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A Direct Three-Component Reaction for the Isolation of a Nonanuclear Iron(III) Phosphonate

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The synthesis, structure, and magnetism of a nonanuclear iron(III) phosphonate, $[Fe_9^{III}(\mu_3\text{-}O)_4(O_3PC_5H_9)_3(O_2CCMe_3)_{13}]\cdot(EtOH)_{0.5}\cdot(Et_2O)_{0.5}$ (**1**), is described. Compound **1** was obtained in the direct reaction of anhydrous ferric chloride, cyclopentylphosphonic acid, and pivalic acid in the presence of triethylamine. Compound **1** possesses a distorted icosahedral structure; nine of the vertices are occupied by Fe^{III}, whereas three others are occupied by the phosphorus atoms of the cyclopentylphosphonate ligand. Mössbauer spectroscopy of **1** confirms the presence of high-spin Fe^{III}. Low-temperature magnetic studies reveal the presence of strong antiferromagnetic coupling between the Fe^{3+} ions.

Introduction

Organophosphonate ligands, $[RPO_3]^{2-}$, are proving to be extremely versatile in the preparation of polynuclear complexes.[1] Their use in the preparation of transition-metal phosphonate coordination polymers that possess extended structures is well established.[2] This is possible because of the multisite coordination capability of these ligands. This feature, which is so useful for the preparation of coordination polymers, is a handicap in isolating molecular complexes. To a large extent this disadvantage can be overcome by two general strategies or a combination of these strategies. The first strategy is to use an appropriate ancillary ligand along with the phosphonic acid.[1,3] The ancillary ligand blocks some of the coordination sites on the transition-metal ion, and therefore even though the phosphonate ligand is multisite-coordinating, it does not have the opportunity to take the structure into a coordination polymer because of the restricted number of coordination sites on the transition-metal ion. The second strategy is to increase the steric bulk on the phosphonic acid, and because of the spatial encumbrance, molecular complexes often result.[4] By utilizing these paradigms, several molecular transition- and main-group-metal phosphonates of varying nuclearity (1 to 36)[1,3–5] have now been prepared. Among the transition-metal ions, Cu^{II} has been the most widely investigated.[1,3–5] In comparison, Fe^{II} and Fe^{III} derivatives are still relatively few in number. A perusal of the literature revealed that only three nonanuclear Fe^{III} phosphonates – $[Fe_9(\mu_3\text{-}O)_4(O_3PPh)_3(O_2CCMe_3)_{13}]$, $[Fe_9(\mu_3\text{-}O)_4(O_2CCMe_3)_{13}(C_{10}PO_3)_3]$ [$C_{10}PO_3H_2$ = camphylphosphonic acid], and $[Fe_9(\mu_3\text{-}O)_4\{O_3PPh(Me)_2\}_3(O_2CCMe_3)_{13}]$ – are known thus far (Scheme 1).[6]

All these compounds were prepared by a cluster expansion strategy that involves the reaction of the trinuclear (Fe^{III}_3O core) ensemble with organophosphonic acids.[6] In view of our experience with $Cu^{II}/Mn^{II}/Mn^{II}–Mn^{III}/V^{III}/Co^{II}$ phosphonates,[1,3–5,7] we were curious to investigate the formation of iron(III) phosphonates in a direct three-component reaction. Surprisingly, in these studies, we were able to isolate only the nonanuclear complex $[Fe_9^{III}(\mu_3\text{-}O)_4(O_3PC_5H_9)_3(O_2CCMe_3)_{13}]\cdot(EtOH)_{0.5}\cdot(Et_2O)_{0.5}$ (**1**). The latter is structurally similar to those shown in Scheme 1. In addition to its synthesis, we describe herein the magnetism and Mössbauer studies of **1**.

