J|A|C|S
COMMUNICATIONS

Oxo-, Hydroxo-, and Peroxo-Bridged Fe(III) Phosphonate Cages

Sanjit Konar,* Nattamai Bhuvanesh, and Abraham Clearfield*

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012

Received May 15, 2006; E-mail: clearfield@mail.chem.tamu.edu

Iron is one of the most essential elements that plays a diverse role in nature, from mineralogy to biology. In most living organisms, iron is stored in the protein ferritin, which can contain up to about 4500 Fe(III) ions in a polymeric oxo hydroxo lattice. Polynuclear iron clusters with oxygen atoms as oxide, hydroxide, and peroxide ligands acting as bridging ligands possess a variety of structures and, therefore, have been pursued as inorganic models for this system and are of current interest in bioinorganic chemistry.[1]

On the other hand, paramagnetic metal cages containing Fe(III) as metal centers have become a focus for a great deal of research since the discovery that certain cages could behave as single-molecule magnets[2] and, therefore, can act as molecular magnetic storage devices. For these reasons, they are objects of both technological and fundamental scientific interest. Phosphonate ligands should be ideal for making discrete molecular assemblies, as they have three O donors and could bind to up to nine metal centers in principle. But except for a few examples,[3] the 3d transition metal phosphonate complexes are restricted to layered structures.[4] They have rarely been used in the synthesis of discrete molecules[3] for their limited solubility. Herein, we report the synthesis and X-ray structure analysis of five Fe(III) phosphonate cage complexes synthesized with carboxylate coligands. The presence of coligands helped these molecules to stay in solution. Reactions of camphyl phosphonic acid ($C_{10}H_{17}PO_3H_2 = C_{10}PH_2$) with the well-known iron(III) carboxylate triangles $[Fe_3O(O_2CCMe_3)_6(H_2O)_3]Cl$[5] results in a unprecedented nonanuclear Fe(III) cluster $[Fe_9(O)_4(O_2CCMe_3)_{13}(C_{10}P)_3]$ (**1**). The X-ray structure analysis of **1** reveals that the entire metal assembly is wrapped in a hydrocarbon sheath of alkyl groups (Figure 1and Figure 1S) emanating either from phosphonate or from carboxylate ligands. The compound contains two subunits. One Fe_6O_3 core is linked with an $Fe_3-\mu_3O$ triangle through three phosphonate groups. The Fe_6O_3 core can be considered to be alternately connected to three Fe(III) (Figure 2; Fe2, Fe3, Fe8) and three oxygens, thereby forming a six-membered ring in chair conformation, where each oxygen is further connected to another Fe(III) center (Fe1, Fe5, Fe9) toward the periphery of the ring. Two of the oxygens (see Supporting Information, Scheme 2) of phosphonates behave as bridging bidentate groups toward two Fe(III) of the $Fe_3-\mu_3O$ triangle and the peripheral irons of the Fe_6O_3 core. The third oxygen is holding an iron at the base of the Fe_6O_3 core. Therefore, each phosphonate is showing a 5.221 (Harris notation)[6] bridging mode. Hexacoordination of irons are fulfilled by oxygens from the coligand, trimethyl acetate. This structural feature of the molecule is responsible for its solubility in a wide range of organic solvents. Additionally, **1** is also stable in air up to 300 °C.

By changing the coligand of the precursor iron(III) triangle from trimethyl acetate to benzoate, that is, using $[Fe_3O(O_2CPh)_6(H_2O)_3]Cl$[5] with $C_{10}PH_2$ in a similar synthetic condition, we have another interesting nonanuclear Fe(III) cluster, $[Fe_9(O)_2(OH)(O_2CPh)_{10}(C_{10}P)_6(H_2O)_2](CH_3CN)_7$ (**2**). The structure consists of two oxo-centered iron triangles linked with an Fe−(OH)−Fe and a single Fe(III) site at the middle by three phosphonate groups from each side (Figure 3). One carboxylate from each edge of the iron triangle precursor has been replaced by three phosphonate groups, which bridged to irons at the middle and, thereby, form a twisted “basket”-like core (Figure 3). In each triangle, for two Fe(III) sites, the water molecules from the precursor are retained, but for the third one, it has been replaced by a carboxylate group, which is further involved in bridging to the Fe−(OH)−Fe subunit. The single Fe(III) site is linked with two monodentate carboxylates and two water molecules in addition to the two phosphonate oxygens and, thereby, appears as a “basket handle”-shaped subunit. Out of six, there are two different types of phosphonates, two of those with 3.111 and the remaining four with 4.211 binding modes.[6] All Fe(III) centers are six-coordinated.

