A Strongly Antiferromagnetically Coupled Dinickel(II) Center Bridged by One Azido and One Alkoxo

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The dinuclear nickel(II) complexes $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]\cdot[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(CH_3OH)](NO_3)_2\cdot H_2O$, (**1**) and $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]NO_3\cdot H_2O$, (**1′**) (HL-Et= *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane) bridged by one alkoxo of $L\text{-}Et^-$ and one azido were prepared and the crystal structure of **1** was determined by X-ray crystallography. Magnetic susceptibility measurements for **1′** from liquid helium temperature to room temperature showed an antiferromagnetically strong interaction ($2J = -187\,cm^{-1}$, $H = -2JS_1 \cdot S_2$).

The azido group is a versatile bridging ligand which can coordinate to nickel(II) ions giving dinuclear complexes either in end-on (μ-1,1-N_3) or in end-to-end (μ-1,3-N_3) mode.[1–10] So far it has generally been known that μ-1,1-coordination gives rise to ferromagnetism, while μ-1,3-coordination results in antiferromagnetic interactions between two nickel(II) ions.[1–10] In the case of the dinuclear complexes with central core $Ni(\mu\text{-}1,3\text{-}N_3)_2$, the dihedral angle between the N–Ni–N plane and the plane formed by the two bridging azido ligands is the main factor which dominates the intensity of the antiferromagnetic interaction.[4] On the other hand, in the dinuclear complexes with a single μ-1,3-azido bridge, the strength of interaction between nickel(II) centers is influenced by the magnitude of the Ni–N–N angle.[1,7] According to the Hoffmann's model,[11] the strongest antiferromagnetic interaction is foreseen to be for the Ni–N–N angle near 110°. However, no strongly antiferromagnetically coupled dinuclear nickel(II) complexes bridged by an azido and the other ligand have been reported so far. We describe here preparation and characterization of the novel dinuclear nickel(II) complexes, $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]\cdot[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(CH_3OH)](NO_3)_2\cdot H_2O$, (**1**), and $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]NO_3\cdot H_2O$, (**1′**) bridged by an azido and an alkoxo of $L\text{-}Et^-$.

Preparation of $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]\cdot[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(CH_3OH)](NO_3)_2\cdot H_2O$, **1** and $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]NO_3\cdot H_2O$, **1′** are as follows. To a methanol solution ($100\,cm^3$) of HL-Et (1.09 g, 1.5 mmol) were added successively NaN_3 (0.20 g, 3.0 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (0.87 g, 3.0 mmol), and NaOH (0.06 g, 1.5 mmol). The reaction mixture was stirred at room temperature for 12 h. After it had been filtered, the filtrate was placed at room temperature for several days to give dark green crystals, **1**.[12] The crystal of **1** is stable in methanol. **1** turns immediately to **1′** by filtration in air. Crystal structure analysis was carried out only for **1** because of the low qualify of the crystal of **1′**. Anal. of **1′**. Calcd for $C_{43}H_{51}N_{17}Ni_2O_5\cdot H_2O$: C, 50.56; H, 5.24; N, 23.32%. Found: C, 50.19; H, 5.07; N, 23.16%.

