Dinuclear Nickel(II) Complexes Containing a Dinucleating Ligand *N,N,N',N'*-Tetrakis-[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane and an Acetate Ion

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(Received April 11, 1996)

The dinuclear nickel(II) complexes $[Ni_2(L^1)(OAc)(MeOH)_2](ClO_4)_2 \cdot H_2O \cdot MeOH$ **1** and $[Ni_2(L^1)(OAc)(H_2O)_2](ClO_4)_2$ **2** (HL^1 = *N,N,N',N'*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane) were prepared. The complex **1** turns to **2** upon exposure to the air. The crystal structure of **1** and the magnetic and spectroscopic properties of **2** were determined.

There has been a current interest in the structure and catalytic function of the active site of nickel containing enzyme, urease which catalyzes the hydrolysis of urea to yield ammonia and carbamate with extreme efficiency. The best studied jack bean urease has two nickel(II) ions per each subunit of enzyme.[1,2] From the electronic absorption and nickel X-ray absorption edge spectra measurements, the nickel(II) coordination environment can be described as six coordinate octahedral or five coordinate with $Ni(N,O)_5$ site.[3-5] More recently, Jabri et al. have reported the crystal structure of bacterial urease isolated from *Klebsiella aerogenes*.[6] The carbamate group of a carbamylated ε-amino residue of lysine 217 bridges two nickel(II) ions in the active site of this enzyme and each nickel(II) is coordinated by two imidazole nitrogens of histidine. One nickel(II) is in three-coordination environment and another is in five-coordination additionally bound by carboxylate oxygen of aspartate 360 and a water molecule. In connection with these investigations,[3-5] some dinuclear nickel(II) complexes have been reported so far as models for the nickel site of urease.[7-13] We also describe here the synthesis, structure, and characterization of the dinuclear nickel(II) complexes **1** and **2** containing *N, N, N',N'*-tetrakis-[(1-ethyl-2- benzimidazolyl)methyl]-2- hydroxy-1,3- diaminopropane (HL^1) and an acetate ion. These complexes can be regarded as a more favorable model of the active site of jack bean or bacterial urease, because they include relevant donor set comprised of imidazole nitrogens and bridging carboxylate oxygens.

$[Ni_2(L^1)(OAc)(MeOH)_2](ClO_4)_2 \cdot H_2O \cdot MeOH$ **1** was prepared by a reaction between $Ni(ClO_4)_2 \cdot 6H_2O$ (0.55 g, 1.5 mmol), HL^1 (0.43 g, 0.60 mmol), $CH_3COONa \cdot 3H_2O$ (0.049 g, 0.6 mmol), and NaOH (0.028 g, 0.7 mmol) in ethanol solution (0.59 g, 86.8% yield). A crystal suitable for X-ray study was obtained by recrystallization from methanol and was sealed in a capillary tube. The complex **1** is stable in methanol solution, but readily turns to $[Ni_2(L^1)(OAc)(H_2O)_2](ClO_4)_2$ **2** upon filtration in the air. A single crystal of **2** was a weak diffractor of X-rays. Anal. Calcd for $C_{45}H_{56}N_{10}O_{13}Cl_2Ni_2$ **2**: C, 47. 68; H, 4. 99; N, 12. 36. Found: C, 47.20; H, 4.84; N, 12.31.

Crystal data for **1**: F_w = 1211.4, triclinic, space group $P\bar{1}$, a = 15.896(2), b = 16.654(2), c = 12.601(1) Å, α = 101.339(8), β = 100.769(9), γ = 64.573(8)°, V = 2934.0(6) Å^3, Z = 2, D_m = 1.35 g cm^{-3}, D_c = 1.37 g cm^{-3}, μ(Mo$K\alpha$) = 8.02 cm^{-1}. A total of 10749 reflections with $2\theta < 50°$ were collected on a RIGAKU AFC7S diffractometer using Mo$K\alpha$ radiation (λ = 0.71069 Å). Absorption correction was applied. The structure was solved by SHELXS 86[14] and refined by full-matrix least-squares to give R = 0.078 and R_w = 0.098 for 7058 observed reflections [$(I > 3\sigma(I)$].[15] One of the perchlorate ions is disordered. The maximum and minimum peaks in the final difference Fourier were 1.28 and -0.81 e Å^{-3}.

An ORTEP[16] view of $[Ni_2(L^1)(OAc)(MeOH)_2]^{2+}$ is shown in Figure 1 with selected bond lengths and angles. The complex has a bioctahedral geometry sharing a corner. Each nickel atom comprises N_3O_3 donor set from a bridging acetato, an alkoxo of L^1, a methanol molecule, a tertially amino and two imidazolyl nitrogen atoms of L^1. The alkoxo oxygen atom of O(1) bridges the corner of the two octahedrons. The Ni(1)—O(1)—Ni(2) angle is 127.9(3)° which is larger than those of hydroxo bridges,[7,17] but Ni(1)—O(1) and Ni(2)—O(1) distances of 1.961(5) and 1.957(5) Å are shorter. The acetato ligand bridges the two Ni atoms with Ni(1)—O(2) and Ni(2)—O(3) bond lengths of 2.031(6) and