Results and Discussion

Synthesis

The synthesis of polynuclear transition-metal complexes in general, and that of molecular transition-metal phosphonates in particular, are beset with some challenges. The most important of these is the ability to control the nuclearity of the complexes and to be able to predispose the

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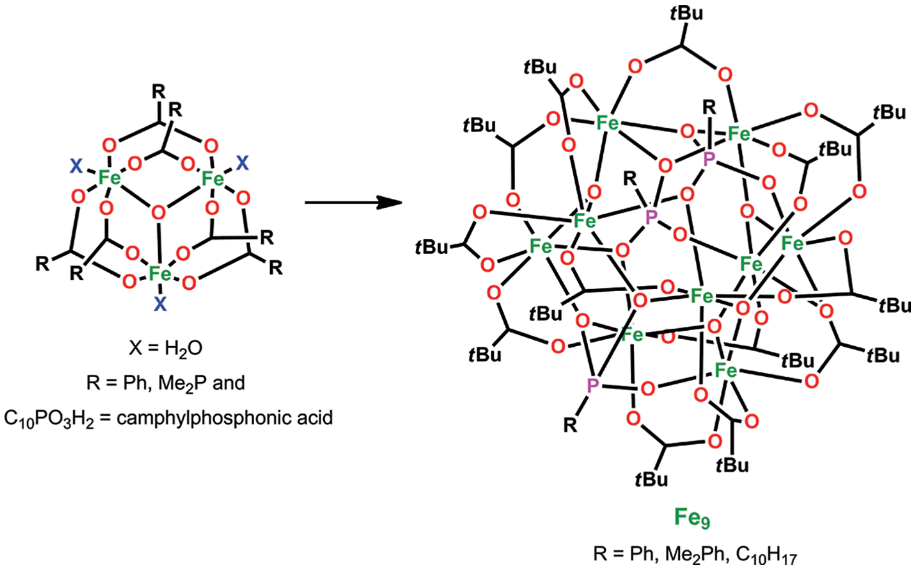
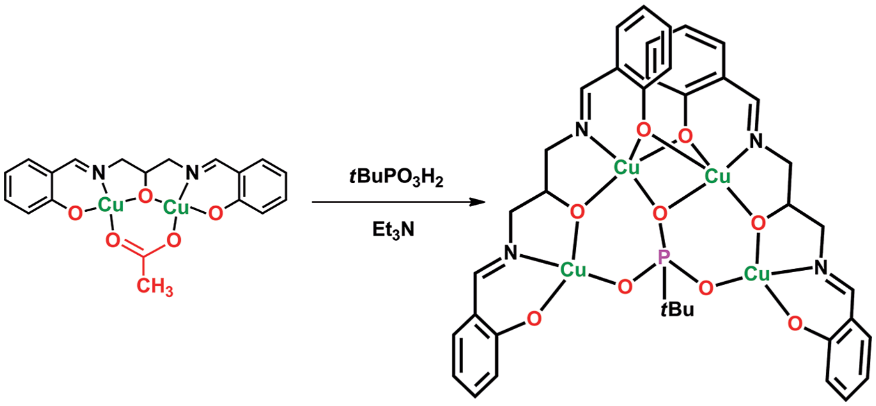


Scheme 1. Synthesis of nonanuclear iron(III) phosphonate complexes by cluster expansion.[6]



Scheme 2. Synthesis of a Cu_4 phosphonate by cluster expansion.[5e]

reaction conditions to deliver a specific product of a definite nuclearity and structure. Although this challenge remains far from solved, some strategies have been developed to address this problem.[1,3,4] An important synthetic strategy for obtaining specific polynuclear products is to utilize di- or trinuclear metal ensembles that contain some replaceable ligands as the building blocks.[6] Stitching these building blocks with appropriate multifunctional ligands can often lead to a polynuclear complex in which the structural integrity of the building block is preserved. Winpenny et al. in particular[6a] (Scheme 1), and to a smaller extent our own research group[5e] (Scheme 2), have shown the efficacy of this approach.

The second strategy is a direct multicomponent reaction that involves the metal salt, phosphonic acid, and an ancillary ligand.[3,5,7] On the face of it, this strategy seems to suffer from lack of control. However, by modulating the steric and electronic features of the ancillary ligands and the nature of the metal salt, it has been possible to tune the nuclearity, particularly in Cu^{II}[5d] and Mn^{II}[7a] phosphonates (Figure 1).

