A Novel Tetranuclear Iron(III) Complex Having L-Alanine Bridges and an Unprecedented $(Fe_4(O_2H))$ Core

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(Received September 28, 1995)

The reaction of L-alanine (L-ala) with $Fe(NO_3)_2\cdot 9H_2O$ in the presence of H_5dhpta (1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid) and base (NaOH) affords the novel tetranuclear complex $Na[Fe_4(dhpta)_2(O)(OH)(L\text{-}ala)_2]\cdot 6H_2O$ having L-alaninato bridges and an $(Fe_4(O_2H))^{9+}$ core whose crystal structure and magnetic properties were determined.

Polynuclear oxo-, hydroxo-, and alkoxo- bridged transition-metal centers have been found in a variety of iron[1] and manganese[2] metalloproteins. In recent years substantial progress[3] has been made in modeling the polynuclear iron centers in haemerythrin, ribonucleotide reductase, purple acid phosphatase, and methane monooxidase.[1] In contrast, non-heme diiron(III) and related polynuclear iron(III) structural model compounds containing amino acid bridge(s) have not been reported except for few examples,[4] though the bridging carboxylate groups are provided by the optically active amino acid residue of the surrounding proteins.

1,3-Diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acid (H_5dhpta) is one of the good bridging ligands and the tetranuclear $Fe(III)_4$[5] and $Mn(II)Mn(III)_3$[6] complexes and the diiron(III)[3m, n] and diruthenium(III)[7] complexes of this ligand were reported. We now wish to report the first synthesis and structure characterization of a tetranuclear iron(III) complex $Na[Fe_4(dhpta)_2(O)(OH)(L\text{-}ala)_2]\cdot 6H_2O$ **1** having amino acid bridges and a novel $(Fe_4(O_2H))^{9+}$ core.

A tetranuclear complex **1** was synthesized as follows. Ferric nitrate, $Fe(NO_3)_3\cdot 9H_2O$ (0.404 g, 1 mmol), and H_5dhpta (0.161 g, 0.5 mmol) were dissolved in 40 ml of water at about 70°C with stirring and the pH was adjusted to 5 by the addition of drops of 1M NaOH solution. After L-alanine (0.445 g, 5 mmol) was added, then the pH was readjusted to 5 by 1M NaOH. The solution was left to stand at room temperature for a few days and the pale-yellow crystals formed were suitable for X-ray crystallography (0.65 g, 53.5% yield). Anal. Calcd for $NaFe_4O_{24}N_6C_{28}H_{41}\cdot 6H_2O$: C, 28.02; H, 4.45; N, 7.00. Found: C, 27.97; H, 4.87; N, 7.09.

Crystal data for $Na[Fe_4(dhpta)_2(O)(OH)(L\text{-}ala)_2]\cdot 6H_2O$ **1** : monoclinic, space group $P2_1$, $a = 11.762(1)$ Å, $b = 15.924(2)$ Å, $c = 12.948(2)$ Å, $\beta = 109.46(1)°$, $V = 2286.6(5)$ Å^3, $Z = 2$, $Dc = 1.743$ gcm^{-3}, $Dm = 1.727$ gcm^{-3}, μ (linear absorption coefficient) = 13.56 cm^{-1}. 5254 independent reflections with $I > 3\sigma(I)$ were collected with Mo Kα radiation ($\lambda = 0.7107$ Å) within the sphere of $2\theta < 60°$ on a Rigaku RASA-7R instrument. The structure was solved by direct methods. The structure was refined with 5254 observed reflections to give $R = 0.035$ and $Rw = 0.046$. The known absolute configuration of the asymmetric carbon atom of L-alanine was used as an internal reference asymmetric center to determine the absolute configuration of the whole complex.

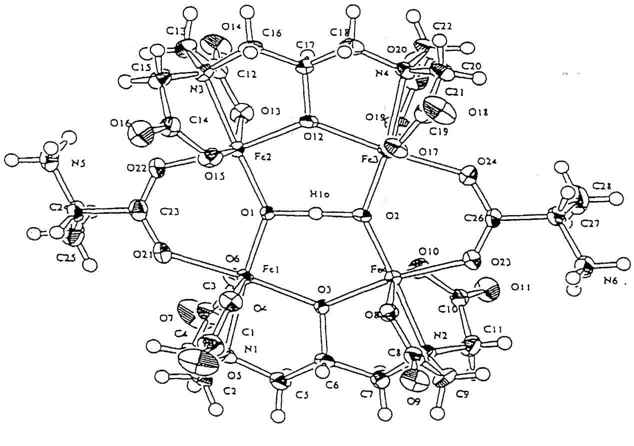

Figure 1. A perspective drawing of the complex anion $Na[Fe_4(dhpta)_2(O)(OH)(L\text{-}ala)_2]\cdot 6H_2O$ **1**. Selected bond distances (Å) and angles (degree): Fe1···Fe2 3.473(12), Fe1···Fe4 3.676(15), O1···O2 2.426(40), Fe1-O1 1.863(4), Fe1-O3 2.015(5), Fe1-O4 2.013(5), Fe1-O6 2.024(4), Fe1-O21 2.076(6), Fe1-N1 2.185(4), Fe2-O1 1.852(4), Fe2-O12 2.020(4), Fe2-O15 2.036(5), Fe2-O13 2.020(5), Fe1-O22 2.097(5), Fe2-N3 2.179(6), O1-H1o 1.22, O2-H1o 1.21, Fe1-O1-Fe2 138.4(3), Fe1-O3-Fe4 131.7(2), O1-Fe1-O3 92.5(2), O1-H1o-O2, 176.1.

