Synthesis and Characterization of Iron(III) Phosphonate Cage Complexes**

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Many groups are now making polymetallic complexes, partly to study the unusual properties they can present, and partly because they represent a significant synthetic challenge. In this field two distinct approaches to synthesis can be found: designed assembly,[1] in which the use of ligands with strongly preferred binding modes leads to structures that could be predicted prior to synthesis, and self or "serendipitous" assembly,[2] in which the ligands are more flexible, and the resulting structures are not predictable. Typical ligands for serendipitous assembly are carboxylates or alkoxides.

Phosphonates are a family of ligands that should be ideal for serendipitous assembly, in that they have three O donors, and could, in principle, bind to up to nine metal centers. They have rarely been used in the synthesis of discrete molecules.[3] An important exception is the work by Zubieta and co-workers in which phosphonate is used to assemble vanadium cages.[4] The problem is the very limited solubility that metal phosphonates have, which results in phosphonates being frequently found in polymeric coordination complexes, for example, in 2D layered structures.[5] To produce cage complexes featuring phosphonates we have begun a project in which phosphonates are introduced with a coligand. In a related paper we report on reactions of cobalt salts involving

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phosphonates and pyridonates;[6] herein we report reactions of phenylphosphonate with the well-known iron(III) carboxylate triangles $[Fe_3O(O_2CR)_6(H_2O)_3]X$, (R = H-, CH_3-, Ph- or -CMe_3; X = NO_3^- or Cl^-).

The variation of R, X, and reaction conditions allows access to a range of polynuclear cages. For example, treatment of $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ with two equivalents of $PhPO_3H_2$ in pyridine (py) gives an orange-red solution. Vapor diffusion of Et_2O into this solution gives crystals of the hexa-iron cluster $[Fe_6O(OH)_3(O_2CMe)_3(O_3PPh)_4(py)_9](NO_3)_2$ **1** (Figure 1).[7] The structure consists of two iron triangles linked through the phosphonate. One triangle is clearly related to the precursor, which contains a μ_3-oxide and three carboxylates bridging the three iron(III) centers; however, three of the carboxylates in the original structure have been replaced by phosphonates. These ligands bridge within the triangle in an identical manner to the carboxylate, but the third O atom of each $PhPO_3$ unit binds to the second triangle. Each edge of the second triangle is bridged by a μ_2-hydroxide, and the "upper" face is occupied by a fourth phosphonate. By the Harris notation,[9] each phosphonate has a 3.111 binding mode. All Fe^{III} centers are six coordinate, with a single pyridine molecule attached to each iron atom in the first triangle, and two pyridine molecules bound to each iron atom of the second.

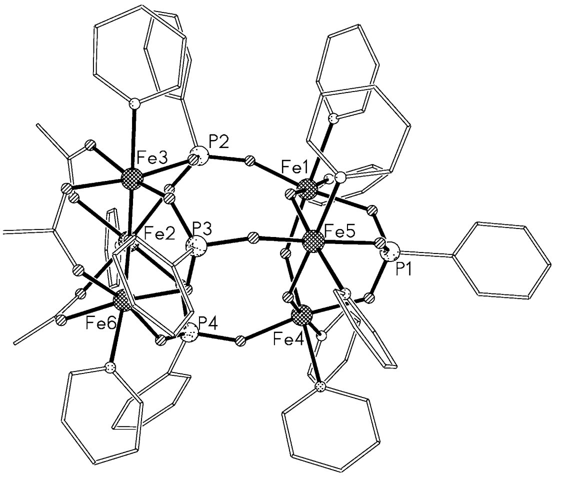

Figure 1. The structure of **1** in the crystal. Bond length ranges [Å]: Fe-O(oxide) 1.911–1.932, Fe-O(OH) 1.979–2.001, Fe-O(O_3PPh) 1.940–1.984, Fe-O(O_2CR) 2.007–2.055, Fe-N 2.164–2.231 (av. estimated standard deviation, esd, 0.005). Shading: Fe atoms, cross-hatched circle; P atoms, light shading; O atoms, diagonal top right–bottom left; N atoms dotted; C atoms drawn as lines. The same scheme is used for all figures.