In view of this, we were interested to investigate the direct three-component reactions for preparing iron(III) phosphonates.

The reaction of anhydrous ferric chloride with cyclopentylphosphonic acid and pivalic acid in a 3:1:3 ratio in the presence of triethylamine afforded $[Fe_9^{III}(\mu_3\text{-}O)_4(O_3PC_5H_9)_3(O_2CCMe_3)_{13}]\cdot(EtOH)_{0.5}\cdot(Et_2O)_{0.5}$ (**1**) (Scheme 3; see the Exp. Sect.).

Several other reaction conditions that involve variations in the stoichiometry of the reactants were tried; we were unable to isolate crystalline products. In some cases, insoluble products were obtained that could not be characterized (see the Supporting Information). As already mentioned above, the other nonanuclear iron(III) phosphonate cages known in the literature have been prepared by the cluster expansion strategy. A summary of the various reaction conditions and the concise structural features of all the nonanuclear iron(III) phosphonate complexes are summarized in Table 1.

Compound **1** crystallizes in the monoclinic system and $P2_1/c$ space group. A comparison of the crystal data of **1**

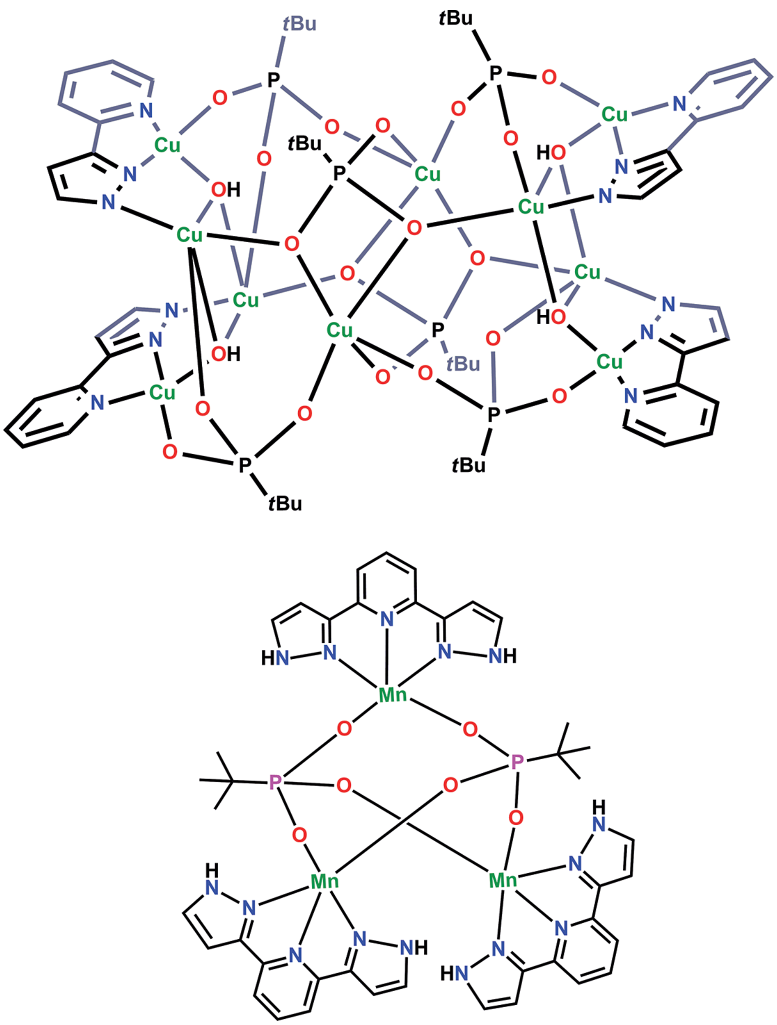
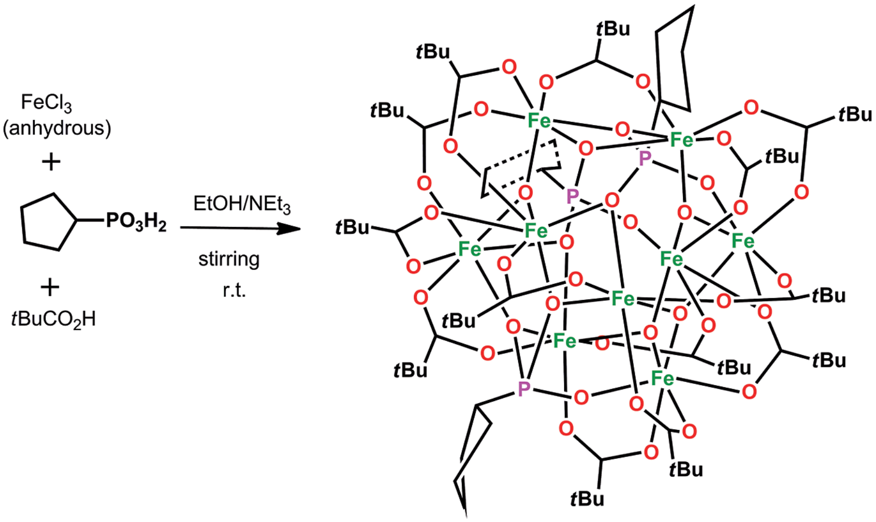


