Cyclic Oligonuclear Fe_6Na_3 Complex with 2,6-Bis(salicylideneaminomethyl)-4-methylphenol

Masahiro Mikuriya,* Shinichiro Ikemi, and Shigetoshi Yao
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501

(Received February 28, 2000; CL-000191)

A cyclic nonanuclear complex with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), $[Fe_6Na_3(L)_3(CH_3COO)_{12}]$, has been synthesized and characterized by X-ray crystallography and magnetic susceptibility measurement.

Oligonuclear metal complexes have been the focus of active research because of their unique structures and magnetic properties.[1] We have been engaged in coordination chemistry of multidentate Schiff-base ligands in order to examine the potential utility as "building blocks" in combination with linkage ligands for oligonuclear or polynuclear formation.[2-5] In the previous study, we isolated a pentanuclear iron(III) complex by the reaction of a Schiff-base ligand 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L) with iron(III) ion in benzene, which is formed by association of the two dinuclear Fe_2L units by virtue of linking to the fifth iron(III) moiety.[2] During the course of our studies on this system, we have found an unprecedented Fe_6Na_3 cyclic core could be achieved when the reaction was performed in acetonitrile. Here we report the synthesis and characterization of $[Fe_6Na_3(L)_3(CH_3COO)_{12}]$ (**1**) as the first example of heterometal cyclic complex with the Schiff-base ligands.

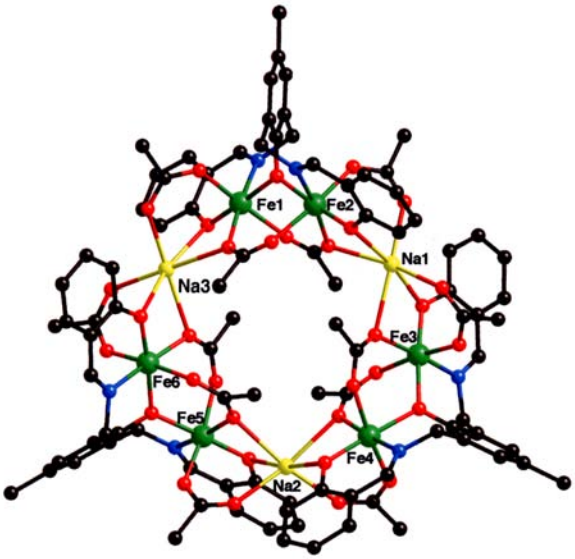

Figure 1. Molecular structure of **1**. Intermetallic distances (Å) and angles (°): Fe1-Fe2 3.539(3), Fe3-Fe4 3.535(3), Fe5-Fe6 3.533(4), Fe2-Na1 3.400(7), Fe3-Na1 3.430(7), Fe4-Na2 3.443(7), Fe5-Na2 3.441(7), Fe6-Na3 3.376(7), Fe1-Na3 3.427(7); Fe1-Fe2-Na1 118.8(2), Fe2-Na1-Fe3 144.2(2), Na1-Fe3-Fe4 119.3(1), Fe3-Fe4-Na2 118.8(1), Fe4-Na2-Fe5 144.0(2), Na2-Fe5-Fe6 118.5(2), Fe5-Fe6-Na3 120.4(2), Fe6-Na3-Fe1 142.1(2), Na3-Fe1-Fe2 121.1(1).

