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Antioxidant potential and secondary reactivity of *bis*{diphenyl(2-pyridyl)phosphino}copper(II) complex

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Abstract: Copper-based complexes with the general formulas $[Cu(L)_2]Cl_2$ (**1**) and $[Cu_2L_2(\mu_2\text{-}L)\mu_{2-}Cl_2]$ (**2**) and a mixed-ligand anionic complex $[Cu(L)_2dedtc][LCl]$ (**3b**), where **L** = diphenyl(2-pyridyl)phosphine and **dedtc** = diethyldithiocarbamate, were synthesized and structurally characterized. X-ray analysis revealed that the coordination environment around the copper atom in complexes **1**–**3** is distorted tetrahedral. In monomeric complexes **1** and **3b** both diphenyl(2-pyridyl) phosphine ligands are monodentate and are coordinated through the P-atom. In complex **3b** two phosphine ligands are attached to copper through the P-atom. The third phosphine ligand acts as a bridged ligand, coordinated to the metal centers through the P-atom and N-atom. Complexes **1** and **3b** were tested for radical scavenging activity using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a free radical. A prominent color change after mixing the solution of complex **1** and DPPH was observed, indicating the efficiency of the compound as antioxidant.

Key words: Cu(II) phosphine complex, secondary reactivity, dithiocarbamate, X-ray structure, antioxidant agent

1. Introduction

Trialkyl- and triarylphosphines are valuable ligands to stabilize metal ions, particularly copper, and afford various geometries depending on the nature of the metal ion and the steric bulk of the phosphine ligand.[1–3] Ligands containing phosphorus and their coordination compounds are abundantly available as they possess versatile electronic, biological, and nonbiological applications.[4–10] This class of ligands has a major contribution in establishing the coordination chemistry of copper.[11] In comparison to triphenylphosphine (Pph_3), diphenyl(o-pyridyl)phosphine is an attractive alternate, which additionally offers the possibility of coordination through the N-atom and can thus act as a bidentate ligand. Due to the presence of two coordination centers in the molecule of the $P(ph)_2py$ ligand (N and P), it has been reported to act either as a bidentate or bridged ligand.[12–17] The oxidation state of the metal ion and the presence of other coligands seem to be the major factors in determining not only the coordination mode of such bidentate ligands but also metal complexes of different nuclearities.[18–22] Since the ligand is neutral, it affords neutral complexes where metal-halogen moiety normally remains intact, which provides the possibility for secondary reactivity. This makes compounds containing phosphine attractive synthons for further transformation. Such secondary reactivity of complexes containing phosphine is rare and

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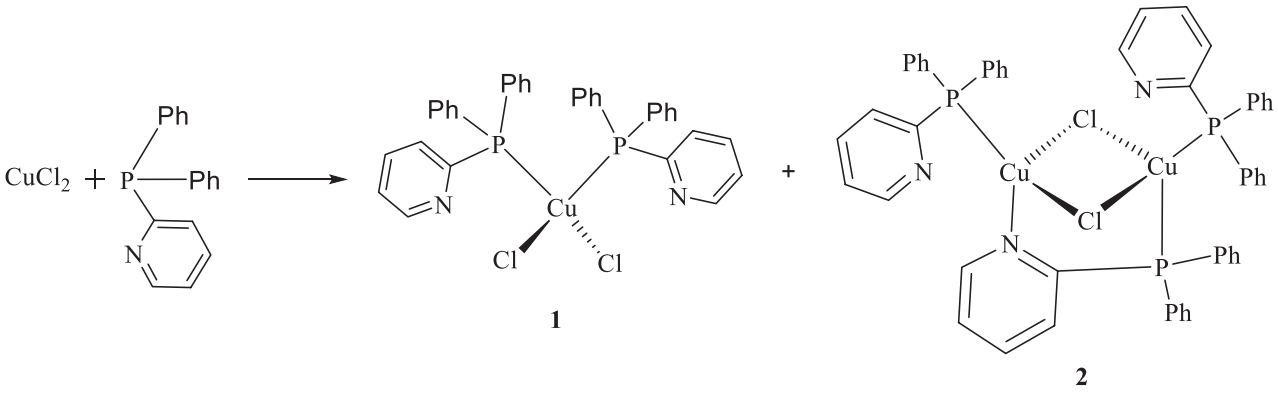
the only example that has been reported is the conversion of a homo-bimetallic copper complex into a trimetallic copper complex.[23] The stoichiometric amount of phosphine ligand in a reaction has a critical role, because its excess amount followed by heating provides a suitable medium for metal reduction.[24] The ruthenium complexes with pyridylphosphine ligand have also been successfully applied in transmetalation to gold and silver.[25] Since the diphenyl(2-pyridyl) phosphine ligand offers two nucleophilic centers, a soft P and a relatively hard N, it thus coordinates the hard or soft metal via N or P, respectively. Despite the fact that the ligand can form chelates and bridged complexes, no mononuclear Cu(II) complexes of it have been reported to date.