Figure 1. Representative examples of Cu$^{II[5d]}$ (top) and Mn$^{II[7a]}$ (bottom) molecular phosphonates.



Scheme 3. Synthesis of **1**.

with those of the literature precedents are given in Table S1 of the Supporting Information. As can be seen, **1** (this work) crystallizes in the monoclinic system, $P2_1/c$; **2** also crystallizes in the monoclinic system in the space group *Cc*.

Table 1. List of structurally related nonanuclear iron(III) phosphonate cages.

	Oxidation state of iron and core topology	Reactants	Bridging oxide groups	Phosphonic and carboxylic acid	Ref.
$[Fe_9(\mu_3\text{-}O)_4(O_3PC_5H_9)_3(O_2CCMe_3)_{13}]$ (**1**)	Fe^{III}, icosahedron	anhydrous $FeCl_3$, $C_5H_9PO_3H_2$, Me_3CCO_2H, NEt_3, EtOH, Et_2O, r.t.	$4\mu_3\text{-}O$	3 $C_5H_9PO_3H_2$ 13 Me_3CCO_2H	this work
$[Fe_9(\mu_3\text{-}O)_4(O_3PPh)_3(O_2CCMe_3)_{13}]$ (**2**)	Fe^{III}, icosahedron	$[Fe_3O(O_2CCMe_3)(H_2O)_3](O_2CCMe_3)\cdot 2Me_3CCO_2H$, $PhPO_3H_2$, MeCN, Et_2O, r.t.	$4\mu_3\text{-}O$	3 $PhPO_3H_2$ 13 Me_3CCO_2H	[6a]
$[Fe_9(\mu_3\text{-}O)_4(O_2CCMe_3)_{13}(C_{10}PO_3)_3]$ (**3**) [$C_{10}PO_3H_2$ = camphylphosphonic acid],	Fe^{III}, icosahedron	$[Fe_3O(O_2CCMe_3)_6(H_2O)_3](NO_3)$, $[Fe_3O(O_2CCMe_3)_6(H_2O)_3]Cl$, NEt_3, CH_3CN, CH_2Cl_2, Et_2O, r.t.	$4\mu_3\text{-}O$	3 $C_{10}PO_3H_2$ 13 Me_3CCO_2H	[6b]
$[Fe_9(\mu_3\text{-}O)_4(O_3PPh(Me)_2)_3(O_2CCMe_3)_{13}]$ (**4**)	Fe^{III}, icosahedron	$[Fe_3O(O_2CCMe_3)_6(H_2O)_3]Cl$, $(Me)_2)_2PhPO_3H_2$, hydrothermal	$4\mu_3\text{-}O$	3 $[(Me_2)_2PhPO_3H_2]$ 13 Me_3CCO_2H	[6c]

By contrast, **4** crystallizes in the triclinic system, $P\bar{1}$ space group. Interestingly, among all the compounds known thus far, **1** possesses the largest volume.

