Structures and Magnetic Properties of Di and Tetranuclear Nickel(II) Complexes with Schiff Base Ligands

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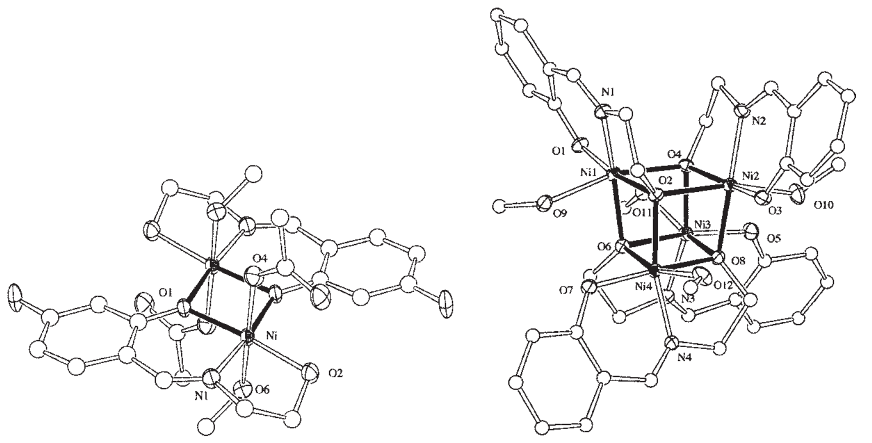
Reactions of $Ni(CH_3COO)_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ with Schiff base ligands yielded di and tetranuclear nickel(II) complexes of $[Ni_2(Hhsae)_2(CH_3COO)_2(MeOH)_2]$ (**1**) and $[Ni_4(sae)_4(MeOH)_4]$ (**2**) (H_2hsae = 2-(5-hydroxysalicylideneamino)ethanol and H_2sae = 2-salicylideneaminoethanol). Magnetic susceptibility measurements revealed that **1** and **2** have singlet and nonet spin ground states, respectively.

Multinuclear metal complexes with high-spin ground states have attached an intense interest due to the possibility of superparamagnetism. Such molecules show magnetic hysteresis[1] and quantum tunneling of magnetization,[2,3] and the molecules are called as signle molecule mangets.[4] The single molecule magnets need to have relatively high spin ground state with a uniaxial magnetic anisotropy. A nickel(II) ion with six coordination geometry is high-spin with magnetic anisotropy. It is, therefore, expected that multi-nuclear nickel(II) complexes can be a good candidate for the single molecule magnet. In this letter, we present syntheses and magnetic properties of dinuclear and tetranuclear nickel(II) complexes with Schiff base ligand.

Reactions of $Ni(CH_3COO)_2{\cdot}4H_2O$ and $NiCl_2{\cdot}6H_2O$ with the Schiff base ligands yielded di- and tetranuclear nickel(II) complexes of $[Ni_2(Hhsae)_2(CH_3COO)_2(MeOH)_2]$ (**1**) and $[Ni_4(sae)_4(MeOH)_4]$ (2) (H_2hsae = 2-(5-hydroxysalicylideneamino)ethanol and H_2sae = 2-salicylideneaminoethanol).[5] Compounds **1** and **2** crystallized in monoclinic space group $P2_1/c$ and $P2_1/n$, respectively,[6] and ortep drawings are presented in Figure 1. Complex **1** is composed of a dinuclear unit and has a inversion centre in the middle of the molecule. Nickel(II) ions in **1** were coordinated by one nitrogen and five oxygen atoms from methanol, acetate, and Schiff base, where the Schiff base ligand is a monoanion with the phenoxo group. The two nickel(II) ions are doubly bridged by the phenoxo group with the Ni···Ni separation of 3.0930(3) Å. Coordination bond lengths of Ni–N(1), Ni–O(1), and Ni–O(4) are in the range of 1.999(1)–2.074(1) Å, while the remaining coordination bond lengths are 2.120(1) and 2.1442 Å. The bridging bond angle of Ni–O1–Ni is 98.95(4)°. The structure of **2** contains a tetranuclear cubane core, of which four nickel(II) ions were bridged by μ_3-alkoxo groups. A cubic array of alternating nickel and oxygen atoms give intracluster metal-metal separations of 3.0347(5)–3.1981(5) Å. The coordination geometry about each nickel(II) ion is an axially elongated octahedron in which the equatorial sites are occupied by a tridentate sae^{2-} ligand and an alkoxo oxygen atom from the next unit of the cube. The coordination bond lengths with equatorial atoms are in the range of 1.976(2)–2.052(2) Å and a tetragonal elongation (2.120(2)–2.191(2) Å) occurs along the trans O–Ni–O bond vector involving methanol and bridging alkoxide. The bridging angles of the Ni–O–Ni bonds in the cube are in the range of 93.53(8)–100.95(8)°.

Temperature dependences of magnetic susceptibility with applying magnetic field of 0.1 T were measured down to 2.0 K for **1** and **2**, and results are depicted in the form of $\chi_m T$ vs.



