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Monodentate, Didentate, and Tridentate Ligation of a Schiff-Base Ligand in a Tetranuclear Zinc(II) Complex

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A tetranuclear zinc(II) complex with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H$_3$L), [Zn$_4$(L)$_2$(pz)$_2$]$\cdot$2CH$_3$CN (Hpz = pyrazole), was synthesized and characterized by ^{1}H NMR spectroscopy and a single-crystal X-ray diffraction method. Each Schiff-base L^{3-} acts as a monodentate, a didentate, and a tridentate ligand for four zinc atoms to form a Z-shaped tetranuclear structure.

2,6-Bis(salicylideneaminomethyl)-4-methylphenol (H$_3$L) is a unique ligand, which affords oligonuclear metal species as well as dinuclear metal complexes.[1–8] Usually, the ligand binds two metal atoms in a tridentate fashion for each metal to give a dinuclear species.[1–3] In the manganese, iron, cobalt, and nickel systems, the dinuclear metal units are associated into tetranuclear, pentanuclear, or hexanuclear metal species by virtue of exogenous ligands.[2–8] In all of these cases, the Schiff-base ligand affords a square-planar, basal, or equatorial plane for each metal atom with an exogenous donor atom. In a previous study, we reported that a chain molecule consisting of ZnZn-Na-zigzag units forms by a reaction of H$_3$L with zinc ion, which may be expected to prefer a tetrahedral geometry as the metal coordination environment.[9] In this complex, sodium ions play an important role in the polymeric assemblage of the dinuclear Zn$_2$(L)$^-$ moieties. During the course of our studies on this system, we have found that an interesting coordination behavior of the Schiff-base ligand could be achieved in a tetranuclear zinc(II) complex, [Zn$_4$(L)$_2$(pz)$_2$] (Hpz = pyrazole) (**1**), when the reaction of H$_3$L with zinc ion was performed in the presence of pyrazole instead of sodium ion. Here, we report on the synthesis and structural characterization of **1**.

The treatment of H$_3$L with Zn(ClO$_4$)$_2$$\cdot$6H$_2$O in acetonitrile containing pyrazole and triethylamine afforded pale-yellow crystals of **1**$\cdot$2CH$_3$CN. An X-ray crystallographic study revealed that the compound is a tetranuclear molecule where the four zinc atoms are arranged in a Z shape [Zn1–Zn2 3.264(1), Zn2–Zn3 3.042(1), Zn3–Zn4 3.248(1)Å; Zn1–Zn2–Zn3 128.80(3), Zn2–Zn3–Zn4 131.00(3)°] (Fig. 1). The outside zinc atoms (Zn1; Zn4) take a similar tetrahedral coordination geometry with two phenoxo-oxygen atoms (O1, O4; O6, O3) and an imino-nitrogen atom (N1; N4) of two L^{3-} ligands and pyrazolato-nitrogen atom (N5; N8), while the geometries of the inside zinc atoms (Zn2; Zn3) are trigonal bipyramidal with a phenoxo-oxygen atom (O2; O5) of L^{3-}, an imino-nitrogen atom of another L^{3-} (N3; N2), and a pyrazolato-nitrogen atom (N6; N7) in the equatorial plane and two phenoxo-oxygen atoms (O4, O5; O3, O2) of L^{3-} at the axial positions. The molecular arrangement of **1**$\cdot$2CH$_3$CN is quite unique in a scarce family of oligonuclear zinc(II) complexes which have appeared recently.[10–13] It is noteworthy that each Schiff-base ligand is bound to four metal atoms. One Schiff-base ligand binds Zn1, Zn2, Zn3, and Zn4 atoms in different ways: it acts as a didentate ligand for tetrahedral Zn1 with the terminal phenoxo-oxygen O1 and imino-nitrogen N1, a monodentate ligand for trigonal-bipyramidal Zn2 with the central phenoxo-oxygen O2, a tridentate ligand for trigonal-bipyramidal Zn3 with a central phenoxo-oxygen O2, an imino-nitrogen N2, and a terminal phenoxo-oxygen O3, and a monodentate ligand for tetrahedral Zn4 with a terminal phenoxo-oxygen O3. The other Schiff-base ligand is bound to Zn1, Zn2, Zn3, and Zn4 atoms in a similar fashion (monodentate with O4 for Zn1, tridentate with O4, N3, and O5 for Zn2, monodentate with O5 for Zn3, and didentate with N4 and O6 for Zn4). This is a novel example of the coexistence of monodentate, didentate, and tridentate ligation of a multidentate ligand in four different bonding modes. This situation may be encountered owing to the flexible coordination behavior of the Schiff-base ligand and the high nuclearity

