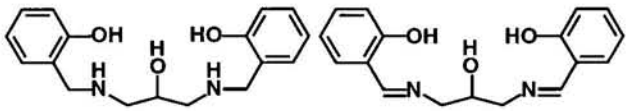
High Nuclearity in a Zinc(II) Complex with 1,3-Bis(salicylamino)-2-propanol

Masahiro Mikuriya,* Noriyo Tsuru, Shinichiro Ikemi, and Shuichi Ikenoue
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662-8501

(Received May 28, 1998; CL-980408)

A zinc(II) complex with 1,3-bis(saliclylamino)-2-propanol (H_3L^a), $[Zn_8L^a_4(OH)_2](ClO_4)_2 \cdot 8CH_3OH$, has been isolated and characterized by X-ray crystallography, which reveals a unique cage structure composed of eight zinc atoms and four alkoxo-oxygen and eight phenoxo-oxygen bridges of L^{a3-}.

Dinucleating ligands are multidentate ligands which have a bridging group to bind two metal atoms in close proximity. A pentadentate Schiff-base ligand, 1,3-bis(salicylideneamino)-2-propanol (H_3L^b) is one of such dinucleating ligands and several investigators prepared dinuclear metal complexes by using this ligand.[1-3] In the dinuclear complexes, the Schiff-base backbone forms a fairly rigid framework for the two metal ions owing to the presence of the two C=N bonds, limiting the variety of the dinuclear species. Hydrogenation of the C=N groups of the Schiff-base may afford a more flexible ligand, 1,3-bis(salicylamino)-2-propanol (H_3L^a), which might enable us to make more interesting metal complexes. In this paper we describe the synthesis and structural characterization of a new zinc(II) complex, $[Zn_8L^a_4(OH)_2](ClO_4)_2$ (**1**), formed by the non-Schiff-base ligand, H_3L^a. In contrast to the cases for the Schiff-base ligand, H_3L^b, this species exhibits a high nuclearity which is unprecedented for zinc(II) complexes.



H_3L^a H_3L^b

When sodium tetrahydroborate was added to a methanol solution of H_3L^b, yellow color of the solution disappeared, suggesting that hydrogenation of the C=N groups of H_3L^b occurred. The reaction of the ligand methanol solution with 2 equiv. of zinc(II) perchlorate resulted in the formation of a colorless solution. After standing the solution overnight, colorless crystals were isolated that have the chemical formula $[Zn_8L^a_4(OH)_2](ClO_4)_2$ (**1**), as inferred from elemental analysis.[4] The IR spectrum of **1** shows a band of ν(NH) at 3303 cm^{-1} which is not observed for that of H_3L^b. On the other hand, the ν(C=N) band at 1633 cm^{-1} of H_3L^b disappears in the spectrum of **1**. These facts are in accordance with the presence of the non-Schiff-base ligand, L^{a3-}. The X-ray crystallography of $\mathbf{1} \cdot 8CH_3OH$ reveals a novel octanuclear Zn^{II} complex cation as shown in Figure 1.[5] The complex cation has a crystallographic inversion center and is formed by eight zinc atoms arranged at vertices of a severely distorted rectangular parallelepiped (edge lenghts 3.313(2)—3.754(3) Å). These zinc atoms are linked through four L^{a3-} ligands. The N_2O_3 donor atomd of L^{a3-} occupies eight coordination sites of four zinc atoms and the central alkoxo oxygen [O2, O5, O2', and O5'; where primes refer to the equivalent position (-x, -y, -z)] acts as the bridging atom binding two zinc atoms. Hydroxide ions (O7, O8, O7', and O8') are incorporated as exogenous bridging groups with an occupancy factor of 0.5, where O7 is for Zn1 and Zn4' and O8 for Zn2 and Zn3, respectively. The presence of the hydroxide ions was confirmed by the IR spectrum of **1** which shows a band of ν(OH) at 3612 cm^{-1}. The two terminal phenoxo oxygens of each L^{a3-} ligand act as bridging groups for two zinc atoms; O1 is for Zn1 and Zn3, O3 for Zn2 and Zn4, O4 for Zn3 and Zn4', and O6 for Zn2 and Zn1', respectively. To our knowledge, this is the first example of observation of an octanuclear zinc assemblage by multidentate chelate ligands. The core structure is shown in Figure 2. The coordination geometry around each zinc atom can be regarded as a severely distorted trigonal bipyramid with an alkoxo-oxygen and two phenoxo-oxygen atoms of two L^{a3-} ligands in the equatorial plane, and an amino nitrogen atom of L^{a3-} and hydroxide ion at the axial positions. The equatorial Zn-O bond lengths are in the range 1.958(10)—2.037(10) Å and the axial Zn-O and Zn-N distances are 2.161(25)—2.322(15) and 2.080(15)—2.104(10) Å, respectively. If we neglect the hydroxide ion, the coordination environment can be described as a distorted tetrahedral geometry which is common in zinc(II) chemistry.

