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Article

Synthesis, Structure, and Magnetism of Hexanuclear Copper(II) Phosphonates

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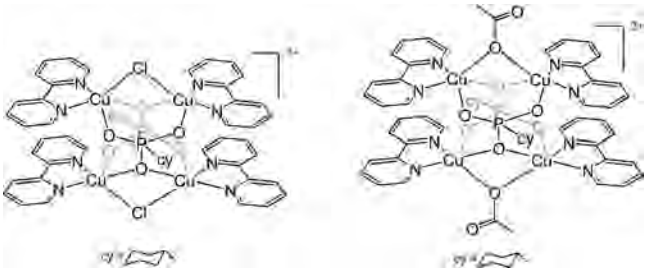
The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with cyclopentylphosphonic acid and 1,10-phenanthroline (phen) in the presence of triethylamine afforded a hexanuclear copper(II) complex $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(MeOH)_4](ClO_4)_4$ (**1**) in over 80% yield. The hexanuclear assembly is held together by the coordination action of four tridentate dianionic $[RPO_3]^{2-}$ ligands giving rise to two $Cu_2P_2O_4$ eight-membered rings in the top and the bottom that are connected to each other by a central Cu_2O_2 four-membered ring. Every copper atom in **1** is bound by a chelating phenanthroline ligand. Each of the two terminal pairs of copper atoms in the hexanuclear assembly contains methanol molecules of coordination. These labile methanol molecules can be replaced by 1,3-bis(4-pyridyl)propane (bpp) to afford $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(bpp)_2](ClO_4)_4$ (**2**) where the pincer-like bipyridine ligand acts as a stopper to close both ends of the open hexanuclear cage. Instead, treatment of the in situ generated $[Cu_6(C_5H_9PO_3)_4(2,2'\text{-bpy})_6(MeOH)_4](ClO_4)_4$ with 4,4′-bipyridine results in the formation of a rail-road-like one-dimensional polymer $[\{Cu_6(C_5H_9PO_3)_4(2,2'\text{-bpy})_6(4,4'\text{-bpy})_2\}(ClO_4)_4]_n$ (**3**). In addition to structural studies, detailed magnetic studies have been carried out on **1**−**3** which reveal an $S = 1$ spin ground-state with low lying excited states.

Introduction

Transition metal phosphonates with extended structures have been known for many years[1] and have attracted interest in view of their interesting structural chemistry, as well as their applications in diverse areas such as catalysis,[2] cation-exchangers,[3] sorption,[4] sensors,[5] and non linear optics.[6] More recently molecular metal phosphonates have also been receiving attention.[7−9] The synthesis of these compounds has become possible by a variety of approaches including (a) the use of sterically hindered phosphonic acids,[10−15] and (b) the use of ancillary ligands such as 3,5-dimethylpyrazole, 2-pyridylpyrazole, hydroxy pyridines,[16−23] and so forth. Although many of the syntheses are serendipity-based and the final outcome of the product was not planned by design, thanks to sustained efforts by a number of research groups, a rationalization of the product formation is emerging. Thus, recently we have been able to plan and assemble a series of tetranuclear copper(II) phosphonates[24] by utilizing copper(II) salts such as copper acetate or copper chloride along with chelating ligands such as 2,2′-bipyridine or 1,10-phenathroline. While the chelating ligands serve to block the coordination sites on the metal, acetate or chloride counter-anions of the starting metal compounds act as bridging ligands to limit the nuclearity of the cluster to four (Chart 1).

Chart 1



In light of this we reasoned that it would be possible to obtain higher-nuclearity clusters if we chose copper salts that contained *non-coordinating* ligands. This expectation was realized, and we were able to isolate $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(MeOH)_4](ClO_4)_4$ (**1**) in over 80% yield in the reaction

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of $Cu(ClO_4)_2 \cdot 6H_2O$, cyclopentylphosphonic acid, and 1,10-phenanthroline. Compound **1** possesses a hexanuclear cage structure. Each copper atom of the two terminal pairs of this ensemble has labile methanol molecules which can be replaced without disturbing the structural integrity of the hexanuclear core. Both intra- and intermolecular tethering of the hexanuclear motifs is possible. Accordingly we isolated $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(bpp)_2](ClO_4)_4$ (**2**) and $[\{Cu_6(C_5H_9PO_3)_4(2,2'\text{-bpy})_6(4,4'\text{-bpy})_2\}(ClO_4)_4]_n$ (**3**). While in the former the two terminal pairs of copper atoms are stitched together by a flexible bipyridine clip, the latter is a *rail-road-like* coordination polymer where pairs of rigid bipyridine ligands bridge successive hexanuclear cores. **1**, **2**, and **3** also represent the first examples of copper phosphonates prepared from cyclopentylphosphonic acid. In addition to structural studies in the solid-state and solution, we have also carried out detailed magnetic studies on these complexes. These studies are reported herein.

Experimental Section

Reagents and General Procedures. Solvents were purified by conventional methods.[25] The following chemicals were used as received: C_5H_9Cl (Aldrich, U.S.A), $Cu(ClO_4)_2 \cdot 6H_2O$ (Fluka, Switzerland), 2,2′-bipyridine (2,2′-bpy) (Aldrich, U.S.A), 1,10-phenanthroline (phen) (Aldrich, U.S.A), 1,3-bis(4-pyridyl)propane (bpp) (Fluka, Switzerland), 4,4′-bipyridine (4,4′-bpy) (Aldrich, U.S.A), $AlCl_3$ (s. d. Fine Chemicals, India), and PCl_3 (s. d. Fine Chemicals, India).

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Electronic spectra were recorded on a Perkin-Elmer-Lambda 20 UV−vis spectrometer and on a Shimadzu UV-160 spectrometer using methanol as the solvent. IR spectra were recorded as KBr pellets on a Bruker Vector 22 FT IR spectrophotometer operating in the range 400−4000 cm^{-1}. Elemental analyses of the compounds were obtained using a Thermoquest CE instrument CHNS-O, EA/110 model. ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. The ionization mechanism used was electro spray in positive ion full scan mode using methanol as 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 CD_3OD solutions on a JEOL JNM LAMBDA 400 model spectrometer operating at 400.0 and 161.7 MHz, respectively. Chemical shifts are reported in ppm and referenced with respect to internal tetramethylsilane (^1H) and external 85% H_3PO_4 (^{31}P).

Magnetic Measurements. Magnetic data were collected at the Unitat de Mesures Magnètiques at the Universitat de Barcelona using crushed crystals of the samples on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T magnet. The data were corrected for TIP, and the diamagnetic corrections were calculated using Pascal's constants; an experimental correction for the sample holder was applied.