The complex **1** is composed of $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]^+$ (**1a**), $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(CH_3OH)]^+$ (**1b**), two NO_3^-, and one H_2O molecule. ORTEP[16] view of **1a** in **1** is shown in Figure 1 with selected bond lengths and angles. **1a** consists of two nickel(II) ions bridged by one alkoxo group of $L\text{-}Et^-$ and one end-to-end type azido. The Ni(1)–O(1)–Ni(2) angle is 132.4(1)° which is larger than those (127.9(3)–128.3(5)°) of the correspoinding $L\text{-}Et^-$-containing complexes, $[Ni_2\ (L\text{-}Et)(OAc)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot CH_3OH$,[17] and $[Ni_2(L\text{-}Et)(OOC\text{–}O\text{–}CH_3)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot CH_3OH$.[18] The Ni(1)–O(1) and Ni(2)–O(1) distances of 1.984(3) and 2.014(3) Å are slightly longer than those (1.954(9)–1.965(9) Å) of $[Ni_2(L\text{-}Et)(OAc)(CH_3OH)_2](ClO_4)\cdot 2H_2O\cdot CH_3OH$[17] and $[Ni_2(L\text{-}Et)(OOC\text{–}O\text{–}CH_3)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot CH_3OH$.[18] The Ni(1)–N(14) and Ni(2)–N(16) distances are 2.122(3) and 2.145(4) Å, respectively. The coordination environment around each nickel atom has N_4O_2 donor set from a bridging azido, an alkoxo of $L\text{-}Et^-$, a methanol or water molecule, a tertiary amino and two imidazolyl nitrogen atoms of $L\text{-}Et^-$. Ni(1)···Ni(2) distance in the dinuclear complex is 3.658(1) Å, which is slightly longer than those (3.521(2)–3.527(3) Å) of $[Ni_2(L\text{-}Et)(OAc)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot$

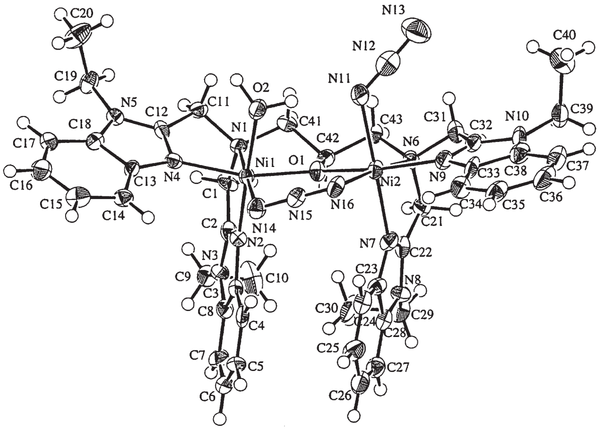

Figure 1. An ORTEP view of $[Ni_2(L\text{-}Et)(\mu\text{-}1,3\text{-}N_3)(N_3)(H_2O)]^+$ **1a**. Selected bond lengths (Å) and angles (°): Ni1···Ni2 3.658(1), Ni1–O1 1.984(3), Ni1–O2 2.149(3), Ni1–N1 2.157(3), Ni1–N2 2.059(3), Ni1–N4 2.052(3), Ni1–N14 2.122(3), Ni2–O1 2.014(3), Ni2–N6 2.144(3), Ni2–N7 2.078(3), Ni2–N9 2.024(3), Ni2–N11 2.161(3), Ni2–N16 2.154(4), N14–N15 1.185(4), N15–N16 1.181(4),Ni1–O1–Ni2 132.4(1), Ni1–N14–N15 106.0(3), N14–N15–N16 178.8(4), Ni2–N16–N15 107.9(3)°.

CH_3OH[17] and $[Ni_2(L\text{-}Et)(OOC\text{–}O\text{–}CH_3)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot CH_3OH$.[18] The dihedral angle between [O(1),N(1), N(4),N(14)] and [O(1),N(6),N(9),N(16)] is 21.71(9)°. The structure of the cation, **1b** is quite similar to that of **1a**.

The complex **1**′ gave the characteristic IR band due to the bridging μ-1,3-azido at 2029 cm^{-1}.