When we tried a similar hydrogenation reaction of H_3L^b in the presence of Mn^{III} or Fe^{III} ions, we could isolate dinuclear species with an unsymmetrical ligand, 1-salicylideneamino-3-salicylamino-2-propanol istead of metal complexes of L^{a3-}.[6] In this case, hydrogenation reaction occurs in only one of the two

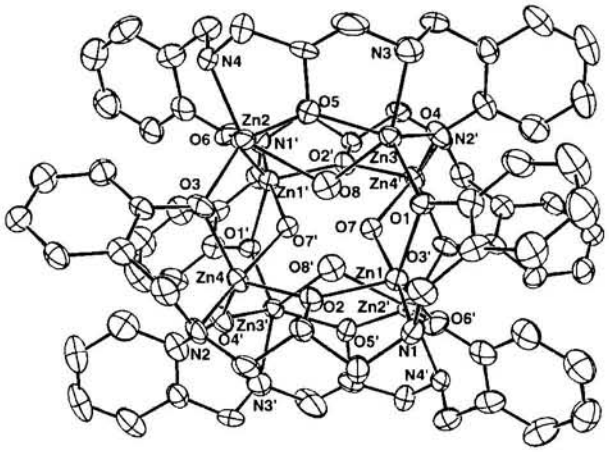


Figure 1. Perspective view of the complex cation of $\mathbf{1} \cdot 8CH_3OH$. Hydrogen atoms are omitted for clarity. Selected bond distances (l/Å) and angles (ϕ/°): Zn1-Zn2' 3.405(2), Zn1-Zn3 3.313(2), Zn1-Zn4 3.754(3), Zn2-Zn3 3.492(3), Zn2-Zn4 3.316(2), Zn3-Zn4' 3.405(2); Zn1-O1-Zn3 111.8(4), Zn1-O2-Zn4 140.4(4), Zn2-O3-Zn4 113.2(4), Zn3-O4-Zn4' 116.6(5), Zn2-O5-Zn3 124.1(7), Zn1'-O6-Zn2 116.4(5), Zn1-O7-Zn4' 136.7(9), Zn2-O8-Zn3 102.9(9).

imino groups of H_3L^b, resulting in the formation of dinuclear species containing Mn^{III} or Fe^{III} centers. The steric accomodation and bridging property of the non-Schiff-base ligand may lead to such a high nuclearity in zinc(II) complexes. The present result suggests that multidentate ligands may be useful to produce high spin clusters which have unique magnetic properties.[7] Further study to extend this system to paramagnetic metal chemistry is now in progress in our laboratory.

