Novel Thiolato-Bridged Tetranuclear Manganese(II) and Iron(II) Complexes with Adamantane-like Cores

Masahiro Mikuriya* and Takanori Kotera
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501

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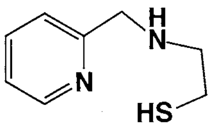
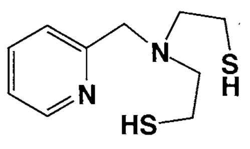
Thiolato-bridged tetranuclear manganese(II) and iron(II) complexes, $[M_4L^b_3Cl]Cl$ (M = Mn and Fe; H_2L^b = 2-[bis(2-mercaptoethyl)aminomethyl]pyridine), have been isolated and characterized by X-ray crystallography, which reveals an adamantane-like M_4S_6 core. Magnetic susceptibility data show an overall antiferromagnetic interaction.

Metal-thiolate compounds have attracted much attention over the past three decades, since they have various coordination structures and potential significance as models for metal-cysteine centers in metalloproteins.[1] We recently described synthesis of dinuclear,[2] trinuclear,[3] and infinite polynuclear[3] complexes which are formed by the use of NNS-donor tridentate ligands including 2-[(2-pyridylmethyl)amino]ethanethiol (HL^a). In the course of this activity, we have found that a new NNSS-donor tetradentate thiolic ligand, 2-[bis(2-mercaptoethyl)aminomethyl]pyridine (H_2L^b), forms from a reaction of 2-(aminomethyl)pyridine with ethylene sulfide for the synthesis of HL^a.[4] Interestingly, this tetradentate ligand affords unique tetranuclear manganese(II) and iron(II) complexes, $[M_4L^b_3Cl]Cl$ (M = Mn (**1**) and Fe (**2**)). Herein we report the synthesis and characterization of these complexes.



HL^a



H_2L^b

Manganese complex **1** was prepared as follows.[5] To a solution of 100 mg (0.438 mmol) of H_2L^b dissolved in 10 cm^3 of methanol was added 1176 mg (5.94 mmol) of manganese(II) chloride tetrahydrate. The solution was heated at *ca.* 60 ℃ for 5 minutes and filtered. The resulting pale yellow solution was allowed to stand overnight at 10 ℃. Salmon-colored crystals deposited were collected by filtration. Yield, 88 mg. Iron complex **2** was prepared in a similar way.[5,6]

The X-ray crystallography of **1** reveals a tetranuclear structure where four Mn atoms occupy the corners of a tetrahedron (Figure 1).[7] The coordination environments of the three Mn atoms (Mn1, Mn2, and Mn3) at the bottom are different from that of of the top Mn atom (Mn4). Each Mn atom of the three MnL^b moieties is surrounded in a distorted trigonal bipyramidal configuration with two thiolato-sulfur atoms and pyridyl nitrogen atom of L^{b2-} in the equatorial plane, and amino nitrogen atom of L^{b2-} and thiolato-sulfur atom of neighboring MnL^b moiety at the axial positions. On the other hand, the vertex Mn4 atom is capped by a chloride ion [Mn4-Cl1 2.307(4) Å], forming a distorted tetrahedral geometry with three thiolato-sulfur atoms. The Mn-S bond distances around the tetrahedral Mn atom [Mn-S 2.447(3)—2.454(3) Å] are slightly shorter than the equatorial Mn-S distances of the trigonal bipyramidal Mn atoms [Mn-S 2.452(4)—2.491(4) Å]. The Mn-Mn distances are 3.954(2)—4.031(2) Å. The Mn_4S_6 core corresponds to an adamantane skeleton. This type of adamantane-like structure is a commonly encountered structural unit in metal-thiolate cage species,[1] however, the majority of which are derived from benzenethiol and very few examples are known for manganese thiolates. The only well-characterized species is $[Mn_4(SC_6H_5)_{10}]^{2-}$.[8] To our knowledge, the present Mn_4S_6 core is the first example of an adamantane-like structure formed by chelated thiolic ligands. The structure of **1** represents a novel example of Mn_4/Cl assemblies showing the involvement of a Cl^- ion in adamantane-like structure, which was proposed as a reaction intermediate in photosynthetic water