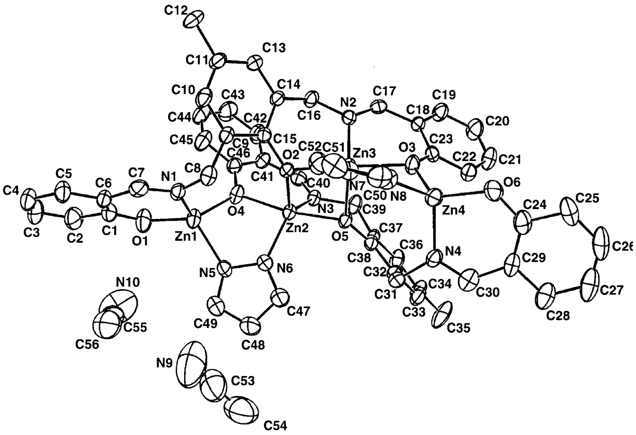

Fig. 1. ORTEP drawing of the structure of **1**$\cdot$2CH$_3$CN showing the 35% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (1/Å) and angles (ϕ/°): Zn1–O1 1.912(6), Zn1–O4 1.962(4), Zn1–N1 1.988(5), Zn1–N5 1.999(7), Zn2–O2 1.997(4), Zn2–O4 2.107(5), Zn2–O5 2.081(5), Zn2–N3 2.037(5), Zn2–N6 1.985(6), Zn3–O2 2.074(4), Zn3–O3 2.084(5), Zn3–O5 2.006(4), Zn3–N2 2.046(6), Zn3–N7 1.999(6), Zn4–O3 1.967(5), Zn4–O6 1.906(6), Zn4–N4 1.984(6), Zn4–N8 1.981(6); O1–Zn1–N1 98.8(2), O4–Zn1–N5 93.4(2), O4–Zn2–N3 88.0(2), O4–Zn2–N6 89.9(2), O5–Zn2–N3 89.8(2), O2–Zn3–N2 89.0(2), O3–Zn3–N2 88.2(2), O3–Zn3–N7 90.4(2), O3–Zn4–N8 94.8(2), O6–Zn4–N4 98.9(3).

of the zinc(II) ion due to strong Lewis acidity.

The ^1H NMR spectrum was measured in $CDCl_3$. All signals can be reasonably assigned based on the 1 : 1 molar ratio of L^{3-} and pz^- ions. This is in harmony with the solid state structure, although a symmetric dinuclear species, $Zn_2(L)(pz)$, is more realistic in solution. In fact, attempts to prepare such a dinuclear species have been unsuccessful.

Experimental

Synthesis of 1. H_3L (18 mg, 0.050 mmol) and pyrazole (7 mg, 0.1 mmol) were combined in a flask and suspended in 5 cm^3 of methanol. Then, 1 cm^3 of an acetonitrile solution of triethylamine (0.15 mol/dm^3) and 37 mg (0.10 mmol) of zinc(II) perchlorate hexahydrate was successively added, and the mixture was stirred under ambient conditions. The resulting pale-yellow solution was filtered. Acetonitrile (5 cm^3) was layered onto the filtrate and the mixture allowed to stand for several days. Pale-yellow plates were deposited, filtered and washed with acetonitrile: Yield, 12 mg (39%). Found: C, 54.38; H, 3.92; N, 9.75%. Calcd for $C_{52}H_{44}N_8O_6Zn_4$: C, 54.86; H, 3.90; N, 9.84%. IR (KBr) ν(C=N) 1625 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, 6H, ArCH_3), 4.63 (s, 8H, ArCH_2N=C–), 6.27 (t, 2H, Ar(pz)*H*), 6.39 (td, 4H, Ar*H*), 6.64 (dd, 4H, Ar*H*), 6.86 (s, 4H, Ar*H*), 7.15 (m, 8H, Ar*H*), 7.88 (d, 4H, Ar(pz)*H*), 8.41 (s, 4H, -N=C*H*Ar).

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm^{-1} region. ^1H NMR spectra were recorded on a Varian UNITY-plus 300 spectrometer .

X-Ray Crystal Structure Analyses. The crystal was sealed in a glass capillary together with the mother liquor and mounted on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo-$K\alpha$ radiation at 25 ± 1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \le 2\theta \le 30°$. The intensitiy data were corrected for Lorentz-polarization effects and for absorption. The structures were solved by direct methods and refined by full-matrix least-squares methods using the weighting scheme $w = 1/[\sigma^2(|F_0|) + (0.02|F_0|)^2 + 1.0]$. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[14]

Crystallographic data: for **1**•$2CH_3CN$; $C_{56}H_{50}N_{10}O_6Zn_4$, *F.W.* = 1220.64, triclinic, space group $P\bar{1}$, $a = 13.996(9)$, $b = 15.484(9)$, $c = 13.187(9)$ Å, $\alpha = 96.97(4)$, $\beta = 107.43(3)$, $\gamma = 87.76(4)°$, $V = 2706(3)$ Å^3, $Z = 2$, $D_m = 1.48$, $D_c = 1.50$ g cm^{-3}, μ(Mo $K\alpha$) = 18.53 cm^{-1}, $F(000) = 1256$, crystal dimensions 0.15 × 0.35 × 0.50 mm, 9529 reflections measured ($2\theta_{max} = 50°$), 5793 [$I \ge 3\sigma(I)$] used in the refinement, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.049$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.057$. The X-ray analysis data have been deposited as Document No. 74001 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 150891.

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