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FACILE OXIDATION OF PHENYLPHOSPHINIC ACID TO PHENYLPHOSPHONIC ACID USING $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$: X-RAY CRYSTAL STRUCTURES OF MONOMERIC $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot 2CH_3OH$ AND $[Cu(PhPO_3H)_2(C_5H_5N)_4]$

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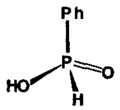
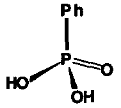
Abstract—Phenylphosphinic acid ($HPhPO_2H$) is oxidized to phenylphosphonic acid ($PhPO_3H_2$) at room temperature using a solution of $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ in pyridine. The phenylphosphonic acid was recovered as the monomeric copper(II) complex $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot H_2O$ (**1a**), and the reaction thought to proceed via a copper(I) intermediate. Recrystallization of **1a** from methanol gave $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot 2CH_3OH$ (**1b**). The unsolvated complex $[Cu(PhPO_3H)_2(C_5H_5N)_4]$ (**1c**) was prepared by refluxing polymeric $[Cu(PhPO_3)(H_2O)]$ (**2**) in pyridine. The X-ray crystal structures of **1b** and **1c** show that in each of these monomeric complexes the copper(II) ion is ligated by four equatorial pyridine molecules and two axial monoanionic phenylphosphonate groups. A cyclic voltammetric study of **1a** revealed a quasi-reversible Cu^{2+}/Cu^{+} couple with $E_{1/2} = +228$ mV (vs Ag/AgCl).

Monobasic phenylphosphinic acid ($HPhPO_2H$) and dibasic phenylphosphonic acid ($PhPO_3H_2$) both form so-called "inorganic coordination polymers" with metal ions, and recently the polymeric layered structures of the phenylphosphinate $[Zn(HPhPO_2)_2]$[1] and the phenylphosphonates, $[Mn(PhPO_3)(H_2O)]$[2] and $[Zn(PhPO_3)(H_2O)]$[3] were confirmed using X-ray crystallography. Clearfield and his co-workers[1] have attributed the subtle differences in the dimensionalities of polymeric phosphinato and phosphonato complexes to the number of oxygen atoms available for bonding to the metal atoms (two for phosphinates and three for phosphonates). Such layered complexes have generated a lot of interest because of their sorptive, catalytic and ion-exchange properties.[4–7]



phenylphosphinic acid



phenylphosphonic acid

In this paper we present details of the synthesis and X-ray crystal structures of the monomeric copper(II) phenylphosphonate complexes $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot 2CH_3OH$ (**1b**) and $[Cu(PhPO_3H)_2(C_5H_5N)_4]$ (**1c**). These complexes contain four pyridine and two monoanionic phenylphosphonate ligands bound to a central copper(II) ion, and to our knowledge are the first structurally characterized, non-polymeric transition metal phenylphosphonates. In the known polymeric phenylphosphonate complexes the phosphonate ligand has always been found to be dianionic and bridging.

Crystals of **1b** were obtained by recrystallizing the monohydrate precursor $[Cu(PhPO_3H)_2$

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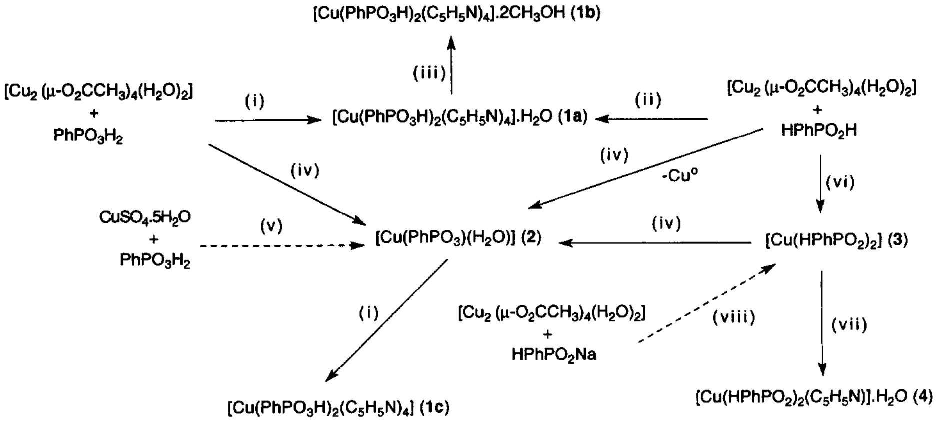
$(C_5H_5N)_4]\cdot H_2O$ (**1a**) from a mixture of pyridine and methanol (Scheme 1). Complex **1a** itself was prepared by two different routes. In the first method dimeric copper(II) acetate was refluxed with a solution of phenylphosphonic acid in pyridine. When this same experiment was conducted in methanol instead of pyridine the polymeric complex $[Cu(PhPO_3)(H_2O)]$ (**2**) was obtained. This complex formulates for one water molecule and one phenylphosphonate dianion per copper and has previously been made by reacting phenylphosphonic acid with a copper(II) salt in either alcoholic[8] or aqueous media.[9] The anhydrous complex $[Cu(PhPO_3)]$ was prepared by heating **2** to 175°C.[8] Thus, it appears that in the reaction between copper(II) acetate and phenylphosphonic acid pyridine is required in order to direct the reaction to a monomeric rather than a polymeric product.