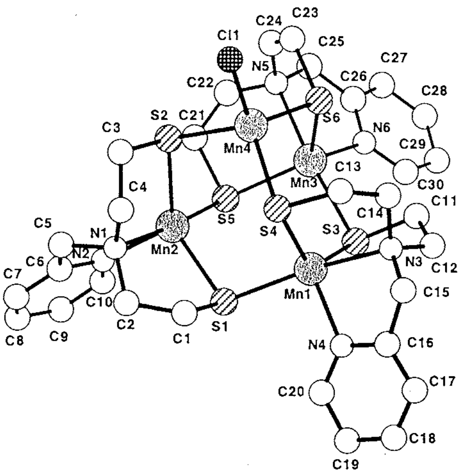


Figure 1. Perspective view of complex cation of **1**, showing the atom-labeling scheme. Selected bond distances (*l*/Å) and angles (*ϕ*/°): Mn1-Mn2 4.033(3), Mn1-Mn3 4.025(2), Mn1-Mn4 3.954(2), Mn2-Mn3 4.031(2), Mn2-Mn4 3.992(3), Mn3-Mn4 4.000(2), Mn1-S1 2.496(4), Mn1-S3 2.461(3), Mn1-S4 2.468(3), Mn1-N3 2.31(1), Mn1-N4 2.200(9), Mn2-S1 2.452(4), Mn2-S2 2.465(3), Mn2-S5 2.503(3), Mn2-N1 2.324(8), Mn2-N2 2.19(1), Mn3-S3 2.498(3), Mn3-S5 2.460(4), Mn3-S6 2.491(4), Mn3-N5 2.307(9), Mn3-N6 2.213(8), Mn4-Cl1 2.307(4), Mn4-S2 2.453(4), Mn4-S4 2.454(3), Mn4-S6 2.447(3); S1-Mn1-S3 101.6(1), S1-Mn1-S4 99.0(1), S1-Mn1-N3 172.5(2), S1-Mn1-N4 97.9(3), S3-Mn1-S4 125.6(1), S3-Mn1-N3 83.7(2), S3-Mn1-N4 110.6(3), S4-Mn1-N3 81.8(3), S4-Mn1-N4 115.5(3), N3-Mn1-N4 75.2(4), S1-Mn2-S2 123.6(1), S1-Mn2-S5 102.3(1), S1-Mn2-N1 83.6(2), S1-Mn2-N2 105.9(2), S2-Mn2-S5 97.9(1), S2-Mn2-N1 81.1(2), S2-Mn2-N2 121.3(3), S5-Mn2-N1 173.4(3), S5-Mn2-N2 100.4(2), N1-Mn2-N2 74.8(3), S3-Mn3-S5 101.1(1), S3-Mn3-S6 99.3(1), S3-Mn3-N5 173.8(3), S3-Mn3-N6 98.7(3), S5-Mn3-S6 124.3(1), S5-Mn3-N5 82.9(3), S5-Mn3-N6 112.0(3), S6-Mn3-N5 82.1(3), S6-Mn3-N6 115.3(3), N5-Mn3-N6 75.4(3), Cl1-Mn4-S2 104.2(2), Cl1-Mn4-S4 111.1(1), Cl1-Mn4-S6 115.2(1), S2-Mn4-S4 110.5(1), S2-Mn4-S6 106.7(1), S4-Mn4-S6 108.9(1).

oxidation.[9] The molecular structure of **2** is very similar to that of **1**.[7] The core structure is shown in Figure 2. The Fe-Fe distances are 3.826(2)—3.967(2) Å. The bond distances around the metal atoms become shortened compared with those of **1**, in accord with the decrease in the Schannon radii.[10]

