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# Dinuclear Copper(II) Phosphonates Containing Chelating Nitrogen Ligands: Synthesis, Structure, Magnetism and Nuclease Activity

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**Keywords:** Copper / Phosphorus / Magnetic properties / Dinuclear complex / N ligands

The reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with $RPO_3H_2$ (R = cyclopentyl, isopropyl, trichloromethyl) in the presence of chelating nitrogen ligands bpya or bpy afforded dinuclear copper phosphonates $[Cu_2(\mu_2\text{-}C_5H_9PO_3)_2(bpya)_2(H_2O)_2]$ $(H_2O)_4$ (**1**), $[Cu_2(\mu_2\text{-}C_3H_7PO_3)_2(bpya)_2(H_2O)_2]$ $(H_2O)_2$ (**2**) and $[Cu_2(\mu_2\text{-}CCl_3PO_3)_2(bpy)_2(MeOH)_2]$ $(H_2O)$ (**3**) [bpya = 2,2′-bipyridylamine, bpy = 2,2′-bipyridine]. The molecular structures of these complexes reveal that they are isostructural and possess two copper centres that are bridged to each other by two isobidentate phosphonate ligands generating an eight-membered $Cu_2O_4P_2$ ring. Magnetic studies on **2** reveal antiferromagnetic behaviour at low temperatures. Dinuclear complexes **1**–**3** were found to be excellent nucleases and can convert supercoiled pBR322 DNA form I into nick form II in only 30 min without the need for any external oxidant through a hydrolytic pathway.


## Introduction

Although transition-metal phosphonates possessing extended structures have been studied for many years,[1] molecular-metal phosphonates have also been attracting interest recently in view of their structural diversity[2] and interesting magnetic properties,[3] as some of these compounds can be used as artificial nucleases.[4] The synthesis of molecular-metal phosphonates is aided by the use of sterically hindered phosphonic acids and ancillary ligands such as pyrazoles and pyridines.[5–11] In recent years, there have been several attempts to understand and control the nuclearity of the metal assemblies by subtle modulation of the phosphonic acid and the ancillary ligand. By utilizing such a variation we successfully prepared dodeca-, deca-, hexa- and tetranuclear copper(II) phosphonates.[4,12–17] We realized that utilization of chelating nitrogen ligands limits the availability of the remaining coordination sites and increase the chances of achieving low-nuclearity assemblies. Accordingly, herein we report the synthesis, structure, magnetic properties and reactivity of the dinuclear copper(II) phosphonates $[Cu_2(\mu_2\text{-}C_5H_9PO_3)_2(bpya)_2(H_2O)_2](H_2O)_4$ (**1**), $[Cu_2(\mu_2\text{-}C_3H_7PO_3)_2(bpya)_2(H_2O)_2](H_2O)_2$ (**2**) and $[Cu_2(\mu_2\text{-}CCl_3PO_3)_2(bpy)_2(MeOH)_2]$ $(H_2O)$ (**3**) [bpya = 2,2′-bipyridylamine, bpy = 2,2′-bipyridine].

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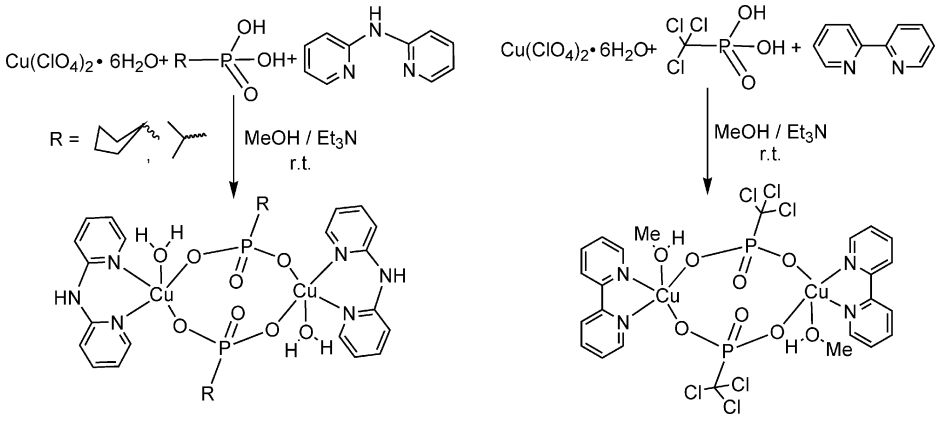
## Results and Discussion