Figure 1 shows an ORTEP drawing of the complex anion. Each Fe has a similar NO_5 distorted octahedral ligand donor set in which the O-donors are supplied by two nonbridging acetate, a bridging oxide, a bridging alkoxide, and a bridging bidentate L-alaninato. The structure can be viewed as a dimer of dimers. In each dimer unit, the dhpta^{5-} ligand binds to two Fe(III) ions bridging with the alkoxy oxygen. The two dimers are linked by the $(O_2H)^{3-}$ and L-alaninato groups as zwitter ionic forms. The four iron atoms are nearly coplanar, with the deviation of 0.007 - 0.003 Å from the best least-squares plane through them. The bridging $(O_2H)^{3-}$ unit is of special interest in connection with the catalytic center of the photosynthetic water splitting apparatus of green plants and cyanobacteria as discussed in the case of a similar tetranuclear manganese complex $(Ba, Ca)_2[Mn_4(dhpta)_2(\mu\text{-}O)(\mu\text{-}OH)(O_2CCH_3)_2]$[6] and approached theoretically by Hoffman et al.[8] The hydrogen atom H, located in the difference Fourier map and subsequently refined (its position was not fixed), is shared by the two bridging oxo groups. The unusually short O1···O2 contact, 2.426(40) Å, indicates a strong hydrogen bond as observed for the tetranuclear manganese complex,[6] and for hydroxy bridged polynuclear iron complexes[9] including $Na_6[Fe_4(dhpta)_2(O)_2(CO_3)_2]\cdot 20H_2O$ **2**.[5] In the case of **2**,[5] Jameson et al., predicted the existence of the bridging $(O_2H)^{3-}$ unit. However, its structure could not be confirmed owing in part to the lattice disorder problem. Therefore, the present complex is the first example of the structurally characterized tetranuclear Fe(III) complex having the bridging $(O_2H)^{3-}$ unit and aminoacidato bridges. The existence e of L-alaninato bridges would give an useful information for model studies of metalloenzymes having the plynuclear iron core.

Na^+ ion joins the tetranuclear core via linear O(11)-Na-O(16) to form infinite Na-$[Fe_4]$-Na chains. Two water molecules are involved in hydrogen bonding to nitrogen atoms of L-ala of the tetranuclear clusters. The coordination geometry of Na(1) is a distorted octahedron formed by bonding four water molecules and the carboxylate O atoms of dhpta [O(11), O(16)]. Within the distorted octahedron, Na-O contacts and O-N-O angles range from 2.378 (6) to 2.629 (7) Å and 78.5 (2) to 91.3 (2)°, respectively. These values are normal for pseudo-octahedrally coordinated sodium.[10] Thus the crystal consists of C_2 symmetric tetranuclear complexes linked by an extensive network involving the Na^+ ions and H_2O molecules.

Magnetic susceptibility data were measured by the Faraday method over a temperature range of 4 - 300 K with a Cahn RH electrobalance. Magnetic susceptibility at room temperature were also obtained by the Gouy method. A diamagnetism of the complexes was corrected from Pascal's constants.[11] The molar susceptibility data were fit to the theoretical equation below which was used for complex **2** by Jameson et al,[5]

$$\chi_M = (P/Q)^2 N g^2 \beta^2 / k(T-\theta) + \mathrm{TIP} + \chi_{para}$$

where χ_M = molar susceptibility , J = intradimer magnetic coupling, J' = interdimer magnetic coupling, $\theta = 2J'(P/Q)$, $P = 2e^A + 10e^B + 28e^C + 60e^D + 110e^E$, $Q = 1 + 3e^A + 5e^B + 7e^C + 9e^D + 11e^E$, $A = 2J/kT$, $B = 6J/kT$, $C = 12J/kT$, $D = 20J/kT$, $E = 30J/kT$, N = Avogadro number, β = Bohr magneton, k = Boltzman constant, TIP = temperature independent paramagnetism, and $\chi_{para} = (\mathrm{PAR})(S)(S+1)(N\gamma^2\beta^2/3k\mathrm{T})$. The last term accounts for the spin-only magnetism associated with a paramagnetic impurity of mole percentage (PAR) and spin S.

The experimental data well fit with J = -44.1 cm^{-1}, J' = -21.7 cm^{-1}, g = 2.0, and TIP = 595 x 10^{-6} cgsu. The intradimer coupling constant is considerably smaller than the values reported for **2**.[5] In contrast, the J' value is fairly larger than the value found for **2**.[5]

A synthesis and characterization of a series of tetranuclear iron(III) complexes which are bridged by 1,3-diamino-2-hydroxypropane-*N,N,N',N'*-tetraacetic acids and other amino acids or carboxylic acids having functional groups are now in progress.

The authors wish to thank Professor Masahiro Mikuriya for his helpful discussions. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Nos. 63612002, 01850190, 03241106, 02854074, 03650687, 07231219, 07215252 and 03555184) and from CIBA-GEIGY Foundation (Japan) for the Promotion of Science and Iwatani Naoji Foundation's Research Grants and Grants from Nippon Itagarasu and Mitsubishi-Yuka Foundations.

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