The second method for the preparation of **1a** involved the reaction between copper(II) acetate and phenylphosphinic acid in pyridine at room temperature. Here the phenylphosphinic acid was smoothly oxidized to phenylphosphonic acid with the latter being isolated as its copper(II) complex **1a**. When this reaction was carried out in methanol instead of pyridine (at *ca* 20°C) oxidation of phenylphosphinic to phenylphosphonic acid did not occur, and only the bis(phenylphosphinate)copper(II) complex $[Cu(HPhPO_2)_2]$ (**3**) was isolated. This complex was further reacted with a mixture of pyridine and ethanol at *ca* 20°C to give $[Cu(HPhPO_2)_2(C_5H_5N)]\cdot H_2O$ (**4**). Complex **3** has previously been prepared by reacting copper(II) acetate with sodium phenylphosphinate in water at 20°C.[10]

When the reaction between copper(II) acetate and phenylphosphinic acid was conducted in refluxing methanol copper metal plated out on the wall of the reaction vessel. The subsequent addition of more copper acetate to the reaction filtrate led, eventually, to the recovery of the phenylphosphonate complex **2** (Scheme 1). Similarly, in a study involving the incorporation of copper(I) ions as an antioxidant in fibre-forming polyamides Tomek[11] polymerized the amide with aqueous potassium phenylphosphinate (as catalyst) in the presence of copper(II) acetate. He found that this combination of reagents resulted in the formation of copper metal during the high-temperature polymerization. However, he later discovered that metal deposition could be avoided by the addition of excess halide ions, which acted to stabilize the metal in the required copper(I) state, The above experiments clearly demonstrate that in reactions involving phenylphosphinic acid and copper(II) ions the choice of both reaction temperature and solvent will dictate the nature of the products formed.

Prolonged reflux of the monophenylphosphonate **2** in pyridine promotes the breakdown of its polymeric structure with the formation of the monomeric bisphenylphosphonate complex $[Cu(PhPO_3H)_2(C_5H_5N)_4]$ (**1c**). In this reaction the phenylphosphonate ligand changes from the dianionic form ($PhPO_3^{2-}$) in **2** to the monoanionic form ($PhPO_3H^-$) in **1c**.

The X-ray crystal structures of **1b** and **1c** are shown in Figs 1 and 2, respectively. In each case the copper(II) ion is ligated by the nitrogen atoms of four equatorial pyridine molecules and a single oxygen atom from each of two axial monoanionic phenylphosphonate groups. As expected, the average Cu—O distance in **1b** and **1c** (Table 1) is significantly longer than that found in M^{2+} complexes



Scheme 1. (i) Refluxing pyridine; (ii) pyridine, 20°C; (iii) pyridine/methanol; (iv) refluxing methanol; (v) water;[9] (vi) methanol, 20°C; (vii) ethanol/pyridine, 20°C; and (viii) water.[10] (---) denotes literature preparation.

