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# Synthesis and Characterization of a New μ-Alkoxodiiron(III) Complex with $NO_5$ Donor Set Environments

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A new dinuclear iron(III) complex, $[Fe_2(hpta)(Obz)(H_2O)_2]$, where $H_5hpta$ is 2-hydroxy-1,3-propanediamine-N,N,N',N'-tetraacetic acid and HObz is benzoic acid, was prepared and characterized. X-Ray structure analysis revealed that the complex has mono-(μ-carboxylato)(μ-alkoxo) diiron(III) core and each iron atom has an $NO_5$ donor set in a distorted octahedron.

The (μ-oxo)diiron(III) unit has been the subject of considerable interest among inorganic chemists for several years.1,2) The interest has further been intensified by the discovery of a (μ-oxo)bis(μ-carboxylato) diiron(III) core in methemerythrin and an analogous (μ-oxo)(μ-carboxylato)diiron(III) core in ribonucleotide reductase(RR).3-7) In RR, two iron atoms are separated by 3.3 Å and the coordination around each iron atom is completed by one histidine imidazole group, carboxylato groups, and a water molecule, so that the metal centers have distinct six-coordinate $NO_5$ environments unlike that of hemerythrin.7) This feature indicates that all the O donor atoms including those in the bridging sites play an important role to form the structure of the active site. In methane monooxygenase(MMO), such an oxo-bridged core structure appears unlikely for the diferric site because of its weaker antiferromagnetic coupling and smaller quadrupole splitting.8,9) The oxygen bridge in the case of MMO is likely to be modified by protonation or alkylation to show properties characteristic of the site.

In the present communication, we report the synthesis of a new dinuclear iron(III) complex with mono(μ-carboxylato)(μ-alkoxo)$Fe_2$ core and $NO_5$ environments, $[Fe_2(hpta)(Obz)(H_2O)_2]\cdot 2H_2O$. The crystal structure, magnetic properties, and Mössbauer spectroscopic data of the complex were determined.

The diiron complex was synthesized as follows. A 0.80 g(2 mmol) of $Fe(NO_3)_3\cdot 9H_2O$ was added gently to an aqueous solution(50 mL) of $H_5$hpta(1 mmol, 0.32 g) and HObz(1 mmol, 0.25 g) at 70°C. The mixture was stirred at this temperature until the iron salt was dissolved, cooled and left standing for 3 days. The microcrystalline yellow solid that formed was filtered. Anal. Found: C, 34.75; H, 4.41; N, 4.55%. Calcd for $Fe_2C_{18}H_{26}N_2O_{15}$: C, 34.75; H, 4.21; N, 4.50%. A plate-like single crystal with dimension of 0.75x0.5x0.1 $mm^3$ was used for X-ray structure analysis. Crystal data: $[Fe_2(hpta)(Obz)(H_2O)_2]\cdot 2H_2O$: F.W.=622.11, triclinic, P$\bar{1}$, a= 7.917(1), b=9.867(2), c=16.257(4) A, $\alpha$=78.07(2)°, $\beta$= 78.48(1)°, $\gamma$= 73.01(2)°, V=1175.2(3) $Å^3$, Z=2, Dc=1.71 g $cm^{-3}$, $\mu$(Mo-K$\alpha$)= 12.36 $cm^{-1}$. Intensity data were collected by a Mac Science MXC18 automatic four circle diffractometer with monochromated Mo-K$\alpha$ radiation. A total of 7477 reflections with $2\theta<55°$ were obtained, of which independent 6125 reflections with $|F_o|>3\sigma|F_o|$ were used for the structure determination. The structure was solved by the Monte Carlo Multan method and refined by the full-matrix least squares method.[10,11] The current R and $R_w$ factors are 0.051 and 0.069, respectively. The crystal structure consists of a dinuclear complex and two water molecules of crystallization. An ORTEP[12] plot of the dinuclear complex is shown in Fig. 1 and the principal structural parameters are listed in Table 1. The structure shows a dimeric unit where the two iron atoms are bridged by the alkoxo oxygen atom and the benzoate oxygen atoms. The two iron(III) atoms are not crystallographically equivalent each other, however, the coordination environments around them are almost the same; each iron atom has an $NO_5$ donor set in a distorted octahedron with a tertiary amine N, acetato O's, and a water molecule, as in the case of RR characterized recently to have a similar $NO_5$ donor set.[7] The two acetate oxygen atoms in hpta$^{5-}$ are in trans position to each other with respect to iron atoms and lie on an axis perpendicular to the $Fe_2O$(alkoxo) plane. The water molecule is found in this plane and the Fe-O length is slightly larger than the bond distances found for the usual

