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Synthesis and Structure of Novel Hexanuclear Iron(III) Complexes with μ-Hydroxo-bis(μ-amino acid-*O,O'*)diiron Cores

Tadashi TOKII,* Kouji IDE, Michio NAKASHIMA, and Masayuki KOIKAWA
Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840

Novel hexanuclear iron(III) complexes with $Fe_2(\mu\text{-}OH)(\mu\text{-}RCOO)_2$ moiety in the molecule (where RCOO is an amphoteric ion of β-alanine (**1**) or glycylglycine) have been prepared. The crystal structure of **1** consists of two μ-hydroxo-bis(μ-β-alanine-*O,O'*)diiron(III) cores and two iron(III) ions bridged by μ-oxo ions at each iron(III) site in the cores.

Binuclear metal units consisting of μ-oxo-bis(μ-carboxylato)-bridges are a potential common structural feature of the active sites of hemerythrins. Many transition metal complexes containing such frameworks, $[M_2(\mu\text{-O or }\mu\text{-OH})(\mu\text{-RCOO})_2]^{n+}$, have been prepared as the model complexes for those metalloproteins.1) However, among polynuclear iron(III) complexes those containing μ-carboxylato species with amino acids as bridging ligands are still rare,2) and no binuclear iron(III) complexes with μ-hydroxo-bis(μ-amino acid-*O,O'*)diiron core are known. We have recently prepared hexanuclear iron(III) complexes with such a core containing an amino acid as a bridging carboxylato. In this paper, we report on the preparation, the structural characterization, and the magnetism of the novel hexanuclear iron(III) complexes with μ-oxo, μ-hydroxo, and μ-β-alanine/glycylglycine-*O,O'* bridges, $Na[Fe_6(O)_4(OH)_2(ami)_4(phen)_8](NO_3)_9\cdot 10H_2O$ (ami = amphoteric ion of β-alanine(**1**) or glycylglycine(**2**); phen = 1,10-phenanthroline).

The complexes were obtained as follows. β-Alanine or glycylglycine (3 mmol) and phen (3 mmol) were suspended in 10 cm^3 of methanol, and to this mixture a solution of iron(III) nitrate enneahydrate (3 mmol) in methanol (10 cm^3) was added under stirring, and the resulting solution was adjusted to pH 5.6 with aqueous NaOH. The earlier precipitates were filtered off, and the filtrate was allowed to stand for several days in a refrigerator. Dark-red crystals were collected by filtration, washed with cold methanol, and dried in air. Anal. Found (**1**): C, 43.39; H, 3.95; N, 13.57; Fe, 11.36%. Calcd for $C_{108}H_{114}Fe_6N_{29}NaO_{51}$: C, 43.35; H, 3.84; N, 13.58; Fe, 11.20%. Found (**2**):C, 42.20; H, 3.65; N, 14.81; Fe, 10.74%. Calcd for $C_{112}H_{118}Fe_6N_{33}NaO_{55}$: C, 42.51; H, 3.76; N, 14.61; Fe, 10.58%. Absorption spectra in H_2O, (λ_{max} / nm) (ε / $dm^3mol^{-1}cm^{-1}$) : **1**: 352 (3380), 570 (sh, 60); **2**: 353 (3840), 578 (sh, 57). Although analogous hexanuclear iron(III) complexes, $Na[Fe_6(O)_4(OH)_2(RCOO)_4(phen)_8](NO_3)_5\cdot 10H_2O$ (where R = $(CH_3)_3C$ or $(C_2H_5)_2CH$), were obtained by use of pivaric acid or 2-ethyl-*n*-butyric acid in stead of amino acids, no hexanuclear iron(III) complexes were precipitated by use of other amino acids instead of β-alanine or glycylglycine under the same reaction conditions described above.

X-Ray structure analysis3) revealed that complex **1** contains six iron atoms arranged in a ring-shaped