The molecular structure of **1** is shown in Figure 2. Compound **1** contains four $\{Fe_3^{III}O\}$ motifs (Figure 3). Presumably, adventitious moisture is involved in coordination to Fe^{III}; hydrolysis of such a coordinated aquo ligand, particularly in the presence of the base triethylamine, can lead to the in situ generation of the oxide ligand. Three phosphonate ligands in a 5.221 coordination mode are involved in holding the nonanuclear core (Figure 4).[8] This coordination results in the formation of several six-membered Fe_2O_3P and four-membered Fe_2O_2 rings (Figure 2). All but one of the thirteen pivalate ligands are involved in stitching the core by a bidentate (μ_2-η^1-η^1) coordination action (Figure 4). One of these pivalate ligands, however, is involved in binding three iron centers. The Fe–O, P–O, C–O, and Fe–O–Fe bond parameters involved in **1** are summarized in Table 2. The Fe–O bond lengths that involve μ_3-O are shorter than those that involve the phosphonate ligands (Table 2). In general, metric parameters found in the current instance are comparable to those found in literature precedents.[6]

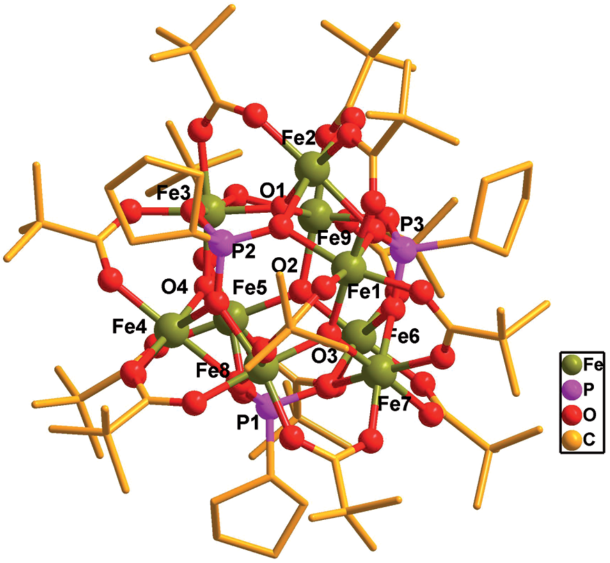


Figure 2. Molecular structure of **1**. All the hydrogen atoms have been omitted for clarity.

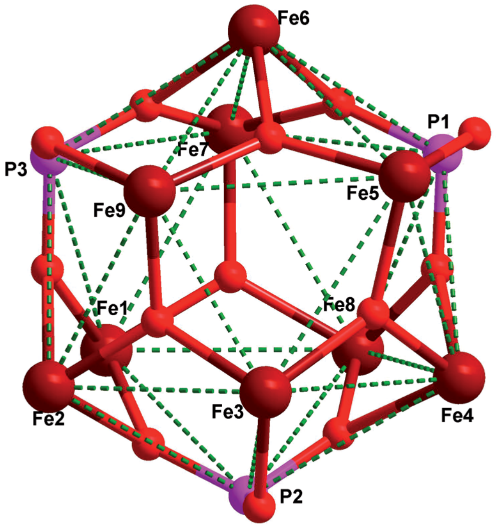
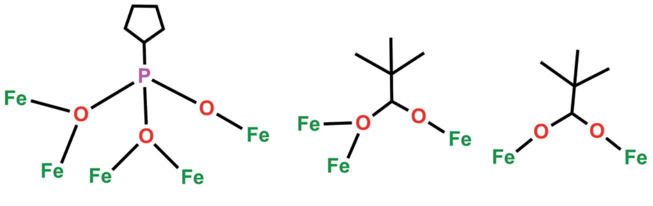


Figure 3. The icosahedral core (Fe_9P_3) structure of **1**.