Synthesis. $C_5H_9P(O)(OH)_2$. Cyclopentyl phosphonic acid has been synthesized by the following procedure. To a cooled mixture of $AlCl_3$ (10.0 g, 75.5 mmol) and PCl_3 (10.4 g, 75.7 mmol) at 0 °C, chlorocyclopentane (10.6 g, 101.2 mmol) was added slowly with stirring. After the addition, the reaction mixture became viscous. After standing overnight, 50 mL of $CHCl_3$ was added to this reaction mixture slowly with stirring at 0 °C. This was added to 150 g of ice and 30 mL of $CHCl_3$. The organic portion was separated and dried over calcium chloride. It was filtered, and the solvent evaporated from the filtrate to afford cyclohexylphosphonyl dichloride. To this 30 mL of water was added and allowed to stir overnight. The solution was evaporated to dryness, and the residue obtained was identified as crude cyclopentylphosphonic acid. This product was recrystallized from a 10:1 mixture of toluene and THF.

Yield: 12.8 g, 72.8% (based on phosphorus). Mp: 132 °C. FT-IR ν/cm^{-1}: 2967 (b), 2321 (b), 1452 (s), 1220 (m), 959 (m), 794 (m), 491 (m). ^1H NMR (CD_3OD): 1.6−2.1 (m). ^{31}P NMR (CD_3OD): 33.2 (s). ESI-MS analysis: *m*/*z*, ion: 151, $\{M + 1\}^+$; Anal. Calcd for $C_5H_{11}PO_3$: C, 40.01; H, 7.39. Found: C, 40.11; H, 7.14.

$[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(MeOH)_4](ClO_4)_4$ (1). A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.20 g, 0.54 mmol), cyclopentylphosphonic acid (0.054 g, 0.36 mmol), and triethylamine (0.11 g, 1.07 mmol) were taken in methanol (30 mL) and stirred for 6 h. A green-colored turbid solution was formed. To this reaction mixture 1,10-phenanthroline (phen) in CH_2Cl_2 (10 mL, 0.107 g, 0.54 mmol) was added, and the reaction mixture stirred for a further 12 h. A clear solution that resulted was concentrated to 15 mL, filtered and left undisturbed to allow crystallization. After 3−4 days blue pure crystalline blocks of **1** were obtained.

Yield: 0.20 g, 84.0% (based on metal). Mp: 270 °C (d). UV−vis (CH_3OH) λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 664 (186). FT-IR ν/cm^{-1}: 3469 (b), 3070 (m), 2950 (s), 2867 (m), 1743 (m), 1629 (s), 1552

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(1) (a) Clearfield, A. *Progress in Inorganic Chemistry: Metal-Phosphonate Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1998; Vol. *47*, pp 371−510; and references therein. (b) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420. (c) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 495. (d) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268. (e) Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1168. (f) Subbiah, A.; Pyle, D.; Rowland, A.; Huang, J.; Narayanan, R. A.; Thiyagarajan, P.; Zoń, J.; Clearfield, A. *J. Am. Chem. Soc.* **2005**, *127*, 10826. (g) Song, S.-Y.; Ma, J.-F.; Yang, J.; Cao, M.-H.; Li, K.-C. *Inorg. Chem.* **2005**, *44*, 2140. (h) Ouellette, W.; Yu, M. H.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **2006**, *45*, 7628. (i) Ouellette, W.; Yu, M. H.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **2006**, *45*, 3224. (j) Burkholder, E.; Golub, V.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **2004**, *43*, 7014. (k) Yang, B.-P.; Mao, J.-G. *Inorg. Chem.* **2005**, *44*, 566.

(2) (a) Wan, B.-Z.; Anthony, R. G.; Peng, G.-Z.; Clearfield, A. *J. Catal.* **1994**, *19*, 101. (b) Deniaud, D.; Schollorn, B.; Mansury, J.; Rouxel, J.; Battion, P.; Bujoli, B. *Chem. Mater.* **1995**, *7*, 995. (c) Hu, A.; Ngo, H.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 11490. (d) Hu, A.; Yee, G. T.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 12486. (e) Nonglaton, G.; Benitez, I. O.; Guisle, I.; Pipeler, M.; Leger, J.; Dubreuil, D.; Tellier, C.; Talham, D. R.; Bujoli, B. *J. Am. Chem. Soc.* **2004**, *126*, 1497.

(3) (a) Clearfield, A. *Inorganic Ion Exchange Materials*; CRC Press: Boca Raton, FL, 1982. (b) Alberti, G. In *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Pergamon: New York, 1996; Vol. *7*, pp 151. (c) Wang, J. D.; Clearfield, A.; Peng, G.-Z. *Mater. Chem. Phys.* **1993**, *35*, 208. (d) Zang, B.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 2751.

(4) (a) Fredoueil, F.; Massiot, D.; Janvier, P.; Gingl, F.; Bujoli-Doeuff, M.; Evian, M.; Clearfield, A.; Bujoli, B. *Inorg. Chem.* **1999**, *38*, 1831. (b) Maeda, K.; Kiyozumi, Y.; Mizukami, F. *J. Phys. Chem. B.* **1997**, *101*, 4402. (c) Yue, Q.; Yang, J.; Li, G.-H.; Li, G.-D.; Chen, J.-S. *Inorg. Chem.* **2006**, *45*, 4431. (d) Gallagher, L. A.; Serron, S. A.; Wen, X.; Hornstein, B. J.; Dattelbaum, D. M.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 2089. (e) Maeda, K. *Microporous Mesoporous Mater.* **2004**, *73*, 47.

(5) (a) Ungashe, S. B.; Wilson, W. L.; Katz, H. E.; Scheller, G. R.; Putvinski, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 8717. (b) Sanchez-Moreno, M. J.; Fernandez-Botello, A.; Gomez-Coca, R. B.; Griesser, R.; Ochocki, J.; Kotynski, A.; Niclos-Gutierrez, J.; Moreno, V.; Sigel, H. *Inorg. Chem.* **2004**, *43*, 1311. (c) Du, Z.-Y.; Xu, H.-B.; Mao, J.-G. *Inorg. Chem.* **2006**, *45*, 6424.

(6) (a) Cabeza, A.; Aranda, M. A. G.; Bruque, S.; Poojary, D. M; Clearfield, A.; Sanz, J. *Inorg. Chem.* **1998**, *37*, 4168. (b) Zhang, B.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1998**, *37*, 249. (c) Ayyappan, P.; Evans, O. R.; Cui, Y.; Wheeler, K. A.; Lin, W. *Inorg. Chem.* **2002**, *41*, 4978.