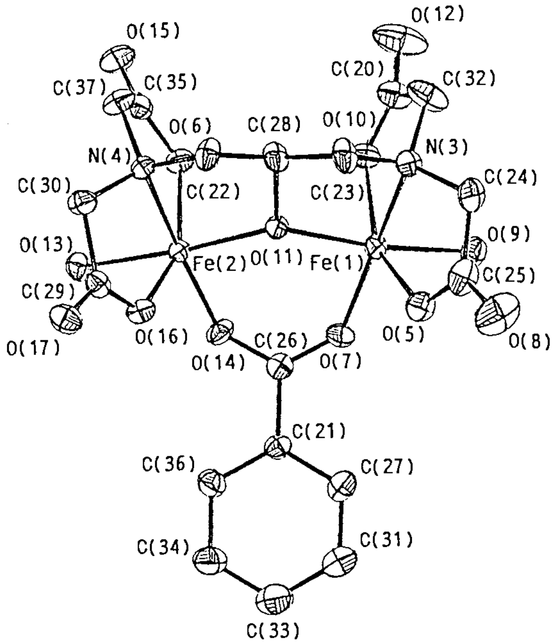

Fig. 1. ORTEP drawing of $[Fe_2(hpta)(Obz)(H_2O)_2]$.

bond length(1.95 to 2.03 Å) in O coordinated compounds, reflecting the trans effect of the alkoxo bridge. The Fe-O(alkoxo) bond lengths(1.986, 2.006 Å) are nearly equivalent and fall in the range reported for various $\mu$-alkoxo or $\mu$-hydroxo diiron complexes.3,4,9,13-15) However, the Fe-Fe distance(3.608 Å) is larger than that of $\mu$-hydroxo ones, probably because of the alkyl chain linkage in hpta formed between the two amine N's.3,4,9,13-15)

An $^{57}$Fe Mössbauer spectrum at 78 K shows a symmetric quadrupole doublet with an isomer shift of $\delta$=0.48 mm s$^{-1}$ and a quadrupole splitting of $\Delta E_q$=0.57 mm s$^{-1}$, indicating that the two iron atoms are in equivalent environment. The isomer shift is well within the range(0.3 to 0.7 mm s$^{-1}$) observed for hydroxo or alkoxo bridged 5-6 coordinate high-spin diferric complexes.3,4,13-15)

Table 1. Selected bond distances(Å) and angles(degree)

| | | | |
|---|---|---|---|
| Fe(1)-Fe(2) | 3.608(1) | Fe(1)-O(11)-Fe(2) | 129.30(7) |
| Fe(1)-N(3) | 2.188(2) | O(7)-Fe(1)-O(9) | 90.55(5) |
| Fe(1)-O(5) | 1.965(5) | O(7)-Fe(1)-O(11) | 91.27(5) |
| Fe(1)-O(7) | 1.945(2) | N(3)-Fe(1)-O(5) | 77.93(6) |
| Fe(1)-O(9) | 2.050(1) | N(3)-Fe(1)-O(9) | 96.34(6) |
| Fe(1)-O(10) | 1.992(1) | N(3)-Fe(1)-O(10) | 79.12(6) |
| Fe(1)-O(11) | 1.986(1) | N(3)-Fe(1)-O(11) | 82.52(5) |
| Fe(2)-N(2) | 2.184(2) | O(14)-Fe(2)-O(13) | 90.74(6) |
| Fe(2)-O(16) | 1.970(1) | O(14)-Fe(2)-O(11) | 91.07(6) |
| Fe(2)-O(14) | 1.969(1) | N(4)-Fe(2)-O(16) | 78.05(5) |
| Fe(2)-O(13) | 2.075(2) | N(4)-Fe(2)-O(13) | 97.68(6) |
| Fe(2)-O(6) | 1.976(1) | N(4)-Fe(2)-O(6) | 78.88(5) |
| Fe(2)-O(11) | 2.006(1) | N(4)-Fe(2)-O(11) | 82.86(6) |

The absence of magnetic hyperfine structure at 8.1 K is consistent with the exchange-coupled diferric structure discussed earlier.3,4)

The results of magnetic susceptibility measurement in a temperature range 4.2 to 280 K is given in Fig. 2. The magnetic behavior can be well simulated based on the general isotropic exchange hamiltonian $H=-2JS_1 \cdot S_2$ with $S_1=S_2=5/2$ using J=-14 cm$^{-1}$, g=2.0, TIP=800x10$^{-6}$, and % monomer=0.02.13,19) Although the |J| value obtained is much smaller than those for $\mu$-oxo diiron(III) complexes, it lies on the range of values(-7 to -17 cm$^{-1}$) found for most $\mu$-hydroxo diiron complexes, indicating the lengthening of the Fe-O(alkoxo) bonds upon alkylation of the oxo-bridge.3,4,13-19) The J value found for the present complex is slightly larger than the J value(-16 cm$^{-1}$) reported for the related tetranuclear complex $[Fe_4O_2(hpta)_2(CO_3)_2]^{6-}$, which