Here we report a mononuclear Cu(II) complex of the diphenyl(2-pyridyl) phosphine ligand with formula $[CoCl_2(Pph_2py)_2]$ (**1**), in which both of the coordinated phosphine ligands are bonded terminally through the P-atom. The reaction mixture also contained an already reported dinuclear Cu(I) compound as a second but minor product (ca. 5%) with three phosphine ligands. Treatment of complex **1** with dithiocarbamate ligand (**dedtc**) afforded a heteroleptic complex $[Cu(Pph_2py)_2dedtc][ph_2cyPCl]$ (**3b**), which was isolated in the solid state. Complexes **1** and **3b** were tested for their antioxidant activities (DPPH assay), and promising results were obtained.

2. Results and discussion

2.1. Chemistry and X-ray crystallography

Reacting two equivalents of diphenyl(2-pyridyl) phosphine with $CuCl_2$ leads to a mixture of compounds **1** (major product) and **2** (minor product) (Scheme 1). Complex **1** was expected to have Cu(II) as the central metal ion while complex **2** contained Cu(I), which was unexpected. Complex **2** has already been reported through the reaction of Cu(I) salt with Ph_2PyP ligand under an inert atmosphere.[26] Reduction of Cu(II) to Cu(I) and some other transition metals such as Re and Tc in excess of phosphine ligand has already been reported previously.[24,27] Separation of complexes **1** and **2** (selected crystallographic details for **2** are given in Supplemental Figure S1 and Tables S1 and S2) was carried out physically under a microscope on the basis of difference in their colors and both compounds were characterized by single-crystal X-ray analysis.



Scheme 1. Synthetic route for complexes **1** (major fraction) and **2** (a minor fraction as side product).

The X-ray structure of complex **1** along with selected bond lengths and angles is shown in Figure 1 and the data pertinent to crystal structure determination and refinements are summarized in Table 1. The complex crystallizes in a monoclinic crystal system with space group $P2_1/n$. The coordination environment around the copper ion is distorted tetrahedral as expected and has twofold (C_2) symmetry as reported for other

compounds.[28] The copper atom is coordinated to the phosphine ligand through a comparatively soft center (phosphorus) and two chlorine atoms. The fine crystals of compound **1** did not allow optimum data collection and could thus suggest a relatively poor diffraction pattern, which ultimately resulted in the higher resolution factor. However, data were good enough to establish connectivity within the molecule. The observed bond angles and lengths are comparable to the reported data for analogous complexes. The bond angles Cl1-Cu1-P2 (113.88°) and Cl2-Cu1-P1 (113.24°) are almost identical with negligible variations. The other two angles, Cl1-Cu1-P1 and Cl2-Cu1-P2, were recorded to be 108.29° and 104.06°, respectively. This variation of angles from that expected for a perfect tetrahedral geometry is due to the presence of different ligands around the metal center. Heteroleptic mononuclear complexes containing the Cu ion and at least one PR_3 ligand are reported to have a P-Cu-P angle in this region of 108–120° and are dependent on the nature of the nonphosphorus ligands in the coordination sphere.[29,30] The bond distances Cu-P and Cu-Cl are 2.266 Å and 2.337 Å, respectively, and are within the expected region (for summarized structural data see Table 2). Compound **1** forms a supramolecular structure stabilized by C-H—Cl type intermolecular hydrogen bonding interactions with an average distance of 2.917 Å. There are intramolecular N—N interactions equivalent to 2.813 Å.

