

# Synthesis and Characterization of High Nuclearity Iron(III) Phosphonate Molecular Clusters

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Three new phosphonic acid ligands (4-*t*-butylphenyl phosphonic acid, 3,5-dimethylphenyl phosphonic acid, and diphenylmethylphosphonic acid) have been synthesized and employed in search of high molecularity iron(III) clusters. The cluster compounds are characterized by single crystal X-ray diffraction and magnetic measurements. The solvothermal reaction of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with diphenylacetic acid and p-*t*-butylphenyl phosphonic acid resulted in an unprecedented dodecanuclear cluster  $[\text{Fe}_{12}(\mu_2\text{-O})_4(\mu_3\text{-O})_4(\text{O}_2\text{CCHPh}_2)_{14}(4\text{-}t\text{-BuPhPO}_3\text{H})_6](1)$  having a double butterfly like core structure.  $[\text{Fe}_{12}(\mu_2\text{-O})_4(\mu_3\text{-O})_4(\text{O}_2\text{CPh})_{14}(\text{C}_{10}\text{H}_{17}\text{PO}_3\text{H})_6](2)$ , another dodecanuclear cluster having core structure similar to 1, has been synthesized in a reaction between  $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6(\text{H}_2\text{O})_3]\text{Cl}$  and camphylphosphonic acid in the presence of triethylamine at ambient condition. 3,5-Dimethylphenyl phosphonic acid reacting solvothermally with an oxo-centered iron triangle  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3]\text{Cl}$  gives a nonanuclear cluster  $[\text{Fe}_9(\mu_3\text{-O})_4(\text{O}_3\text{PPh}(\text{Me})_2)_3(\text{O}_2\text{CCMe}_3)_3](3)$  having icosahedral type core structure where three positions of the iron atoms have been replaced by phosphorus. Another nonanuclear  $[\text{Fe}_9(\text{O})_3(\text{OH})_3(\text{O}_3\text{PCHPh}_2)_6(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3](4)$ , having a distorted cylindrical core structure, has been synthesized in a similar solvothermal reaction between  $[\text{Fe}_3\text{O}(\text{O}_2\text{CCMe}_3)_6(\text{H}_2\text{O})_3]\text{Cl}$  and biphenylmethyl phosphonic acid. All compounds are characterized by IR spectra, elemental analysis, as well as single crystal X-ray analysis. Magnetic measurements for all the compounds reveal that there are antiferromagnetic interactions between the metal centers.

## Introduction

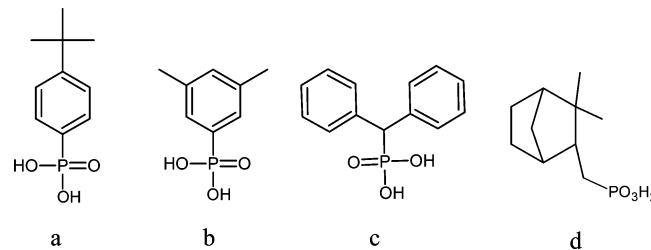
Synthesis and characterization of molecular clusters are among the most important areas of inorganic as well as materials chemistry research. The reason is their relevance to two fields, bioinorganic chemistry<sup>1,2</sup> and molecular materials science.<sup>3,4</sup> Iron-oxo centers are found in several

nonheme metalloproteins, for example, hemerythrin, ribonucleotide reductase, and methane monooxygenase. In most living organisms, iron is stored in the protein ferritin which can contain up to about 4500 Fe<sup>III</sup> ions in a polymeric oxo hydroxo lattice. The search for large clusters of paramagnetic transition metal ions has also been stimulated by the discovery of single-molecule magnetism.<sup>5</sup> High nuclearity transition metal clusters with appropriate topologies can

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sometimes possess large ground-state spin ( $S$ ) values and can even occasionally function as single-molecule magnets (SMMs). Numerous transition metal cluster compounds have been reported in the literature synthesized using carboxylates or alkoxides as ligand.<sup>6</sup> But, there are two major difficulties in the use of phosphonate ligands for making transition metal clusters. One is their unique tendency to form layered structures and the other is the restricted solubility of the product compound. Often they form insoluble or intractable compounds. Recently a few papers have reported<sup>7</sup> on transition metal-phosphonate clusters mainly by Winpenny and co-workers,<sup>7b–f</sup> as well as a few other groups including ours.<sup>7h</sup> The first problem has been solved by using some presynthesized small clusters as a starting material, and the solubility problem has been taken care of by incorporating some coligand like carboxylate, in addition to the phosphonates, to increase the organic part of the compound. This paper reports the synthesis of three new phosphonic acid ligands (4-*t*-butylphenyl phosphonic acid[4-*t*-buPhPO<sub>3</sub>H<sub>2</sub>], 3,5-dimethylphenyl phosphonic acid[H<sub>2</sub>O<sub>3</sub>PPh(Me)<sub>2</sub>], and diphenylmethylphosphonic acid [Ph<sub>2</sub>CHPO<sub>3</sub>H<sub>2</sub>], Scheme 1a,b,c, respectively) following Arbuzov<sup>8</sup> and Michalis-Arbuzov reactions.<sup>9</sup> Two structurally analogous dodecanuclear iron-phosphonate cluster compounds having molecular formula