5.221 3.21 2.11

Figure 4. Coordination modes shown by the $[C_5H_9PO_3]^{2-}$ and $[Me_3CCOO]^{-}$ ligands in the present study.

Considering only the Fe_9P_3 core, it can be seen that these atoms occupy the vertices of an icosahedron (Figure 3). The Fe_9 core, as described previously,[6a] occupies the vertices of a tridiminished icosahedron. The coordination geometry around each iron center (6O) of **1** is distorted octahedral (Table S2 in the Supporting Information).

Further evidence of the oxidation state and nature of the iron centers in **1** has been obtained by a room-temperature solid-state Mössbauer spectrum (Figure 5). This reveals a doublet with a small quadrupole splitting [$\delta(\Delta E_q)$: 0.24

Table 2. Selected bond lengths [Å] and angles [°] of **1**.

Fe–O [Å]	Fe–O–Fe [°]	C–O [Å]	P–O [Å]
Fe2–O1 1.838(4)	Fe7–O3–Fe8 119.73(19)	O33–C65 1.272(7)	P1–O12 1.507(4)
Fe3–O1 1.916(4)	Fe1–O3–Fe8 119.8(2)	O32–C65 1.259(7)	P1–O11 1.549(4)
Fe9–O1 1.935(4)	Fe1–O3–Fe7 120.3(2)	O30–C60 1.301(7)	P1–O13 1.556(4)
Fe6–O2 1.861(4)	Fe6–O2–Fe9 117.9(2)	O54–C95 1.274(7)	P2–O7 1.516(4)
Fe9–O2 1.944(4)	Fe6–O2–Fe5 119.8(2)	O19–C26 1.248(8)	P2–O5 1.551(4)
Fe5–O2 1.957(4)	Fe9–O2–Fe5 121.5(2)	O36–C59 1.260(7)	P2–O6 1.552(4)
Fe1–O3 1.927(4)	Fe4–O4–Fe3 118.1(2)	O39–C50 1.266(7)	P3–O9 1.515(4)
Fe7–O3 1.950(4)	Fe4–O4–Fe5 119.0(2)	O24–C39 1.257(7)	P3–O10 1.538(4)
Fe8–O3 1.951(4)	Fe5–O4–Fe3 122.3(2)	O22–C44 1.252(8)	P3–O8 1.548(4)
Fe4–O4 1.862(4)	Fe3–O1–Fe9 106.42(18)	O23–C44 1.245(8)	
Fe5–O4 1.951(4)	Fe2–O1–Fe3 122.3(2)	O25–C39 1.241(7)	
Fe3–O4 1.953(4)	Fe2–O1–Fe9 123.6(2)	O31–C60 1.239(7)	
		O20–C34 1.269(8)	
		O21–C34 1.239(7)	

(0.74) mm s^{-1}]. These data are consistent with a high-spin Fe^{III}.[9] This is corroborated further by magnetic measurements as described below.

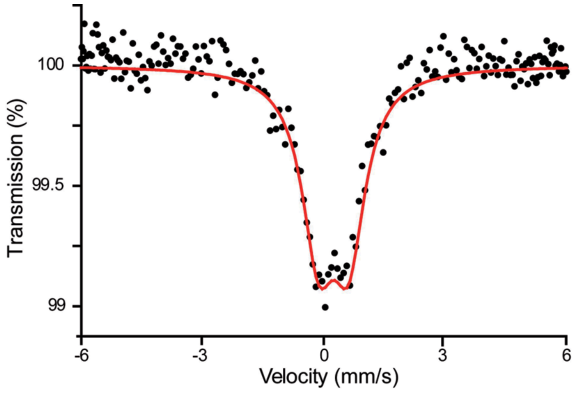


Figure 5. Mössbauer spectrum of **1** at 295 K.