Compound **2** was obtained as a minor side product during the course of reaction and was separated manually as discussed earlier under a microscope. The central metal atom (Cu) was found in reduced form

Table 1. Crystal data and structure refinement of **1** and **3b**.

Crystal parameter	**1**	**3b**
Empirical formula	$C_{34}H_{30}Cl_2CuN_2OP_2$	$C_{56}H_{52}ClCuN_4P_3S_2$
Formula weight	678.98	1037.03
Temperature (K)	296	133
Wavelength (Å)	0.71073	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$/n	$P2_1$/c
a	8.9924(13)	24.528(8)
b	17.37(3)	12.313(4)
c	20.587(4)	16.592(5)
β	102.102	97.651(3)
Volume (Å^3)	3228.6(9)	4966.4(3)
μ (mm^{-1})	0.97	0.72
Z	4	4
Density (Mg m^{-3})	1.397	1.387
F (0,0,0)	1396	2156.0
(h, k, l) min	(–10, –22, –26)	(–30, –15, –20)
(h, k, l) max	(11, 22, 11)	(30, 15, 20)
Theta (max)	27.3	26.3
Absorption correction	None	Numerical
R (ind. reflection/restraints/parameters)	0.099(7060/2/289)	0.117(9986//0606)
wR_2	0.304(7060)	0.333
Goodness of fit (S)	1.013	1.199

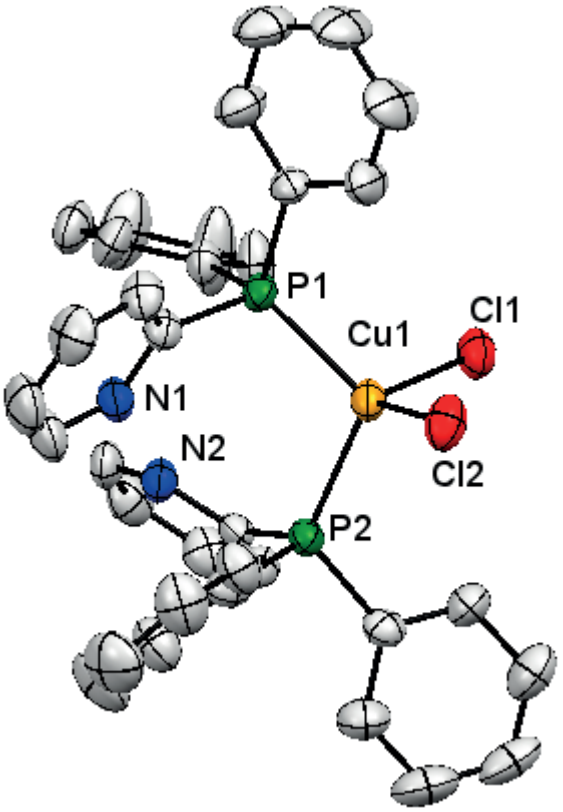


Figure 1. Molecular structure of compound **1**, 50% probability thermal ellipsoids, all hydrogen atoms are omitted, and only noncarbon atoms are numbered. For selected bond lengths and angles, see Table 2.

Table 2. Selected bond lengths (Å) and bond angle (°) of compounds **1** and **3b**.

Complex **1**	Bond distances		Bond angles	
	Cu1-Cl1	2.337(2)	P1-Cu1-P2	110.63(8)
	Cu1-Cl2	2.350(2)	P1-Cu1-Cl1	108.29(9)
	Cu1-P1	2.266(2)	P2-Cu1Cl1	113.88(9)
	Cu1-P2	2.267(2)	P2-Cu1-Cl2	104.05(9)
			Cl1-Cu1-Cl2	106.76(9)
Complex **3b**	Bond distances		Bond angles	
	Cu1-P1	2.2311(19)	P1-Cu1-P2	114.99(7)
	Cu1-P2	2.2312(18)	P1-Cu1-S2	107.06(8)
	Cu1-S1	2.3870(2)	P2-Cu1-S2	119.39(7)
	Cu1-S2	2.3650(2)	P1-Cu1-S1	120.97(8)
	P3-Cl1	1.9350(3)	P2-Cu1-S1	112.98(7)
			S2-Cu1-S1	75.77(7)