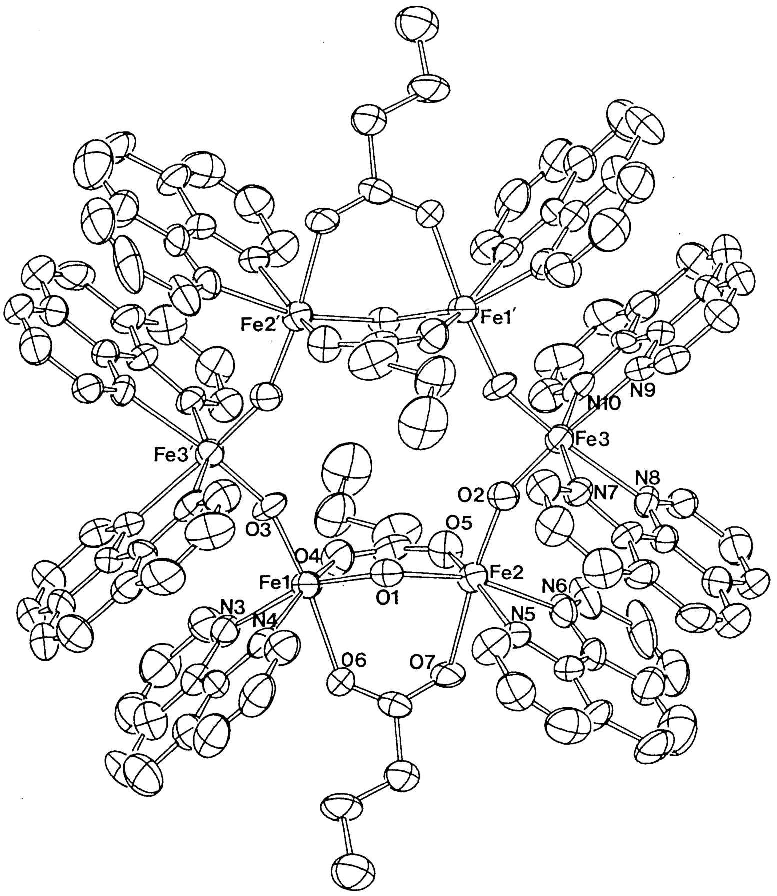

Fig. 1. ORTEP drawing for the complex cation **1** with thermal ellipsoids scaled at the 50% probability level.

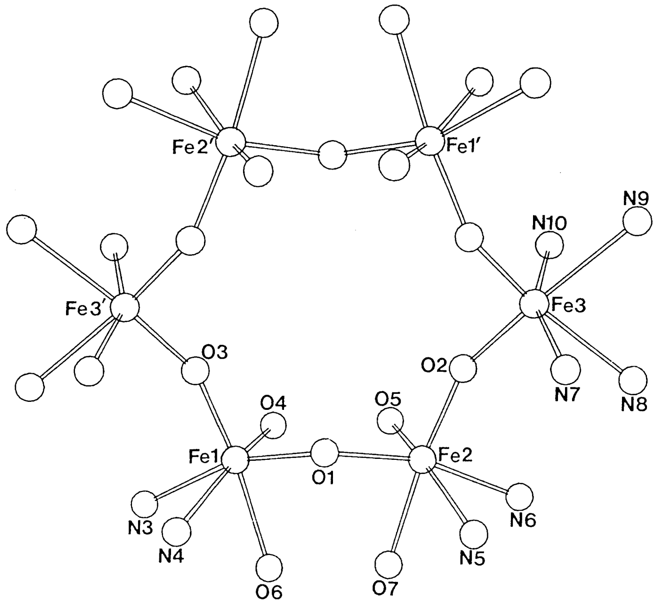

Fig. 2. Coordination spheres of six Fe(III) sites.

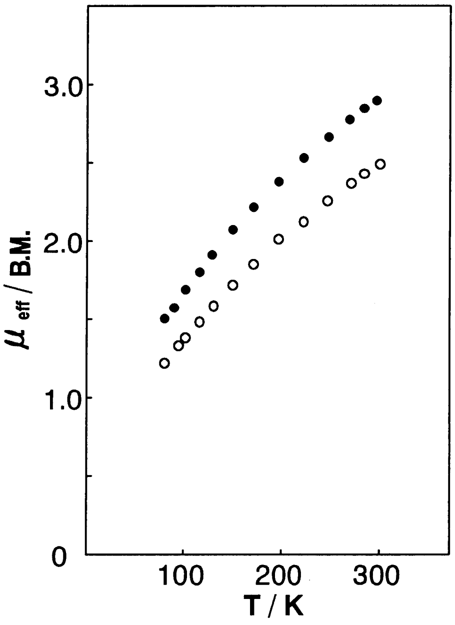

Fig. 3. Temperature dependence of magnetic moments for **1**(○) and **2**(●)

Table 1. Selected bond lengths (Å) and angles (°) of **1**

Fe1–O1	1.91(1)	Fe2–O1	1.970(9)	Fe3–O2	1.85(1)
Fe1–O3	1.82(1)	Fe2–O2	1.87(1)	Fe3–O3	1.86(1)
Fe1–O4	2.04(1)	Fe2–O5	2.02(1)	Fe3–N7	2.15(1)
Fe1–O6	2.15(1)	Fe2–O7	2.12(1)	Fe3–N8	2.27(1)
Fe1–N3	2.17(1)	Fe2–N5	2.15(1)	Fe3–N9	2.27(1)
Fe1–N4	2.17(1)	Fe2–N6	2.17(1)	Fe3–N10	2.18(1)
Fe1...Fe2	3.426(8)	Fe2...Fe3	3.643(9)	Fe1...Fe3'	3.581(3)
O1–Fe1–N3	161.6(4)	O1–Fe2–N6	164.6(4)	O2–Fe3–N9	164.6(4)
O3–Fe1–O6	174.1(4)	O2–Fe2–O7	173.6(4)	O3'–Fe3–N8	163.5(5)
O4–Fe1–N4	159.7(5)	O5–Fe2–N5	160.4(5)	N7–Fe3–N10	158.9(5)
Fe1–O1–Fe2	123.8(4)	Fe2–O2–Fe3	156.0(6)	Fe1–O3–Fe3	154.3(6)