Table 1. Crystal and Structure Refinement Parameters for Compounds **1**−**3**

parameters	**1**	**2**	**3**
empirical formula	$C_{98}H_{108}Cl_4Cu_6N_{12}O_{34}P_4$	$C_{124}H_{114}Cl_8Cu_6N_{16}O_{32}P_4$	$C_{112}H_{114}Cl_4Cu_6N1_8O_{32}P_4$
formula weight	2644.88	3129.04	2871.13
temperature	293 (2) K	293(2)K	293(2) K
wavelength	0.71069 Å	0.71073 Å	0.71073 Å
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$
unit cell dimensions	$a = 12.649(5)$ Å	$a = 15.017(5)$ Å	$a = 14.7064(15)$Å
	$b = 15.225(5)$ Å	$b = 24.962(5)$ Å	$b = 14.8112(15)$Å
	$c = 15.896(5)$ Å	$c = 17.015(5)$ Å	$c = 15.2607(15)$Å
	$\alpha = 111.439(5)°$	$\alpha = 90.000(5)°$	$\alpha = 110.074(2)°$
	$\beta = 95.405(5)°$	$\beta = 93.554(5)°$	$\beta = 97.147(2)°$
	$\gamma = 109.795(5)°$	$\gamma = 90.000(5)°$	$\gamma = 106.121(2)°$
volume, Z	2596.7(16) Å^3, 2	6366(3) Å^3, 4	2909.1(5)Å^3, 1
density (calculated)	1.691 Mg/m^3	1.632 mg/m^3	1.639 mg/m^3
absorption coefficient	1.462 mm^{-1}	1.288 mm^{-1}	1.313 mm^{-1}
F (000)	1354	3192	1470
crystal size	0.20 × 0.08 × 0.07 mm^3	0.20 × 0.15 × 0.10 mm	0.10 × 0.08 × 0.07 mm^3
θ range for data collection	2.17 to 26.00°.	2.02 to 26.00°	2.11 to 26.00 °
limiting indices	$-15 \le h \le 15$,	$-18 \le h \le 9$,	$-18 \le h \le 14$,
	$-18 \le k \le 18$,	$-30 \le k \le 27$,	$-18 \le k \le 17$,
	$-8 \le l \le 19$	$-20 \le l \le 20$	$-18 \le l \le 18$
reflections collected	14826	35439	16425
independent reflections	10021 [R(int) = 0.0599]	12474 [R(int) = 0.0561]	11192 [R(int) = 0.0412]
completeness to θ	98.0% (θ = 26.0)	99.7% (θ = 26.0)	97.9% (θ = 26.0)
data/ restraints/ parameters	10021/0/724	12474/0/871	11192/0/783
goodness-of-fit on F^2	0.963	1.025	1.040
final R indices [$I > 2\sigma(I)$]	R1 = 0.0708,	R1 = 0.0806,	R1 = 0.0767,
	wR2 = 0.1459	wR2 = 0.2254	wR2 = 0.1962
R indices (all data)	R1 = 0.1302,	R1 = 0.1184,	R1 = 0.1055,
	wR2 = 0.1831	wR2 = 0.2583	wR2 = 0.2222
largest diff. peak and hole	0.936 and −0.630 e Å^{-3}	1.866 and −1.070 e A^{-3}	1.456 and −0.956 e Å^{-3}

(s), 1140 (s), 872 (s), 838 (s) 647 (s). ESI-MS *m*/*z*, ion: 513.51 $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6]^{4+}$, 423.06 $[Cu(1,10\text{-phen})_2]^+$, 242.98 $[Cu(1,10\text{-phen})]^+$. Anal. Calcd for $C_{96}H_{96}Cu_6N_{12}O_{16}P_4$: C, 52.91; H, 4.44; N, 7.71. Found: C, 53.05; H, 4.56; N, 7.38.

$[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(bpp)_2](ClO_4)_4$ (2). A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.20 g, 0.54 mmol), cyclopentylphosphonic acid (0.054 g, 0.36 mmol), and triethylamine (0.11 g, 1.07 mmol) were taken in methanol (30 mL) and stirred for 6 h resulting in a green turbid solution. To this, 1,10-phenanthroline in CH_2Cl_2 (10 mL, 0.107 g, 0.54 mmol) was added and stirred for a further 12 h affording a clear blue solution. To this was added 1,3-bis(4-pyridyl)propane, and stirred for another 12 h. The reaction mixture was concentrated to 15 mL, filtered and left undisturbed to allow crystallization. After 3−4 days blue crystalline blocks of **2** were obtained.

Yield: 0.205 g, 72.8% (based on metal). Mp: 250 °C (d). UV−vis (CH_3OH) λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 676 (186). FT-IR ν/cm^{-1}: 3441 (b), 3068 (b), 2928 (s), 2864 (m), 1743 (s), 1608 (s), 1585 (s), 1137 (s), 871 (s), 778 (s), 645 (s). ESI-MS *m*/*z*, ion: 513.51 $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6]^{4+}$, 423.06 $[Cu(1,10\text{-phen})_2]^+$, 242.98 $[Cu(1,10\text{-phen})]^+$. Anal. Calcd for $C_{118}H_{112}Cu_6N_{16}O_{12}P_4$: C, 57.81; H, 4.61; N, 9.14. Found: C, 57.96; H, 4.76; N, 9.06.

$[\{Cu_6(C_5H_9PO_3)_4(2,2'\text{-bpy})_6(4,4'\text{-bpy})_2\}(ClO_4)_4]_n$ (3). A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.20 g, 0.54 mmol), cyclopentylphosphonic acid (0.054 g, 0.36 mmol), and triethylamine (0.11 g, 1.07 mmol) were taken in methanol (30 mL) and stirred for 6 h. To the resultant green turbid solution, 2,2′-bipyridine dissolved in CH_2Cl_2 (10 mL, 0.085 g, 0.54 mmol) was added and stirred for a further 12 h affording a clear blue solution. At this stage, 4,4′-bipyridine (0.043 g, 0.27 mmol) was added and the reaction mixture stirred for another 12 h. This was concentrated to 15 mL, filtered, and left undisturbed to allow crystallization. After 3−4 days a blue crystalline product was obtained by slow evaporation.

Yield: 0.198 g, 76.6% (based on metal). Mp: 260 °C (d). UV−vis (CH_3OH) λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 670 (186). FT-IR ν/cm^{-1}: 3430 (b), 3085 (m), 2927 (s), 2868 (m), 1603 (s), 1493 (s), 1090(s), 1027 (m), 768 (s), 622 (s). ESI-MS *m*/*z*, ion: 477.52 $[Cu_6(C_5H_9PO_3)_4(bpy)_6]^{4+}$, 375.06 $[Cu(bpy)_2]^+$, 218.98 $[Cu(bpy)]^+$. Anal. Calcd for $C_{120}H_{116}Cu_6N_{20}O_{12}P_4$: C, 56.84; H, 4.61; N, 11.05;. Found: C, 57.08; H, 4.96; N, 10.90.

X-ray Crystallography. The crystal data and the cell parameters for compounds **1**−**3** are given in Table 1. 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** have been collected on a Bruker SMART CCD diffractometer using a Mo Kα 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,d] for space group and structure

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(7) (a) Chandrasekhar, V.; Kingsley, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2320. (b) Chandrasekhar, V.; Kingsley, S.; Vij, A.; Lam, K. C.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 3238. (c) Chandrasekhar, V.; Kingsley, S.; Hatigan, B.; Lam, M. K.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1030. (d) Chandrasekhar, V.; Nagarajan, L.; Gopal, K.; Baskar, V.; Kögerler, P. *Dalton Trans.* **2005**, 3143. (e) Chandrasekhar, V.; Sasikumar, P.; Boomishankar, R.; Anantharaman, G. *Inorg. Chem.* **2002**, *41*, 1030.