(Cu^{2+} to Cu^{1+}). The reduction phenomenon of the metal ion has been attributed to an excess amount of Pph_2py ligand[24] or oxygen being provided under aerobic conditions.[27]

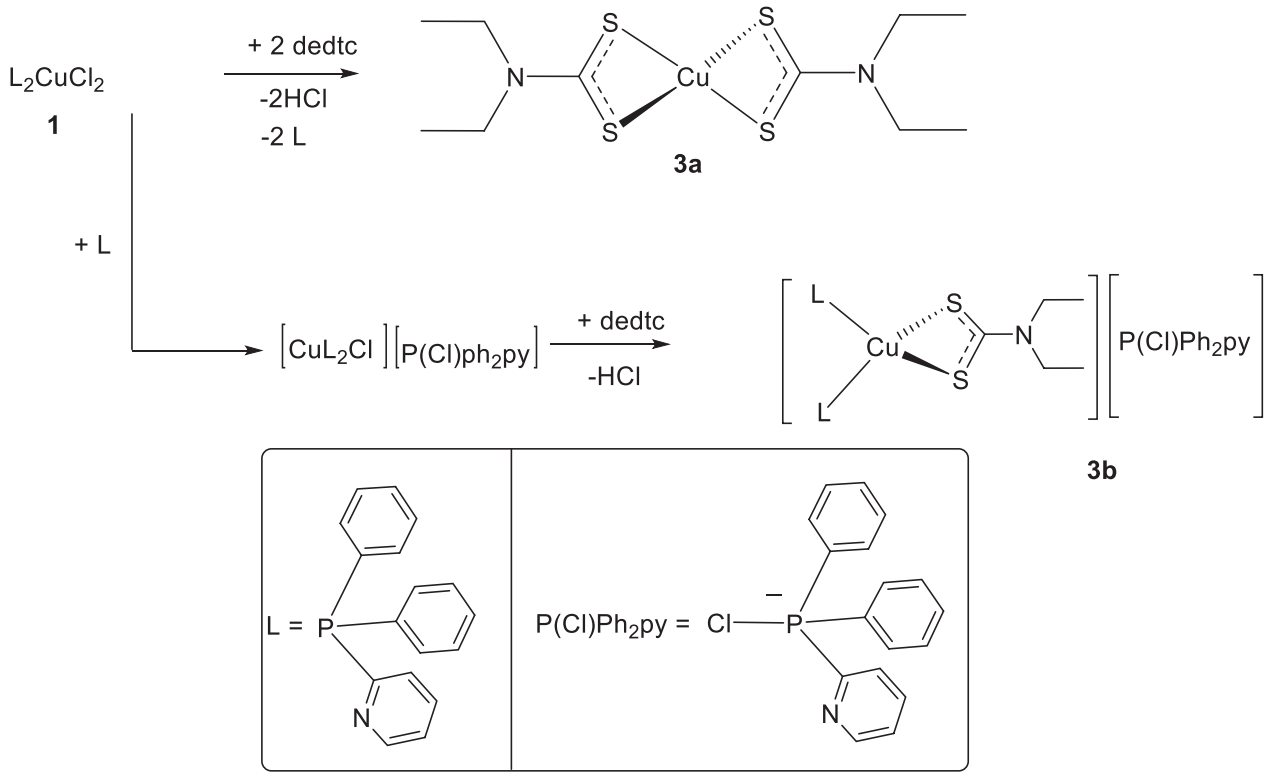
2.2. Secondary reactivity of complex 1

We have previously reported octahedral complexes of general formula L_4CuCl_2 where **L** = indazole ligand[31] and we were thus interested in studying the secondary reactivity of structurally analogous complexes by replacing the two Cl^- ligands present in compound **1**. The diethyldithiocarbamate ligand was selected in this study in order to get the targeted octahedral compounds. However, treating two equivalents of diethyldithiocarbamate (**dedtc**) with compound **1** in methanol instead afforded two different products $[Cu(dedtc)_2]$ (**3a**) and $[Cu(L)_2dedtc][LCl]$ (**3b**) (structure of **L** is given in Scheme 2). Compound **3a** is soluble in MeOH while **3b** precipitates out as a green solid. Compound **3a** was identified as the bis(dithiocarbamato)Cu(II) complex that has already been reported.[32–36] The precipitate was separated and redissolved in hot EtOH, which afforded green crystals of **3b** in a few days. Compound **3b** crystallizes in a monoclinic crystal system with space group $P2_1/c$. X-ray analysis of **3b** reveals that it is a mixed-ligand anionic complex and copper is bonded to two phosphine ligands through the P-atom and a chelating **dedtc** ligand through two sulfur atoms (Scheme 2; Figure 2). The geometry around Cu can best be described as distorted tetrahedral. The distortion from normal tetrahedral geometry around the copper is due to the expected acute angle formed by the **dedtc** bidentate ligand (S1-Cu1-S2 75.77°), which is in good agreement with the reported data.[37–39] The angles S1-Cu1-P2, P2-Cu1-P1, and P1-Cu1-S2 were in the range of 107.06–114.99°. The P-Cu-P angle is wider because of the bulk of the P-ligand compared to the bidentate **dedtc** ligand. The observed distortion and planarity of -NCSS moiety represent the resonance phenomenon in the -NCSS group, which is common in complexes containing dithiocarbamate ligands.[40] The Cu-S bond distance is in the range of 2.365–2.387 Å and the Cu-P bond distance is 2.231 Å, comparable to the reported data.