Magnetic Properties

The magnetic properties of complex **1** are shown in Figure 6. The magnetic susceptibility as a function of temperature (χT) data are measured in an applied field of 0.3 T and decrease continuously on cooling from 300 to 2 K, thus demonstrating large antiferromagnetic couplings between the Fe^{3+} ions. At 300 K the χT value reaches 3.0×10^{-4} m^3 K mol^{-1}. The value expected for a single Fe^{3+} $S = 5/2$, $g = 2$ ion is 5.5×10^{-5} m^3 K mol^{-1}. Thus, for a molecule that consists of nine such ions the value of χT would approach 4.95×10^{-4} m^3 K mol^{-1} at sufficiently high temperatures. A similar temperature dependence of χT was observed for complexes **2** and **3**;[6a,6c] however, the high-temperature χT value for **1**–**3** varies over a wide range owing to the difference in the couplings in **1**–**3**. At 300 K the χT value for complex **1** sits between those of complex **2** (1.6×10^{-4} m^3 K mol^{-1})[6a] and **3** (4.8×10^{-4} m^3 K mol^{-1}),[6c] which suggests the presence of an intermediate overall antiferromagnetic coupling between Fe^{3+} ions in complex **1**. The inset of Figure 6 shows the magnetization measured at a temperature of 2.0 K; it increases steadily across the whole field range studied.

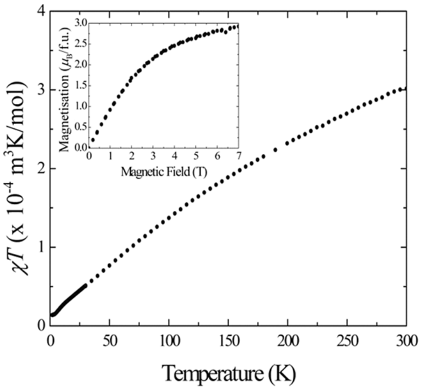


Figure 6. Temperature dependence of χT data of complex **1** measured in an applied magnetic field of 0.3 T. The inset shows the magnetization measured at 2.0 K.

The ac susceptibility was measured for complex **1** in an oscillating field of 0.05–1.5 kHz (Figure S1 in the Supporting Information). Complex **1** has a very small in-phase susceptibility ($\approx 4 \times 10^{-6}$ m^3 mol^{-1}) and no observable out-of-phase susceptibility in the temperature and frequency range studied. This is likely due to the strong antiferromagnetic couplings between the Fe^{3+} ions, which leads to a molecular low-spin ground state and, hence, a reduction of the relaxation barrier.

Conclusion

In summary, we describe a direct three-component reaction protocol to afford a nonanuclear iron(III) ensemble. It is possible that variation in the steric and electronic features of the phosphonate ligand might modulate the nuclearity of the iron(III) phosphonate cage. Such studies should be of interest, particularly given the paucity of iron(III) phosphonate complexes.

Experimental Section

Reagents and General Procedures: Solvents and other general reagents used in this work were purified according to standard procedures.[10] Anhydrous $FeCl_3$, $AlCl_3$, PCl_3, pivalic acid

(Me_3CCO_2H) (S. D. Fine Chemicals, India), and cyclopentyl chloride (C_5H_9Cl) (Aldrich, USA) were used as received. Cyclopentylphosphonic acid ($C_5H_9PO_3H_2$) was prepared by using a known literature procedure.[11]

Instrumentation: ^{1}H and ^{31}P NMR spectra were recorded with a JEOL-JNM Lambda 400 model NMR spectrometer operating at 400.0 and 161.7 MHz, respectively, for solutions of samples in $CDCl_3$. Chemical shifts are referenced with respect to tetramethylsilane. IR spectra were recorded as KBr pellets with a Bruker Vector 22 FTIR spectrophotometer operating from 400 to 4000 cm^{-1}. Elemental analysis was obtained with a Thermoquest CE instrument CHNS-O, EA/110 model. ESI-MS spectra were recorded with a Micromass Quattro II triple quadrupole mass spectrometer. Thermogravimetric analysis (heating rate of 10 °C min^{-1}) was carried out with a Perkin–Elmer Pyris 6 machine. ^{57}Fe Mössbauer spectra were recorded with a Wissel 1200 spectrometer. ^{57}Co(Rh) in a constant acceleration mode was used as the radioactive source. Isomer shifts (δ) are given related to α-iron foil at room temperature. Magnetic measurements were carried out with a Quantum Design MPMS-5XL SQUID magnetometer using the DC measurement mode. Polycrystalline samples were loaded in to gelatin capsules mounted on a carbon-fiber rod. Susceptibility data were recorded on cooling.