### Synthesis

Complexes **1**–**3** were prepared (Scheme 1) in high yields from the reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with $RPO_3H_2$ in the presence of bpya or bpy. In each case, the synthesis was carried out such that every copper was chelated with one bidentate bpya or bpy ligand. All three complexes are held together by the bidentate coordination mode of the two phosphonate ligands. The electronic spectra of **1**–**3** reveal the presence of a broad d–d transition in the region $650 \pm 10$ nm. The MS (ESI) spectra of **1**–**3** were recorded in the positive ion mode to study the stability of the dinuclear core structures in solution. These show peaks at $m/z$ = 765.08, 713.04 and 834.73 corresponding to $[Cu_2(C_5H_9PO_3)_2(bpya)_2]^+$, $[Cu_2(C_3H_7PO_3)_2(bpya)_2]^+$ and $[Cu_2(Cl_3CPO_3)_2(bpy)_2]^+$ moieties, respectively (Supporting Information, Figures S1–S3), and indicate that the dinuclear structures are stable in solution. All three complexes were found to be quite active in the catalytic oxidative coupling of 2,6-dimethylphenol to afford poly(phenyl ether) (PPE) and diphenylquinone (DPQ) in varying quantities (Supporting Information).




Scheme 1. Synthesis of dinuclear copper phosphonates **1**–**3**.

## Molecular Structures of 1–3

The molecular structures of complexes **1**–**3** are shown in Figures 1, 2 and 3. Selected bond lengths and angles can be found in Tables 1–3. The dinuclear structures of all three complexes are similar. Two $[RPO_3]^{2-}$ {R = $C(CH_3)_2$, $C_5H_9$, $CCl_3$} ligands are involved in holding the dinuclear assembly together. This is accomplished by a bridging isobidentate coordination action of the phosphonate ligands; in each case, the third oxygen atom of the phosphonate ligand is not involved in coordination. Generally, dianionic $[RPO_3]^{2-}$ ligands hold multiple metals together[9–11] and the situation found in the current instance is quite rare. As a result of the bridging coordination of the phosphonate ligand, the core of the dinuclear copper complex contains a puckered eight-membered $Cu_2P_2O_4$ ring. The two copper atoms and the two phosphorus atoms in the eight-membered ring lie on the same plane, whereas the oxygen atoms are located above and below the axis plane.

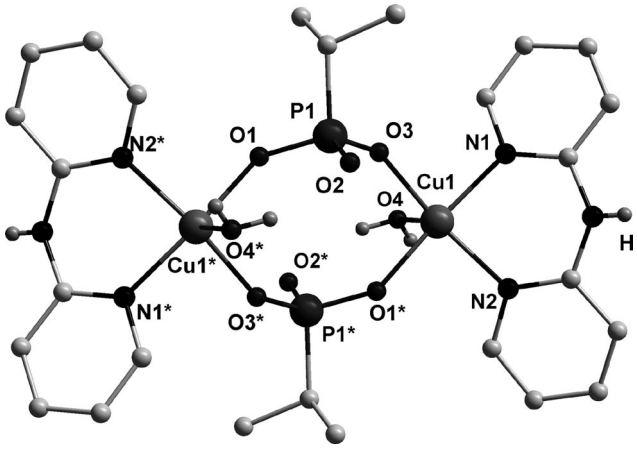



Figure 2. Molecular structure of complex **2**. Hydrogen atoms have been removed from the aromatic ring and alkyl group for the sake of clarity.

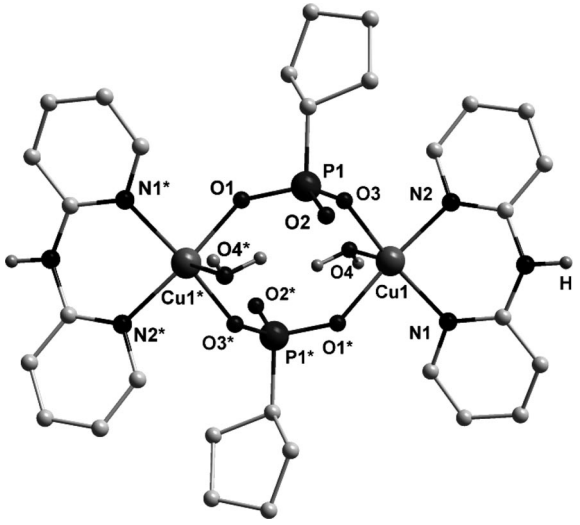



Figure 1. Molecular structure of complex **1**. Hydrogen atoms have been removed from the aromatic and cyclopentyl ring for the sake of clarity.