[41] Various attempts to suppress the formation of **3a** were unsuccessful despite using equimolar quantities of **1** and **dedtc** ligand. It is proposed that less volatile $P(ph)_2py$ ligands are released during the course of the reaction, which trap a Cl ion from complex **1**, making it coordinatively unsaturated and acting as an intermediate (Scheme 2). The reactive intermediate thus allows one equivalent of **dedtc** ligand to coordinate with the metal center and affords complex **3b**.

Compound **3b** shows a supramolecular structure that is stabilized by N—H-C and Cl—H-C intermolecular interaction with a distance of 2.615 Å and 2.287 Å, respectively. Parameters related to the structure solution and refinements and selected structural properties are summarized in Table 1 and Table 2, respectively.

2.3. Determination of antioxidant activities of copper complexes (1 and 3b)

The free radical scavenging activities of complexes **1** and **3b** were determined against 2,2-diphenyl-1-picrylhydrazyl (DPPH). The results obtained are represented in Figures 3 and 4 and the calculated values are summarized in Table 3. DPPH has a purple color in its free state and has λ_{max} = 517 nm (shown on the extreme right in Figure 3). This absorbance is affected by the addition of an antioxidant and the decrease in the absorption intensity depends on the interaction between these two species. Adding 20 ppm solution of compound **1** not only led to a color change but also caused a sudden drop in absorption intensity, with an observed inhibition of 16%. By increasing the concentration of **1** to 40 and 60 ppm the absorbance further decreased with an increased inhibition of 19% and 27.9%, respectively, for the two concentrations. With a further increase in the concentration of complex **1** to 80 and 100 ppm, the absorbance decreased accordingly and the color of the solution mixture changed to yellow. For higher concentrations of 80 and 100 ppm, the observed inhibitions were very close to each other, i.e. 57% and 58%, respectively (see Figures 4 and 5).



Scheme 2. The proposed reaction pathway for the formation of complexes **3a** and **3b**.

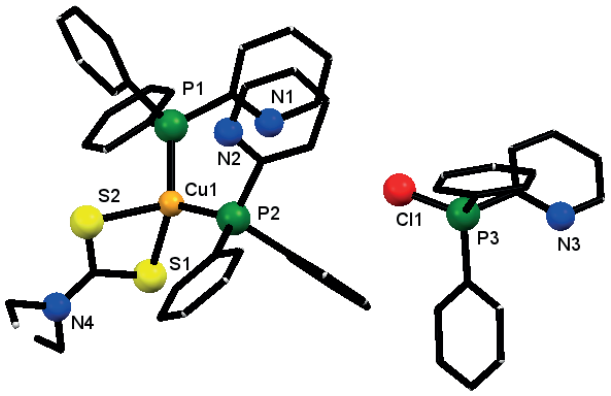


Figure 2. Molecular structure of compound **3b** with partial numbering scheme, where noncarbon atoms are shown as balls and all carbon atoms are represented as capped sticks for clarity reasons. Hydrogen atoms are also omitted for the same reason.