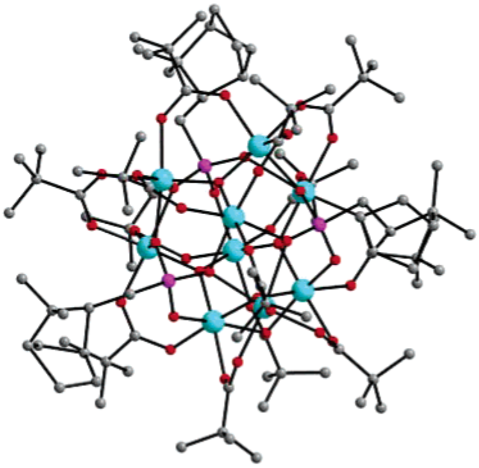

Figure 1. Molecular structure of **1** in the crystal. Color code: cyan, iron; purple, phosphorus; red, oxygen; gray, carbon. Hydrogen atoms are omitted for clarity.

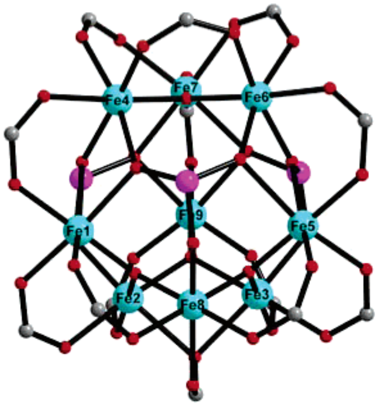

Figure 2. Core structure of **1**. Color code: same as Figure 1. Bond length ranges [Å]: Fe−O(oxo) 1.843(3)−1.958(3); Fe−O($C_{10}P$) 1.939(3)−2.327(3); Fe−O(O_2CCMe_3) 1.979(3)−2.156(3).

10.1021/ja063388s CCC: $33.50

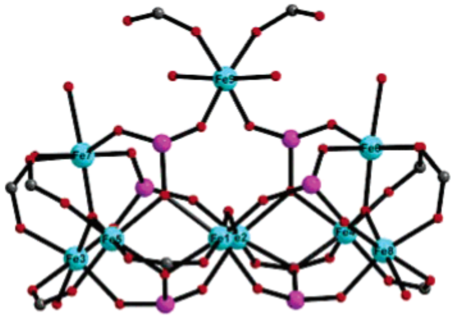

Figure 3. Core structure of **2** in the crystal. Color code: same as Figure 1. For molecular structure, see SI. Bond length ranges [Å]: Fe−O(oxo) 1.894(5)−1.926(5); Fe−O($C_{10}P$) 1.989(5)−2.071(5); Fe−O(O_2CPh) 1.917(5)−2.160(5); Fe−O(H_2O) 2.084(5)−2.129(6); Fe−O(hydroxo) 1.911(5)−1.928(5).

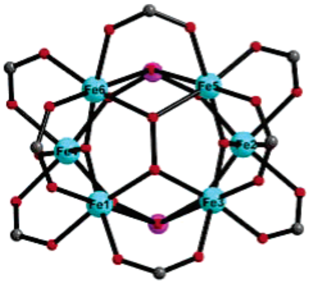

Figure 4. Core structure of **3**. Color code: same as Figure 1. Bond length ranges [Å]: Fe−O(oxo) 1.884(4)−1.910(4); Fe−O(peroxo) 2.021(4)−2.046(5); Fe−O($C_{10}P$) 1.938(4)−2.116(5); Fe−O(O_2CCMe_3) 1.972(4)−2.115(4); Fe−O(H_2O) 2.095(5)−2.106(5).

While repeating the same synthesis as **1** in the presence of a peroxide source, with the intention to making a peroxo-bridged Fe−phosphonate cluster, the hexanuclear iron cage $[Fe_6O_2(O)_2(O_2CCMe_3)_8(C_{10}P)_2(H_2O)_2](CH_3CN)_4$ (**3**) formed. The structure of **3** shows (Figure 4) that the molecule contains two Fe(III) triangles connected by two phosphonates, two carboxylates, and a peroxide in 2.11 binding mode and, thereby, forms a "butterfly"-like $Fe_6(O_2)(O)_2$ core structure (Figure 4). The P atoms and the peroxide lie on a crystallographic mirror plane and, thereby, make the cage more regular.