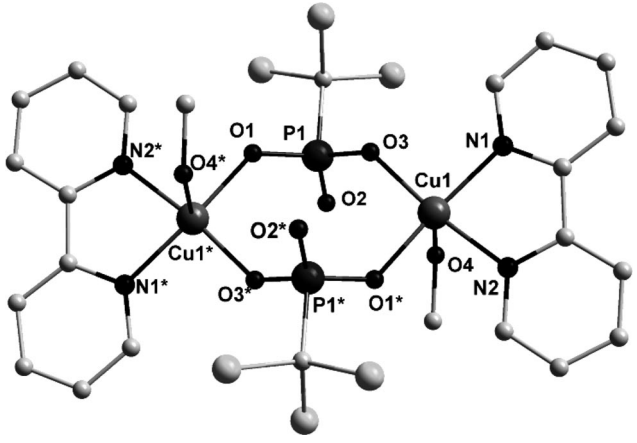



Figure 3. Molecular structure of complex **3**. Hydrogen atoms have been removed for the sake of clarity.

Apart from the phosphonate ligands, the remaining coordination environment around the two copper centres in each of the complexes comprises a chelating ligand (bpya

Table 1. Selected bond lengths [Å] and angles [°].[a]

| | | | |
|---|---|---|---|
| Cu1–O1 | 1.956(3) | Cu1–O3 | 1.935(3) |
| Cu1–O4 | 2.270(3) | Cu1–N1 | 2.007(3) |
| Cu1–N2 | 2.001(3) | P1–O1 | 1.536(3) |
| P1–O2 | 1.538(3) | | |
| O1–Cu1–N2 | 171.28(13) | O3–Cu1–N1 | 165.27(13) |
| O3–Cu1–N2 | 87.79(13) | O3–Cu1–O1* | 94.02(12) |
| N2–Cu1–N1 | 88.41(14) | N2–Cu1–O4 | 95.75(13) |
| N1–Cu1–O4 | 101.42(13) | O3–Cu1–O4 | 93.12(13) |
| O1*–Cu1–O4 | 92.67(12) | O1*–Cu1–N1 | 87.71(13) |

[a] Symmetry transformations used to generate equivalent atoms: * = $-x$, $-y$, $-z + 1$.

Table 2. Selected bond lengths [Å] and angles [°].[a]

| | | | |
|---|---|---|---|
| Cu1–O1 | 1.953(2) | Cu1–O3 | 1.926(3) |
| Cu1–O4 | 2.253(3) | Cu1–N1 | 2.010(3) |
| Cu1–N2 | 2.013(3) | P1–O1 | 1.536(3) |
| P1–O2 | 1.527(3) | | |
| O1*–Cu1–N1 | 172.04(11) | O3–Cu1–O1* | 93.50(11) |
| O3–Cu1–N1 | 88.10(12) | O3–Cu1–N2 | 165.71(11) |
| O1*–Cu1–N2 | 89.08(11) | N1–Cu1–N2 | 87.50(12) |
| O3–Cu1–O4 | 91.98(11) | O1*–Cu1–O4 | 92.37(10) |
| N1–Cu1–O4 | 95.37(11) | N2–Cu1–O4 | 101.97(12) |

[a] Symmetry transformations used to generate equivalent atoms: * = $-x + 1$, $-y$, $-z$.

Table 3. Selected bond lengths [Å] and angles [°].[a]

| | | | |
|---|---|---|---|
| Cu1–O3* | 1.934(3) | Cu1–O1 | 1.941(3) |
| Cu1–O4 | 2.298(4) | Cu1–N2 | 1.996(4) |
| Cu1–N1 | 2.012(4) | P1–O1 | 1.514(4) |
| P1–O2 | 1.512(4) | | |
| O3*–Cu1–O1 | 96.13(15) | O3*–Cu1–N2 | 173.08(16) |
| O1–Cu1–N2 | 90.14(16) | O3*–Cu1–N1 | 92.57(16) |
| O1–Cu1–N1 | 161.78(16) | N2–Cu1–N1 | 80.59(17) |
| O3*–Cu1–O4 | 91.18(14) | O1–Cu1–O4 | 89.61(15) |
| N2–Cu1–O4 | 91.78(15) | N1–Cu1–O4 | 106.22(15) |