**Scheme 1.** Schematic Drawing of the Phosphonic Acid Ligands**Table 1.** Crystallographic Data For 1–4

	1	2	3	4
crystal system	triclinic	triclinic	triclinic	triclinic
empirical	C <sub>266</sub> H <sub>245</sub> Fe <sub>12</sub>	C <sub>158</sub> H <sub>182</sub> Fe <sub>12</sub>	C <sub>90</sub> H <sub>146</sub> C <sub>12</sub>	C <sub>118</sub> H <sub>184</sub> Fe <sub>9</sub>
formula	N <sub>5</sub> O <sub>6</sub> P <sub>6</sub>	O <sub>5</sub> P <sub>6</sub>	Fe <sub>9</sub> O <sub>41</sub> P <sub>3</sub>	N <sub>5</sub> O <sub>53</sub> P <sub>6</sub>
space group	P\bar{1}	P\bar{1}	P\bar{1}	P\bar{1}
a [Å]	20.777(3)	16.408(4)	16.354(4)	15.8291(19)
b [Å]	22.558(3)	17.026(4)	16.243(2)	18.960(5)
c [Å]	30.174(5)	19.956(7)	27.438(3)	27.402(7)
α [°]	78.142(3)	109.105(4)	73.260(2)	72.051(3)
β [°]	88.054(3)	105.886(4)	80.522(2)	88.824(3)
γ [°]	88.211(3)	105.955(3)	61.460(2)	74.839(3)
V [Å <sup>3</sup> ]	13828(4)	4641(2)	5931.9(12)	7785(4)
Z	2	1	2	2
T (K)	110	110	110	110
wavelength [Å]	0.71073	0.71073	0.71073	0.71073
D (cal.)	1.286	2.044	1.787	2.155
reflns.	85727	38796	49182	65357
ind. reflns				
reflns.	39992	13554	17341	22728
with	21610	9105	10889	18976
[I > 2σ(I)]				
gof on F <sup>2</sup>	1.024	1.067	1.057	1.043
final R indices	R <sub>1</sub> =	R <sub>1</sub> =	R <sub>1</sub> =	R <sub>1</sub> =
[I > 2σ(I)] <sup>a</sup>	0.0860	0.0755	0.0724	0.0652
wR <sub>2</sub>	wR <sub>2</sub> =	wR <sub>2</sub> =	wR <sub>2</sub> =	wR <sub>2</sub> =
	0.2349	0.2434	0.1840	0.1943

<sup>a</sup>  $R_1 = (\sum |F_o| - |F_c|)/\sum |F_o|$ ;  $wR_2 = \{\sum [(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]\}^{1/2}$ , where  $w = 1/[\delta^2(F_o^2) + (aP)^2 + bP]$  and  $P = [\max(0, F_o^2) + 2F_c^2]/3$ .

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## Experimental Section

**Materials and Methods.** The starting materials FeCl<sub>3</sub>, 1-bromonaphthalene 1,3-diisopropylbenzene, triethyl phosphate, 1-bromo-4-*t*-butyl benzene, 1-bromo-3,5-dimethylbenzene, and diphenylmethyl bromide were obtained from Aldrich. Camphyl phosphonic acid was obtained from Donjindo chemicals company, Japan. It was recrystallized before using. Elemental analyses were done by Robertson Microlit Laboratories, Madison, NJ. Infrared (IR) spectra were measured as KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer with spectral resolution of 2.00 cm<sup>-1</sup>. Magnetic susceptibility and magnetization measurements were carried out on

a Quantum Design SQUID magnetometer MPMS-XL. Direct current magnetic measurements were performed with an applied field of 1000 G in the 2–300 K temperature range. Diamagnetic corrections were made from the Pascal constants.<sup>5a</sup>

**X-ray Crystallography.** Data collection of the compounds were performed at 110 K on a Bruker Smart CCD-1000 diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation using a cold nitrogen stream (Oxford). Data reduction and cell refinements were performed with the SAINT program,<sup>10</sup> and the absorption correction program SADABS<sup>11</sup> was employed to correct the data for absorption effects. Crystal structures were solved by direct methods and refined with full-matrix least-squares (SHELXTL-97)<sup>12</sup> with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The crystallographic data are summarized in Table 1. SHELXTL, Mercury, and Diamond software programs were used to visualize the structures. The waters of crystallization in all molecules were not assigned any hydrogen atoms. For **2**, two of the phenyl rings of the carboxylic acid are disordered in two positions and occupancies were refined. The disordered parts are omitted from the diagrams. The camphyl phosphonic acid ligands in **2** are also disordered, which is common for this type of big organic alkyl moiety.

**Synthesis of Ligands. 4-Butylphenylphosphonic Acid.** 1-Bromo-4-tert-butyl benzene (1.06 g, 5.0 mmol) in 1,3-diisopropylbenzene (10 mL, distilled under atmospheric pressure before use) and triethyl phosphite (2 mL, 11.7 mmol as the first addition and 1 mL, 5.6 mmol as the second addition after 24 h) were coupled using NiBr<sub>2</sub> (0.10 g, 0.46 mmol as the first addition and 0.05 g, 0.23 mmol as the second addition) at 160–165 °C under nitrogen for 48 h. 1,3-Diisopropylbenzene and excess of triethyl phosphite were distilled off under a reduced pressure to obtain a viscous oil which was characterized as 4-butyl-diethylphenylphosphonate (0.915 g, 68%).

p-Butyl-diethylphenylphosphonate was refluxed with 6 M HCl and hydrolyzed to p-Butylphenylphosphonic acid. The phosphonate ester as well as the acid was characterized by <sup>1</sup>H NMR and ESI mass spectra.