Treatment of H_3L with basic iron(III) acetate in acetonitrile containing a methanol solution of sodium hydroxide resulted in deposition of black crystals (**1**).[6] X-Ray crystallography of **1** revealed the compound to be a rare example of a cyclic nonanuclear structure as shown in Figure 1.[7] The molecule contains six iron and three sodium atoms in an alternating cyclic arrangement of $[Fe_2(L)(CH_3COO)_2]^-$ and sodium ions. Each pair of iron atoms is bridged by the central phenoxo-oxygen atom (O2, O5, and O8) of L^{3-} (Figure 2). The Fe-Fe distances are in the range from 3.533(4) to 3.539(3) Å. Two acetate ions are incorporated in each dinuclear iron units as exogenous *syn-syn* bridges. Each iron atom adopts a distorted octahedral coordination geometry with Fe-O and Fe-N distances in the ranges 1.91(1)—2.10(1) and 2.12(1)—2.16(1) Å, respectively. The two terminal phenoxo-oxygen atoms (O1, O3; O4, O6; O7, O9) of each L^{3-} act as bridging groups as further coordinated to sodium atom with one of the exogenous acetate bridges in a monatomic bridging, resuting in η^3 bridges of the acetate ions. Interestingly, the iron and sodium atoms are further bridged by an acetate ion in a *syn-syn* mode. Each sodium atom takes a

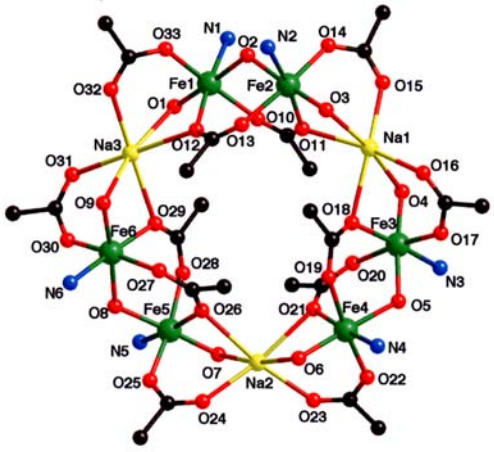

Figure 2. Nonanuclear core showing coordination spheres in **1**. Selected bond distances (Å) and angles (°): Fe1-O1 1.94(1), Fe1-O2 2.03(1), Fe1-O10 2.06(1), Fe1-O12 2.05(1), Fe1-O33 1.97(1), Fe1-N1 2.13(1), Fe2-O2 2.002(9), Fe2-O3 1.93(1), Fe2-O11 2.05(1), Fe2-O13 2.07(1), Fe2-O14 1.98(1), Fe2-N2 2.13(1), Fe3-O4 1.93(1), Fe3-O5 2.021(9), Fe3-O17 1.97(1), Fe3-O18 2.03(1), Fe3-O20 2.06(1), Fe3-N3 2.13(1), Fe4-O5 2.036(9), Fe4-O6 1.91(1), Fe4-O19 2.08(1), Fe4-O21 2.02(1), Fe4-O22 1.98(1), Fe4-N4 2.12(1), Fe5-O7 1.92(1), Fe5-O8 2.02(1), Fe5-O25 1.96(1), Fe5-O26 2.03(1), Fe5-O28 2.10(1), Fe5-N5 2.14(1), Fe6-O8 2.01(1), Fe6-O9 1.93(1), Fe6-O27 2.06(1), Fe6-O29 2.06(1), Fe6-O30 1.94(1), Fe6-N6 2.16(1), Na1-O3 2.56(1), Na1-O4 2.56(1), Na1-O11 2.46(1), Na1-O15 2.30(1), Na1-O16 2.29(1), Na1-O18 2.52(1), Na2-O6 2.58(1), Na2-O7 2.58(1), Na2-O21 2.54(1), Na2-O23 2.28(1), Na2-O24 2.28(1), Na2-O26 2.50(1), Na3-O1 2.55(1), Na3-O9 2.51(1), Na3-O12 2.56(1), Na3-O29 2.48(1), Na3-O31 2.38(1), Na3-O32 2.30(2); Fe1-O2-Fe2 122.9(5), Fe2-O3-Na1 97.3(5), Na1-O4-Fe3 98.7(5), Fe3-O5-Fe4 121.2(4), Fe4-O6-Na2 98.8(5), Na2-O7-Fe5 98.9(5), Fe5-O8-Fe6 122.6(5), Fe6-O9-Na3 98.1(5), Na3-O1-Fe1 98.5(5).

