# $[Cu(H_2dped)](BF_4)_2$ ($H_2dped$ = *N,N'*-bis(2-(diphenylphosphino)phenyl)ethane-1,2-diamine): a Stable Phosphine Complex of Copper(II)

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Controlled potential oxidation of $[Cu(H_2dped)]^{1+}$ **1** in 1,2-dichloroethane or reaction of $[Cu(H_2O)_6](BF_4)_2$ with $H_2dped$ in acetone affords the complex $[Cu(H_2dped)]^{2+}$ **2** *i.e.* a $Cu^{II}$ species stabilized by a soft–hard ($P_2N_2$) ligand set.

The synthesis of phosphine complexes of copper(II) has been attempted for decades.[1] The coexistence of a $Cu^{II}$ centre and a phosphine coordinating site inside the same metal coordination sphere being the main obstacle and, in oxygen-containing solvents or in the presence of even minute amounts of water, the practically unavoidable reduction of $Cu^{II}$ to $Cu^{I}$ and the concomitant oxidation of the phosphine coordination site to phosphine oxide are observed.[1,2]

Two binuclear copper(II) complexes containing 8-quinoldiphenylphosphine were described by Issleib *et al.*[3] but the complexes were not structurally characterized fully. The surprising[2] existence of $Cu^{II}$ complexes of bis(diphenylphosphino)ethane and of bis(diphenylphosphino)propane as a component of new anion sensor materials was claimed in 1990[4] and the formation of a $Cu^{II}$ complex with the ligand *N,N'*-bis(2-diphenylphosphino)phenyl)propane-1,3-diamine at the water–1,2-dichloroethane interphase has been proposed by Schiffrin and coworkers.[5] In this last instance, however, a $Cu^{I}$ species is likely to be responsible for the observed facilitated transfer of copper(II) from the water to the organic phase.[6]

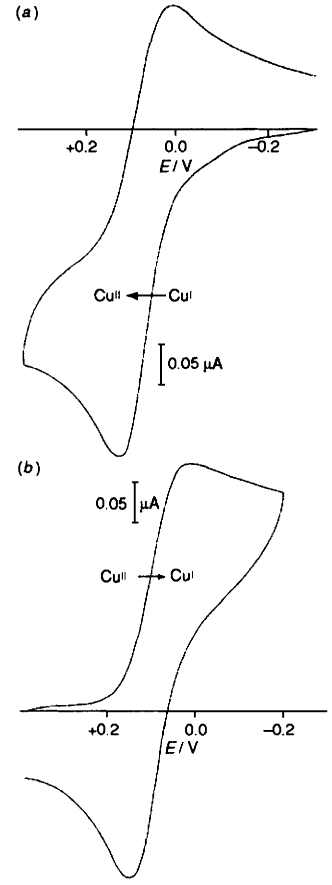

**Fig. 1** Cyclic voltammograms of **1** (*a*) and of **2** (*b*) recorded in dichloroethane using a Pt electrode at a scan rate of 50 mV $s^{-1}$. Potentials are referred to the ferrocenium/ferrocene redox couple ($E_{1/2}$ = +0.42 V *vs.* aqueous SCE) (conditions; (Cu) = 1.60 $10^{-3}$ mol $dm^{-3}$, tetrabutylammonium perchlorate 0.2 mol $dm^{-3}$ as supporting electrolyte).

We report the synthesis of a well-characterized (ESR and electrochemical analyses) tetracoordinated complex of *N,N'*-bis[2-(diphenylphosphino)phenyl]ethane-1,2-diamine.

The complex cation $[Cu(H_2dped)]^{2+}$ **2** can be quantitatively (chronoamperometric tests) obtained in dichloroethane† upon controlled potential one-electron oxidation of $[Cu(H_2dped)]^{1+}$ **1**.[6] The dark-red $Cu^{II}$ complex precipitates as perchlorate salt from 0.025 mol $dm^{-3}$ solutions of the $Cu^{I}$ precursor. Complex **2** can also be chemically synthesized upon treating $[Cu(H_2O)_6](BF_4)_2$ with a stoichiometric amount of $H_2dped$ in acetone or dichloromethane at room temp.‡ Complex **2** behaves as a 2 : 1 electrolyte in acetonitrile ($\Lambda_M$ = 291.5 $\Omega^{-1}$ $cm^2$ $mol^{-1}$). Its electronic spectrum in dichloromethane displays a very broad charge-transfer band (LMCT) in the 250–1500 nm range, tailing away into the end of the VIS spectrum, known to be responsible for the red colour of a number of copper(II) complexes.[7]

Solutions of **2** in dichloroethane exhibit a CV pattern [Fig. 1(*b*)] stable for days and identical to that obtained in the one-electron electrochemical oxidation of **1** [Fig. 1(*a*)].