**3,5-Dimethylphenylphosphonic Acid.** 1-Bromo-3,5-dimethylbenzene (1.85 g, 10.0 mmol) in 1,3-diisopropylbenzene (15 mL, distilled under atmospheric pressure before use) and triethyl phosphite (2.5 mL, 14.7 mmol as the first addition and 1 mL, 6 mmol as the second addition after 24 h) were coupled using NiBr<sub>2</sub> (0.20 g, 0.92 mmol as the first addition and 0.10 g, 0.46 mmol as the second addition) at 180–185 °C under nitrogen for 48 h. 1,3-Diisopropylbenzene and excess of triethyl phosphite were distilled off under a reduced pressure to obtain a viscous oil. The product ester was refluxed with 6 M HCl and hydrolyzed to 3,5-dimethylphenylphosphonic acid. The phosphonate ester as well as the acid was characterized by <sup>1</sup>H NMR and ESI mass spectra. Final yield was 1.43 g, 71%.

**Diphenylmethylphosphonic Acid.** A mixture of biphenylmethylbromide (2.47 g, 10 mol) and triethyl phosphite (22.6 g, 0.135 mol) was heated for 6 h at 165 °C under a gentle stream of nitrogen. After cooling down, excess triethylphosphite and ethylbromide (generated as byproduct) were distilled off. Then, the crude product was refluxed with 6 M HCl to be hydrolyzed to the final product diphenylmethylphosphonic acid. The acid was recrystallized from aqueous MeOH. The phosphonate ester, as well as the acid, was characterized by <sup>1</sup>H NMR and ESI mass spectra. Final yield was 2.1 gm, 90%.

(10) SAINT, Program for Reduction of Area Detector Data, V6.63; BRUKER AXS Inc.: Madison, WI.

(11) Sheldrick, G. SADABS, Program for Absorption Correction of Area Detector Frames; BRUKER AXS Inc.: Madison, WI.

[Fe<sub>3</sub>O(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl and [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl were prepared by a literature method.<sup>13</sup>

**Synthesis of 1.** FeCl<sub>3</sub>•6H<sub>2</sub>O (0.32 g, 2.0 mmol), diphenylacetic acid (0.45 g, 4.0 mmol), 4-butylphenyl phosphonic acid (0.21 g, 1.0 mmol), and triethylamine (0.50 g, 5.0 mmol) in methanol were placed in a Teflon-lined steel autoclave and heated at 125 °C for 18 h. The product brown powder was filtered out, washed thoroughly with methanol, and air-dried. The yield of the reaction was ~25% (non optimized). The compound was then dissolved in an acetonitrile–dichloromethane (1:1) mixture, and the final solution was kept at room temperature. X-ray quality single crystals had grown after a few days. Elemental analysis calcd (%) for C<sub>266</sub>H<sub>245</sub>Fe<sub>12</sub>N<sub>5</sub>O<sub>62</sub>P<sub>6</sub>: C 59.60, H 4.60, N 1.30; found: C 58.95, H 4.55, N 1.78. Selected IR data (KBr pellet): 3425(br), 2932 (m), 2860(m), 1583(w), 1442(w), 1278(w), 1226(m), 1055(s), 787(m), 795(m), 573(m), 463(s) cm<sup>-1</sup>.

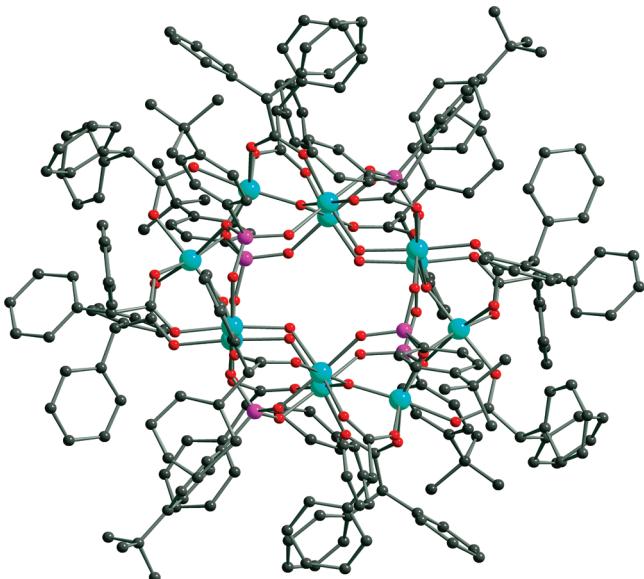
**Synthesis of 2.** [Fe<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl (0.099 g, 0.10 mmol), camphyl phosphonic acid (0.022 mg, 0.1 mmol), and triethylamine (0.01 g, 0.1 mmol) were added to CH<sub>3</sub>CN (5 mL), and the solution was stirred overnight. The red-orange solution was filtered, and Et<sub>2</sub>O (5 mL) was added before it was allowed to evaporate slowly at 4 °C. Red crystals were collected after a few days. Yield of the reaction was ~50% (on the basis of Fe). Elemental analysis calcd (%) for C<sub>158</sub>H<sub>182</sub>Fe<sub>12</sub>O<sub>56</sub>P<sub>6</sub>: C 49.50, H 4.78; found: C 49.85, H 4.19. Selected IR data (KBr pellet): 3419(br), 2942(m), 2853(m) 1573(w), 1446(w), 1279(w), 1232(m), 1051(s), 783(m), 796(m), 577(m), 460(s) cm<sup>-1</sup>.