If the same reaction is performed starting with $[Fe^{III}_3O(O_2CPh)_6(H_2O)_3]Cl$, a tetranuclear iron cage is formed: $[Fe_4OCl(O_2CPh)_3(O_3PPh)_3(py)_5]$ **2** (Figure 2). Complex **2** again contains a triangle similar to that of the starting material, but from which three carboxylates have been displaced. In **2** the three O_3PPh units bind to a single Fe^{III} site, producing a capped tetrahedron. Two pyridine molecules and a chloride ion complete the coordination at this iron center. The three phosphonates again show the 3.111 binding mode (Harris notation).

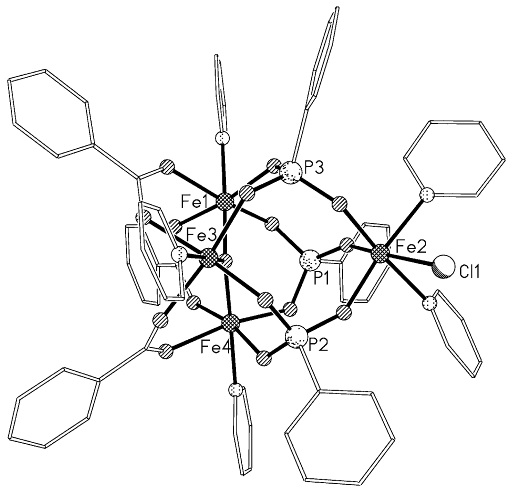

Figure 2. The structure of **2** in the crystal. Bond length ranges [Å]: Fe-O(oxide) 1.927–1.948, Fe-O(O_3PPh) 1.922–1.990, Fe-O(O_2CR) 2.032–2.067, Fe-N 2.177–2.291 (av esd 0.003).

A reduction in the amount of pyridine present changes the reaction path. Thus the sequential addition of $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$, six equivalents of pyridine, and two equivalents of $PhPO_3H_2$ to $MeNO_2$ gave a red solution from which crystals of $[Fe_7O_2(O_2CMe)_9(O_3PPh)_4(py)_6]$ **3** could be grown by diffusion of Et_2O into the solution. Similar hepta-iron compounds $[Fe_7O_2(O_2CPh)_9(O_3PPh)_4(py)_6]$ **4** and $[Fe_7O_2(O_2CPh)_8(NO_3)(O_3PPh)_3(py)_6]$ **5** were formed when the iron(III) acetate triangle was replaced by $[Fe^{III}_3O(PhCOO)_6(H_2O)_3]Cl$ and $[Fe^{III}_3O(PhCOO)_6(H_2O)_3](NO_3)$ respectively.

Complexes **3**–**5** have similar structures (Figure 3). The structures are built from two oxo-centered triangles in which two carboxylates on one edge are replaced by phosphonates, which both bridge to a single Fe^{III} site. Thus this central iron site links the two triangles into a heptanuclear cage, and is bound to four O donors from four distinct phosphonates, and two further O donors from a chelating group. In **3** and **4**, this group is a carboxylate, while in **5** it is a nitrate. Pyridine ligands complete the coordination spheres of the iron atoms