It is interesting to note that **1** and **2** could also be synthesized in a one-pot reaction with $FeCl_3$, camphyl phosphonic acid, and trimethyl acetic acid/benzoic acid in the presence of excess triethylamine. Similar syntheses with pyridine instead of triethylamine result in two new tetra-iron cages: $[Fe_4(O)(O_2CCMe_3)_4(C_{10}P)_3(Py)_4](CH_3CN)_3$ (**4**) and $[Fe_4(O)(O_2CPh)_4(C_{10}P)_3(Py)_4](Py)_3](CH_3CN)_2$ (**5**; Py = pyridine) with the same core structure (Figure 5). These molecules could also be described as derivatives of Fe_3−carboxylate triangle from which three carboxylate groups have been displaced by three phosphonates, of which the third oxygen of each phosphonate unit binds to a single Fe(III) site. The hexacoordination of this iron is fulfilled by a chelation carboxylate and a pyridine molecule. All the phosphonates show 3.111 binding mode.

We have described the synthesis of five novel Fe(III) cluster compounds mediated by camphyl phosphonic acid and coligand carboxylates, without producing insoluble or intractable material.

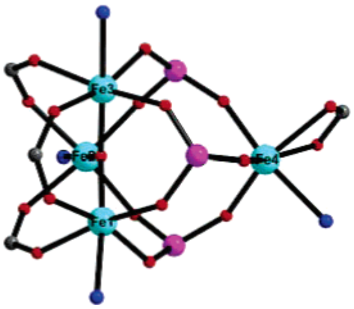

Figure 5. Core structure of **4** and **5**. For molecular structure, see SI. Color code: cyan, iron; purple, phosphorus; red, oxygen; black, carbon; blue, nitrogen. Bond length ranges for **4** and **5** [Å]: Fe−O(oxo) 1.928(3)−1.961(3); Fe−O($C_{10}P$) 1.896(4)−1.992(4); Fe−O(carboxylate) 2.027(4)−2.165(4); Fe−N(Py) 2.220(5)−2.252(7).

None of the phosphonate groups behave as chelating ligands in all of the five complexes, which is a more common feature of the layered phosphonates. The choice of coligand is highly influential on the structure of the final product. Currently, we are adopting this methodology for assembling cages by displacing carboxylates with biphosphonates.

Acknowledgment. This work was carried out with funds from the National Science Foundation (DMR 0332453) and Robert A. Welch Foundation (Grant No. A-0673), for which grateful acknowledgment is made.

Supporting Information Available: Synthetic procedures, TGA, drawing of the molecular structures (Figures 1S−5S), schemes, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823. (b) Crichton, R. R. *Angew. Chem., Int. Ed.* **1973**, *12*, 57. (c) Taft, K. L.; Papaefthymiou, G. C.; Lippard, S. J. *Science* **1993**, *259*, 1302. (d) Tshuva, E. Y.; Lippard, S. J. *Chem. Rev.* **2004**, *104*, 987. (e) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Jr. *Chem. Rev.* **2004**, *104*, 939. (f) Rohde, J. U.; In, J. H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Muenck, E.; Nam, W.; Que, L., Jr. *Science* **2003**, *299*, 1037.

(2) (a) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993. (b) Aubin, S. M. J.; Wemple, M. W.; Adams, D. M.; Tsai, H.-L.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 7746. (c) Barra, A. L.; Gatteschi, D.; Sessoli, R. *Chem.−Eur. J.* **2000**, *6*, 1608. (d) Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Inorg. Chem.* **1999**, *38*, 229. (e) *Magnetism: Molecules to Materials III*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: New York, 2002.

(3) (a) Khan, M. I.; Zubieta, J. *Prog. Inorg. Chem.* **1995**, *43*, 1. (b) Walawalker, M. G.; Roesky, H. W.; Murugavel, R. *Acc. Chem. Res.* **1999**, *32*, 117. (c) Chandrasekhar, V., Kinghsley, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2320. (d) Maheswaran, S.; Chastanet, G.; Teat, S. J.; Mallah, T.; Sessoli, R.; Wernsdorfer, W.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 5044. (e) Tolis, E. I.; Helliwell, M.; Langley, S.; Raftery, J.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3804.

(4) (a) Clearfield, A. Metal phosphonate chemistry. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1998, p 371 and references therein. (b) Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801. (c) Clearfield A.; Wang, Z. *Dalton Trans.* **2002**, 2937. (d) Fanucci, G. E.; Krzystek, J.; Meisel, M. W.; Talham, D. R. *J. Am. Chem. Soc.* **1998**, *120*, 5469.

(5) Blake, A. B.; Fraser, L. R. *J. Chem. Soc., Dalton Trans.* **1975**, 193.

(6) Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349.

JA063388S