**Synthesis of 3.** [Fe<sub>3</sub>O(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl (0.86 g, 1.0 mmol) and 3,5-dimethylphenylphosphonic acid (0.065 g, 0.3 mmol) and MeOH (9 mL) were placed in a sealed Teflon-lined steel container and heated for 12 h at 125 °C. The product, a brown powder, was filtered out, washed thoroughly with methanol, and air-dried. The yield of the reaction was ~85%. The compound was then dissolved in an acetonitrile–dichloromethane (1:1) mixture, and the final solution was kept at 4 °C. X-ray quality single crystals were grown after a few days. Elemental analysis calcd (%) for C<sub>90</sub>H<sub>146</sub>C<sub>12</sub>Fe<sub>9</sub>O<sub>41</sub>P<sub>3</sub>: C 42.38, H 5.77; found: C 42.65, H 5.53. Selected IR data (KBr pellet): 2924(w), 2830(m) 1553(w), 1452(w), 1273(w), 1232(m), 1065(s), 750(m), 570(m) cm<sup>-1</sup>.

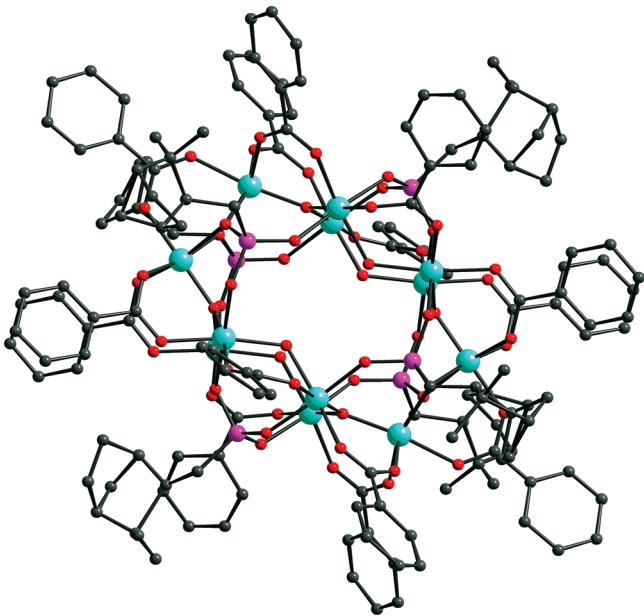
**Synthesis of 4.** [Fe<sub>3</sub>O(O<sub>2</sub>CCMe<sub>3</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl (0.86 g, 1.0 mmol) and biphenylmethyl phosphonic acid (0.025 g, 0.1 mmol) were placed in a sealed Teflon-lined steel container and heated for 12 h at 125 °C. The product, a brown powder, was filtered out, washed thoroughly with methanol, and air-dried. The yield of the reaction was ~45%. The compound was then dissolved in a methanol–acetonitrile (1:1) mixture, and the final solution was kept at room temperature. Red crystals were collected from solution after few days. Elemental analysis calcd (%) for C<sub>118</sub>H<sub>184</sub>Fe<sub>9</sub>N<sub>5</sub>O<sub>53</sub>P<sub>6</sub>: C 44.19, H 5.72, N 2.18; found: C 44.05, H 5.19, N 2.09. Selected IR data (KBr pellet): 3427(s), 2936(m), 2860(m), 1579(w), 1442(w), 1282(w), 1227(m), 1055(s), 797(m), 573(m), 463(s) cm<sup>-1</sup>.

## Results and Discussions

**Synthesis.** Reaction of the oxo-centered iron triangle with phosphonic acids generated a series of high nuclearity clusters. The structure of the final product cluster compounds were profoundly affected by the starting oxo-centered triangle. We also discuss a new one step route for synthesizing iron-phosphonate clusters starting from an inorganic iron salt (FeCl<sub>3</sub>). Our attempt to synthesize **1** at ambient condition (following the same route as taken for **2**) failed as the precursor [Fe<sub>3</sub>O(O<sub>2</sub>CCHPh<sub>2</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl is not soluble in most of

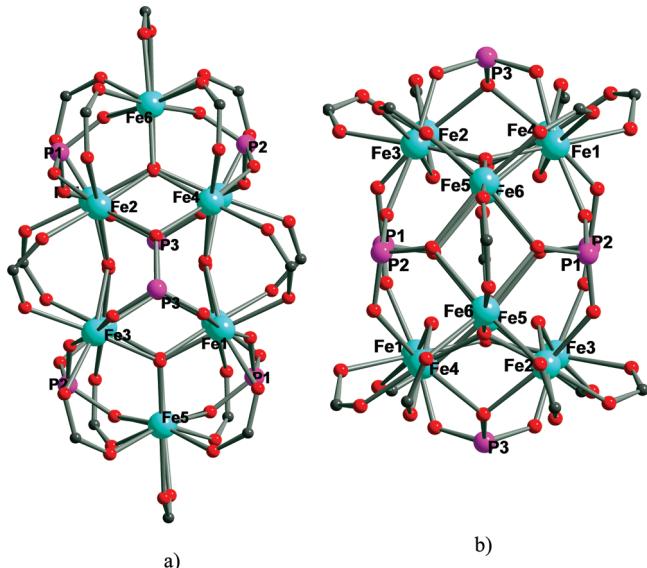


**Figure 1.** Molecular structure of **1** in the crystal. Color code: cyan, iron; purple, phosphorus; red, oxygen; grey, carbon. Hydrogen atoms are omitted for clarity.