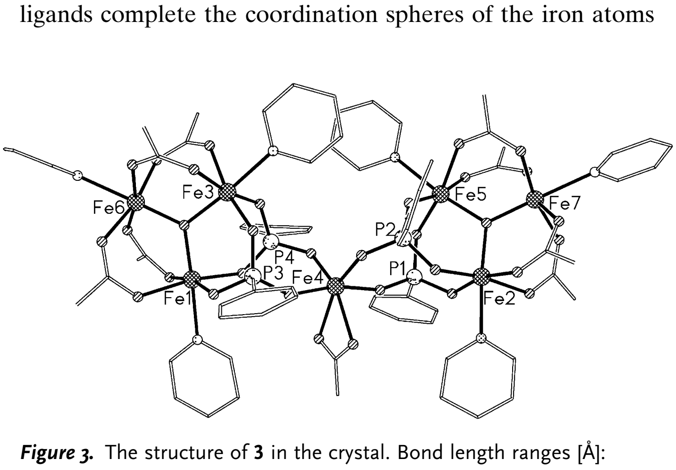

Figure 3. The structure of **3** in the crystal. Bond length ranges [Å]: Fe-O(oxide) 1.859–1.951, Fe-O(O_3PPh) 1.916–1.971, Fe-O(O_2CR) 2.007–2.203, Fe-N 2.171–2.262 (av. esd 0.011).

within the triangles. As before the phosphonates show the 3.111 mode.

With pivalate as the carboxylate, and excluding pyridine entirely, the chemistry produces a much larger cluster. $[Fe_3O(O_2CCMe_3)_6(H_2O)_3](NO_3)$ was treated with one equivalent of $PhPO_3H_2$ in MeCN giving an orange-red solution, from which crystals of $[Fe_{14}O_4(O_2)_2(O_2CCMe_3)_{12}(O_3PPh)_8(H_2O)_{12}](NO_3)_2$ **6** were grown by the addition of Et_2O, followed by slow evaporation of the solvent. The structure (Figure 4) contains two "dimers of triangles", which form distorted trigonal prisms, with two phosphonates bridging in a 4.211 mode on two of the three "rectangular" sides of the prism, and with the μ_2 O-atom in each case bound to one Fe^{III} ion from each triangle. The third side of the prism is occupied by a peroxide binding in the 4.22 mode (O78 and O82 in Figure 4). Peroxides have been found previously in reactions of iron carboxylate triangles,[10] and have shown interesting reactivity in Gif type oxidations.[11]

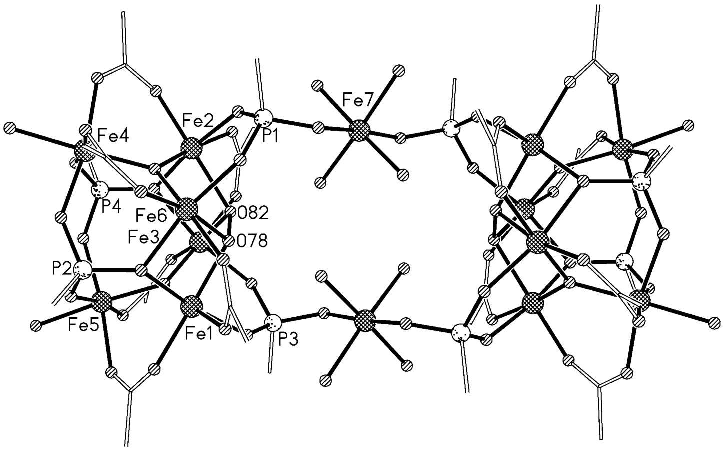

Figure 4. The structure of **6** in the crystal. Phenyl rings and methyl groups omitted for clarity. Bond length ranges [Å]: Fe-O(oxide) 1.879–1.925, Fe-O(peroxide) 2.083–2.101, Fe-$O(O_3PPh)$ 1.938–1.996, Fe-μ_2-$O(O_3PPh)$ 2.056–2.108, Fe-$O(O_2CR)$ 1.963–2.052, Fe-$O(H_2O)$ 2.006–2.095 (av. esd 0.005).

