Structures and Magnetic Properties of Di- and Trinuclear Nickel(II) Complexes with Phenoxo and Acetato Bridges

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Reactions of $NiCl_2 \cdot 6H_2O$ and $Ni(CH_3COO)_2 \cdot 4H_2O$ with tridentate ligand yielded di- and trinuclear nickel(II) complexes of $[Ni_2(HL1)_2Cl_2(MeOH)_2]$ (**1**) and $[Ni_3(HL2)_2(CH_3COO)_4(MeOH)_2]$ (**2**) (H_2L1 = *N*-(2-hydroxybenzyl)ethanolamine), H_2L2 = *N*-(2-hydroxybenzyl)propanolamine), respectively; the magnetic susceptibility measurements revealed that **1** and **2** have singlet and septet spin ground states, respectively.

There have been considerable interests in multinuclear metal complexes because of their relevance to many areas such as nanoscale magnetic materials,[1] bioinorganic chemistry,[2] and oxidation of organic compounds.[3] We have been working on preparing high-spin molecules[1d,1e,4] which might be single molecule magnets (SMMs). A nickel(II) ion with six coordination geometry is in the high-spin state with the magnetic anisotropy. It is, therefore, expected that multinuclear nickel(II) complexes can be a good candidate for the SMMs. We report here syntheses, structures and magnetic properties of di- and trinuclear nickel(II) complexes with ligands prepared by the reduction of Schiff base precursors.

The ligands H_2L1 and H_2L2 were obtained by the following literature procedures.[5,6] A reaction of $NiCl_2 \cdot 6H_2O$ with H_2L1 and NEt_3 in MeOH gave a clear green solution. After concentration of the resulting solution upon heating, the solution was stored for several days at $-20\,^{\circ}C$ to yield pale green crystals of dinuclear nickel(II) complex, $[Ni_2(HL1)_2Cl_2(MeOH)_2]$ (**1**). Green crystals of $[Ni_3(HL2)_2(CH_3COO)_4(MeOH)_2]$ (**2**) were obtained by the reaction of $Ni(CH_3COO)_2 \cdot 4H_2O$ with H_2L2 and NEt_3 in the same manner as **1**. Compounds **1** and **2** crystallized in monoclinic space group $P2_1/c$ and $P2_1/n$, respectively,[7] and ORTEP drawings are shown in Figure 1. Complex **1** is composed of a dinuclear unit which has an inversion center. In **1**, coordination geometry about each nickel(II) ion is an axially elongated octahedron with $N_1O_4Cl_1$ chromophores provided by methanol molecule, chloride ion, and the tridentate ligand ($HL1^-$). Coordination bond lengths about the nickel(II) ions are in the range of 2.017(2)–2.108(2) Å for Ni–O1, Ni–O2, and Ni–N1, while the remaining coordination bonds are elongated with bond lengths of 2.439(2) Å for Ni–Cl, and 2.161(2) Å for Ni–O3. The two nickel(II) ions are doubly bridged by the phenoxo group with the Ni···Ni separation of 3.112(1) Å and the bridging bond angle (Ni–O1–Ni) is 100.75(8)°. Complex **2** has a linear trinuclear unit doubly bridged by phenoxo and acetate ions, where the central nickel(II) ion sits on the center of symmetry. Each terminal nickel(II) ion has quasi-octahedral coordination geometry with N_2O_4 atoms from $HL2^-$, methanol, bridging monodentate and bidentate acetate ions. The central nickel ion is coordinated by O_6 atoms from the two bridging phenoxo groups and four bridging acetate ions. The nickel ions are separated by 3.069(1) Å, and the coordination bond lengths about the central nickel ion are 2.025(5), 2.014(5), 2.127(5) Å for Ni2–O1, Ni2–O4, Ni2–O5, respectively. The coordination bond lengths about terminal nickel ions are in the range of 1.988(5)–2.145(5) Å. The bridging bond angles of the Ni1–O1–Ni2 and of the Ni1–O5–Ni2 are 99.8(2) and 94.1(2)°, respectively.

Temperature dependence of magnetic susceptibility with applying magnetic field of 0.5 T was measured down to 1.8 K for **1** and **2**, and the results are depicted in the form of $\chi_m T$ vs temperature (Figure 2). The $\chi_m T$ value at 300 K for **1** is 2.32 emu mol^{-1} K, which is close to the value (2.21 emu mol^{-1} K, $g = 2.1$) expected for the isolated two nickel(II) ions. The $\chi_m T$ values for **1** show a gradual decrease as the temperature is lowered, and this behavior is characteristic for the occurrence of antiferromagnetic interactions between two nickel(II) ions. The magnetic susceptibility data were analyzed by a two spin model with a coupling constant J, ($H =$