(a) (b)

Figure 1. Ortep diagrams of **1** (a) and **2** (b). Selected interatomic distances (Å) for **1**: Ni–N(1) 1.9987(11), Ni–O(1) 2.0160(9), Ni–O(1)* 2.0530(9), Ni–O(4) 2.0735(10), Ni–O(2) 2.1197(10), Ni–O(6) 2.1442(10) (key to symmetry operation 1-x, 2-y, z); for **2**: Ni(1)–O(2) 2.0218(19), Ni(1)–O(6) 2.0469(19) Ni(1)–O(4) 2.1207(18), Ni(2)–O(4) 2.0376(19), Ni(2)–O(8) 2.0522(19), Ni(2)–O(2) 2.1299(18), Ni(3)–O(4) 2.0331(19), Ni(3)–O(6) 2.0397(18), Ni(3)–O(8) 2.1197(19), Ni(4)–N(4) 1.989(2), Ni(4)–O(2) 2.0249(19), Ni(4)–O(8) 2.0257(18), Ni(4)–O(6) 2.1384(19).

temperature (Figure 2). The $\chi_m T$ value at 300 K for **1** is 2.19 emu^{-1} K mol^{-1}, which would be expected for the isolated two nickel(II) ions. The $\chi_m T$ values for **1** showed gradual decrease as the temperature is lowered, and this behavior is characteristic of antiferromagnetic interactions being operated between two nickel(II) ions. The magnetic susceptibility data were analyzed by the two spin model with a coupling constant J, representing the intra-molecular magnetic interaction ($H = -2J(S_1 \cdot S_2)$). The least squares calculation, where the contribution of paramagnetic impurity (p) was included, gave the best fit parameters of $g = 2.196$, $J = -6.9\,\mathrm{cm}^{-1}$, and $p = 0.07$. Temperature dependence of $\chi_m T$ values for **2** are, on the other hand, quite different from that for **1**. The room temperature $\chi_m T$ value ($= 4.99$ emu mol^{-1} K) corresponds to the isolated four nickel(II) ions. Upon cooling, $\chi_m T$ increased to a maximum value of 8.76 emu mol^{-1} K at 8 K. This magnetic behavior is indicative of ferromagnetic interactions among the nickel(II) centers and predicts an $S = 4$ spin ground state for **2**. A sudden decrease of $\chi_m T$ values below 8 K is due to an inter-cube antiferromagnetic interaction and/or zero-field splitting. The magnetic data were analyzed by using Heisenberg spin Hamiltonian $H = -2J\Sigma S_i \cdot S_j$ and the resulting expression of $\chi_m T$ was derived by the Kambe's method.[7] The least squares calculation yielded the best fit parameters of g and J values being 2.171 and 3.2 cm^{-1}, respectively.[8] Some alkoxo bridged Cu(II), Ni(II), and Fe(II) cubes were reported to have intracluster ferromagnetic interactions with S = 2, 4, and 8 spin ground states, respectively.[9] In summary, we have synthesized the di- and tetranulcear nickel(II) complexes. Magnetic susceptibility measurements showed that the compounds **1** and **2** have singlet and nonet spin ground states, respectively.

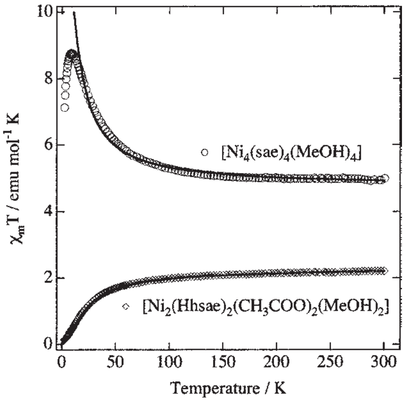


Figure 2. $\chi_m T - T$ plots for **1** (◯) and **2** (◇). The solid lines correspond to the theoretical curves, parameters of which are given in the text.

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5 The ligand H_2hase and H_2sae were prepared by the condensation reactions of 5-hydroxysalicylaldehyde and salicylaldehyde with 2-aminoethanol in methanol, respectively.

6 Crystal data for **1**: $C_{24}H_{34}N_2Ni_2O_{12}$, $M = 659.93$, monoclinic space group $P2_1$/c, $a = 9.4504(5)$ Å, $b = 9.8801(5)$ Å, $c = 15.4983(8)$ Å, $\beta = 98.3100(10)^\circ$, $V = 1431.90(13)$ Å^3, $Z = 2$, $d_{calc} = 1.535$ Mg/m^3, $R1 = 0.0206$, w$R2 = 0.0553$ for 3272 unique reflections ($I_0 > 2\sigma(I_0)$); Crystal data for **2**: $C_{40}H_{52}N_4Ni_4O_{12}$, $M = 1051.65$, monoclinic space group $P2_1$/n, $a = 13.1087(9)$ Å, $b = 18.3344(12)$ Å, $c = 18.8023(13)$ Å, $\beta = 110.1680(10)^\circ$, $V = 4241.9(5)$ Å^3, $Z = 4$, $d_{calc} = 1.590$ Mg/m^3, $R1 = 0.0452$, w$R2 = 0.1129$ for 9601 unique reflections ($I_0 > 2\sigma(I_0)$). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-187069 and 187070.

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8 Analysis of the magnetic data for **2** was performed by using the data above 20 K, which minimizes the influence of the zero-field splitting and inter-cubane interaction.

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