[a] Symmetry transformations used to generate equivalent atoms: * = $-x + 1$, $-y$, –z.

in **1** and **2**; bpy in **3**) and a solvent molecule (water in the case of **1** and **2** and methanol in the case of **3**). Thus, in all three complexes **1**–**3** the coordination environment of both copper centres is similar (five-coordinate, 2 N, 3O coordination environment). The stereochemistry of the copper centres in **1**–**3** is best described as distorted square-pyramidal [The degree of distortion ($\tau$) can be estimated according to the Addison method.[18] For an ideal trigonal bipyramid, $\tau = 1$, whereas for square-pyramid, $\tau = 0$.] The calculated $\tau$ values for **1** and **2** are 0.10, whereas for **3** it is 0.19. In each case, the basal plane comprises the two chelating nitrogen atoms and the two oxygen atoms of the phosphonate ligands. The axial site is occupied by the water molecule. In each case, the copper atoms are displaced out of the square plane.

Among the Cu–O bond lengths, those involving the phosphonate oxygen atoms are shorter than those involving the Cu–$O_{solvent}$ [For **1**: Cu1–O3 1.935(3) Å, Cu1–O1* 1.956(3) Å, Cu1–O4 2.270(3) Å; for **2**: Cu1–O3 1.926(3) Å, Cu1–O1* 1.953(2) Å, Cu1–O4 2.253(3) Å; for **3**: Cu1–O3 1.934(3) Å, Cu1–O1* 1.941(3) Å, Cu1–O4 2.298(4)]. The P–O distances for the phosphonate ligands are nonequivalent [cf. for complex **1**: P1–O1 1.536(3) Å, P1–O2 1.538(3) Å, P1–O3 1.526(3) Å; for other bond parameters see Tables 1, 2 and 3]. It may be mentioned that the Cu–O bond lengths found in the present instance are comparable to that found in structurally similar dinuclear phosphates.[19]

## Magnetic Properties of 2

The magnetic susceptibility measurements as a function of the temperature for compound **2** are shown as an $\chi T$ vs. $T$ plot in Figure 4. Lowering the temperature, the $\chi T$ product that reaches 0.81 $cm^3 K mol^{-1}$ at room temperature is first roughly constant and then continuously decreases down to 1.8 K. At 1.8 K, the $\chi T$ product is 0.24 $cm^3 K mol^{-1}$. This magnetic behaviour is typically observed for complexes that possess an intra-complex antiferromagnetic interaction. A simple dinuclear Heisenberg $S = 1/2$ model[20] was used to fit the magnetic susceptibility by considering the following spin Hamiltonian: $H = -2J\{\boldsymbol{S}_{Cu1}\cdot\boldsymbol{S}_{Cu2}\}$ (where $\boldsymbol{S}_{Cu1}$ and $\boldsymbol{S}_{Cu2}$ are the spin operators with $S_{Cu1} = S_{Cu2} = 1/2$). The best set of parameters obtained for **2** by using the above model is: $J/k_B = -2.21(5)$ K and $g = 2.08(2)$.

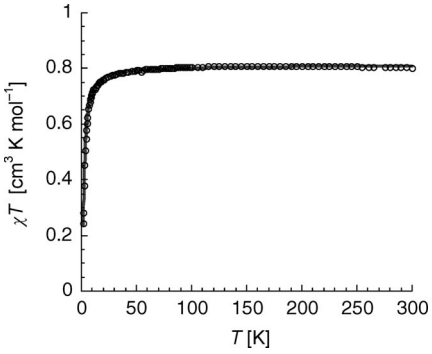



Figure 4. $\chi T$ vs. $T$ data (where $\chi = M/H$) for compound **2** measured at 1000 Oe. The solid line is the best fit obtained with the dinuclear Heisenberg model described in the text.

## Cleavage of Plasmid DNA

Complexes **1**–**3** are ideal to be tested as DNA cleavage reagents[21] in view of the fact that in each case the copper centre has a labile water molecule/solvent. Further, cooperativity effects can be expected because of the presence of two copper centres. Accordingly, in each case time-course experiments revealed that **1**–**3** were able to mediate complete conversion of supercoiled pBR322 DNA form I to nick form II in only 30 min for **1** and **2** and 40 min for **3** without the need for any external oxidant (Figure 5).