The magnetic moments of **1** and **2** at room temperature (8.73 and 8.35 B.M., respectively) suggest that the metal ions are in the high-spin state, although these values are significantly lower than those expected for non-interacting four metal atoms. The magnetic moments of **1** measured down to 80 K are plotted in Figure 3 and indicate antiferromagnetic interactions of J = -10.5 cm^{-1} and J' = -5.0 cm^{-1}.[11] Similar antiferromagnetic behavior was observed for **2**.[11]

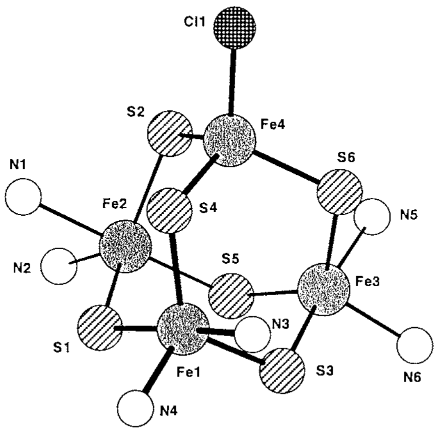


Figure 2. Perspective view of coordination spheres of cation of **2**. Selected bond distances (l/Å) and angles (ϕ/°): Fe1-Fe 3.967(2), Fe1-Fe3 3.962(3), Fe1-Fe4 3.826(2), Fe2-Fe3 3.960(3), Fe2-Fe4 3.860(3), Fe3-Fe4 3.888(3), Fe1-S1 2.399(5), Fe1-S3 2.362(5), Fe1-S4 2.381(4), Fe1-N3 2.26(1), Fe1-N4 2.13(1), Fe2-S1 2.342(3), Fe2-S2 2.381(4), Fe2-S5 2.412(5), Fe2-N1 2.28(1), Fe2-N2 2.13(1), Fe3-S3 2.405(4), Fe3-S5 2.365(5), Fe3-S6 2.401(5), Fe3-N5 2.275(9), Fe3-N6 2.14(1), Fe4-Cl1 2.256(4), Fe4-S2 2.385(4), Fe4-S4 2.357(4), Fe4-S6 2.370(5); S1-Fe1-S3 100.4(2), S1-Fe1-S4 97.2(2), S1-Fe1-N3 173.7(4), S1-Fe1-N4 97.3(4), S3-Fe1-S4 123.3(2), S3-Fe1-N3 84.3(4), S3-Fe1-N4 111.7(4), S4-Fe1-N3 83.4(3), S4-Fe1-N4 118.8(4), N3-Fe1-N4 77.0(5), S1-Fe2-S2 121.7(1), S1-Fe2-S5 100.2(1), S1-Fe2-N1 84.1(2), S1-Fe2-N2 108.1(3), S2-Fe2-S5 97.5(2), S2-Fe2-N1 82.5(3), S2-Fe2-N2 123.0(2), S5-Fe2-N1 174.8(3), S5-Fe2-N2 99.1(4), N1-Fe2-N2 76.7(5), S3-Fe3-S5 99.5(2), S3-Fe3-S6 97.1(1), S3-Fe3-N5 175.3(4), S3-Fe3-N6 98.5(3), S5-Fe3-S6 122.7(2), S5-Fe3-N5 84.0(4), S5-Fe3-N6 113.5(4), S6-Fe3-N5 83.5(4), S6-Fe3-N6 117.6(4), N5-Fe3-N6 77.1(4), Cl1-Fe4-S2 104.2(1), Cl1-Fe4-S4 110.8(2), Cl1-Fe4-S6 114.7(2), S2-Fe4-S4 111.3(2), S2-Fe4-S6 106.7(2), S4-Fe4-S6 109.0(1).