The two trigonal prisms are linked through single Fe^{III} sites, which adopt a similar structural role to the linking sites in **3**–**5**. The phosphonates bridging to these sites adopt the 3.111 mode, and the coordination geometry of the Fe sites is completed by four molecules of H_2O in each case. Assignment of the bridging peroxide appears to be the only rational choice for a two-atom fragment adopting this binding motif. Raman spectroscopy of a solid sample of **6** shows a peak at 852 cm^{-1}, which is very close to ν(O–O) stretch reported previously for peroxides with 4.22 binding.[10]

The inclusion of peroxide in **6** was unexpected. We therefore repeated the experiment, but added a source of peroxide. On this occasion a hexanuclear iron cage formed: $[Fe_6O_2(O_2)(O_2CCMe_3)_8(O_3PPh)_2(H_2O)_2]$ **7**. The structure of **7** (Figure 5) is clearly related to **6**, and contains two oxo-centered Fe^{III} triangles bridged by two phosphonates binding in the 4.211 mode; phosphonates and a peroxide binding in the 4.22 mode. The pivalates binding in the 2.11 mode also bridge the two edges of the rectangular face containing the peroxide, in addition to the pivalates bridging the edges of the triangular faces. The P atoms and the peroxide lie on a crystallographic mirror plane, making the cage much more regular than the equivalent units in **5**. We assign a Raman band at 859 cm^{-1} to the ν(O–O) stretch for **7**. The O–O bond is 1.468(2) Å long in **7**, compared with 1.480(5) Å in **6**.

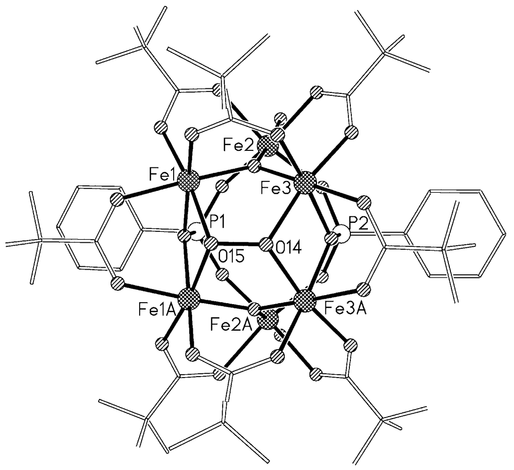

Figure 5. The structure of **7** in the crystal. Bond length ranges [Å]: Fe-O(oxide) 1.892–1.905, Fe-O(peroxide) 2.029–2.042, Fe-$O(O_3PPh)$ 1.963–1.967, Fe-μ_2-$O(O_3PPh)$ 2.089, Fe-$O(O_2CR)$ 1.972–2.098, Fe-$O(H_2O)$ 2.123 (av. esd 0.001).

The reactions reported show that phosphonate can be introduced into polynuclear iron(III) chemistry, without producing insoluble and intractable materials. This may be because of the presence of the carboxylate coligand. An interesting observation is that use of preformed clusters—triangles in this case—leads to structures in which the precursor cage motif is highly influential in the structure of the final complex. This result suggests that phosphonate could be used to link cages into larger arrays by displacement reactions with carboxylates.

Experimental Section

Iron oxo-centred carboxylate triangles were made by literature methods.[13]

1: $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ (0.34 g, 0.49 mmol) and $PhPO_3H_2$ (0.16 g,0.99 mmol) were added to pyridine (10 mL) and the reaction stirred for 24 h. The solution was filtered, and Et_2O was allowed to diffuse into the red filtrate. This gave crystals of **1**. Yield: 0.11 g (19.4 % based on Fe) Elemental analysis calcd (%) for **1**$\cdot 0.5py\cdot 8H_2O$ ($C_{77.5}H_{95.5}Fe_6N_{11.5}O_{36}P_4$): C 41.87, H 4.33, N 7.25, Fe 15.07, P 5.57; found: C 41.56, H 3.51, N 7.74, Fe 14.79, P 5.48. IR (KBr): $\tilde{\nu}$ = 1604 (m), 1578 (s), 1567 (s), 1446 (s), 1384 (vs), 1119 (s), 1068 (s), 1014 (s), 994 (s), 697 (s), 550 cm^{-1} (m).