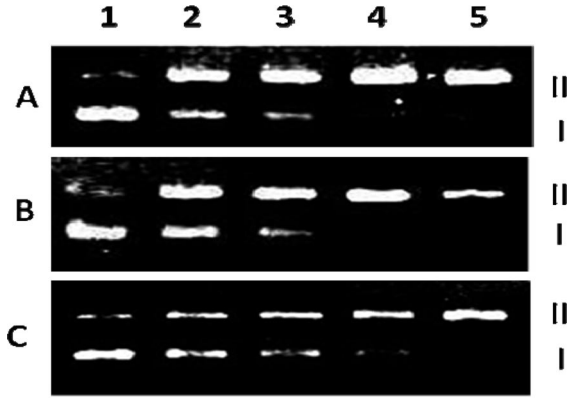



Figure 5. Complexes **1**–**3** (complex **1** corresponds to gel A, **2** to gel B and **3** to gel C) mediated DNA (pBR322) cleavage experiment at different time intervals. Lane 1: pBR322 alone; lane 2–5: pBR322 + complexes **1**–**3** (10, 20, 30 and 40 min, respectively).

### DNA Cleavage Mechanism

Copper-based artificial nucleases function through oxidative and/or hydrolytic pathways. In view of this, as well as the fact that metal complexes containing axially bound water molecules participate in DNA cleavage,[21e] we probed the cleavage mechanism of **1**–**3**. In the presence of EDTA, the cleavage reaction was completely inhibited, which demonstrates that the copper present in the complexes is crucial for plasmid modification. Dimethyl sulfoxide (DMSO), D-mannitol or *tert*-butyl alcohol do not inhibit cleavage reactions, which demonstrates that diffused radicals are not involved in the cleavage process. $NaN_3$ is a well-known quencher of singlet oxygen. $NaN_3$ also does not inhibit the cleavage reaction, which demonstrates that singlet oxygen[22] is not involved in the cleavage process (Figure 6). Also, DNA cleavage does not decrease under anaerobic conditions (Figure 7).

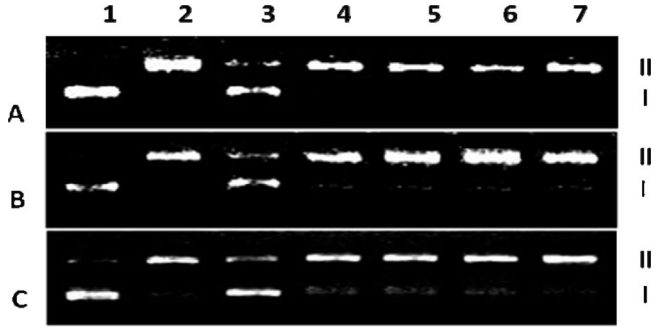



Figure 6. pBR322 cleavage experiments in the presence of free radical scavengers and singlet oxygen quencher assisted by complexes **1**–**3** (complex **1** corresponds to gel A, **2** to gel B and **3** to gel C) in a 30 min reaction. Lane 1: pBR322 alone; lane 2: pBR322 + **1**–**3**; lane 3: pBR322 + **1**–**3** + EDTA; lane 4: pBR322 + **1**–**3**+ NaN3; lane 5: pBR322 + **1**–**3** + *tert*-BuOH; lane 6: pBR322 + **1**–**3** + D-manitol; lane 7: pBR322 + **1**–**3** + DMSO.

This cumulative circumstantial evidence points to the possibility of the hydrolytic pathway being the dominant process in plasmid modification in the current instance.

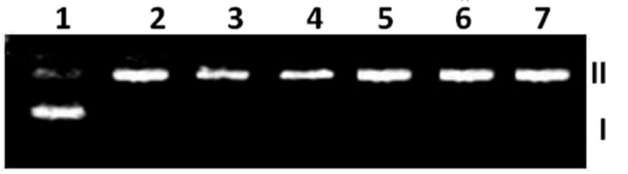



Figure 7. pBR322 cleavage under anaerobic conditions by **1**–**3** at a time intervalof 40 min. Lane 1: pBR322 alone; lanes 2 and 3: complex **1** + pBR322; lanes 4 and 5: complex **2** + pBR322; lanes 6 and 7: complex **3** + pBR322 (lanes 2, 4 and 6 aerobic conditions; lanes 3, 5 and 7 anaerobic conditions).