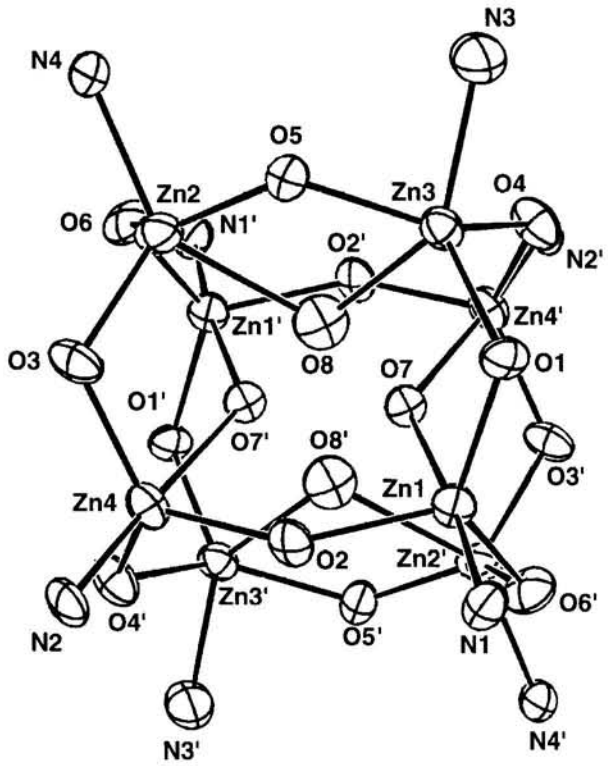


Figure 2. Core structure of the complex cation of $1 \cdot 8CH_3OH$. Selected bond distances (l/Å) and angles (ϕ/°): Zn1-O1 2.009(9), Zn1-O2 2.015(9), Zn1-O6' 1.970(9), Zn1-O7 2.254(16), Zn1-N1 2.104(10), Zn2-O3 1.972(9), Zn2-O5 1.964(17), Zn2-O6 2.037(10), Zn2-O8 2.301(24), Zn2-N4 2.094(12), Zn3-O1 1.991(9), Zn3-O4 2.044(8), Zn3-O5 1.988(13), Zn3-O8 2.161(25), Zn3-N3 2.080(15), Zn4-O2 1.976(10), Zn4-O3 2.000(10), Zn4-O4' 1.958(10), Zn4-O7' 2.322(15), Zn4-N2 2.093(9); O1-Zn1-O2 114.9(4), O1-Zn1-O6' 128.2(4), O1-Zn1-O7 86.9(5), O1-Zn1-N1 93.4(4), O2-Zn1-O6' 115.3(4), O2-Zn1-O7 88.3(5), O2-Zn1-N1 85.9(4), O6'-Zn1-O7 82.5(5), O6'-Zn1-N1 102.2(4), O7-Zn1-N1 173.8(6), O3-Zn2-O5 116.9(5), O3-Zn2-O6 108.6(4), O3-Zn2-O8 98.0(6), O3-Zn2-N4 115.8(4), O5-Zn2-O6 130.8(5), O5-Zn2-O8 64.9(7), O5-Zn2-N4 84.7(5), O6-Zn2-O8 91.9(6), O6-Zn2-N4 92.2(4), O8-Zn2-N4 142.5(7), O1-Zn3-O4 105.0(4), O1-Zn3-O5 115.7(4), O1-Zn3-O8 96.5(6), O1-Zn3-N3 121.9(5), O4-Zn3-O5 135.6(5), O4-Zn3-O8 92.1(6), O4-Zn3-N3 91.2(4), O5-Zn3-O8 67.3(8), O5-Zn3-N3 82.2(6), O8-Zn3-N3 139.0(8), O2-Zn4-O3 115.3(4), O2-Zn4-O4' 117.9(4), O2-Zn4-O7' 87.9(5), O2-Zn4-N2 86.1(4), O3-Zn4-O4' 124.3(4), O3-Zn4-O7' 85.0(5), O3-Zn4-N2 94.3(4), O4'-Zn4-O7' 81.6(5), O4'-Zn4-N2 104.4(4), O7'-Zn4-N2 173.0(6).

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 08404046) and Grant-in-Aid for Scientific Research on Priority Areas (No. 10149255 "Metal-assembled Complexes") from the Ministry of Education, Science, Sports and Culture, Japan.

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4 To a methanol solution of 1.3-bis(salicylideneamino)-2-propanol (30 mg, 0.10 mmol), sodium tetrahydroborate (8 mg, 0.21 mmol)) was added with stirring. After stirring for 2 h, a methanol solution of zinc(II) perchlorate hexahydrate (74 mg, 0.20 mmol) was added to the solution. The resulting solution was left to stand overnight. Colorless plates were deposited; they were collected by filtration and dried in vacuo over P_2O_5 (yield 28 mg). Found: C, 41.80; H, 4.37; N, 5.32%. Calcd for $C_{68}H_{78}Cl_2N_8O_{22}Zn_8$ (**1**): C, 41.81; H, 4.02; N, 5.74%.

5 Crystallographic data: for $1 \cdot 8CH_3OH$; $C_{76}H_{110}Cl_2N_8O_{30}Zn_8$, $F.W.$ = 2209.8, monoclinic, space group $P2_1/n$, a = 17.406(9), b = 15.977(5), c = 17.484(7) Å, β = 108.58(2)°, V = 4608(3) Å^3, Z = 2, D_m = 1.63, D_c = 1.59 gcm^{-3}, μ(Mo Kα) = 22.3 cm^{-1}, 8416 reflections measured ($2\theta_{max}$ = 50°), 3555 [$I \geq 3\sigma(I)$] used in the refinement, R = 0.068, R_w = 0.078. 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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