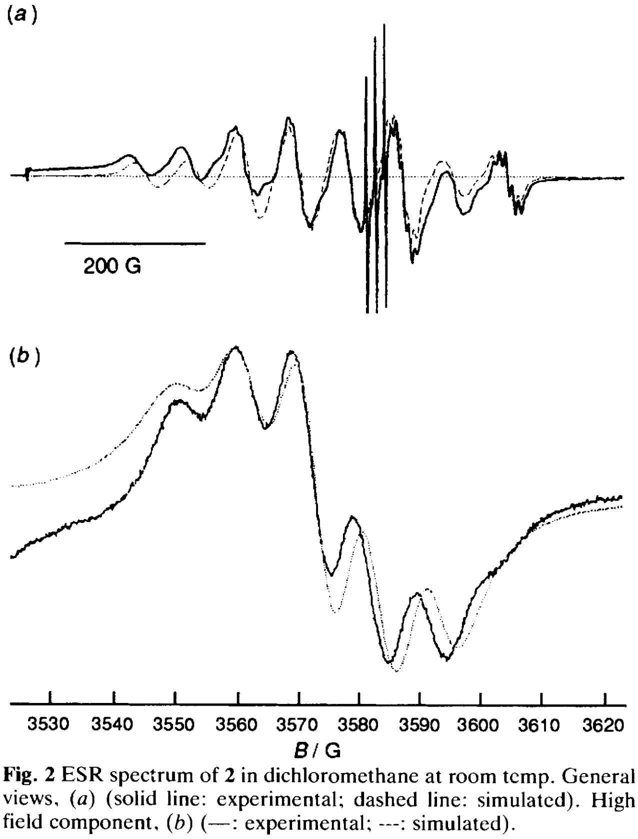

**Fig. 2** ESR spectrum of **2** in dichloromethane at room temp. General views, (*a*) (solid line: experimental; dashed line: simulated). High field component, (*b*) (—: experimental; ---: simulated).

The $Cu^I \rightleftarrows Cu^{II}$ redox interconversion is a quasireversible process ($\Delta E_p$ is 132 as opposed to 60 mV expected for a fully reversible one-electron transfer), centred at $E_{1/2} = 0.080$ V *vs.* ferrocenium/ferrocene as mean value of the potentials for the cathodic and anodic peak currents. Control experiments showed that uncoordinated $H_2$dped is oxidized at far more anodic potentials ($E_p{}^a$ *ca.* 0.500 V *vs.* ferrocenium/ferrocene), further anodically shifted upon metal coordination ($E_p{}^a$ *ca.* 0.700 V).

The nature of **2** is unambigously demonstrated by ESR spectroscopy in dichloroethane [Fig. 2(*a*) and (*b*)]. The spectrum is typical of a spin $S = 1/2$ species and is centred at a $g$ value (corrected by second-order shift), $g_{iso}$ 2.057. The spectrum consists of several hyperfine components covering a range of *ca.* 600 G. The pattern can be fully analysed in terms of the hyperfine interaction of the unpaired electron with one spin $I = 3/2$ nucleus ($^{63}$Cu and $^{65}$Cu), with two equivalent spin $I = 1/2$ nuclei ($^{31}$P) and with two equivalent $I = 1$ nuclei ($^{14}$N). The hyperfine splitting constants are: $A_{iso}{}^{Cu} = 84$, $A_{iso}{}^{P} = 164$, $A_{iso}{}^{N} = 10$ G; these constants compare well with those reported for well characterized square planar copper(II) complexes.[8]

Because of the large couplings, second-order effects[9] have to be considered as well as the presence of the two Cu isotopes in the natural isotopic mixture. Moreover, the line intensities in the first derivative spectrum do not follow the expected ratio corresponding to the degeneracy of the ESR transitions because the linewidths change across the spectrum.

The linewidth variation is typical of $Cu^{II}$ complexes in solution and it is due to the incomplete averaging of the $g$ and $A$ tensor anisotropies by the molecular tumbling motion.[10] The variation has been accounted for by eqn. (1),

$$1/T_2 = A + B\,m_I + Cm_I{}^2 \qquad (1)$$

where $m_I$ is the Cu spin quantum number and $A$, $B$ and $C$ are constants related to the anisotropies of the $g$ and Cu hyperfine tensor. The constants $A$, $B$ and $C$ also depend on the rotational correlation time.

Fig. 2(*a*) shows the spectrum together with its computer simulation, while Fig. 2(*b*) shows the highfield components and the relevant simulation. The very good agreement supports a molecular structure in which a $Cu^{II}$ centre is coordinated to two phosphorus and two nitrogen ligating sites. The linewidths were found to be independent of the $^{14}$N and $^{31}$P spin components, thus indicating a smaller value of the hyperfine tensor anisotropies for those nuclei. As shown in Fig. 2(*a*), the experimental spectrum also displays an evident, albeit weak, triplet centred at $g$ 2.008 (separation = 14 G) attributable to the presence of a nitroxide-like radical likely produced by the interaction of **2** with trace amounts of water.

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## Footnotes

† 0.450 g (0.615 mmol) of **1** $BF_4$ in dichloroethane (25 ml) are exhaustively (1 F $mol^{-1}$) oxidized at a platinum gauze electrode at +0.850 V *vs.* SCE. **2**$(ClO_4)_2$ precipitates spontaneously (*ca.* 70% yield) after a few hours at room temp. Most of the remaining **2**$(ClO_4)_2$ can be obtained as microcrystals upon cooling to −20 °C.

‡ $[Cu(H_2dped)](BF_4)_2$ is obtained as follows: solid $H_2$dped (101 mg, 0.17 mmol) is added to a light-blue solution of $[Cu(H_2O)_6](BF_4)_2$ (60 mg, 0.17 mmol) dissolved in acetone (10 ml) with stirring, at room temp.; the solution immediately turns dark red and is stirred for an additional 10 min till complete ligand dissolution. Addition of diethyl ether (50 ml) leads to the precipitation of a dark-red microcrystalline powder, which is collected upon filtration and dried *in vacuo* (yield = 91%). The complex is soluble in dimethylformamide, MeCN, chlorinated solvents and nitromethane.

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