## Conclusions

In conclusion, in the presence of chelating nitrogen ligands the reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with lipophilic phosphonic acids affords the first examples of dinuclear copper(II) phosphonates. Previously, we showed the assembly of molecular copper(II) phosphonates where the nuclearity varied from twelve to four. The copper phosphonates found in the present instance represent the simplest structural forms of this structurally diverse family. All the compounds reported in the present study retain their dinuclear structures in solution. The presence of labile solvent molecules in the coordination sphere of the two copper centres makes these compounds quite attractive for building larger ensembles and for their use in applications such as nuclease activity. Whereas the latter has been reported in this work, we are exploring the former.

## Experimental Section

**Materials and Physical Methods:** Solvents were purified by conventional methods.[23] The following chemicals were used as received: $C_5H_9Cl$ (Aldrich, USA), $Cu(ClO_4)_2{\cdot}6H_2O$ (Fluka, Switzerland), 2,2′-bipyridine (bpy) (Aldrich, USA), 2,2′-bipyridylamine (bpya) (Aldrich, USA), $AlCl_3$ (s.d. Fine Chemicals, Mumbai, India), $PCl_3$ (s.d. Fine Chemicals, Mumbai, India), supercoiled plasmid DNA (pBR322) (Bangalore Genei, India), ethidium bromide (LOBA Chemie Pvt. Ltd. Mumbai, India), sodium cacodylate buffer (SRL, Mumbai, India), ethylenediaminetetraacetic acid (EDTA), DMSO, *tert*-butyl alcohol and D-mannitol (s.d Fine Chemicals, Mumbai, India). All buffer solutions were prepared by using millipore water.

**Instrumentation:** Melting points were measured with a JSGW melting point apparatus and are uncorrected. Electronic spectra were recorded with a Perkin–Elmer-Lambda 20 UV/Vis spectrometer and with a Shimadzu UV-160 spectrometer by using methanol as the solvent. IR spectra were recorded as KBr pellets with a Bruker Vector 22 FTIR spectrophotometer operating from 400–4000 $cm^{-1}$. MS (ESI) analyses were performed with a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. Electrospray ionization mechanism was used in positive ion full scan mode by employing methanol as the solvent and nitrogen gas for desolvation. Capillary voltage was maintained at 3 kV and cone voltage was kept at 30 V. The temperature maintained for the ion source was 100 °C and for desolvation 250 °C. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solutions with a JEOL JNM LAMBDA 400 model spectrometer operating at 400.0 and 161.7 MHz respectively. Chemical shifts are reported in ppm and are referenced with respect to internal tetramethylsilane ($^1H$) and external 85% $H_3PO_4$

($^{31}$P). Elemental analyses were carried out by using a Thermoquest CE instruments CHNS-O, EA/110 model elemental analyzer.

**Magnetic Measurements:** The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL housed at the Centre de Recherche Paul Pascal. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from –7 to 7 T. Measurements were performed on a polycrystalline sample of 26.41 mg for complex **2**. The absence of extrinsic ferromagnetic impurities was checked by measuring the magnetization as a function of the field at 100 K. The magnetic data were corrected for the sample holder and the diamagnetic contributions.

**Synthesis:** The phosphonic acids $C_5H_9P(O)(OH)_2$, $C_3H_7P(O)(OH)_2$ and $CCl_3P(O)(OH)_2$ were prepared by literature procedures.[24,25] The synthetic procedure used for the preparation of the dinuclear copper(II) phosphonates (**1**–**3**) was similar. As an illustrative example the procedure for the preparation of **1** is given below.

**$[Cu_2(\mu_2\text{-}C_5H_9PO_3)_2(bpya)_2(H_2O)_2](H_2O)_4$ (1):** A mixture of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.2 g, 0.54 mmol), 2,2′-bipyridylamine (bpya; 0.092 g, 0.54 mmol), cyclopentylphosphonic acid (0.081 g, 0.54 mmol) and triethylamine (0.11 g, 1.09 mmol) in methanol (60 mL) was stirred for 2 h. The blue-coloured reaction mixture was filtered, and the filtrate was concentrated in vacuo to afford a blue solid that was recrystallized from methanol. Yield: 0.358 g, 81% (based on metal). M.p. 228 °C (decomp.). UV/Vis ($CH_3OH$): $\lambda$ ($\varepsilon$, $L\,mol^{-1}\,cm^{-1}$) = 645 (186) nm. FTIR: $\tilde{\nu}$ = 3449 (b), 2938 (s), 2738 (s), 2677 (s), 2491 (m), 1643 (s), 1588 (s), 1532 (s), 1398 (s), 1480 (s) 1116 (b), 772 (s), 534 (s) $cm^{-1}$. MS (ESI): *m*/*z* = 765.08 $[Cu_2(C_5H_9PO_3)_2(bpya)_2]^+$, 405.08, 407.08, 383.03, 385.04, 279, 281, 234, 173.09, 172.08. $C_{30}H_{48}Cu_2N_6O_{12}P_2$ (873.78): calcd. C 41.24, H 5.54, N 9.62; found C 41.30, H 5.61, N 9.42.