2: As for **1**, but replacing $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ with $[Fe^{III}_3O(O_2CPh)_6(H_2O)_3]Cl$. Yield: 0.19 g (51.1 % based on Fe) Elemental analysis calcd (%) for **2**$\cdot H_2O$ ($C_{64}H_{57}Fe_4N_5O_{17}ClP_3$): C 50.57, H 3.78, N 4.61, Cl 2.33, Fe 14.70, P 6.11; found: C 50.70, H 3.71, N 4.49, Cl 2.49, Fe 14.77, P 5.80. IR (KBr): $\tilde{\nu}$ = 1601 (s), 1561 (s), 1412 (vs), 1138 (s), 1095 (s), 1068 (s), 1011 (s), 994 (s), 719 (s), 696 (s), 547 (m), 470 cm^{-1} (s).

3: $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ (0.42 g, 0.61 mmol), pyridine (0.29 ml, 3.7 mmol) and $PhPO_3H_2$ (0.19 g, 1.22 mmol) were added to $MeNO_2$ (10 ml) and the mixture stirred for 5 h, then filtered. Et_2O

was allowed to diffuse into the red filtrate giving crystals suitable for X-Ray analysis. Yield: 0.12 g (20.1 % based on Fe) Elemental analysis (%): calcd for **3**·3 CH_3NO_2 ($C_{75}H_{86}Fe_7N_9O_{38}P_4$): C 40.28, H 3.88; N 5.64; Fe 17.48, P 5.54, found: C 40.35, H 3.56, N 5.17, Fe 17.50, P 5.45. IR (KBr): $\tilde{\nu} = 1604$ (vs), 1446 (vs), 1137 (m), 1089 (s), 1067 (s), 1010 (s), 994 (s), 718 (w), 697 (m), 547 (m), 473 cm^{-1} (w).

4: As for **3**, but replacing $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ with $[Fe^{III}_3O(O_2CPh)_6(H_2O)_3]Cl$, and use of 1:1 CH_3CN/CH_2Cl_2 as the solvent in place of $MeNO_2$. Yield: 0.14 g (19.3 % based on Fe) Elemental analysis calcd (%) for **4**·0.5 CH_2Cl_2 ($C_{117.5}H_{96}Fe_7N_6O_{32}ClP_4$): C 53.17, H 3.65, N 3.17, Fe 14.73, P 4.67; found: C 52.94, H 3.70, N 3.18, Fe 15.25, P 4.73. IR (KBr): $\tilde{\nu} = 1611$ (s), 1570 (s), 1550 (s), 1411 (vs), 1136 (m), 1100 (s), 1067 (s), 1009 (s), 994 (s), 719 (s), 697 (s), 547 (s), 471 cm^{-1} (s).

5: As for **3**, but replacing $[Fe_3O(O_2CMe)_6(H_2O)_3](NO_3)$ with $[Fe^{III}_3O(O_2CPh)_6(H_2O)_3](NO_3)$, and use of 1:1 CH_3CN/CH_2Cl_2 as the solvent in place of $MeNO_2$. Yield: 0.05 g (10.0 % based on Fe) Elemental analysis (%): calcd for **5**·0.5 CH_2Cl_2 ($C_{110.5}H_{91}Fe_7N_7O_{33}ClP_4$): C 51.14, H 3.53; N 3.78; Fe 15.06; found: C 51.32, H 3.58, N 3.82, Fe 15.16. IR (KBr): $\tilde{\nu} = 1611$ (s), 1570 (s), 1548 (s), 1411 (vs), 1136 (m), 1098 (s), 1067 (s), 1011 (s), 994 (s), 719 (s), 697 (s), 547 (s), 471 cm^{-1} (s).