(8) (a) Brechin, E. K.; Coxall, R. A.; Parkin, A.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2700. (b) Maheswaran, S.; Chastanet, G.; Teat, S. J.; Mallah, T.; Sessoli, R.; Wernsdorfer, W.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5044. (c) Tolis, E. I.; Helliwell, M.; Langley, S.; Raftery, J.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3804. (d) Langley, S. J.; Helliwell, M.; Sessoli, R.; Rosa, P.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. Commun.* **2005**, 5029. (e) Langley, S.; Helliwell, M.; Raftery, J.; Tolis, E. I.; Winpenny, R. E. P. *Chem. Commun.* **2004**, 142.

(9) (a) Walawalkar, M. G.; Roesky, H. W.; Murugavel, R. *Acc. Chem. Res.* **1999**, *32*, 117. (b) Chakraborty, D.; Chandrasekhar, V.; Bhattacharjee, M.; Krätzner, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2000**, *39*, 23. (c) Anantharaman, G.; Walawalkar, M. G.; Murugavel, R.; Gábor, B.; Regine, H.-I.; Baldus, M.; Angerstein, B.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4482.

determination and least-squares refinements on F^2. All the structures were solved by direct methods 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 model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The disordered water molecules were refined isotropically. The crystallographic figures have been generated using Diamond 3.1e software.[26f]

Results and Discussion

Synthetic Aspects. The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with cyclopentylphosphonic acid and 1,10-phenanthroline (phen) in the presence of triethylamine afforded the hexanuclear copper(II) complex **1** in over 80% yield (see Supporting Information, Scheme S1). A 1:1 ratio of $Cu(ClO_4)_2 \cdot 6H_2O$ and phen ensured that two coordination sites of every copper were blocked by the chelating ligand. Adjusting the stoichiometric ratio of Cu(II) salt : phosphonic acid at 3:2 allowed the isolation of the hexanuclear complex $[Cu_6(C_5H_9PO_3)_4(1{,}10\text{-phen})_6(MeOH)_4](ClO_4)_4$ (**1**) (see Supporting Information, Chart S1). Each terminal copper atom of **1** has a labile methanol molecule. The *cis* orientation of the methanol ligands on either end of the hexanuclear cage allowed their facile replacement by two flexible bipyridine ligands to afford $[Cu_6(C_5H_9PO_3)_4(1{,}10\text{-phen})_6(bpp)_2](ClO_4)_4$ (**2**). Each of the pincer-like bipyridine ligands acts as a stopper to close both ends of the open hexanuclear cage (see Supporting Information, Scheme S1; Chart S1). If instead of a flexible bipyridine ligand, the rigid 4,4′-bipyridine is used, a rail-road-like one-dimensional polymer of Cu_6 units linked by the 4,4′-bipyridine linkers of formula $[\{Cu_6(C_5H_9PO_3)_4(2{,}2'\text{-bpy})_6(4{,}4'\text{-bpy})_2\}(ClO_4)_4]_n$ (**3**) is formed (see Supporting Information, Scheme S1; Chart S1). It is to be noted that we were able to crystallize **3** by using 2,2′-bipyridine instead of 1,10-phenanthroline. Electronic spectra of **1**−**3** reveal a broad d-d transition in the region of 670 ± 10 nm similar to that observed for the tetranuclear compounds prepared by us earlier.[24] ESI-MS spectra of **1**−**3** were recorded in the positive ion mode to study the stability of the hexanuclear cores in solution. For all the three complexes (**1**−**3**) it was confirmed that the hexanuclear core structure is stable in solution as evidenced by the observation of major peaks at 513.51 for complexes **1** and **2**, corresponding to $[Cu_6(C_5H_9PO_3)_4(1{,}10\text{-phen})_4]^{4+}$ and a major peak at 477.52 for **3** arising because of $[Cu_6(C_5H_9PO_3)_4(bpy)_4]^{4+}$ in their ESI-MS spectra (Supporting Information, Figures S1−S3).

X-ray Crystallography of 1−3. Compounds **1**−**3** are tetracationic hexanuclear complexes containing non-coordinating perchlorate anions. Selected bond parameters for these compounds are summarized in Table 2 and Tables S1 and S2 (see Supporting Information). The structures of the complexes **1**−**3** are given in Figures 1−3. The hexanuclear core is similar and isostructural in all the three complexes. We will, therefore, describe the structural details of only **1**.

Complex **1** is made up of two symmetrically related tricopper units (Figure 1). The entire hexanuclear ensemble is held together by the coordination action of four tridentate dianionic $[RPO_3]^{2-}$ ligands. Each of the two pairs of terminal copper atoms (Cu2 and Cu3; Cu2* and Cu3*) are connected by two O−P−O bridges to afford puckered $Cu_2P_2O_4$ eight-membered rings. Two oxygen atoms (O5 and O5*) from the symmetry related phosphonate ligands (P2 and P2*) function as single atom bridges and hold the central copper atoms Cu1 and Cu1* in a four-membered Cu_2O_2 ring. The remaining two oxygen atoms (O1 and O1*) derived from the phosphonates P1 and P1* act as terminal ligands for the central copper atoms Cu1 and Cu1*, respectively. The structure of the complex is completed by the coordination of methanol to each of the terminal copper atoms. This is the key structural feature that allows the facile synthesis of complexes **2** and **3** by substitution of the terminal ligands in