**$[Cu_2(\mu_2\text{-}C_3H_7PO_3)_2(bpya)_2(H_2O)_2](H_2O)_2$ (2):** $Cu(ClO_4)_2{\cdot}6H_2O$ (0.2 g, 0.54 mmol), 2,2′-bipyridylamine (bpya) (0.092 g, 0.54 mmol), isopropylphosphonic acid (0.067 g, 0.54 mmol) and triethylamine (0.11 g, 1.09 mmol). Yield: 0.353 g, 85.1% (based on metal). M.p. 254 °C (decomp.). UV/Vis ($CH_3OH$): $\lambda$ ($\varepsilon$, $L\,mol^{-1}\,cm^{-1}$) = 649 (186) nm. FTIR: $\tilde{\nu}$ = 3203 (b), 2967 (s), 2738 (s), 2866 (m), 2679 (m), 1659 (s), 1587 (s), 1573 (m), 1477 (s), 1111 (s), 1050 (s), 1011 (s), 766 (m), 568 (m) $cm^{-1}$. MS (ESI): *m*/*z* = 713.04 $[Cu_2(C_3H_7PO_3)_2(bpya)_2]^+$, 172, 233, 275.8, 406.6. $C_{26}H_{40}Cu_2N_6O_{10}P_2$ (785.68): calcd. C 39.75, H 5.13, N 10.70; found C 40.02, H 5.16, N 10.62.

**$[Cu_2(\mu_2\text{-}Cl_3CPO_3)_2(bpy)_2(MeOH)_2](H_2O)$ (3):** $Cu(ClO_4)_2{\cdot}6H_2O$ (0.2 g, 0.54 mmol), 2,2′-bipyridine (bpy; 0.085 g, 0.54 mmol), trichloromethylphosphonic acid (0.11 g,0.54 mmol) and triethylamine (0.11 g, 1.09 mmol). Yield: 0.372 g, 75.2% (based on metal). M.p. 228 °C (decomp.). UV/Vis ($CH_3OH$): $\lambda$ ($\varepsilon$, $L\,mol^{-1}\,cm^{-1}$) = 669 (186) nm. FTIR: $\tilde{\nu}$ = 3455 (b), 3113 (m), 2929 (m), 2678 (m), 2491 (m), 1604 (s), 1473 (m), 1447 (s), 1163 (s), 1098 (s) 773 (s) 624 (s) 573 (s) $cm^{-1}$. MS (ESI): *m*/*z* = 834.73 $[Cu_2(Cl_3CPO_3)_2(bpy)_2]^+$, 770.76, 526.35, 375.06, 253.96, 218.99, 101.12. $C_{25}H_{28}Cl_6Cu_2N_4O_9P_2$ (930.28): calcd. C 32.28, H 3.03, N 6.02; found C 32.16, H 3.12, N 5.97.

**X-ray Crystallography:** The crystal data and the cell parameters for compounds **1**–**3** are given in Table 4. Single crystals suitable for X-ray crystallographic analyses were obtained by slow evaporation of methanol/dichloromethane mixture (**1**–**3**). The crystal data for compounds **1**–**3** were collected with a Bruker SMART CCD diffractometer by using a Mo-$K_\alpha$ sealed tube. The program SMART[26a] was used for collecting frames of data, indexing reflections and determining lattice parameters; SAINT[26a] for integration of the intensity of reflections and scaling; SADABS[26b] for absorption correction and SHELXTL[26c,26d] for space group and structure determination and least-squares refinements on $F^2$. All structures were solved by direct methods by using the program SHELXS-97[26e] and refined by full-matrix least-squares methods against $F^2$ with SHELXL-97.[26e] Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding

Table 4. Crystal and structure refinement parameters for compounds **1**–**3**.

