sigma^2(|F_o|)+k|F_o|$; severe disorder in ClO_4^- and trapped solvent molecules; for **2a** benzene was treated as a rigid body. All calculations performed using SHELXTL PLUS.[4] Scattering factors for all the atoms were taken from ref. 5.

Crystal data for **2a**: $C_{45}H_{42}Cl_2CuN_2O_8P_2$, *M* = 935.2, monoclinic, space group $P2_1/c$ (no. 14), *a* = 13.011(3), *b* = 17.424(4), *c* = 18.780(5) Å, β = 91.37(2)°, *U* = 4256(2) Å^3, *Z* = 4, D_c = 1.459 g cm^{-3}, *F*(000) = 1932, μ(Mo-Kα) = 7.7 cm^{-1}, specimen 0.15 × 0.15 × 0.20 mm^3. 5941 unique reflections for $2\theta \leqslant 46°$, of which 3009 with $|F_o| \geqslant 4\sigma(|F_o|)$ were used in the refinement, *R* = 0.079, *R'* = 0.087, *S* = 2.00 and largest difference peak of 1.1 e Å^{-3}.

For **2b**: $C_{39.5}H_{37}Cl_3CuN_2O_8P_2$, *M* = 899.5, monoclinic, space group *P*2/*c* (no. 14), *a* = 13.150(6), *b* = 16.890(4), *c* = 18.692(7) Å, β = 92.92(3)°, *U* = 4146(3) Å^3, *Z* = 4, D_c = 1.441 g cm^{-3}, *F*(000) = 1848, μ(Mo-Kα) = 8.5 cm^{-1}, specimen 0.10 × 0.15 × 0.18 mm^3. 5418 unique reflections for $2\theta \leqslant 45°$, of which 2354 with $|F_o| \geqslant 4\sigma(|F_o|)$ were used in the refinement, *R* = 0.089, *R'* = 0.096, *S* = 1.44 and largest difference peak of 0.95 e Å^{-3}.

The cations of **2a** and **2b** are essentially superimposable, the weighed root-mean square deviation being 0.066 Å, if the fitting is performed on basal plane and C(1)–(15) atoms, with maximum deviation (0.53 Å) by O(1). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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Received, 3rd October 1995; Com. 5/06503H