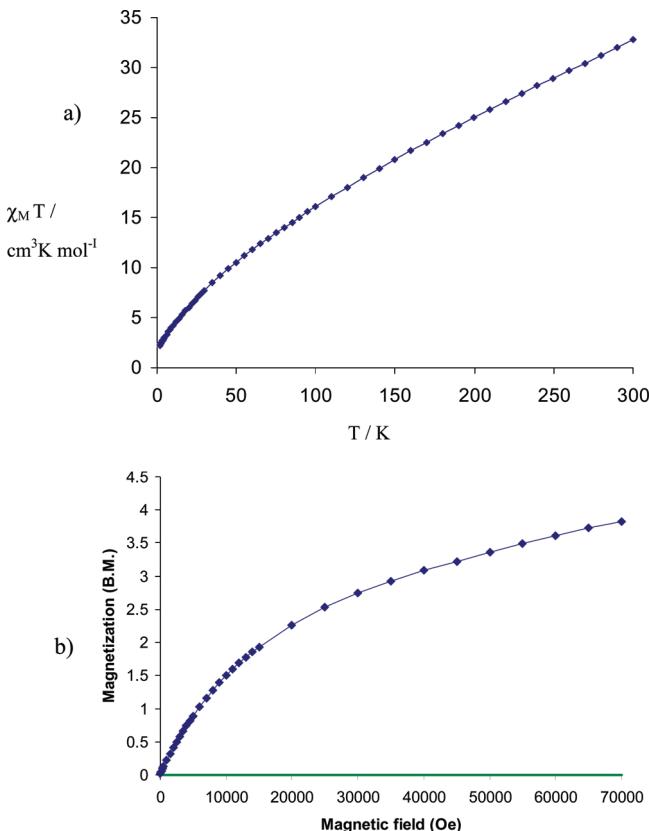


**Figure 2.** Molecular structure of **2** in the crystal. Color code: cyan, iron; purple, phosphorus; red, oxygen; grey, carbon. Hydrogen atoms are omitted for clarity.

the common organic solvents. In another attempt, the reaction of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , diphenylacetic acid, 4-tbutylphenyl phosphonic acid, and triethylamine in methanol at room temperature resulted in a brown oil. Recently we have reported a nonanuclear cluster,  $[\text{Fe}_{12}(\text{O})_2(\text{OH})(\text{O}_2\text{CPh})_{10}(\text{C}_{10}\text{P})_6(\text{H}_2\text{O})_2] \cdot (\text{CH}_3\text{CN})_7^{\text{th}}$  formed on reaction between  $[\text{Fe}_3\text{O}(\text{O}_2\text{CPh})_6 \cdot (\text{H}_2\text{O})_3]\text{Cl}$  and camphylphosphonic acid. Interestingly, the addition of a small amount of triethylamine in the same synthesis resulted in a novel dodecanuclear cluster  $[\text{Fe}_{12}(\mu_2\text{-O})_4(\mu_3\text{-O})_4(\text{O}_2\text{CPh})_{14}(\text{C}_{10}\text{H}_{17}\text{PO}_3\text{H})_6](\text{2})$ . The small amount of triethylamine added during the synthesis does not effectively change the pH of the solution but rather played an important role to change the mechanism of the reaction and thereby yielded a new compound. Attempts to synthesize **3**



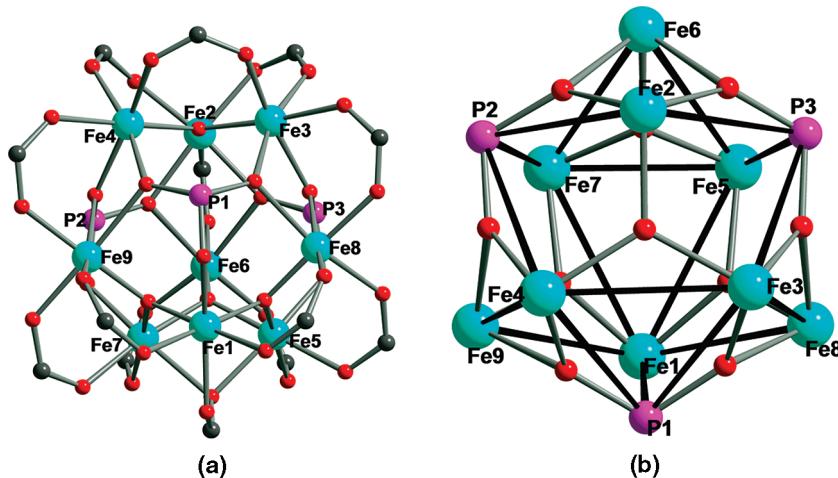
**Figure 3.** Core structure of **1** and **2**. (a) One “butterfly” overlapped another. (b) Two “butterfly” units face-to-face sharing four phosphonates and two carboxylate ligands. Color code same as in Figure 1.