X-ray Crystallography: Single-crystal X-ray structural studies of **1** were performed with a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystals did not degrade/decompose during data collection. Data collection, structure solution, and refinement were performed by using the SMART, SAINT, and SHELXTL programs, respectively.[12a–12f] All the calculations for the data reduction were carried out using the Bruker SADABS program. All the non-hydrogen atoms were refined anisotropically using full-matrix least-squares procedures. All the hydrogen atoms were included in idealized positions and a riding model was used. All the mean plane analyses as well as molecular drawings were obtained from DIAMOND (version 3.1). The crystal data and the cell parameters for **1** are summarized in Table 3.

Table 3. Crystal data and structure refinement parameters of compound **1**.

Formula	$C_{166}H_{304}Fe_{18}O_{80}P_6$
M_r	4771.23
T [K]	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	16.306(2)
b [Å]	26.577(4)
c [Å]	52.036(7)
$\alpha = \gamma$ [°]	90
β [°]	91.553(3)
V [Å^3]; Z	22543(5); 4
$D_{calcd.}$ [Mg m^{-3}]	1.406
μ [mm^{-1}]	1.242
F (000)	9992
Crystal size [mm]	0.12 × 0.11 × 0.09
θ range [°]	1.90 to 25.50
Limiting indices	$-18 \leq h \leq 19$ $-30 \leq k \leq 32$ $-48 \leq l \leq 63$
Reflections collected	119645
Unique reflections [R_{int}]	41628 [0.0704]
Completeness to θ [%]	99.2 (25.50°)
Data/restraints/parameters	41628/1621/2396
GoF on F^2	1.024
Final R indices ($I>2\sigma(I)$)	R_1 = 0.0724, wR_2 = 0.1831
R indices (all data)	R_1 = 0.1081, wR_2 = 0.2130
Largest residual peaks [e Å^{-3}]	1.950 and –1.950

CCDC-1006656 (for **1**) contains the 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.

Synthesis of $[Fe^{III}_9(\mu_3\text{-}O)_4(O_3PC_5H_9)_3(O_2CCMe_3)_{13}]\cdot(EtOH)_{0.5}\cdot(Et_2O)_{0.5}$ (1): Anhydrous $FeCl_3$ (0.147 g, 0.900 mmol) was dissolved in ethanol (15 mL). A solution of cyclopentylphosphonic acid ($C_5H_9PO_3H_2$) (0.045 g, 0.300 mmol) and triethylamine (0.152 g, 1.500 mmol) in ethanol (15 mL) were added to this, and the mixture was stirred at room temperature for 3 h. At this stage, pivalic acid (0.092 g, 0.900 mmol) was added to the reaction mixture. The resulting clear brown solution was stirred for an additional 12 h. The solution was evaporated and the residue obtained was redissolved in ethanol and diethyl ether, filtered, and kept for crystallization. After 10 d, brown block-shaped crystals of **1** were obtained, yield 0.096 g, 40% (based on Fe). $C_{83}H_{152}Fe_9O_{40}P_3$ (2385.61): calcd. C 41.79, H 6.42; found C 41.56, H 6.26. IR (KBr): ṽ = 3429 (s), 2952 (w), 2868 (w), 1622 (m), 1576 (s), 1515 (s), 1451 (s), 1425 (s), 1342 (s), 1301 (w), 1222 (s), 1148 (s), 1116 (s), 1089 (s), 1056 (s), 987 (s), 931 (s), 863 (s), 852 (s), 842 (s), 779 (s), 765 (s), 728 (s), 622 (s), 578 (s), 534 (w), 418 (m) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Crystallographic comparison data, ac susceptibility, TGA, bond lengths, and angles.

Acknowledgments

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