6: $[Fe_3O(piv)_6(H_2O)_3](NO_3)$(0.26 g, 0.28 mmol) and $PhPO_3H_2$ (45.1 mg,0.28 mmol) were added to CH_3CN (7 ml) and the solution stirred overnight. The solution was filtered, and Et_2O (5 ml) added before the solution was allowed to evaporate slowly. Yield: 0.04 g (18.0 % based on Fe) Elemental analysis (%): calcd for **6** ($C_{96}H_{172}Fe_{14}N_2O_{74}P_8$): C 34.94, H 4.67, N 0.75; found: C 34.68, H 4.95, N 0.66. IR (KBr): $\tilde{\nu} = 2964$ (m) 1530 (s), 1485 (s), 1426 (s) 1383 (s), 1141 (s), 1064 (s), 1012 (s), 995 (s), 752 (m) 721 (m), 696 (m), 603 (s), 556 (s), 440 cm^{-1} (s).

7. $[Fe_3O(piv)_6(H_2O)_3](NO_3)$(0.26 g, 0.28 mmol) and $PhPO_3H_2$ (45.1 mg,0.28 mmol) were added to CH_3CN (7 ml) and 2 drops of H_2O_2 (30 % in H_2O) were added. The solution stirred for 1 h after which it turned red. Then the solution was allowed to stand undisturbed at 4 °C for few days. Dark red crystals suitable for X-ray analysis formed. Yield: 0.1 g (31.6 % based on Fe) Elemental analysis calcd (%) for **7**·0.5 MeCN ($C_{53}H_{87.5}Fe_6N_{0.5}O_{28}P_2$): C 40.37, H 5.59, N 0.44, P 3.93; found: C 39.88, H 5.61, N 0.47, P 4.02; IR (KBr): $\tilde{\nu} = 2963$ (m) 1552 (s), 1485 (s), 1427 (s) 1380 (m), 1231 (m), 1130 (m), 1039 (w), 979 (s), 788 (w), 600 (m), 440 cm^{-1} (m).

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Keywords: cage compounds · iron · phosphonates · supramolecular chemistry