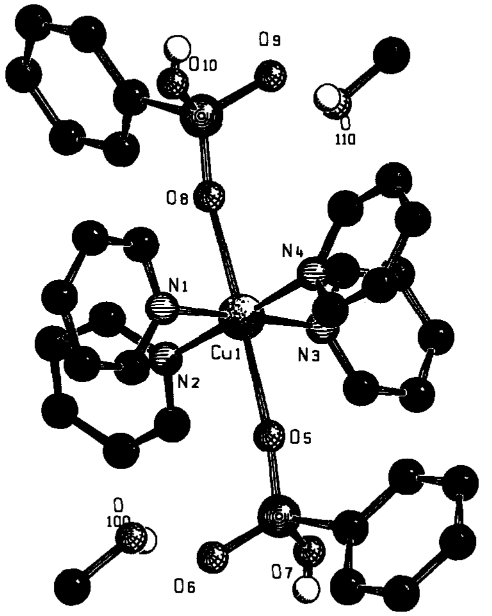


Fig. 1. X-ray crystal structure of $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot 2CH_3OH$ (**1b**).

containing the phenylphosphonate dianionic ligand, e.g. $[Mn(PhPO_3)(H_2O)]^2$ [mean Mn—O (phosphonate) distance = 2.174 Å] and $[Zn(PhPO_3)(H_2O)]^3$ [mean Zn—O(phosphonate) distance = 2.12 Å]. The phosphorus–oxygen bond lengths for the oxygens not attached to copper were found to be asymmetric, with a short (*ca* 1.50 Å) and a long (*ca* 1.57 Å) bond, which correspond to a double bond (P=O) and a single bond (P—O), respectively.

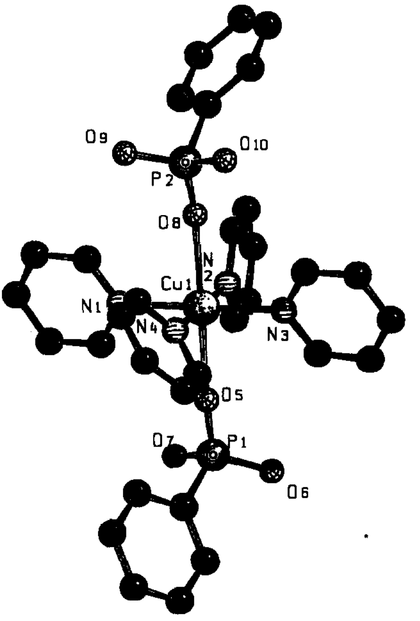


Fig. 2. X-ray crystal structure of $[Cu(PhPO_3H)_2(C_5H_5N)_4]$ (**1c**).

This is reinforced by the presence of intermolecular hydrogen bonds (see Table 1). For **1b** the hydrogens themselves were located. However, for **1c** they were not located, but inter-oxygen distances suggest that they are present. In all cases it was found that the pair of oxygens with short intermolecular contact distances consisted of one with a short phosphorus bond distance and one with a long distance. This offers support for both the asymmetry of the phosphorus coordination and also the presence of hydrogen bonds.

There does not seem to be any significant difference between the two molecules obtained from structure determination. It would appear therefore that the different crystal forms observed are due to the presence of co-crystallized solvent in **1b** and not in **1c**.

The room-temperature magnetic moment of $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot H_2O$ (**1a**) was in the range expected for normal mononuclear copper(II) complexes. The cyclic voltammogram of the complex is shown in Fig. 3, and as the ligands are electro-inactive in the potential range studied the redox activity displayed by the complex is attributable to changes in the oxidation state of the copper. In the potential range +0.8 to −0.3 V only the quasi-reversible couple $Cu^{2+} + e \leftrightarrow Cu^{+}$ (peaks A and D) is observed ($\Delta E = 406$ mV; $E_{1/2} = +228$ mV; $i_c/i_a = 1$). When the switching potentials are extended to the range +1.0 to −0.7 V two more peaks appear. Cathodic peak B represents the further reduction $Cu^{+} + e \rightarrow Cu^{0}$ ($E_c = -543$ mV), and the large anodic stripping peak C ($E_a = -237$ mV) comes from the reoxidation of the copper metal on the electrode surface. This redox behaviour of **1a** is quite similar to that which we recently reported[12] for the copper(II) complex $[Cu(C_5H_5N)_4((+)\text{-phos})((-)\text{-phos})]$ (phos = 1,1′-binaphthyl-2,2′-diyl hydrogen phosphate anion).