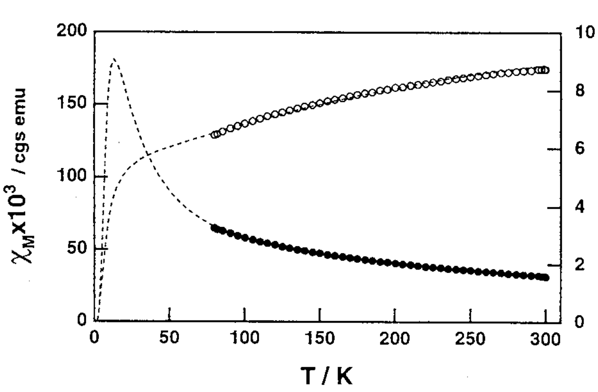


Figure 3. Magnetic susceptibility data (●) and effective magnetic moments (○) of **1**. The dashed lines were calculated from the van Vleck equation based on Heisenberg model.[11]

Contrary to the case for the tridentate L^{a-} ligand which gives rise to a polymeric chain compound [Mn(L^a)Cl]$_n$,[3] further polymerization to form larger aggregates seems to be difficult for the L^{b2-} complexes, because the tetradentate ligand occupies four of the five available sites for each metal atom. The oligonuclear formation may be accomplished by the introduction of the additional 2-mercaptoethyl group to the tridentate ligand.

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References and Notes

1 For example, see B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, **30**, 769 (1991).

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4 Ethylene sulfide (6.8 g) was added to a toluene solution (15 cm^3) containing 2-aminomethylpyridine (6.4 g). The mixture was heated at reflux for 30 h in a sealed bottle. The product was collected by distillation at 130—134 ℃/2 mmHg and 2.3 grams were obtained. ^{1}H NMR measurements showed that the product contained small amount of diethyl disulfide which could not be excluded by distillation.

5 All maniplations were performed under argon by using standard Schlenk techniques.

6 To a methanol solution (5 cm^3) of H$_2$L^b (50 mg, 0.22 mmol) was added iron(II) chloride tetrahydrate (600 mg, 3.0 mmol). The resulting brown solution was allowed to stand overnight at 10 ℃. Brown plates deposited were collected by filtration. Yield, 17 mg.

7 Crystallographic data: for **1**·1/2(C_2H_5S)$_2$·2CH_3OH; $C_{34}H_{55}Cl_2Mn_4N_6O_2S_7$ $F.W.$ = 1094.97, triclinic, space group $P\bar{1}$, a = 11.293(5), b = 15.816(7), c = 16.342(7) Å, α = 61.13(4), β = 79.17(2), γ = 81.81(3)°, V = 2506(2) Å^3, Z = 2, D_m = 1.58, D_c = 1.45 gcm^{-3}, μ(Mo Kα) = 14.15 cm^{-1}, 7394 reflections measured ($2\theta_{max}$ = 47°), 5241 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.073, R_w = 0.090. For **2**·1/2(C_2H_5S)$_2$·CH_3OH; $C_{33}H_{51}Cl_2Fe_4N_6OS_7$ $F.W.$ = 1066.56, triclinic, space group $P\bar{1}$, a = 15.719(4), b = 16.128(5), c = 11.239(3) Å, α = 93.69(2), β = 98.29(2), γ = 118.45(1)°, V = 2450(1) Å^3, Z = 2, D_m = 1.57, D_c = 1.45 gcm^{-3}, μ(Mo Kα) = 15.90 cm^{-1}, 7689 reflections measured ($2\theta_{max}$ = 48°), 4930 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.073, R_w = 0.100. 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.

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11 The magnetic susceptibilities were measured by the Faraday method over the 80—300 K temperature range. The magnetic data were analyzed with van Vleck equation based on the Heisenberg model [$\mathcal{H} = -2J(S_{M1}\cdot S_{M4} + S_{M2}\cdot S_{M4} + S_{M3}\cdot S_{M4}) - 2J'(S_{M1}\cdot S_{M2} + S_{M2}\cdot S_{M3} + S_{M1}\cdot S_{M3})$ ($S_{M1} = S_{M2} = S_{M3} = S_{M4}$ = 5/2 for **1**, $S_{M1} = S_{M2} = S_{M3} = S_{M4}$ = 2 for **2**)]; the best fitting parameters are: J = -10.5 cm^{-1}, J' = -5.0 cm^{-1}, g = 1.98, θ = -0.9 K for **1**; J = -10.7 cm^{-1}, J' = -3.4 cm^{-1}, g = 2.05, θ = -2.8 K for **2**.