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{30}H_{48}Cu_2N_6O_{12}P_2$ | $C_{26}H_{40}Cu_2N_6O_{10}P_2$ | $C_{25}H_{28}Cl_6Cu_2N_4O_9P_2$ |
| Crystal System | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| *a* [Å] | 8.000 (5) | 7.956 (5) | 12.1096(10) |
| *b* [Å] | 10.408 (5) | 10.560 (5) | 9.7982(8) |
| *c* [Å] | 22.563 (5) | 19.296 (5) | 15.8403(13) |
| $\beta$ [°] | 94.652(5) | 92.040 (5) | 101.367(2) |
| *V* [Å$^3$] | 1872.5 (15) | 1588.5(13) | 1842.6(3) |
| *Z* | 4 | 4 | 2 |
| $M_r$ | 872.13 | 784.08 | 930.279 |
| $d_{calcd.}$ [$Mg\,m^{-3}$] | 1.550 | 1.643 | 1.734 |
| Absorption coefficient [$mm^{-1}$] | 1.288 | 1.504 | 1.733 |
| *F*(000) | 908 | 812 | 972 |
| $\theta$ range [°] | 2.64 to 28.27 | 2.21 to 27.0 | 2.36 to 28.30 |
| Reflections measured | 11764 | 8435 | 11825 |
| Limiting indices | $-10 \le h \le 10$ | $-5 \le h \le 10$ | $-15 \le h \le 16$ |
| | $-13 \le k \le 13$ | $-13 \le k \le 13$ | $-13 \le k \le 9$ |
| | $-13 \le l \le 30$ | $-24 \le l \le 23$ | $-20 \le l \le 21$ |
| Reflections unique [$R_{int}$] | 4542 [0.0340] | 3423 [0.0357] | 4534 [0.0372] |
| Parameters refined | 263 | 230 | 233 |
| GooF on $F^2$ | 1.164 | 1.102 | 1.165 |
| Final *R* indices | $R_1$ = 0.0477 | $R_1$ = 0.0429 | $R_1$ = 0.0491 |
| [$I>2\sigma$ (*I*)] | $wR_2$ = 0.0969 | $wR_2$ = 0.1024 | $wR_2$ = 0.1095 |
| *R* indices | $R_1$ = 0.0658 | $R_1$ = 0.0562 | $R_1$ = 0.0763 |
| (all data) | $wR_2$ = 0.1390 | $wR_2$ = 0.1287 | $wR_2$ = 0.1684 |
| Largest residual peaks [e Å$^{-3}$] | 1.092, –0.723 | 0.933, –0.797 | 1.078, –1.221 |

model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The crystallographic figures were generated by using Diamond 3.1e software.[26f]

**pBR322 Cleavage Assay:** Plasmid cleavage reactions were performed in sodium cacodylate buffer (10 mmol, pH 7.5, 32 °C) containing pBR322 (8 ng$\mu L^{-1}$, Bangalore Genei). A solution of complexes **1**–**3** (1 mM) in distilled methanol was used for DNA cleavage. Typically, for each cleavage reaction, 16–18 μL of pBR322 supercoiled DNA and 2 μL of the complex-containing solution was used. For scavenger experiments, concentrations used were 100 mM. All cleavage reactions were quenched with 5 μL of loading buffer containing 100 mM of EDTA, 50% glycerol in Tris–HCl, pH 8.0. The samples were loaded on 0.7% agarose gel (Biozym) containing ethidium bromide (1 μg/1 mL). Electrophoresis was done for 1 h at constant current (80 mA) in 0.5 X TBE buffer. Gels were imaged with a PC-interfaced Bio-Rad Gel Documentation System 2000.

**Plasmid cleavage under Anaerobic Conditions:** Oxygen-free nitrogen was bubbled through cacodylate buffer, which was then subjected to four freeze–thaw cycles. All reagents were transferred in a glove bag under an argon atmosphere, and Eppendorf tubes were tightly sealed with parafilm under the argon atmosphere. Reactions were quenched with loading buffer and efforts were made to ensure strict anaerobic conditions during irradiation and quenching.

CCDC-715762 (for **1**), -715763 (for **2**) and -715764 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): MS spectra of **1**–**3**; general procedure for the catalytic oxidative coupling of 2,6-dimethylphenol; conversion of 2,6-dimethylphenol into poly(phenyl ether).

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