**Figure 4.** (a) Temperature dependence of  $\chi_M T$  for a powder sample of **1** and (b) magnetization curve for **1** (measured at 2 K).

and **4** at room temperature resulted in no reaction at all for **3** and less than 5% yield for **4**.

**Crystal Structure and Magnetic Measurements.**  $[\text{Fe}_{12}(\mu_2\text{-O})_4(\mu_3\text{-O})_4(\text{O}_2\text{CCHPh}_2)_{14}(4\text{-tBuPhPO}_3\text{H})_6]$  (**1**) and  $[\text{Fe}_{12}(\mu_2\text{-O})_4(\mu_3\text{-O})_4(\text{O}_2\text{CPh})_{14}(\text{C}_{10}\text{H}_{17}\text{PO}_3\text{H})_6]$  (**2**). The core structure of both compounds is similar, which can be best described as an  $\text{Fe}_{12}$  central core wrapped in a hydrophobic sheath of alkyl or aryl groups (Figures 2). The central  $\text{Fe}_{12}$  core is



**Figure 5.** (a) Core structure of **3**. (b) Icosahedral view of the core. Unlabeled atoms are oxygen atoms.

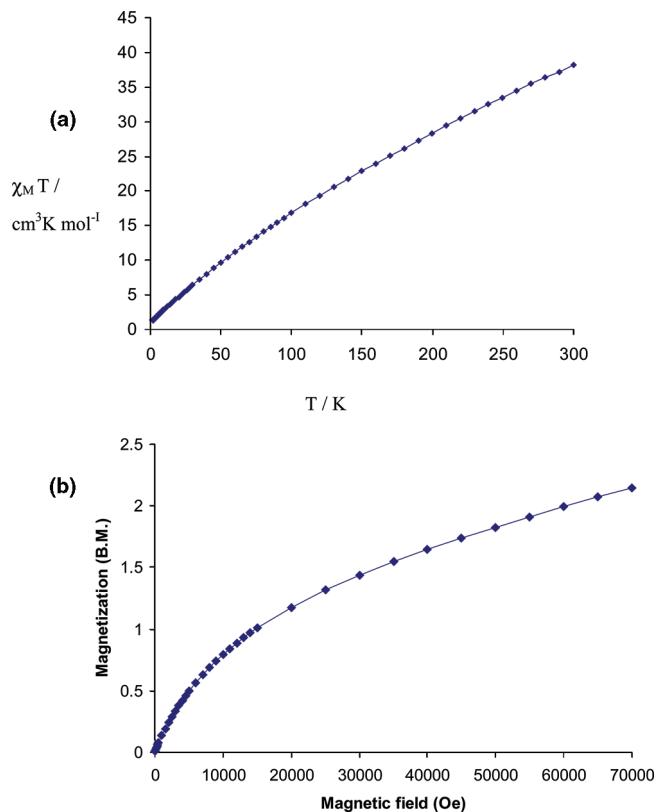
formed by the attachment of two symmetry related  $\text{Fe}_6$  units. Each  $\text{Fe}_6$  unit has a butterfly type shape formed by two  $\text{Fe}_3\text{O}$  triangles (Figure 3a). The body of the butterfly consists of four  $\text{Fe}^{\text{III}}$  ions, two of each are from two triangles and are connected by a phosphonate group having 4.211 binding mode [Harris Notation],<sup>14</sup> two  $\mu_2$ -oxo and two carboxylate ligands (Figure 3b). These four  $\text{Fe}^{\text{III}}$  ions ( $\text{Fe}1$ ,  $\text{Fe}2$ ,  $\text{Fe}3$ ,  $\text{Fe}4$ ) form a rectangle with  $\text{Fe}-\text{Fe}$  distances ranging from  $3.083(4)$  Å to  $3.522(4)$  Å (for **1**) and  $3.078(5)$  Å to  $3.568(5)$  Å (for **2**). The remainder of the two  $\text{Fe}^{\text{III}}$  ions ( $\text{Fe}5$ ,  $\text{Fe}6$ , one from each triangle) of the  $\text{Fe}_6$  unit do not lie in the same plane with the rectangle. They are displaced toward and bonded with the other  $\text{Fe}_6$  unit through phosphonate groups as well as through two carboxylate ligands and thereby form a highly puckered cyclic molecule. Interestingly, all the phosphonate groups in both compounds are singly protonated with a long ( $1.546(6)$ – $1.566(6)$  Å)  $\text{P}-\text{O}$  bond. The magnetic measurements for **1** are shown in the form of  $\chi_M T$  ( $\chi_M$  is the molecular magnetic susceptibility) versus temperature ( $T$ ) plot in Figure 4a. The room temperature  $\chi_M T$  value for **1** is  $31.2 \text{ cm}^3 \text{ K mol}^{-1}$ , which is much less than the calculated value  $52.5 \text{ cm}^3 \text{ K mol}^{-1}$  ( $g = 2$ ) for isolated twelve  $\text{Fe}^{\text{III}}$  centers. This may be due to the presence of a strong intramolecular antiferromagnetic interaction in the molecule. The  $\chi_M T$  values decrease smoothly on lowering the temperature, indicating the presence of antiferromagnetic interaction between the metal centers. The magnetization experiment (at 2 K) does not show any saturation even at the highest field measured (Figure 4b). This behavior could be due to having low-lying excited states which become populated at higher field. Compound **2** has shown magnetic behavior similar to **1**. The  $\chi_M T$  versus  $T$  plot and the magnetization curve are given in the Supporting Information.