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(10) (a) Konar, S.; Bhuvanesh, N.; Clearfield, A. *J. Am. Chem. Soc.* **2006**, *128*, 9604. (b) Plutner, J.; Rohovec, J.; Kotek, J.; Žák, Z.; Lukeś, I. *Inorg. Chim. Acta* **2002**, *335*, 27. (c) Liu, B.; Li, Y.-Z.; Zheng, L.-M. *Inorg. Chem.* **2005**, *44*, 6921. (d) Cao, D.-K.; Li, Y.-Z.; Zheng, L.-M *Inorg. Chem.* **2005**, *44*, 2984. (e) Yao, H.-C.; Li, Y.-Z.; Song, Y.; Ma, Y.-S.; Zheng, L.-M.; Xin, X.-Q. *Inorg. Chem.* **2006**, *45*, 59. (f) Yao, H.-C.; Wang, J.-J.; Ma, Y.-S.; Waldmann, O.; Du, W.-X.; Song, Y.; Li, Y.-Z.; Zheng, L.-M.; Decurtins, S.; Xin, X.-Q. *Chem. Commun.* **2006**, 1745. (g) Kratochvil, J.; Necas, M.; Petricek, V.; Pinkas, J. *Inorg. Chem.* **2006**, *45*, 6562. (h) Kontturi, M.; Laurilla, E.; Mattsson, R.; Peräniemi, S.; Vepsäläinen, J. J.; Ahlgrèn, M. *Inorg. Chem.* **2005**, *44*, 2400. (i) Mehring, M.; Guerrero, G.; Dahan, F.; Mutin, P. H.; Vioux, A. *Inorg. Chem.* **2000**, *39*, 3325. (j) Otieno, T.; Mokry, L. M.; Bond, M. R.; Carrano, C. J.; Dean, N. S. *Inorg. Chem.* **1996**, *35*, 850. (k) Clarke, R.; Latham, K.; Rix, C.; Hobday, M.; White, J. *CrystEngComm* **2004**, *6*, 42. (l) Clarke, R.; Latham, K.; Rix, C.; Hobday, M.; White, J. *CrystEngComm* **2005**, *7*, 28. (m) Yao, H.-C.; Li, Y.-Z.; Zheng, L.-M; Xin, X.-Q. *Inorg. Chim. Acta* **2005**, *358*, 2523. (n) Yao, H.-C.; Li, Y.-Z.; Gao, S.; Song, Y.; Zheng, L.-M.; Xin, X.-Q. *J. Solid State Chem.* **2004**, *177*, 4557. (o) Zhao, Q.-H.; Du, L.; Fang, R.-B. *Acta Crystallogr.* **2006**, *E62*, m219. (p) Yi, X.-Y.; Liu, B.; Jiménez-Aparico, R.; Urbanos, F. A.; Gao, G.; Xu, W.; Chen, J.-S.; Song, Y.; Zheng, L.-M. *Inorg. Chem.* **2005**, *44*, 4309. (q) Fan, Y.-T.; Xue, D.-X.; Li, G.; Hou, H.-W.; Du, C.-X.; Lu, H.-J. *J. Mol. Struct.* **2004**, *693*, 217. (r) Kontturi, M.; Peräniemi, S.; Vepsääinen, J. J.; Ahlgrèn, M. *Polyhedron* **2005**, *24*, 305. (s) Finn, R. C.; Zubieta, J. *Inorg. Chim. Acta* **2002**, *332*, 191.

(11) Yang, Yu.; Walawalkar, M. G.; Pinkas, J.; Roesky, H. W.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **1998**, *37*, 96.

(12) Baskar, V.; Shanmugam, M.; Sañudo, E. C.; Shanmugam, M.; Collison, D.; McInnes, E. J. L.; Wei, Q.; Winpenny, R. E. P. *Chem. Commun.* **2007**, 37.

(13) Anantharaman, G.; Walawalkar, M. G.; Murugavel, R.; Gábor, B.; Herbst-Irmer, R.; Baldus, M.; Angerstein, B.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4482.

(14) Anantharaman, G.; Chandrasekhar, V.; Walawalkar, M. G.; Roesky, H. W.; Vidovic, D.; Magull, a J.; Noltemeyer, M. *Dalton Trans.* **2004**, 1271.

(15) Yang, Y.; Schmidt, H.-G.; Noltemeyer, M.; Pinkas, J.; Roesky, H. W. *J. Chem. Soc., Dalton Trans.* **1996**, 3609.

(16) Chandrasekhar, V.; Kingsley, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2320.

(17) Chandrasekhar, V.; Kingsley, S.; Vij, A.; Lam, K. C.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 3238.

(18) Chandrasekhar, V.; Kingsley, S.; Hatigan, B.; Lam, M. K.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1030.

(19) Chandrasekhar, V.; Sasikumar, P.; Boomishankar, R.; Anantharaman, G. *Inorg. Chem.* **2006**, *45*, 3344.

(20) Chandrasekhar, V.; Nagarajan, L.; Gopal, K.; Baskar, V.; Kögerler, P. *Dalton Trans.* **2005**, 3143.

(21) Chandrasekhar, V.; Nagarajan, L.; Clerac, R.; Ghosh, S.; Senapati, T.; Verma, S. *Inorg. Chem.* **2008**, *47*, 5347.

(22) Chandrasekhar, V.; Nagarajan, L.; Clerac, R.; Ghosh, S.; Verma, S. *Inorg. Chem.* **2008**, *47*, 1067.

(23) Langley, S.; Helliwell, M.; Sessoli, R.; Teat, S. J.; Winpenny, R. E. P. *Inorg. Chem.* **2008**, *47*, 497.

(24) Chandrasekhar, V.; Azhakar, R.; Senapati, T.; Thilagar, P.; Ghosh, S.; Verma, S.; Boomishankar, R.; Steiner, A.; Koegerler, P. *Dalton Trans.* **2008**, *9*, 1150.

(25) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman: London, 1989.

Table 2. Bond Lengths [Å] and Bond Angles [deg] for **1**

Cu(3)−O(2) 1.912(4)	Cu(1)−O(1) 1.946(4)	Cu(2)−O(3) 1.941(4)
Cu(3)−O(4) 1922(4)	Cu(1)−O(5) 1.965(4)	Cu(2)−O(6) 1.943(4)
Cu(3)−N(5) 2.016(6)	Cu(1)−N(2) 2.015(5)	Cu(2)−N(3) 2.024(6)
Cu(3)−N(6) 2.039(6)	Cu(1)−N(1) 2.032(6)	Cu(2)−N(4) 2.036(5)
Cu(3)−O(7) 2.280(5)	Cu(1)−O(5^{a}) 2.242(5)	Cu(2)−O(8) 2.036(5)
O(2)−Cu(3)−O(4) 97.83(19)	O(2)−Cu(3)−O(7) 89.62(19)	O(5)−Cu(1)−N(2) 171.6(2)
O(2)−Cu(3)−N(5) 90.5(2)	O(4)−Cu(3)−O(7) 94.44(19)	O(1)−Cu(1)−N(1) 163.2(2)
O(4)−Cu(3)−N(5) 166.7(2)	N(5)−Cu(3)−O(7) 96.0(2)	O(5)−Cu(1)−N(1) 92.6(2)
O(2)−Cu(3)−N(6) 166.5(2)	N(6)−Cu(3)−O(7) 101.6(2)	N(2)−Cu(1)−N(1) 80.6(2)
O(4)−Cu(3)−N(6) 88.7(2)	O(1)−Cu(1)−O(5) 96.95(18)	O(1)−Cu(1)−O(5^{a}) 94.25(18)
N(5)−Cu(3)−N(6) 81.0(2)	O(1)−Cu(1)−N(2) 88.5(2)	O(5)−Cu(1)−O(5^{a}) 83.21(18)
N(2)−Cu(1)−O(5^{a}) 102.83(19)	O(6)−Cu(2)−O(8) 96.1(2)	N(3)−Cu(2)−N(4) 80.8(2)
N(1)−Cu(1)−O(5^{a}) 100.59(19)	N(3)−Cu(2)−O(8) 94.4(2)	Cu(1)−O(5)−Cu(1^{a}) 96.79(18)
O(3)−Cu(2)−O(6) 94.24(19)	N(4)−Cu(2)−O(8) 95.9(2)	O(3)−Cu(2)−O(8) 95.4(2)
O(3)−Cu(2)−N(3) 168.6(2)	O(3)−Cu(2)−N(4) 92.5(2)	O(6)−Cu(2)−N(4) 165.7(2)
O(6)−Cu(2)−N(3) 90.4(2)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 2$, $-y$, $-z + 2$.