Because the complex **1** cannot be existed in solid state as described above, magnetic susceptibility measurement was carried out for **1**′. The magnetic moment of **1**′ at room temperature is 2.32 BM/Ni. The data of temperature-dependence magnetic susceptibility of **1**′ show a peak near 260 K, indicating an antiferromagnetic interaction between two nickel(II) ions (Figure 2). The magnetic parameters can be estimated as $g = 2.51$, $2J = -187\,\mathrm{cm}^{-1}$ ($H = -2JS_1 \cdot S_2$), $p = 0.0017$, and $N\alpha = 450 \times 10^{-6}\,\mathrm{cgs\,emu\,mol}^{-1}$ from the best fit of the χ_A values to the Eq 1,[19]

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{[5+\exp(4x)](1-p)}{5+3\exp(4x)+\exp(6x)} + \frac{(2Ng^2\beta^2)p}{3kT} + N\alpha. \qquad (1)$$

where x, g, p, and $N\alpha$ are $-J/kT$ (J: the exchange integral), g factor, the rate of the paramagnetic impurity, and T.I.P., respectively. This result shows that a very strong antiferromagnetic spin-coupling occurs in **1**′. This is probably due to two reasons: (i) The Ni(1)–N(14)–N(15) and Ni(2)–N(16)–N(15) angles in **1a** are 106.0(3)° and 107.9(3)°, respectively, which are close to 110°.[11] (ii) The Ni(1)–O(1)–Ni(2) angle is much larger than the corresponding angle (105.7°) of the similar complexes $[Ni_2(L\text{-}Et)(OAc)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot CH_3OH$[17] and $[Ni_2(L\text{-}Et)(OOC\text{–}O\text{–}CH_3)(CH_3OH)_2](ClO_4)_2\cdot H_2O\cdot CH_3OH$.[18] The antiferromagnetic exchange interaction appears to increase with the increase of the bridging angles described above.

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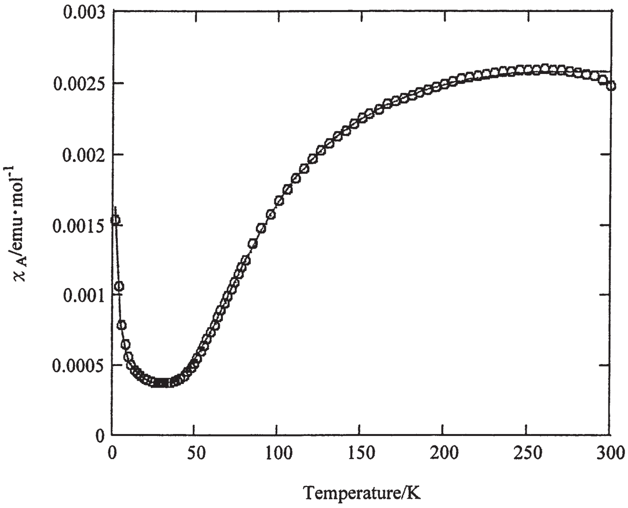

Figure 2. Temperature dependence of the magnetic susceptibility for **1**′. The solid line shows the theoretical susceptibility calculated using Eq 1.[19]

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12 Crystal data for **1**: fw = 2134.94, triclinic, space group $P\bar{1}$, $a = 13.5847(9)$, $b = 15.8921(9)$, $c = 23.4943(8)$ Å, $\alpha = 95.5533(7)$, $\beta = 96.449(1)$, $\gamma = 97.5139(9)°$, $V = 4964.7(5)\,\mathrm{cm}^3$, $Z = 2$, $D_{\mathrm{calcd}} = 1.428\,\mathrm{g\,cm}^{-3}$, $\mu(\mathrm{Mo\ K}\alpha) = 8.26\,\mathrm{cm}^{-1}$. The data were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer using graphite monochromated μ(Mo Kα) radiation ($\lambda = 0.71069$ Å) at -160 ± 1 °C. Out of 43132 reflections, 22160 were unique ($R_{\mathrm{int}} = 0.059$) and 19591 were considered as observed. An absorption correction was applied using ABSCOR program.[13] The maximum and minimum transmission factors were 0.775 and 0.944, respectively. The structure was solved by direct methods[14] and refined on F^2 by full-matrix least-squares to give $R = 0.107$ and $R_w = 0.113$ for 19591 observed reflections [$I > 0.00\sigma(I)$].[15]
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