Copyright © 2000 The Chemical Society of Japan

distorted octahedral geometry with Na-O distances in the range 2.28(1)—2.58(1) Å. The Fe-Na distances are in the range 3.376(7)—3.443(7) Å. Thus, the adjacent metal-metal separations alternate between two short (Fe-Na) and one long (Fe-Fe) contacts in the distorted nonagon. The interior Fe-Fe-Na and Fe-Na-Fe angles of the nonagon are 118.5(2)—120.4(2)° and 142.1(2)—144.2(2)°, respectively. This kind of cyclic nonanuclear species is unknown, although few cyclic hexanuclear iron(III) complexes have been reported recently.[8-11] In some of the latter cases, the alkali ion is incorporated in the center of the cyclic ring. The present complex is very unique in this regard, because the alkali ions take part in making up the ring. The *syn-syn* bridging form including the η^3 bridging of the carboxylate groups can be confirmed by the infrared spectrum of **1** [ν_{as}(COO) 1585, ν_s(COO) 1441 cm^{-1}].[12]

Room temperature magnetic moment of **1** is 12.59 B.M. per nonanuclear molecule. The value is indicative of the presence of an antiferromagnetic interaction, because the spin-only value is 14.49 B.M. for the six local S = 5/2 and three diamagnetic S = 0 spins. As shown in Figure 3, the magnetic moment

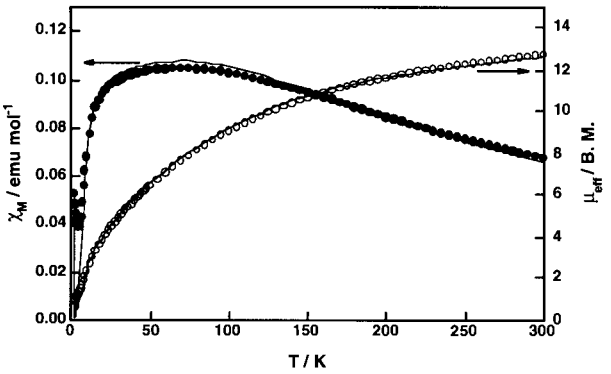

Figure 3. Temperature dependence of magnetic susceptibilities (●) and effective magnetic moments (○) of **1**.