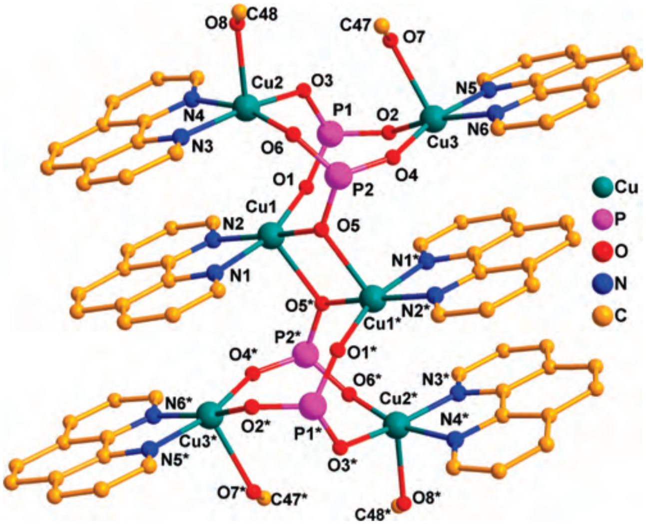

Figure 1. Cationic complex **1**. Cyclopentyl groups and hydrogen atoms have been removed for the sake of clarity.

complex **1** and the in situ generated [$\{Cu_6(C_5H_9PO_3)_4(2,2'$-bpy$)_6(MeOH)_2\}(ClO_4)_4$], respectively.

Of the four phosphonate ligands present in **1** two are of one type (P1 and P1*) which bind to three copper atoms in a 3.111 coordination mode.[27] The other two phosphonates (P2 and P2*) hold four copper atoms in a 4.211 coordination mode[27] (see Supporting Information, Chart S2). The Cu(II) ions are pentacoordinated to three O and two N atoms in a distorted square-pyramidal fashion (see Supporting Information, Table S3 for τ values).

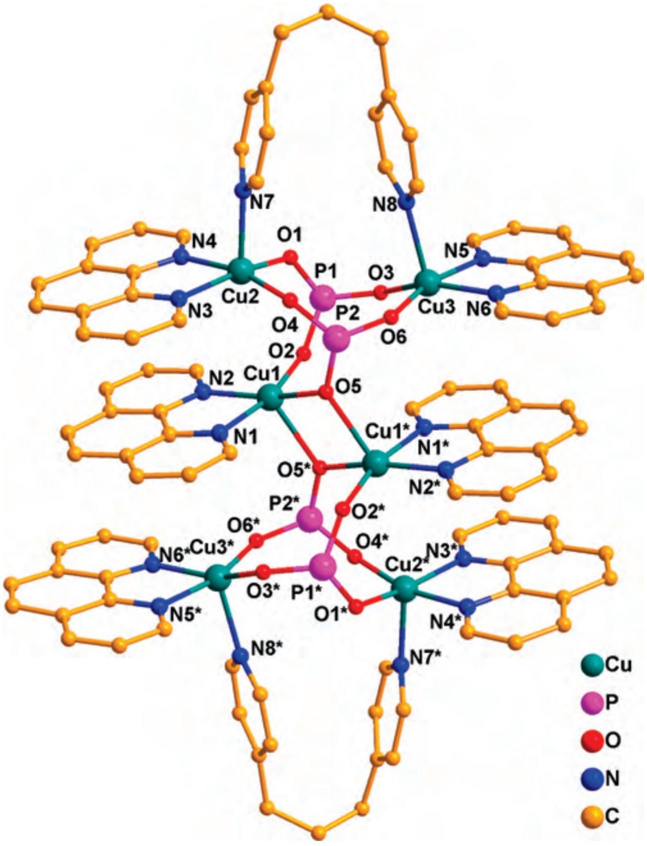

Figure 2. Cationic complex **2**. Cyclopentyl groups and hydrogen atoms have been removed for the sake of clarity.

Two types of Cu−O distances are found for the terminal copper atoms; those involving the phosphonate oxygen atoms are shorter: Cu3−O2 [1.912(4) Å] and Cu3−O4 [1.922 (4) Å]. In contrast the Cu−O bond distance involving the methanol ligand is slightly longer [Cu3−O7, 2.280(5) Å]. The Cu−O distances of the central copper atoms involving the phosphonate ligands are not very dissimilar [Cu1−O1, 1.946(4) Å; Cu1−O5, 1.965(4) Å] from those observed for the terminal copper atoms.

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(26) (a) *SMART & SAINT Software Reference manuals*, Version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2003. (b) Sheldrick, G. M. *SADABS a software for empirical absorption correction*, Ver. 2.05; University of Goettingen: Goettingen, Germany, 2002. (c) *SHELXTL Reference Manual*, Ver. 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000. (d) Sheldrick, G. M. *SHELXTL*, Ver. 6.12; Bruker AXS Inc.: Madison, WI, 2001. (e) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Geottingen: Goettingen, Germany, 1997. (f) Bradenburg, K. *Diamond*, Ver. 3.1eM; Crystal Impact GbR: Bonn, Germany, 2005.

(27) Coxall, R. A.; Harris, S. G.; Henderson, S.; Parsons, S.; Taskar, R. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, *14*, 2349.

(28) (a) Fernandez-Botello, A.; Escure, A.; Solans, X.; Font-Bardia, M.; Holy, A.; Sigel, H.; Moreno, V. *Eur. J. Inorg. Chem.* **2007**, 1867. (b) Itoh, M.; Nakazawa, J.; Maeda, K.; Kano, K.; Mizutani, T.; Kodera, M. *Inorg. Chem.* **2005**, *44*, 691. (c) Liu, X.; McLaughlin, A. C.; de Miranda, M. P.; McInnes, E. J. L.; Kilner, C. A.; Halcrow, M. A. *Chem. Commun.* **2002**, 2978. (d) Mezei, G.; Baran, P.; Raptis, R. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 574. (e) Mohamed, A. A.; Burini, A.; Galassi, R.; Paglialunga, D.; Galan-Mascaros, J.-R.; Dunbar, K. R.; Fackler, J. P., Jr. *Inorg. Chem.* **2007**, *46*, 2348. (f) Sakai, K.; Yamada, Y.; Tsubomura, T.; Yabuki, M.; Yamaguchi, M. *Inorg. Chem.* **1996**, 542.