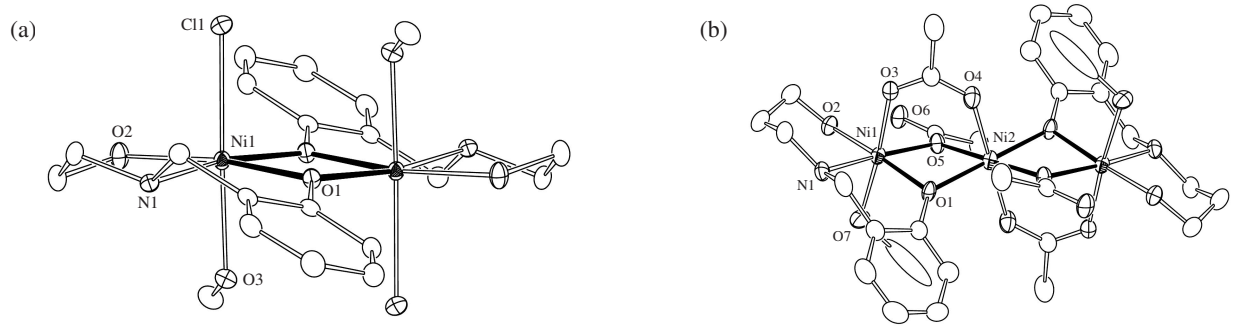

Figure 1. ORTEP diagrams of **1** (a) and **2** (b). Selected interatomic distances (Å) for **1**: Ni–N(1) 2.055(2), Ni–O(1) 2.017(2), Ni–O(1)* 2.024(2), Ni–O(2) 2.108(2), Ni–O(3) 2.161(2), Ni–Cl 2.439(1). Key to symmetry operation of *: $-x+1$, $-y$, $-z$. **2**: Ni(1)–N(1) 1.988(5), Ni(1)–O(1) 1.988(5), Ni(1)–O(2) 2.063(5), Ni(1)–O(3) 2.046(5), Ni(1)–O(5) 2.066(5), Ni(1)–O(7) 2.145(5), Ni(2)–O(1) 2.025(5), Ni(2)–O(4) 2.014(5), Ni(2)–O(5) 2.127(5). Key to symmetry operation of *: $-x$, $-y+2$, $-z+2$.

$-2JS_1 \cdot S_2$). The least squares calculation by using the data above 15 K gave the best fit parameters of $g = 2.146(4)$, $J = -4.6(1)\,\mathrm{cm}^{-1}$. The discrepancy between the observed and theoretical $\chi_m T$ values is due to a paramagnetic impurity. Temperature dependence of $\chi_m T$ values for **2** is quite different from that for **1**. The $\chi_m T$ value (3.76 emu mol^{-1} at 300 K for **2** corresponds to the isolated three nickel(II) ions. Upon cooling, the $\chi_m T$ values slightly increased to a maximum value of 4.01 emu mol^{-1} K at 8 K. This magnetic behavior is indicative of weak ferromagnetic interactions among the nickel(II) ions, giving rise to an $S = 3$ spin ground state. A sudden decrease of $\chi_m T$ values below 8 K is due to an intermolecular antiferromagnetic interaction and/or zero-field splitting. The magnetic data above 10 K were analyzed by a Heisenberg model ($H = -2J\Sigma S_i \cdot S_j$) and the resulting expression of $\chi_m T$ was derived by the Kambe's method.[8] The exchange coupling constant J was estimated to be $0.47(1)\,\mathrm{cm}^{-1}$ with $g = 2.2(1)$. The occurrence of the ferromagnetic interaction can be understood by the mismatch of the magnetic orbitals of the nickel(II) ions. The dihedral angle of O1–Ni1–O5 and O1–Ni2–O5 planes is 155.1(1)°, and this implies the negligible overlap of the magnetic orbitals. In summary, we prepared the two types of nickel(II) complexes bridged by phenoxo and acetate group. Magnetic susceptibility measurements reveal the antiferromagetic interactions for **1** and the weak ferromagnetic interactions for **2** between nickel(II) ions, respectively.

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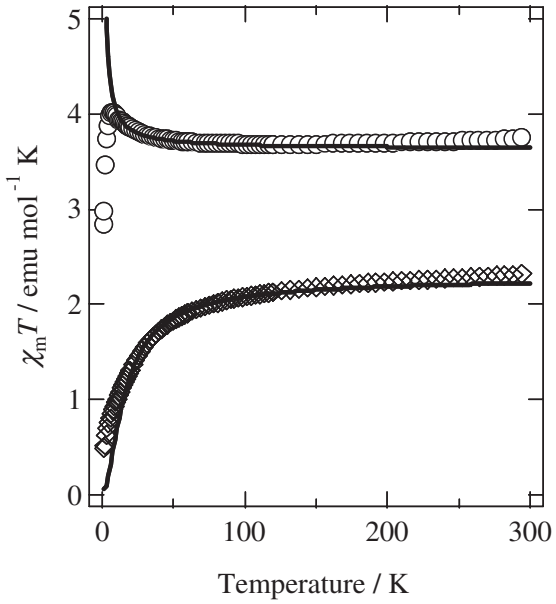

Figure 2. $\chi_m T$–T plots for **1** (◇) and **2** (○). The solid lines correspond to the theoretical curves, parameters of which are given in the text.

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7 Crystal data: **1**: $C_{22}H_{38}Cl_2N_2Ni_2O_8$ (including solvate molecules), $M_r = 646.86$, monoclinic space group $P2_1/c$, $a = 9.642(1)$, $b = 8.010(1)$, $c = 17.985(3)$ Å, $\beta = 100.798(2)°$, $V = 1364.5(3)$ Å^3, $Z = 2$, $T = -70$ °C. A total of 6483 were collected ($3° < 2\theta < 50°$) of which 1954 unique reflections (R(int) = 0.0194) were measured. Residual R and wR were 0.0241 and 0.0722, respectively, from the refinement on F^2 with $I > 2\sigma(I)$. **2**: $C_{30}H_{44}N_2Ni_3O_{14}$, $M_r = 832.80$, monoclinic space group $P2_1/n$, $a = 10.0184(9)$, $b = 11.0632(9)$, $c = 17.070(1)$ Å, $\beta = 103.564(2)°$, $V = 1839.2(3)$ Å^3, $Z = 2$, $T = 20$ °C. A total of 8878 were collected ($3° < 2\theta < 50°$) of which 2652 unique reflections (R(int) = 0.0834) were measured. Residual R and wR were 0.0723 and 0.1659, respectively, from the refinement on F^2 with $I > 2\sigma(I)$. In the structure analyses, non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. The large anisotropy observed in carbon atoms of methanol molecules for **2** is due to the disorder.

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