[ $\text{Fe}_9(\mu_3\text{-O})_4(\text{O}_3\text{PPh}(\text{Me})_2)_3(\text{O}_2\text{CCMe}_3)_{13}$ ] (**3**). The core structure of **3** could be best described as a combination of two fragments, an oxo-centered triangle [ $\text{Fe}2$ ,  $\text{Fe}3$ ,  $\text{Fe}4$ , see

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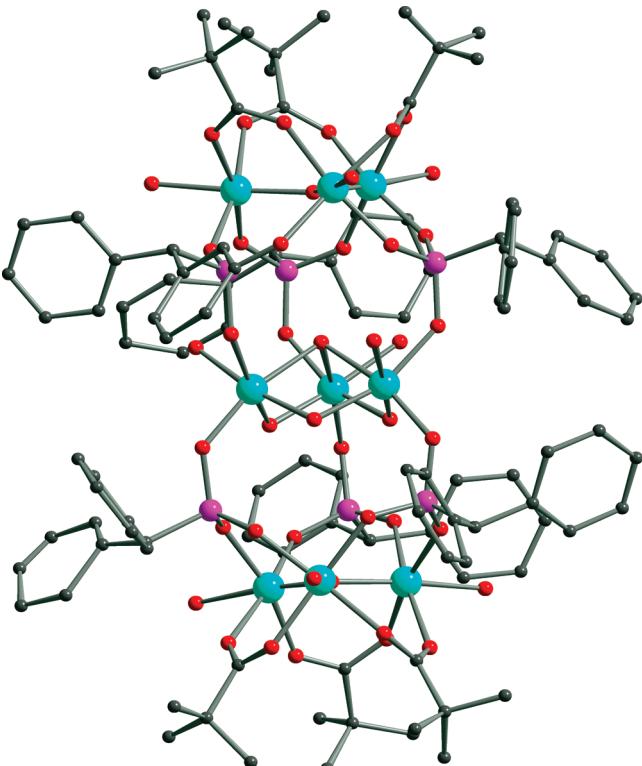
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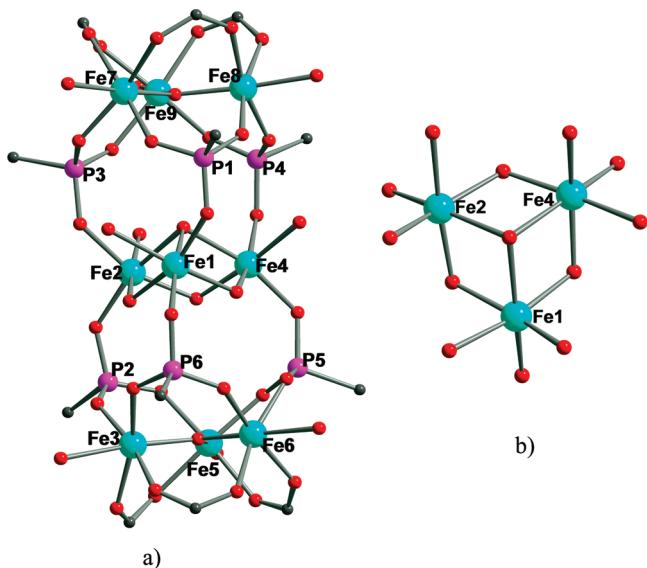


**Figure 6.** (a) Temperature dependence of  $\chi_M T$  for a powder sample of **3** and (b) magnetization curve for **3** (measured at 2 K).

Figure 5a] bonded with a  $[\text{Fe}_6\text{O}_3]$  subunit formed by three edge sharing  $\text{Fe}_3\text{O}$  triangles through three phosphonate ligands. A better picture might be available after removing all the carbons and hydrogens (Figure 5b). Each phosphorus is surrounded by five neighboring irons, and each iron is surrounded by five atoms (includes both iron and phosphorus) and thereby forms an  $\text{Fe}_9\text{P}_3$  icosahedron. Two compounds having similar core structures with different phosphonic acids have been reported elsewhere.<sup>7f,h</sup> Figure 6a shows the  $\chi_M T$  versus  $T$  plot for **3**.  $\chi_M T$  has a value of  $38.2 \text{ cm}^3 \text{ K mol}^{-1}$  at  $300 \text{ K}$  which is very close to the spin-only value of  $39.4 \text{ cm}^3 \text{ K mol}^{-1}$  (for  $g = 2$ ) as expected for a nine quasi-isolated  $\text{Fe}^{\text{III}}$  center.  $\chi_M T$  starts to decrease gradually upon decreasing