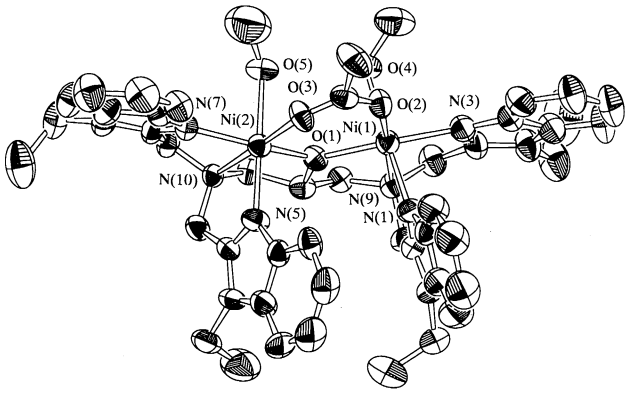

Figure 1. An ORTEP view of $[Ni_2(L^1)(OAc)(MeOH)_2]^{2+}$. Selected bond lengths(Å) and angles(°): Ni(1)· · · Ni(2) 3.520(2), Ni(1)—O(1) 1.961(5), Ni(1)—O(2) 2.031(6), Ni(1)—O(4) 2.255(7), Ni(1)—N(1) 2.038(7), Ni(1)—N(3) 2.042(7), Ni(1)—N(9) 2.187(7), Ni(2)—O(1) 1.957(5), Ni(2)—O(3) 2.022(6), Ni(2)—O(5) 2.193(7), Ni(2)—N(5) 2.048(7), Ni(2)—N(7) 2.048(7), Ni(2)—N(10) 2.193(6) Å; Ni(1)—O(1)—Ni(2) 127.9(3), O(1)—Ni(1)—O(2) 97.0(2), O(1)—Ni(1)—O(4) 82.7(2), O(2)—Ni(1)—O(4) 84.1(2), O(1)—Ni(1)—N(1) 98.6(3), O(2)—Ni(1)—N(1) 97.7(3), O(1)—Ni(2)—O(3) 96.8(2), O(1)—Ni(2)—O(5) 81.1(2), O(3)—Ni(2)—O(5) 87.9(3), O(1)—Ni(2)—N(5) 93.3(3), O(3)—Ni(2)—N(5) 100.1(3)°.

2.022(6) Å. The bonds between Ni and methanol O atoms [Ni(1)—O(4) 2.255(7) and Ni(2)—O(5) 2.193(7) Å] are rather long.[18] The Ni—N [tertially amine] bond lengths are longer than those of the Ni—N (imidazolyl). The planes defined by O(1), O(2),N(3),N(9), and Ni(1) atoms, and O(1), O(3),N(7),N(10), and Ni(2) atoms are almost planar: maximum deviation of the atom is 0.23 Å of N(7). The two planes make an angle of 10.5°. The Ni· · ·Ni distance in the dinuclear complex is 3.520(2) Å.

The coordination of the present dinuclear complex is symmetric and each Ni(II) atom is in a distorted octahedral environment. However, the structure is similar to the active site of the bacterial urease in several points. (1) One acetato ligand bridges between two Ni(II) atoms as Ni-O-C-O-Ni. (2) Each Ni(II) is coordinated by two imidazolato groups. (3) The Ni· · · Ni distance in the dinuclear complex is extremely close to that (3.5 Å) in the native urease. Similar values are also observed in some acetato-bridged dinuclear nickel(II) complexes.[9,10]

The magnetic moment of **2** at room temperature is 2.94 BM. The data of temperature-dependence magnetic susceptibility of **2** show a peak near 50 K and a rapid decrease at lower temperature, indicating an antiferromagnetic interaction between the two nickel atoms. The magnetic parameters can be estimated as $g = 2.24$, $J = -21.6$ cm^{-1} ($H = -2JS_1 \cdot S_2$) and p=0.044 from the best fit of the χ_A values to the equation (1).[19]

$$\chi_A = (Ng^2\beta^2)/(kT) \times [5 + \exp(4x)]\,(1-p)/[(5 + 3\exp(4x) + \exp(6x)] + (2\,Ng^2\beta^2)p/(3kT) \quad (1)$$

where x, g, and p are $-J/kT$(J: the exchange integral), g factor, and the rate of the paramagnetic impurity, respectively. The similar interaction is seen in the magnetic data ($J = -6.3$ cm^{-1}) for jack bean urease.[3] The molar conductance, Λ of **2** in N,N-dimethylformamide (DMF) solution showed 145 S cm^2 mol^{-1}, indicating that the complex is 1:2 electrolyte. Accordingly, the structure in the solid state of **2** is supposed to be maintained in DMF. The electronic absorption spectrum of DMF solution showed that λ_{max} of **2** are 1017(ε, 23), 644(ε, 23), and 407nm(ε, 39), and those of jack bean urease are 1060(ε, 10), 745(ε, 46), and 407nm(sh).[20] The preparation and characterization of a series of dinuclear nickel(II) complexes which are bridged by an alkoxo of L^1 and a simple bridging ligand such as propionato are now in progress.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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