A thermogravimetric study of **1a** showed the loss of the water and pyridine molecules in a series of events (not perfectly resolved) over the temperature range 60–240°C. No further weight loss occurred until *ca* 380°C, where decomposition of the residual $[Cu(PhPO_3H)_2]$ began. In the case of the polymeric complex $[Zn(PhPO_3)(C_5H_5N)]$ it was found[13] that after the loss of pyridine (at *ca* 200°C) the breakdown of the remaining $[Zn(PhPO_3)]$ polymer started at *ca* 500°C. Similarly, for the polymeric monohydrates $[M(PhPO_3)(H_2O)]$ (M = Co, Zn)[6] decomposition of the anhydrous $[M(PhPO_3)]$ residue began at *ca* 500°C. It seems reasonable to assume that as the water and pyridine molecules are progressively removed from the monomeric complex **1a**, the complex undergoes a change in its bonding in the solid state in an attempt to satisfy the

Table 1. Selected bond lengths (Å) and angles (°) for **1b** and **1c**. A similar numbering scheme was used for both complexes

	Complex **1b**	Complex **1c**
Cu—N	2.049[a]	2.071[a]
Cu—O	2.409(4), 2.43(4)	2.298(6), 2.342(7)
P(1)—O(5)	1.496(4)	1.497(7)
P(1)—O(6)	1.501(4)	1.510(7)
P(1)—O(7)	1.565(4)	1.575(7)
P(2)—O(8)	1.496(4)	1.504(7)
P(2)—O(9)	1.509(4)	1.519(7)
P(2)—O(10)	1.563(4)	1.565(7)
P—C	1.809(5), 1.803(4)	1.818(7), 1.819(7)
O···O	2.593, 2.603	2.525, 2.519
O—Cu—O	177.7(1)	176.9(3)
O—Cu—N	90.0[a]	90.0[a]
N—Cu—N	90.0,[a] 178.1[a]	90.0,[a] 178.1[a]
O(6)—P(1)—O(5)	116.8(2)	115.8(4)
O(7)—P(1)—O(5)	107.0(2)	109.5(4)
O(7)—P(1)—O(6)	110.6(2)	109.9(4)
O(9)—P(2)—O(8)	115.7(2)	113.7(4)
O(10)—P(2)—O(8)	108.1(2)	111.3(4)
O(9)—P(2)—O(10)	110.3(2)	110.2(4)
O(5)—P(1)—C	108.3(2)	106.6(4)
O(6)—P(1)—C	108.3(2)	108.9(3)
O(7)—P(1)—C	105.2(2)	105.6(4)
O(8)—P(2)—C	108.3(2)	106.9(4)
O(9)—P(2)—C	108.5(2)	108.4(4)
O(10)—P(2)—C	105.4(2)	105.6(4)
Cu—O(5)—P(1)	168.0(2)	165.5(5)
Cu—O(8)—P(2)	164.5(2)	163.8(5)

[a] Figures obtained by averaging values.

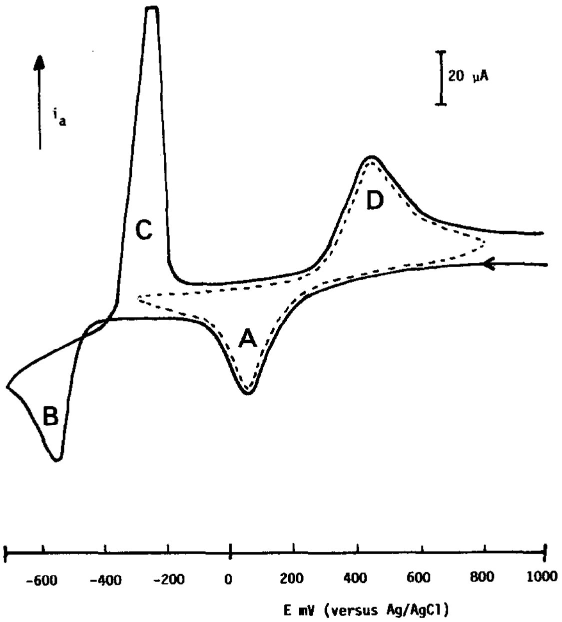


Fig. 3. Cyclic voltammogram of $[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot H_2O$ (**1a**). Scan rate = 50 mV s^{-1}.

coordination requirements of the copper. This modification in the bonding will undoubtedly involve a rearrangement of the initially unidentate $PhPO_3H^-$ ligands in such a way as to allow more of the oxygen atoms to coordinate (i.e. to bridge) to neighbouring copper atoms and thus to form a polymeric network. Polymerization is probably not as extensive or as well developed as that found in the known metal phenylphosphonate coordination polymers, as judged by the lower decomposition temperature of the $[Cu(PhPO_3H)_2]$ residue (380°C as opposed to 500°C).