configuration with two $[Fe_2(OH)(Ala)_2(phen)_2]^{4+}$ cores and the other two iron atoms linked two cores through two μ-oxo single bridge. This is the first example of the structurally characterized hexanuclear Fe(III) complex with μ-oxo/hydroxo-bis(μ-carboxylato)iron(III) cores. A perspective view of **1** and the coordination spheres of six Fe(III) sites are shown in Figs. 1 and 2, respectively. Complex **1** resides on an inversion center so that only half of the molecule is crystallographically unique. The six iron atoms are essentially coplanar, with the deviation of only 0.001–0.002 Å from the best least-squares plane through them. The $Fe–O_{hydroxo}$ bond distances (Fe1–O1, 1.91; Fe2–O1, 1.970 Å) are significantly longer than the $Fe–O_{oxo}$ distances (1.82–1.86 Å). The lengthening of the $Fe–O_{hydroxo}$ distances agrees with results for other hydroxo-bridged diiron(III) complexes.$^{4)}$ The longer Fe–O distances lead to a greater Fe...Fe distance. The Fe...Fe distance in $[Fe_2(OH)(Ala)_2(phen)_2]^{4+}$ core (3.426(8) Å) is comparable to that in the μ-hydroxo-bis(μ-acetato)iron(III) complex, $[Fe_2(OH)(OAc)_2(HB(pz)_3)_2]^+$ (3.439(1) Å),$^{5)}$ and is much longer than those found in μ-oxo-bis(μ-carboxylato)-bridged iron(III) complexes (3.06–3.18 Å).$^{4)}$ Another two Fe...Fe distances held by the single μ-oxo bridge are not equivalent (Fe1...Fe3' = 3.581(3) Å , Fe2...Fe3 = 3.643(9) Å), and are slightly longer than those in μ-oxo-bridged iron(III) complexes (3.39–3.56 Å).$^{4)}$ Four sets of the adjacent phen ligands in Fig. 1 are nearly paralleled to one another (dihedral angles 2.8 and 5.6°) and have an average separation of 3.41 Å. Rotations of Fe1 by 18° about the Fe1–O3 bond and of Fe2 by 15° about the Fe2–O2 bond would bring each set of the phen rings into the eclipsed configuration. The shortest C...C distance between the stacked phen rings is 3.29 Å. This distance is shorter than those of $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)_2{\cdot}4H_2O$,$^{6)}$ $[Fe_2(O)(phen)_4(H_2O)_2](NO_3)_4{\cdot}5H_2O$,$^{7)}$ and $[Ru_2(O)(bpy)_4(H_2O)_2](ClO_4)_4{\cdot}2H_2O$,$^{8)}$ $[Tc_2(O)Cl_2(phen)_4]Cl_2{\cdot}4H_2O$$^{9)}$ (3.48, 3.45, 3.53, and 3.47 Å respectively), and is somewhat shorter than twice of the van der Waals radius of aromatic carbon atom (1.77 Å).$^{10)}$ For complex **2**, X-ray structure analysis is in progress, and the current *R* value is 0.11. The elemental analysis and the X-ray analytical data for **2** definitely show that the complex has the same hexanuclear structure with the stacked phen rings as **1**. These stacked phen rings are likely to play a role of stabilization in the present complexes.

The variations of the effective magnetic moments with temperature for **1** and **2** are shown in Fig. 3. The magnetic moments per iron(III) ion are 2 [illegible]9 B.M. for **1** and 2.89 B.M. for **2** at room temperature, and gradually decrease with the lowering of temperature (Fig. 3). This behavior indicates that antiferromagnetic interaction is operative in these complexes.

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3) The crystal data for **1**: $C_{108}H_{114}Fe_6N_{29}NaO_{51}$, Mw = 2992.32, monoclinic, *C2/c*, $a = 31.70(9)$, $b = 15.710(6)$, $c = 28.41(4)$ Å, $\beta = 114.5(1)°$, $V = 12871(38)$ Å^3, $Z = 4$, $\mu(\text{Mo } K\alpha) = 7.59$ cm^{-1}, $D_m = 1.54$, $D_x = 1.544$ g cm^{-3}, $R = 0.077$, $R_w = 0.102$. Intensity measurements were carried out for $2\theta < 45°$ on a Rigaku AFC5S four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Of the 8788 reflections measured, the unique 4338 reflections with $I > 3.00\sigma(I)$ were considered as observed. The structure was solved by direct methods and refined by the full-matrix least-squares method using TEXRAY software package programs (TEXSAN). The non-hydrogen atoms were refined with anisotropic thermal parameters. Six of the ten water molecules of crystallization were located on the difference synthesis. All of the hydrogen atoms were inserted at their calculated positions.
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