These findings indicate that compound **1** is an efficient antioxidant agent as compared to our recently studied copper complexes.[31] The optimum inhibitory concentration of complex **1** is impressive and it is a more efficient antioxidant than the gold-based complex reported previously.[40]

On the other hand, **3b** proved to be much less efficient under the same experimental conditions. Maximum percent inhibition of 18.5% could be achieved by adding a solution of 100 ppm concentration of **3b**.

Table 3. Free radical scavenging activity (DPPH) of compounds **1** and **3b**.

	Complex 1	Complex 3b
Conc. (ppm)	% RSA (DPPH)	% RSA (DPPH)
20	16.0	12.4
40	19.1	13.3
60	27.9	16.7
80	57.4	18.4
100	58.1	18.5

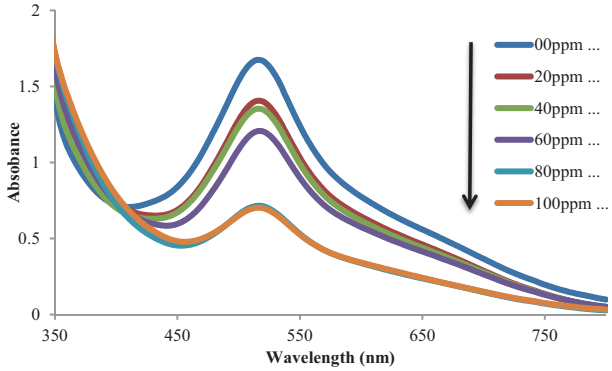


Figure 3. Absorption spectra of DPPH in the absence and in the presence of compound **1**. The arrow shows the change in the spectra on increasing the concentration of the compound.

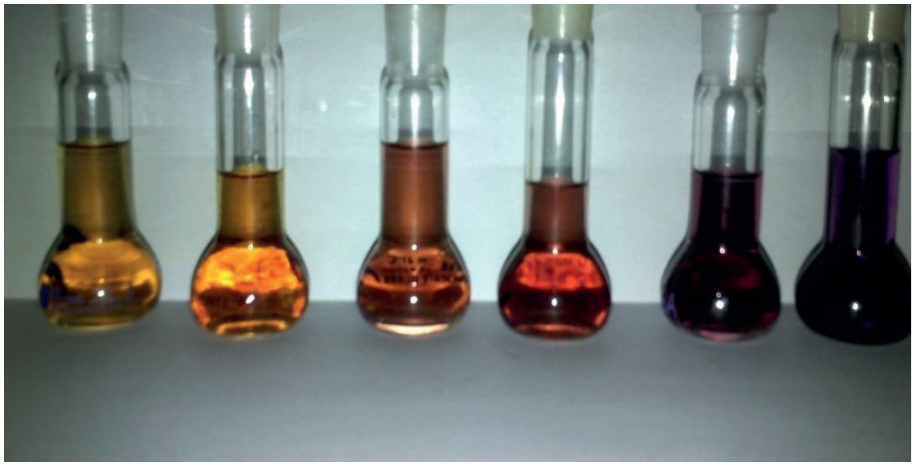


Figure 4. Color change of DPPH radical scavenging activity of compound **1**; the concentration of compound **1** increases from right to left (100, 80, 60, 40, 20, 0 ppm).

2.4. Conclusion

Bis(diphenylpyridyl)phosphinodichlorocopper(II) complex **1** has been synthesized under aerobic conditions and further studied as a starting precursor for secondary reactivity. The M-Cl functionality in the complex is easily replaceable with an anionic ligand like dithiocarbamate. During the course of the reaction the phosphine ligand is released as a result of disproportionation reaction, which acts as a Cl^- ion acceptor and provides a better