Let us now consider the mechanism by which phenylphosphinic acid is oxidized to phenylphosphonic acid in the preparation of **1a**. It is well known that certain redox-active transition metal ions in aqueous media [e.g. chromium(VI),[14] iron (III),[15] manganese(III)[16] and vanadium(V)[17]] catalyse the oxidation of phenylphosphinic acid to phenylphosphonic acid. The reaction stoichiometry for the oxidation using vanadium(V)[17] is outlined in eq. (1).

$$HPhPO_2H+2V^V+H_2O \longrightarrow PhPO_3H_2 + 2V^{IV}+2H^+ \quad (1)$$

Our reaction between copper(II) acetate and phenylphosphinic acid in pyridine was initiated under anaerobic conditions and after *ca* 3 h the original blue solution had changed to a yellow colour. When this yellow solution was exposed to air it went green over a period of *ca* 20 min. When the green solution was deoxygenated again (using nitrogen) it went back to yellow. This green ↔ yellow cycle was repeated a number of times. Finally, the green solution was stirred in air for 2 days, and during this period the blue complex **1a** gradually precipitated. We believe that the green copper(II) complex is catalysing the oxidation of phenylphosphinic acid to phenylphosphonic acid, and that the metal is being reduced in the process to a yellow copper(I) complex [cf. reduction of vanadium(V) to vanadium(IV) in eq. (1)]. Furthermore, the presence of pyridine in the reaction mixture probably helps stabilize the copper(I) ion in much the same way as the added halide ion does.[11] Subsequent aerial oxidation then restores the metal to the initial copper(II) state.

Supporting evidence for the green copper (II) ↔ yellow copper(I) interplay comes from the ^1H NMR spectra of the reaction solution in which deuteriopyridine (C_5D_5N) was used as the solvent. As expected, the initial blue solution gave a broad NMR spectrum due to the effects of the paramagnetic copper(II) ion. When the solution changed to the yellow colour the NMR spectrum became sharp and well defined, suggesting the formation of a diamagnetic copper(I) complex [i.e. either a copper(I)-phenylphosphinate-pyridine complex or a copper(I)-phenylphosphonate-pyridine complex]. All attempts to try and isolate a copper(I) complex from the yellow solution were unsuccessful as this solution proved to be extremely air-sensitive.

EXPERIMENTAL

Chemicals were purchased from commercial sources and used without further purification. Solvents were not pre-dried before use. IR spectra (KBr discs) were recorded in the 4000–200 cm^{-1} region on a Perkin–Elmer 783 grating spectrometer, and room-temperature magnetic susceptibility measurements were made on a Johnson–Matthey magnetic susceptibility balance. NMR spectra were run on a Bruker AC 80 spectrometer using deuteriopyridine (C_5D_5N) as the solvent. Thermogravimetric analyses (under nitrogen) were performed on a Stanton Redcroft TG750/770 instrument which was coupled to a Houston Instrument Omniscribe (series D5000) recorder. Heating rate was 10°C 10°C min^{-1}. Cyclic voltammograms were recorded (*ca* 20°C and under nitrogen) using an EG&G Model 264A polarographic analyser, and the data was analysed using the EG&G Condecon software package. A platinum bead and a platinum wire were used as the working and counter electrodes, respectively. Potentials were recorded with respect to a silver–silver chloride reference electrode, against which the ferrocene/ferrocenium(1+) couple had $E_{1/2} = +567$ mV. Tetraethylammonium perchlorate (0.1 M) dissolved in a 4 : 1 mixture of methanol : pyridine was used as the supporting electrolyte/solvent system. Sample concentration was 4.0×10^{-3} M and the scan rate was 50 mV s^{-1}. Elemental analyses were carried out by the Microanalytical Laboratory, University College, Cork, Ireland.

Crystallography

Complex **1b**. A blue rectangular-shaped crystal of approximate size $0.3 \times 0.2 \times 0.15$ mm^3 was mounted on an Enraf–Nonius CAD4 diffractometer, and the intensities of 4391 reflections in the range $1° < \theta < 22°$ were measured using Mo-K_α radiation with a graphite monochromator. The cell coordinates were determined by refining the setting angles of 25 reflections in the θ range 15–18°. 3600 reflections with $|F_{obs}| > 4\sigma|F_{obs}|$ were used in the structure solution and refinement.