gradually decreases upon cooling from 12.59 B.M. at 300 K to 1.13 B.M. at 4.0 K. Fitting of the data gives values of J = -9.3 cm^{-1}, θ = 2.0 K, and g = 2.01.[13] The result shows that the intradimer (within the $[Fe_2(L)(CH_3COO)_2]^-$ unit) interaction is antiferromagnetic. It is known that the bridging angle is important in determining the nature of the magnetic exchange interaction.[14] The Fe-O-Fe angles within the dinuclear units of **1** are 121.2(4)—122.9(5)°, resulting in the long Fe-Fe distances. Similar structural parameters are found in few dinuclear iron(III) complexes containing the (μ-phenoxo)(μ-acetato)$_2$ structural entity [Fe-Fe 3.528(8) Å and Fe-O-Fe 118.3(4)° for $[Fe_2(bbpmp)(CH_3COO)_2]ClO_4$ (H_3bbpmp = 2,6-bis[(2-hydroxybenzyl)(2-pyridylmethyl)aminomethyl]-4-methylphenol),[15] 3.567(3) Å and 117.5(3)° for $[Fe_2(biomp)(CH_3COO)_2]ClO_4$ (H_3biomp = 2,6-bis[((2-hydroxybenzyl)((1-methylimidazol-2-yl)methyl)amino)methyl]-4-methylphenol)[16]]. In these complexes, an antiferromagnetism was observed and similar J values (-6.0 and –6.4 cm^{-1}) were reported. Therefore, the present J value is not unusual as the intradimer interaction and the θ value of 2.0 K could be due to the weak ferromagnetic interaction caused by the cyclic assemblage of the dinuclear iron and sodium ions.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No.11136250 “Metal-assembled Complexes) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 S. Parsons and R. E. P. Winpenny, *Acc. Chem. Res.*, **30**, 89 (1997).
2 M. Mikuriya and K. Nakadera, *Chem. Lett.*, **1995**, 213.
3 M. Mikuriya, Y. Hashimoto, and S. Nakashima, *Chem. Commun.*, **1996**, 295.
4 M. Mikuriya and M. Fukuya, *Chem. Lett.*, **1998**, 421.
5 M. Mikuriya and S. Tashima, *Polyhedron*, **17**, 207 (1998).
6 H_3L (18 mg, 0.05 mmol) was dissolved in 5 cm^3 of acetonitrile, and to the solution was added 1 cm^3 of methanol solution (0.15 M) of sodium hydroxide. To the resulting solution was added basic iron(III) acetate (23 mg, 0.07 mmol) to give a dark reddish brown solution. The solution was filtered and allowed to stand several days at room temperature. Black crystals deposited were collected by filtration (yield 12 mg).
7 Crystallographic data: for $\mathbf{1}\cdot 4CH_3CN\cdot 1.5CH_3OH\cdot H_2O$; $C_{102.5}H_{113}Fe_6N_{10}Na_3O_{35.5}$, *F.W.* = 2457.12, triclinic, space group $P\bar{1}$, a = 17.607(15), b = 23.706(15), c = 15.498(11) Å, α = 97.72(4), β = 100.65(4), γ = 87.33(5)°, V = 6298(8) Å^3, Z = 2, D_m = 1.35, D_c = 1.30 gcm^{-3}, μ(Mo Kα) = 7.59 cm^{-1}, crystal dimensions 0.15×0.45×0.50 mm^3, 23041 reflections measured ($2\theta_{max}$ = 50°), 7816 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.085, R_w = 0.099. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using a MolEN program package.
8 T. Tokii, K. Ide, M. Nakashima, and M. Koikawa, *Chem. Lett.*, **1994**, 441.
9 A. Caneschi, A. Corvia, and S. J. Lippard, *Angew. Chem.*, **107**, 511 (1995).
10 A. Caneschi, A. Corvia, A. C. Fabretti, S. Foner, D. Gatteschi, R. Grandi, and L. Schenetti, *Chem. Eur. J.*, **2**, 1379 (1996).
11 G. L. Abbati, A. Corvia, A. C. Fabretti, W. Malavasi, L. Schenetti, A. Caneschi, and D. Gatteschi, *Inorg. Chem.*, **36**, 6443 (1997).
12 K. Nakamoto, “Infrared and Raman Spectra of Inorganic and Coordination Compounds,” 4th ed, Wiley Interscience, New York (1986), p. 230.
13 The magnetic data were fitted with the van Vleck equation including a Weiss temperature θ based on the Heisenberg model $\mathbf{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$ ($S_1 = S_2 = 5/2$), $\chi_M = \{2Ng^2\beta^2/k(T-\theta)\}(55+30x^{10}+14x^{18}+5x^{24}+x^{28})/(11+9x^{10}+7x^{18}+5x^{24}+3x^{28}+x^{30}))$, where $x = \exp(-J/kT)$; the other symbols have their usual meanings.
14 M. Mikuriya, Y. Kakuta, K. Kawano, and T. Tokii, *Chem. Lett.*, **1991**, 2031.
15 A. Neves, M. A. de Brito, I. Vencato, V. Drago, K. Griesar, W. Haase, and Y. P. Mascarenhas, *Inorg. Chim. Acta*, **214**, 5 (1993).
16 H. Nie, S. M. J. Aubin, M. S. Mashuta, C.-C. Wu, J. F. Richardson, D. N. Hendrickson, and R. M. Buchanan, *Inorg. Chem.*, **34**, 2382 (1995).