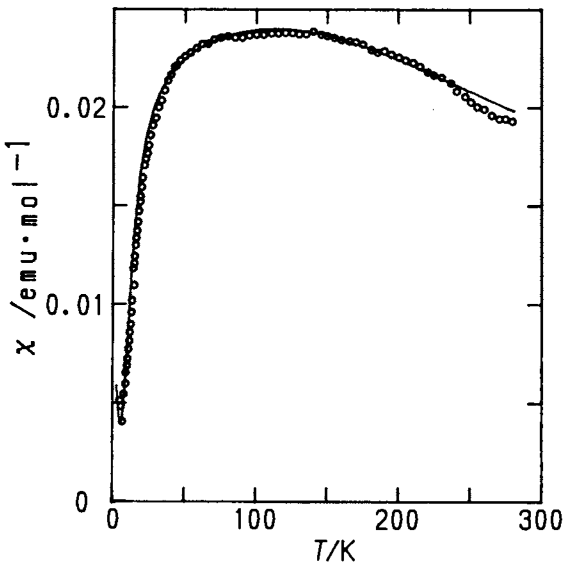

Fig. 2. Temperature dependence of the magnetic susceptibility. The solid line is calculated with the value listed in the text.

has an average Fe-O(alkoxo) distance of 2.05 Å.[18] These results suggest that Fe-O distance is the key factor to determine the exchange coupling.[17]

Both the results of magnetic properties and Mössbauer spectroscopic data indicate that the bridged core is related with the smaller $|J|$ value($J$: -20 $cm^{-1}$) in MMO compared with those for oxo-bridged diiron complexes, such as hemerythrin. Investigations of the reactivities of the present complex and the well-defined related derivatives with $H_2O_2$ and other substrates lead to better understanding of the activation mechanisms for the RR and other non-heme iron proteins, which are now in progress in our laboratory.

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References

1) S. J. Lippard, Angew. Chem., Int. Ed. Engl., 27, 344(1988).
2) R. D. Cannon and R. P. White, Prog. Inorg. Chem., 36, 195(1988).
3) D. M. Kurtz, Jr., Chem. Rev., 90, 585(1990).
4) J. B. Vincent, G. L. Olivier-Lilley, and B. A. Averill, Chem. Rev., 90, 1447(1990).
5) P. C. Wilkins and G. G. Wilkins, Coord. Chem. Rev., 79, 195(1987).
6) R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, Acta Crystallogr., Sect. B, 39, 697(1983).
7) P. Nordlund, B.-M. Sjöberg, and H. Eklund, Nature, 345, 593(1990).
8) B. G. Fox, K. K. Surerus, E. Münck, and J. Lipscomb, J. Biol. Chem., 263, 10553(1988).
9) E. P. Day, S. S. David, J. Peterson, W. R. Dunham, J. J. Bonvoisin, R. H. Sands, and L. Que, Jr., J. Biol. Chem., 263, 15561(1988).
10) A. Furusaki, Acta Crystallogr., Sect. A, 35, 220(1979).
11) P. Main, S. E. Hull, L. Lessimger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN 78, Univ. of York, England, and Louvain, Belguim.
12) C. K. Johnson, ORTEP, Report ORNL-3794 (1965). Oak Ridge National Laboratory, Tennessee.
13) S. Menage and L. Que, Jr., Inorg. Chem., 29, 4293(1990).
14) F.-J. Wu, D. M. Kurtz, Jr., K. S. Hagen., P. D. Nyman, P. G. Debrunner, and V. A. Vankai, Inorg. Chem., 29, 5174(1990).
15) K. L. Taft and S. J. Lippard, J. Am. Chem. Soc., 112, 9629(1990).
16) K. S. Murray, Coord. Chem. Rev., 12, 1(1974).
17) C. J. O'Connor, J. Prog. Inorg. Chem., 29, 204(1979).
18) D. L. Jameson, C.-L. Xie, D. N. Hendrickson, J. A. Potenza, and H. Schugar, J. Am. Chem. Soc., 109, 740(1987).
19) Q. Chen, J. B. Lynch, P. Gomez-Romero, A. Ben-Hussein, G. B. Jameson, C. J. O'Connor, and L. Que, Jr., Inorg. Chem., 27, 2673(1988).
20) S. M. Gorun and S. J. Lippard, Inorg. Chem., 30, 1625(1991).

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