Crystal data for $CuP_2O_6N_4C_{32}H_{32} \cdot 2CH_3OH$ (**1b**): $Mr = 758.14$, triclinic, space group P-1 (no. 2) $a = 9.148(3)$, $b = 11.366(4)$, $c = 17.466(5)$ Å, $\alpha = 84.43(8)°$, $\beta = 86.89(8)°$, $\gamma = 84.62(8)°$, $U = 1797(1)$ Å^3, $D_c = 1.4004$ g cm^{-3}, $Z = 2$, $F(000) = 790$, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 7.13 cm^{-1}. The structure was solved by hand interpretation of the Patterson method by SHELXS, and was refined by full-matrix least-squares to an R factor of 0.0565. The non-hydrogen atoms of the non-solvent molecules were all refined with anisotropic temperature factors. The hydrogen atoms of the phenyl and pyridine rings were placed geometrically and refined with temperature factors of 0.105(6) and 0.070(4), respectively. The hydrogens of the intermolecular hydrogen bonds were located and allowed to refine with a single temperature factor. The final difference-Fourier map had a highest peak of 0.77 e Å^{-3} and a goodness of fit of 1.68.

Complex **1c**. A blue rectangular-shaped crystal was mounted on the above-mentioned diffractometer and the intensities of 2164 reflections were measured in the range $1° < \theta < 22°$ using the same set-up as before. The cell coordinates were determined by refining the setting angles of 25 reflections, $14^\circ < \theta < 16^\circ$. The data were merged to give 2029 unique reflections, $R_{\text{merg}} = 0.0139$; of these, 1758 had $|F_{\text{obs}}| > 4\sigma|F_{\text{obs}}|$ and were used for the structure solution and refinement.

Crystal data for $CuP_2O_6N_4C_{32}H_{32}$ (**1c**): $Mr = 694.12$, monoclinic, space group $P2_1$ (no. 4), $a = 9.821(1)$, $b = 17.176(1)$, $c = 10.688(1)$ Å, $\beta = 117.269(6)^\circ$, $U = 1602.6(3)$ Å^3, $D_c = 1.44$ g cm^{-3}, $Z = 2$, $F(000) = 718.0$, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 7.92$ cm^{-1}. The structure was solved in the space group $P2_1$ by both the Patterson and direct methods of SHELXS. The structure was refined to an R factor of 0.0470 (223 parameters—copper, phosphorus and oxygen atoms anisotropic, the phenyl ring with constrained geometry and the hydrogens in fixed positions). The hydroxyl hydrogens could not be located from difference-Fourier synthesis, but the oxygen contact distances at 2.53 and 2.52 Å, respectively, suggest that they are however present. The final difference-Fourier had a goodness of fit of 1.43 and a highest peak of 0.48 eÅ^{-3}.

The programs SHELXS and SHELX 76 were used with the kind permission of Prof. G. F. Sheldrick (Universität Göttingen).

$[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot H_2O$ (1a)

Method (a). To a dark-blue solution of $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (0.31 g, 0.78 mmol) in pyridine (50 cm^3) was added phenylphosphonic acid (1.0 g, 6.3 mmol). The mixture was brought to reflux, and after 4 h the solution had changed to a mint green colour. Reflux was continued for a further 24 h without any noticeable change, and on cooling to room temperature the blue product precipitated. The solid was filtered off, washed with diethyl ether and then dried *in vacuo*. Yield: 0.90 g (81%).

Method (b). $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (0.31 g, 0.78 mmol) was dissolved in pyridine (50 cm^3) at room temperature and under nitrogen to give a dark blue solution. Phenylphosphinic acid (0.89 g, 6.3 mmol) was added and the mixture was stirred for 3 h to give a bright yellow solution. When this solution was exposed to air it changed to a mint green colour within 20 min. Deoxygenating the solution (using nitrogen) turned the solution yellow again, and subsequent re-exposure to air regenerated the mint green colour. This green↔yellow cycle was repeated a number of times and finally, the green solution was stirred in air for 2 days. Over this period **1a** slowly precipitated. (Note: It is not necessary to go through the green↔yellow cycles in order to obtain the product. If the initial yellow solution is stirred in air for 2 days, then the product forms as before.) The solid was recovered, washed and dried as outlined in method (a). Yield: 0.23 g (22%). Complex **1a** is soluble in DMF and alcohol (ethanol or methanol) containing a few drops of pyridine. Found: C, 53.6; H, 4.5; N, 7.5. Calc.: C, 53.9; H, 4.8; N, 7.8%. $\mu = 1.9$ B.M. (room temperature). IR: 3070, 1605, 1445, 1135, 1065, 900, 695 cm^{-1}.