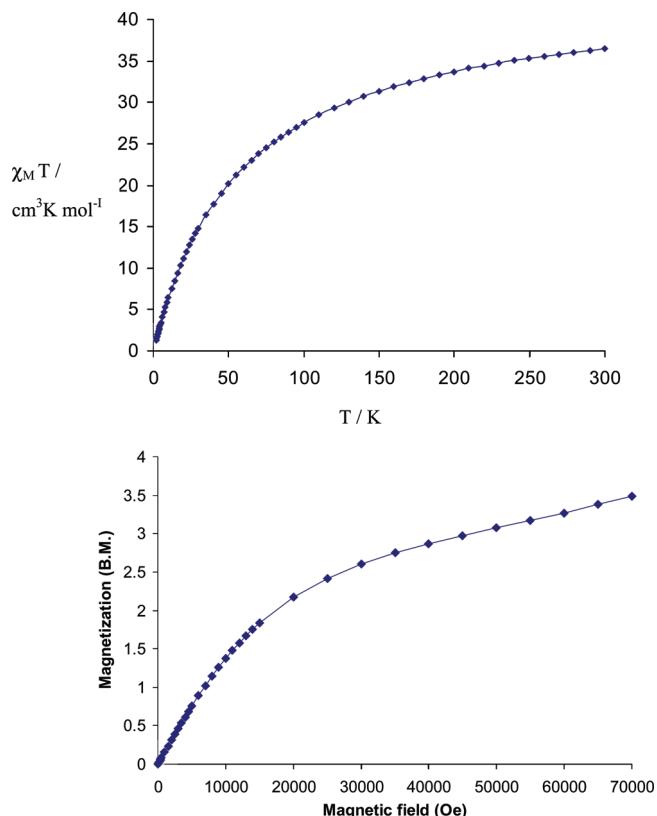


**Figure 7.** Molecular structure of **4** in the crystal. Color code: cyan, iron; purple, phosphorus; red, oxygen; grey, carbon. Hydrogen atoms are omitted for clarity.



**Figure 8.** (a) Core structure of **4**. Color code: same as in Figure 7. (b) View of the central triangle.

the temperature as expected for antiferromagnetically coupled metal centers and reaches a minimum value of  $0.791 \text{ cm}^3 \text{ K mol}^{-1}$  at 2.0 K. The magnetization experiment (at 2 K) does not show any saturation even at the highest field measured (Figure 6b) as expected for this type of compound. The magnetic susceptibility of **3** was also measured in zero applied field down to temperatures as low as 1.4 K by the use of an alternating current (ac) susceptometer, but no imaginary component of the ac susceptibility was observed.



**Figure 9.** (a) Temperature dependence of  $\chi_M T$  for a powder sample of **4**; (b) magnetization curve for **4** (measured at 2 K).

[ $\text{Fe}_9(\mu_3\text{-O})_3(\mu_2\text{-OH})_3(\text{O}_3\text{PCHPh}_2)_6(\text{O}_2\text{CMe}_3)_6$ ] (**4**). The structure consists of a total of three iron triangles, of which two  $\mu_3$ -oxo centered triangles are symmetrically linked to another one at the middle by three phosphonate groups from each side (Figure 7). The edges of the peripheral triangles are bridged by a carboxylate group, as well as a phosphonate ligand, of which the third oxygen is bound to the triangle at the middle from both sides and thereby form a distorted cylindrical core structure (Figure 8a). The edges of the central triangles are bridged by  $\mu_2$ -OH groups and capped by a  $\mu_3$ -oxo group. Interestingly, the  $\mu_3$ -oxo group does not lie on the same plane with the triangle as revealed for most of the iron  $\mu_3$ -oxo compounds reported so far (Figure 8b). They are out of plane and pointing toward the opposite side of the  $\mu_2$ -OH groups. All nine  $\text{Fe}^{III}$  sites of the molecule retained a coordinated water molecule from the precursor.

Figure 9a shows the  $\chi_M T$  versus  $T$  plot for **4**.  $\chi_M T$  has a value of  $36.45 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K which is very close to the spin-only value of  $39.4 \text{ cm}^3 \text{ K mol}^{-1}$  (for  $g = 2$ ) as expected for a nine quasi-isolated  $\text{Fe}^{III}$  center.  $\chi_M T$  starts to decrease gradually upon decreasing the temperature as expected for antiferromagnetically coupled metal centers and reaches a minimum value of  $1.37 \text{ cm}^3 \text{ K mol}^{-1}$  at 2.0 K. Similar to the other two compounds, a magnetization experiment (at 2 K) does not show any saturation even at the highest field measured (Figure 9b) as expected.

## Conclusion

Solvothermal techniques were originally used and developed by geochemists to mimic mineral growth and have long

been used for crystallization of inorganic materials.<sup>15</sup> Recently, several papers have reported on the solvothermal synthesis of molecular cluster compounds.<sup>16</sup> But this technique is not well established for synthesizing high nuclearity molecular clusters using phosphonate as ligands. We have employed solvothermal chemistry in a very efficient way to synthesize and crystallize high nuclearity molecular phosphonate clusters directly from the reaction mixture in good yield. This paper also reports the hydrothermal synthesis of iron-phosphonate clusters for the first time. This propensity for the hydrothermal synthesis and crystal growth will be enormously important in cluster chemistry given the reliance on X-ray diffraction as the main tool for product identification. Preliminary magnetic data of the compounds (**1**, **3**, and

**4**) showed antiferromagnetic interaction between the metal centers. But the magnetization experiments for each of these compounds do not achieve saturation. According to Christou and co-workers,<sup>4b,c</sup> the energy gap for these types of high nuclearity clusters is small between the ground-state and the excited states which become populated at higher field and prevent any saturation. Finally, the present results illustrate once again the versatility and aesthetic beauty of the hydrothermal technique as well as metal–phosphonate chemistry.

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**Supporting Information Available:** X-ray crystallographic data in CIF format, tables with selected bond distances, and a figure showing magnetic properties for **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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