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[7] Crystal data for **1**: ($C_{95}H_{94}Fe_6N_{14}O_{25}P_4$; $M_r = 2290.82\ g\,mol^{-1}$): brown wedge, triclinic, space group $P\bar{1}$, $a = 14.1201(13)$, $b = 14.5564(14)$, $c = 27.185(3)$ Å, $\alpha = 104.009(2)°$, $\beta = 100.447(2)°$, $\gamma = 98.644(2)°$, $V = 5219.9(9)$ Å^3, $Z = 2$, $T = 100(2)$ K, $\rho = 1.458\ g\,cm^{-1}$, $F(000) = 2356$, $\mu(Mo_{K\alpha}) = 0.951\ mm^{-1}$. Crystal data for **2**: ($C_{261}H_{210}Cl_3Fe_{12}N_{24}O_{54}P_9$; $M_r = 5601.81\ g\,mol^{-1}$), brown prism, rhombohedral, space group $R\bar{3}$, $a = b = 41.1922(18)$, $c = 29.1310(17)$ Å, $V = 42\,807(4)$ Å^3, $Z = 6$, $T = 100(2)$ K, $\rho = 1.304\ g\,cm^{-1}$, $F(000) = 17\,244$, $\mu(Mo_{K\alpha}) = 0.742\ mm^{-1}$. Crystal data for **3**: ($C_{72}H_{64}Fe_7N_6O_{32}P_4$; $M_r = 2040.12\ g\,mol^{-1}$): brown plate, triclinic, space group $P\bar{1}$, $a = 16.104(2)$, $b = 19.212(2)$, $c = 20.976(3)$ Å, $\alpha = 66.906(2)°$, $\beta = 72.105(2)°$, $\gamma = 87.153(2)°$, $V = 5662.4(12)$ Å^3, $Z = 2$, $T = 100(2)$ K, $\rho = 1.197\ g\,cm^{-1}$, $F(000) = 2072$, $\mu(Mo_{K\alpha}) = 0.992\ mm^{-1}$. Crystal data for **4**: ($C_{119}H_{98}Fe_7N_7O_{32}P_4$; $M_r = 2652.88\ g\,mol^{-1}$), orange plate, orthorhombic, space group $Pca2_1$, $a = 27.865(3)$, $b = 20.534(2)$, $c = 20.583(3)$ Å, $V = 11\,777(2)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.496\ g\,cm^{-1}$, $F(000) = 5436$, $\mu(Mo_{K\alpha}) = 0.974\ mm^{-1}$. Crystal data for **5**: ($C_{113.5}H_{95.5}ClFe_7N_{8.5}O_{33}P_4$; $M_r = 2656.76\ g\,mol^{-1}$), red rectangle, monoclinic, space group Cc, $a = 22.4543(18)$, $b = 19.9800(16)$, $c = 26.985(2)$ Å, $\beta = 96.270(2)°$, $V = 12\,034.0(17)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.466\ g\,cm^{-1}$, $F(000) = 5436$, $\mu(Mo_{K\alpha}) = 0.976\ mm^{-1}$. Crystal data for **6**: ($C_{120}H_{130}Fe_{14}N_8O_{82}P_8$; $M_r = 4025.96\ g\,mol^{-1}$), brown plate, orthorhombic, space group $Pnn2$, $a = 23.3688(19)$, $b = 26.584(2)$, $c = 15.2904(12)$ Å, $V = 9499.0(13)$ Å^3, $Z = 2$, $T = 100(2)$ K, $\rho = 1.408\ g\,cm^{-1}$, $F(000) = 4092$, $\mu(Mo_{K\alpha}) = 1.188\ mm^{-1}$. Crystal data for **7**: ($C_{56}H_{92}Fe_6N_2O_{28}P_2$; $M_r = 1638.36\ g\,mol^{-1}$), brown plate, orthorhombic, space group $Pnma$, $a = 17.0228(15)$, $b = 18.6228(17)$, $c = 22.836(2)$ Å, $V = 7239.3(11)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\rho = 1.503\ g\,cm^{-1}$, $F(000) = 3408$, $\mu(Mo_{K\alpha}) = 1.294\ mm^{-1}$. Data were collected on Bruker SMART CCD diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å). In all cases the selected crystals were mounted on a Hamilton cryoloop using Flombin oil and placed in the cold flow (100 K) produced with an Oxford Cryocooling device. Complete hemispheres or spheres of data were collected using ω-scans (0.3°, up to 30 seconds/frame). Integrated intensities were obtained with SAINT+[8] and when they were corrected for absorption SADABS was used.[8] Structure solution and refinement was performed with the SHELXTL-package.[8] The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 to give: for **1**: using 1043 parameters, $wR_2 = 0.3115$ (23 730 unique reflections), $R_1 = 0.0933$ (13 448 reflections with $I > 2\sigma(I)$); for **2**: using 950 parameters, $wR_2 = 0.2018$ (22 991 unique reflections), $R_1 = 0.0579$ (14 468 reflections with $I > 2\sigma(I)$); for **3:** using 1022 parameters, $wR_2 = 0.4381$ (24 767 unique reflections), $R_1 = 0.1293$ (7773 reflections with $I > 2\sigma(I)$); for **4:** using 1479 parameters and 1 restraint, $wR_2 = 0.1194$ (22 844 unique reflections), $R_1 = 0.0530$ (17 174 reflections with $I > 2\sigma(I)$); for **5:** using 1421 parameters and 776 restraints, $wR_2 = 0.1515$ (20 236 unique reflections), $R_1 = 0.0545$ (17 322 reflections with $I > 2\sigma(I)$); for **6:** using 913 parameters and 37 restraints, $wR_2 = 0.1804$ (19 287 unique reflections), $R_1 = 0.0599$ (16 810 reflections with $I > 2\sigma(I)$); for **7:** using 465 parameters, $wR_2 = 0.0740$ (7661 unique reflections), $R_1 = 0.0269$ (7010) reflections with $I > 2\sigma(I)$). CCDC 208769 to 208775 contain the supple-

mentary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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