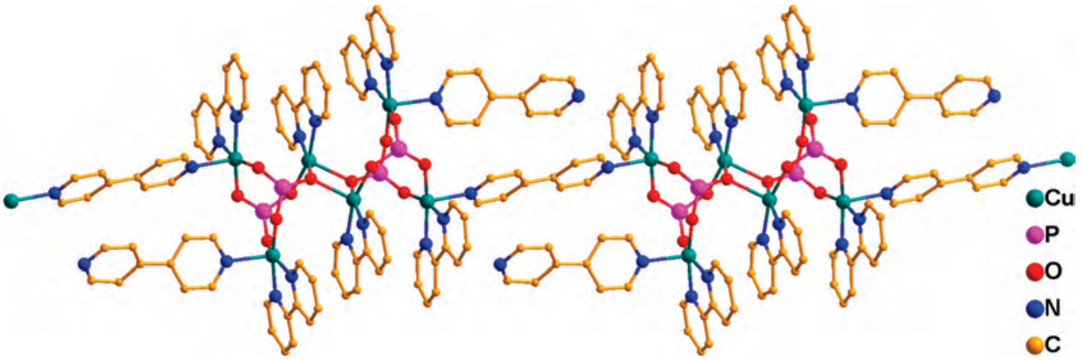

Figure 3. Cationic complex **3**. Cyclopentyl groups and hydrogen atoms have been removed for the sake of clarity.

It is interesting to compare the structural features of **1** with some hexanuclear copper complexes known in the literature. Only one hexanuclear copper phosphonate is known in literature, $[Cu_6(2,2'\text{-bpy})_6(PMEDAPy)_4][ClO_4]_8 \cdot 2H_2O$ (PMEDAPy = 2,4-diamino-1-[2-(phosphonomethoxy)ethyl]pyrimidine) whose core structure is similar to that of **1**. In this case also the chelating bipyridine ligands serve to block two coordination sites on copper while four dianionic phosphonate ligands are involved in holding the six copper atoms together.[28a] The metric parameters found are very similar to those observed for **1**. In another example of a phosphate ligand-assisted hexanuclear complex $[Cu_6(L)_3((PhOPO_3)_4][ClO_4]_4$ (L= 1,2-bis(2-((methyl(pyridylmethyl)amino)methyl)-6-pyridyl)-ethane), the ensemble contains two symmetry related tricopper units bridged to each other by the hexadentate amino ligand L. Two dianionic phosphate ligands are involved in holding each of the subunits.[28b] In addition a few other hexanuclear copper complexes are known which contain ligands such as pyrazole, imidazole, hydroxide, fluoride, or carboxylate ligands.[28c−f] However, the structures of these complexes are vastly different from those observed in the present instance.

As described above, **1** contains two pairs of copper centers on either end of the hexanuclear framework. Each copper atom of a given pair has a labile methanol molecule present in the apical coordination site of square-pyramid geometry. The *cis* orientation of the methanol molecules in a pair of copper atoms (Cu2 and Cu3; Cu2* and Cu3*) renders them to be replaced by a suitable bridging ligand. Accordingly, reaction of **1** with a flexible 1,3-bis (4-pyridyl)propane (bpp), allows the formation of **2** whose molecular structure is shown in Figure 2. The trimethylene spacer that separates the two pyridine subunits is sufficiently flexible and allows the coordination of the two pyridine arms to occur smoothly *without* causing any structural change in the hexanuclear core. The copper atoms Cu2, Cu3, and their symmetry related counterparts Cu2* and Cu3* have a 3N, 2O coordination environment in a square-pyramidal geometry. The basal plane is occupied by the two chelating nitrogen atoms of the 1,10-phenanthroline ligand and the two oxygen atoms of the phosphonate ligands while the apical site is occupied by the nitrogen of the bridging bipyridyl ligand. The $Cu-N_{apical}$ distance (Cu2−N7, 2.193(7) Å) is slightly longer than the $Cu-N_{basal}$ (Cu3−N5, 2.048(6) Å; Cu3−N6, 2.065(6) Å) distances. The other bond parameters of **2** are given in Table S1 (see Supporting Information).

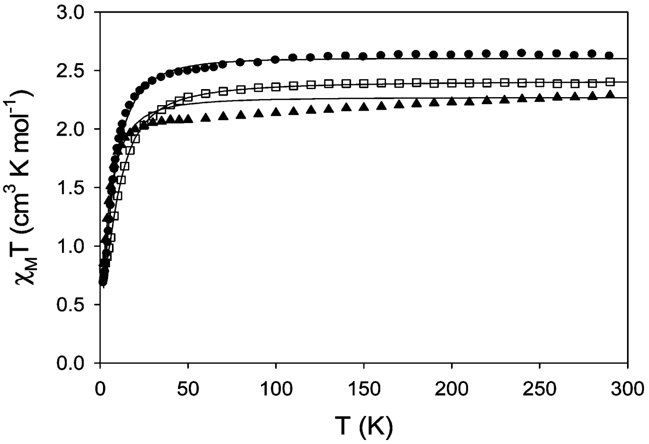

Figure 4. $\chi_M T$ vs *T* plot for **1** (circles), **2** (squares), and **3** (triangles). The solid line is the best fit, see text for the fitting parameters.

Reaction of the in situ generated $[Cu_6(C_5H_9PO_3)_4(1,10\text{-phen})_6(MeOH)_4](ClO_4)_4$ with a rigid bidentate ligand such as 4,4′-bipyridine ensures that chelation involving the intramolecular reaction does not occur. Instead, bridging coordination involving an intermolecular reaction occurs leading to the formation of a one-dimensional coordination polymer which has a *rail-road-like* architecture containing two parallel interconnected strands (Figure 3). In spite of the fact that four replacement reactions have to occur to generate the polymer, the coordination polymer containing alternately the hexanuclear core and two bipyridine bridges is the sole product. As in the case of **2** the formation of **3** occurs without any structural change to the Cu_6 core. The bond parameters of **3** are summarized in Table S2 (see Supporting Information).

Magnetic Studies. Figure 4 shows $\chi_M T$ plots for complexes **1** (circles), **2** (triangles), and **3** (squares), measured at 1.0 T applied field in the 2 to 300 K temperature range. In all cases, measurements were performed at an additional field below 30 K, and no field dependence of the susceptibility was observed. The Cu-phosphonate core of the three complexes **1**−**3** is very similar, the main difference lies in the terminal ligands, which are MeOH molecules in **1**, a pincer ligand in **2** that links Cu3−Cu4 and Cu5−Cu6 (see Scheme 1 for labeling of the Cu ions), and 4,4′-bipyridine ligands in **3** that link the complexes into a one-dimensional chain. The 4,4′-bipyridine groups hold the Cu_6 complexes

Scheme 1. Coupling Scheme Used to Fit the Magnetic Data of **1**, **2**, and **3**

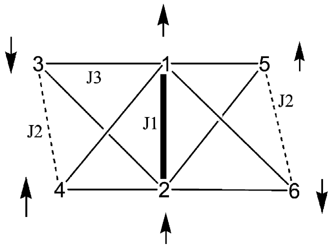

Table 3. Fitting Parameters for Complexes **1**, **2**, and **3** Using Magpack

	g	J1 (cm^{-1})	J2 (cm^{-1})	J3 (cm^{-1})	J' (cm^{-1})
1	2.15	20.31	−2.35	−1.63	
2	2.07	15.44	−1.64	−2.41	
3	2.01	15.00	−0.23	−0.002	−0.90

in **3** 11.633 Å apart; this is known to lead to very weak (<1 cm^{-1}) magnetic coupling. The $\chi_M T$ values at 300 K for complexes **1** (2.62 cm^3 K mol^{-1}), **2** (2.39 cm^3 K mol^{-1}), and **3** (2.29 cm^3 K mol^{-1}) are well in agreement with the value of 2.25 cm^3 K mol^{-1} expected for six non-interacting Cu(II) ions with $S = 1/2$ and $g = 2.0$. As the temperature decreases, the $\chi_M T$ values for **1** and **2** remain nearly constant down to 30 K for **1** and 50 K for **2**. At lower temperatures the $\chi_M T$ rapidly decreases to values of 0.68 cm^3 K mol^{-1} and 0.80 cm^3 K mol^{-1} for **1** and **2** at 2 K, respectively. The $\chi_M T$ value for **3** slowly decreases from 2.29 cm^3 K mol^{-1} at 300 K, until it reaches a plateau of 2.08 cm^3 K mol^{-1} between 100 and 20 K. Below 20 K, a sharp decrease is observed down to 0.85 cm^3 K mol^{-1} at 2 K.