$[Cu(PhPO_3H)_2(C_5H_5N)_4]\cdot 2CH_3OH$ (1b)

Crystals of this complex were formed by recrystallizing **1a** from a 50:50 mixture of pyridine and methanol. IR: 3500, 3070, 1605, 1450, 1135, 1065, 900, 695 cm^{-1}.

$[Cu(PhPO_3H)_2(C_5H_5N)_4]$ (1c)

Complex **1c** was prepared by refluxing **2** (see below) in pyridine for 12 h under nitrogen. The resulting blue suspension was filtered and **1c** slowly crystallized from the filtrate.

$[Cu(PhPO_3)(H_2O)]$ (2)

Method (a). $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (0.46 g, 1.15 mmol) and phenylphosphonic acid (1.0 g, 6.3 mmol) were refluxed in methanol (50 cm^3) for 12 h. The hot suspension was filtered and the blue solid product was washed with methanol and then dried *in vacuo*. Yield: 0.46 g (84%).

Method (b). $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (0.29 g, 0.73 mmol) and phenylphosphinic acid (0.62 g, 4.36 mmol) were stirred together in methanol (50 cm^3) at room temperature and under nitrogen. The resulting pale blue suspension was brought to reflux and over a period of 1.5 h copper metal plated out on the reaction flask. The metal was filtered off and more copper acetate (0.29 g, 0.73 mmol) was added to the colourless filtrate. On refluxing this mixture for a further 1 h under nitrogen more copper plated out. The metal was removed as before and a further batch of copper acetate (0.29 g, 0.73 mmol) was added. After refluxing for another 2 h the resulting pale blue suspension was filtered to give **2**. The solid was washed and dried as outlined above.

Method (c). Complex **3** (see below) (0.16 g, 0.46 mmol) was refluxed in methanol (20 cm^3) under nitrogen for 12 h. During this time copper metal deposited on the walls of the flask and the solution became colourless. The nitrogen blanket was removed and refluxing was continued in air for a further 20 min. The copper metal slowly redissolved to give a blue solution, from which **2** subsequently precipitated. The solid was recovered as outlined above. Yield: 0.03 g (30%). Note: complex **2** prepared by this method was contaminated with a small amount of **3** as indicated by the presence of a small P—H band at 2360 cm^{-1} in the IR spectrum of the product. Found: C, 31.8; H, 3.1. Calc.: C, 30.3; H, 2.9%. IR: 3320, 3050, 1085, 1045, 700 cm^{-1}.

$[Cu(HPhPO_2)_2]$ (**3**)

The following reaction was carried out at room temperature and under nitrogen. To a suspension of $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]$ (1.27 g, 3.2 mmol) in methanol (150 cm^3) was added phenylphosphinic acid (2.78 g, 19.6 mmol). A pale blue solution immediately formed, and upon stirring for *ca* 3 min the pale blue product precipitated. The resulting suspension was stirred for a further 12 h and then the product was filtered off, washed with methanol and then dried *in vacuo*. Yield: 2.16 g (98%). Complex **3** was soluble in pyridine and aqueous ammonia, and insoluble in common organic solvents. Found: C, 42.4; H, 3.6. Calc.: C, 41.7; H, 3.5%. $\mu = 2.0$ B.M. (room temperature). IR: 3050, 2360, 1150, 1115, 585, 550 cm^{-1}.

$[Cu(HPhPO_2)_2(C_5H_5N)] \cdot H_2O$ (**4**)

To a suspension of **3** (0.25 g, 0.72 mmol) in ethanol (20 cm^3) under nitrogen was added pyridine (1 cm^3). The resulting dark blue solution was stirred at room temperature for 1 h. On concentrating the solution to low volume the product precipitated as blue microcrystals. The solid was filtered off, washed with ethanol and then dried *in vacuo*. Yield: 0.11 g (34%). Found: C, 46.0; H, 4.4; N, 3.2. Calc.: C, 46.1; H, 4.3; N, 3.2%. IR: 3045, 2340, 1605, 1450, 1135, 1040, 560 cm^{-1}.

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