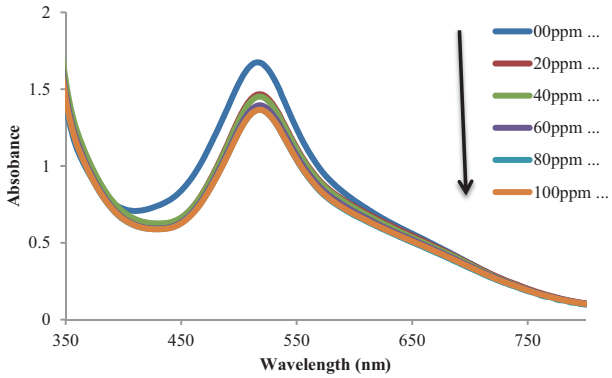


Figure 5. Absorption spectra of DPPH in the absence (blue) and in the presence of compound **3b**. Arrow shows the change in spectra on increasing the concentration of compound.

medium for stabilizing the cationic complex ion. The phenomenon probably occurs as a result of the steric bulk of the phosphine ligand, which does not allow two equivalents of **dedtc** ligand to coordinate to copper in **3b**. Compounds **1** and **3b** are crystalline in nature. Compound **1** exhibits excellent antioxidant efficiency. Further reactivity with the dithiocarbamate ligand did not enhance the efficiency of the complex.

3. Experimental

3.1. General

Handling of all chemicals and reagents used in this study was carried out in open air. The ligand diphenylpyridylphosphine (Ph_2PyP), copper(II) chloride, and solvents used in this study were obtained from commercial sources and were used without further purifications. The dithiocarbamate ligand was prepared by following the literature procedure.[42] Melting points (uncorrected) of the synthesized complexes were determined in sealed capillary tubes with the help of a BioCote Stuart-SMP10 (Japan).

3.2. X-ray structure determination

The single-crystal X-ray diffraction data (Mo-Kα, λ= 0.71073 A) were collected using a Bruker κAPEXII CCD diffractometer (**1**, **2**) and STOEIPDSII/STADIVARI (**3**). The latter was fitted with a low-temperature unit. Crystals of compound **3** were selected in perfluorinated oil at room temperature[43] and diffraction data were collected at low temperature. Crystal structures were refined with the help of SIR97,[44] SHELXL97,[45] WinGX,[46] and PLATON.[47]

3.3. Free radical scavenging activities

Antioxidant potentials of complexes **1** and **3b** were assessed following the well-known reported method.[48,49] Different concentrations of complexes **1** and **3b** were prepared and were mixed with DPPH solution according to the procedure outlined in our recently reported work.[31] A 30-min incubation at room temperature was observed for all the samples and the absorbance of the resultant mixture was recorded at 517 nm.

3.4. Synthesis of copper(II) complexes 1 and 2

Methanolic solutions of $CuCl_2.2H_2O$ (0.2301 g, 1.35 mmol) and diphenyl(2-pyridyl)phosphine (0.9775 g, 2.7 mmol) were prepared in separate Schlenk tubes (20 mL). Salt solution was slowly added to the ligand solution with vigorous stirring. A sudden change in the color of the solution from green to yellow was observed. The color of the solution on further stirring became dark yellow and after 30 min orange precipitates were formed. The solid from the reaction mixture was separated and was dissolved in about 3 mL of hot ethanol (40 °C). By slow evaporation of the solution, crystals were obtained after a few days. A close view under microscope shows two types of crystals: i) orange (major fraction, ≈95% based on solid crystalline material of **1**) and ii) light yellow (minor fraction, ca. 5%, complex **2**). The color of these crystals allowed us to separate them manually under a microscope. Crystals of suitable dimensions were picked out and analyzed by X-ray diffraction.

3.5. Synthesis of [Cu(dedtc)bis(ph_2py)P][(ph_2py)PCl], 3b

A Schlenk tube was charged with compound **1** (0.1 g, 0.152 mmol) in methanol (20 mL), to which a solution of diethyldithiocarbamate (0.28 g, 0.152 mmol) in methanol (20 mL) was added. A sudden change in color occurred and shortly after the addition of the ligand dark green precipitates were formed. The solid was separated and was dissolved in hot ethanol (2 mL, 40–45 °C). This solution was allowed to evaporate slowly to afford green crystals of **3b** after a few days. Crystals were isolated and studied with the help of X-ray crystallography. Methanol filtrate from the first step was allowed to evaporate under ambient temperature, which gave block-shaped crystals of complex **3a**, which is a well-established compound.[50–54]

3.6. Supplementary data

The crystallographic data corresponding to compounds **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary publications nos. CCDC 1830413 and 1830414. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). For supplementary data related to complex **2**, see Figure S1 and Tables S1 and S2.