The Magpack software[29] was used to model the magnetic data. Weak intermolecular interactions were included in the case of **3**, as a perturbation (J') using the mean-field theory.[30] The coupling scheme, shown in Scheme 1, was simplified to three J values. The dominant interaction is J1, the one between the two central Cu(II) ions bridged by two μ-oxygen atoms from two phosphonate ligands. The Cu−Cu distance is between 3.151 and 3.257 Å for the three compounds, and the Cu−O−Cu angles have values of 96.79° (**1**), 100.68° (**2**), and 96.85° (**3**), respectively. J2 was defined as the exchange parameter between each pair of peripheral Cu ions (Cu3 and Cu4, and Cu5 and Cu6 as labeled in Scheme 1, shown as a dashed line). All of the other exchange contacts (shown as a solid line in Scheme 1) are grouped in J3, these include Cu−Cu distances between 3.352 to 6.046 Å, through one or two phosphonate ligands. Most of these interactions will be very weak because of the long Cu−Cu separation, but cannot be left out of the model since it is known that phosphonate ligands provide efficient pathways for magnetic exchange.[12] The best fittings are shown in Figure 4 as solid lines, and the fitting parameters are shown in Table 3. The J1 values are all ferromagnetic and relatively weak, as expected for the interaction between a full d_{z^2} Cu(II) orbital and a half-full $d_{x^2-y^2}$ orbital through a μ-oxide.[30] The J2 and J3 values are both weak, and antiferromagnetic, as expected by examination of the structural parameters. Similar values have been reported by Baskar et al. for similar Cu-phosphonate complexes.[12] Clearly, the worst agreement is that of **3** where the intermolecular interaction is 0.90 cm^{-1}. J' is of the same order of magnitude as J2 and J3; thus, the perturbational treatment applied is not the most appropriate in this case, but it is the best approximation possible, since a chain of Cu$_6$ clusters cannot be modeled. Magnetization versus field data was collected at 2 K for all the three samples. The magnetization versus field plots are shown in Figure 5 and they indicate $S = 1$ as the ground state for the three complexes. As can be clearly seen, magnetization does not saturate, indicating the presence of excited states low lying in energy. This fact is in agreement with the susceptibility data fitting results, which predict the first and second excited states at less than 5 cm^{-1} from the spin ground state. The solid line is the Brillouin function for $S = 1$ and $g = 2.0$, the ground-state predicted by the fitting of the susceptibility data. The $S = 1$ ground state of the hexanuclear Cu complexes can be easily rationalized, as shown in Scheme 1, where the spin on each Cu(II) ion is pictured as an arrow. J1 is larger in absolute value than J2 and J3. With J1 being ferromagnetic, a central $S = 1$ unit resulting from the ferromagnetic coupling of two Cu(II) ions with $S = 1/2$ dominates the magnetic properties of complexes **1**, **2**, and **3**. The exchange constants J2 and J3 are of the same order and antiferromagnetic, thus leading to an $S = 1$ spin ground-state with low lying excited states, as seen experimentally with the magnetization data.

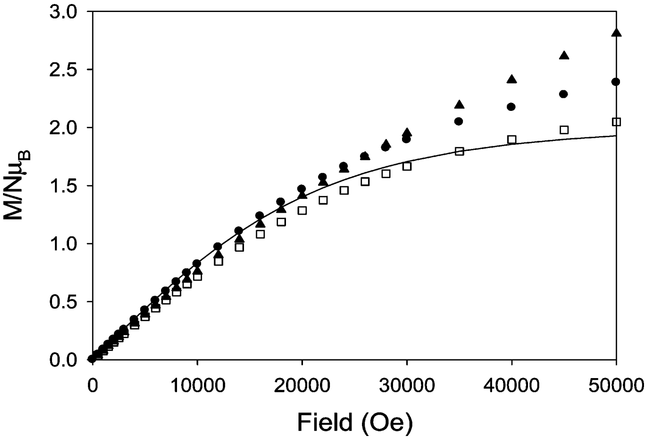

Figure 5. Magnetization vs field plot at 2.0 K for **1** (circles), **2** (squares), and **3** (triangles). The solid line is the Brillouin function for $S = 1$ and $g = 2.0$.

Conclusion

In summary, we have developed a new synthetic strategy involving the reaction of Cu(ClO$_4$)$_2$·6H$_2$O with cyclopentylphosphonic acid and 1,10-phenanthroline (phen) or 2,2′-bipyridine for assembling the hexanuclear copper(II) complex [Cu$_6$(C$_5$H$_9$PO$_3$)$_4$(1,10-phen)$_6$(MeOH)$_4$](ClO$_4$)$_4$ (**1**). The chelating ligand blocks two coordination sites on each copper atom while four tridentate phosphonate ligands allow six copper centers to be stitched together. The two pairs of copper centers in **1** contain labile methanol ligands which can be replaced by 1,3-bis(4-pyridyl)propane (bpp) to afford [Cu$_6$-

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[29] Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *(Magpack Software) J. Comp. Chem.* **2001**, *2*, 2985.

[30] Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993; p 26.

$(C_5H_9PO_3)_4(1,10\text{-phen})_6(\text{bpp})_2](ClO_4)_4$ (**2**) where the pincer-like bipyridine ligand acts as a stopper to close both ends of the open hexanuclear cage. On the other hand treatment of the in situ generated $[Cu_6(C_5H_9PO_3)_4(2,2'\text{-bpy})_6(\text{MeOH})_4](ClO_4)_4$ with the rigid ligand, 4,4′-bipyridine, results in the formation of a rail-road-like one-dimensional polymer $[\{Cu_6(C_5H_9PO_3)_4(2,2'\text{-bpy})_6(4.4'\text{-bpy})_2\}(ClO_4)_4]_n$ (**3**). The magnetic behavior of **1**−**3** was modeled using a full-matrix diagonalization method, showing that the hexanuclear Cu(II) complexes display an $S = 1$ spin ground state with low lying excited states.

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Supporting Information Available: Scheme S1, Charts S1 and S2, Figures S1−S3, and Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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