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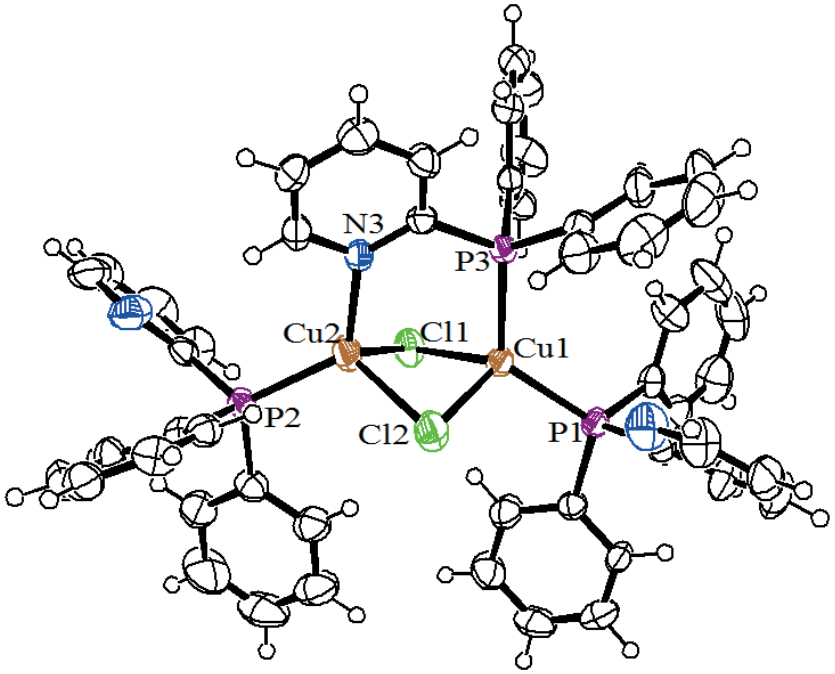

Figure S1. Molecular structure of compound **2** with partial numbering scheme and 50% probability ellipsoids; all hydrogens are omitted for clarity. See ref. 26 for full details.

Table S1. Selected bond lengths (Å) and angles (^{o}) of compounds **1**, **2**, and **3**.

Complex **2**	Bond distances	Cu2-Cl1	2.3953(10)	Cu2-N3	2.1150(2)
		Cu1-Cl1	2.4451(9)	Cu2-P2	2.2265(9)
		Cu1-Cl2	2.3915(10)	Cu2-Cl2	2.4327(9)
				P3-Cu1	2.2486(8)
	Bond angles	P1-Cu1-P3	124.21(3)	P1-Cu1-Cl2	110.09(3)
		P3-Cu1-Cl2	104.31(4)	P3-Cu1-Cl1	100.36(3)
		P1-Cu1-Cl1	108.29(9)	P1-Cu1-Cl1	115.83(3)
		P2-Cu1-Cl1	113.88(9)	Cl2-Cu1-Cl1	98.56(3)
		Cu2-Cl1-Cu1	73.00(3)	Cu2-Cu1-P3	85.28(2)
		P2-Cu2-Cl2	114.33(4)	Cu2-Cu1-P1	150.46(3)
		P2-Cu2-Cl1	107.05(3)	P2-Cu2-N3	123.12(7)
		N3-Cu2-Cl2	99.03(7)	N3-Cu2-Cl1	111.84(8)

Table S2. Crystal data and structure refinement of **2**.

Crystal parameter	**2**		
Empirical formula	$C_{51}H_{42}Cl_2Cu_2N_3P_3$	Formula weight	987.76
Temperature (K)	296	Wavelength (Å)	0.71073
Crystal system	Monoclinic	Space group	$P2_1/n$
a	14.2412	Volume (Å^3)	4501.5(3)
b	18.2910	μ (mm^{-1})	1.21
c	17.4979	Z	4
β	99.027	F (0, 0, 0)	2024
Density (Mg m^{-3})	1.457	Theta (max)	27.0
(h, k, l) min	(–18, –20, –22)	R (reflection)	0.045(9816)
(h, k, l) max	(17, 23, 21)	wR_2	0.123(9816)
Goodness of fit	1.031		