

Oligonuclear Metal-Assembly of Antiferromagnetic Ni₄ and Ferromagnetic Ni₆ Clusters with Non-Schiff-Base Tetradentate Ligand

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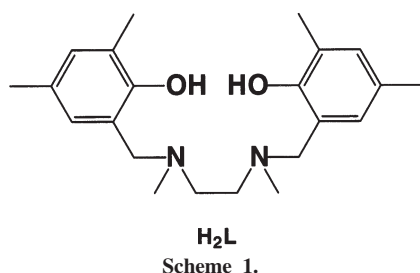
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Tetranuclear and hexanuclear nickel(II) complexes with *N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N,N'*-dimethyl-1,2-ethanediamine (H₂L), [Ni₄L₂(CH₃COO)₄]-4THF and [Ni₆L₃(OH)₄(NO₃)₂(H₂O)₂]-2DMF, have been synthesized and characterized by X-ray crystallography, electronic spectroscopy and magnetic susceptibility measurement.

Bis(salicylidene)ethylenediamine (H₂salen) is a famous Schiff-base ligand, giving an equatorial planar environment for metal ions due to the rigid framework including the two C=N bonds.¹ Especially, square-planar arrangement with the N₂O₂ donor atoms of salen is encountered for nickel(II) ion. On the other hand, coordination chemistry of the corresponding non-Schiff-base ligands such as *N,N'*-bis(2-hydroxy-3,5-dimethylbenzyl)-*N,N'*-dimethyl-1,2-ethanediamine (H₂L) is not well developed. In the previous study, we found that hydrogenation of C=N groups of the pentadentate Schiff-base ligand, 1,3-bis(salicylideneamino)-2-propanol afford a more flexible ligand, 1,3-bis(salicylamino)-2-propanol, which enables us to produce a high nuclearity of an octanuclear zinc(II) species.² Oligonuclear metal complexes are of current interest since the discovery of Mn₁₂ cluster as single molecule magnets.³ So far, we explored ways to design the synthesis of oligonuclear metal complexes with organic ligands.⁴ In the course of this activity, we expected that such a high nuclearity of nickel(II) ion which is potentially paramagnetic, can be achieved by the use of the non-Schiff-base tetradentate ligand H₂L and found that the anionic ligand L²⁻ forms two new oligonuclear clusters containing four and six nickel(II) ions, respectively.



Reaction of H₂L with Ni(CH₃COO)₂·4H₂O in THF gave yellowish green crystals (**1**).⁵ Similarly, treatment of H₂L with Ni(NO₃)₂·6H₂O led to green crystals (**2**).⁶ X-Ray structural determination of **1** reveals a novel tetranuclear nickel complex [Ni₄L₂(CH₃COO)₄]-4THF having an eight-membered cyclic core with four nickel atoms and four phenoxo-oxygen atoms of L²⁻ (Figure 1).⁷ The tetranuclear molecule has three C₂ symmetry with the crystallographic twofold axes passing through Ni1 and

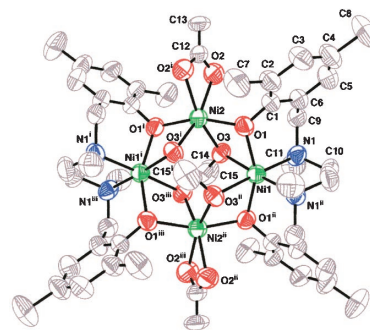


Figure 1. Perspective view of **1**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (*d*/Å) and angles (*φ*/°): Ni1–Ni2 3.109(1), Ni1–O1 2.040(2), Ni1–O3 2.200(2), Ni1–N1 2.076(3), Ni2–O1 2.037(2), Ni2–O2 2.086(3), Ni2–O3 2.077(2); Ni1–O1–Ni2 99.39(10), Ni1–O3–Ni2 93.23(10). Symmetry codes: i: $-x+1/4, -y+1/4, z$; ii: $-x+1/4, y, -z+1/4$; iii: $x, -y+1/4, -z+1/4$.

Ni1ⁱ, Ni2 and Ni2ⁱⁱ, and C14, C14ⁱ, C15, and C15ⁱ. Thus, the four nickel atoms are located at the corners of a square of edge length Niⁱ–Ni of 3.109(1) Å. The Ni1 atom is octahedrally coordinated by O1, O1ⁱⁱ, N1, and N1ⁱⁱ of one L²⁻ ligand and O3 and O3ⁱⁱ of two acetato ligands, whereas the Ni2 atom is octahedrally coordinated by O1 and O1ⁱ of two L²⁻ ligands, O3 and O3ⁱ of two acetato ligands, and O2 and O2ⁱ of one bidentate acetato ligand. One of the most interesting features in **1** is coexistence of *syn-syn* bridging and bidentate modes of the four acetato ligands. Particularly, each acetato ligand bridges four nickel atoms in the *syn-syn* bridging, which is the first example of μ_4 -bridging mode in metal carboxylate chemistry.

On the other hand, the crystal structure of **2** shows unprecedented hexanuclear cluster [Ni₆L₃(OH)₄(NO₃)₂(H₂O)₂]-2DMF, which has C₂ symmetry with a crystallographic twofold axis passing through Ni3 and Ni4 (Figure 2).⁷ The six nickel atoms are roughly coplanar and the five nickel atoms (Ni1, Ni2, Ni3, Ni1ⁱ, and Ni2ⁱ) are located at the vertices of a pentagon around the central Ni4 atom. The Ni3 atom is octahedrally coordinated by O3, O3ⁱ, N3, N3ⁱ of one L²⁻ ligand and μ_3 -hydroxo-oxygen atoms (O8 and O8ⁱ). The Ni2 atom is octahedrally coordinated by O1, O2, N1, and N2 of one L²⁻ ligand, μ_3 -hydroxo-oxygen atom (O7), and μ_2 -aqua-oxygen atom (O9). The Ni1 atom is coordinated by O2 and O3 of two L²⁻ ligands, two μ_3 -OH (O7 and O8), and one bidentate nitrate ligand (O4 and O5). Finally the Ni4 atom is coordinated by six oxygen atoms [four μ_3 -OH (O7, O7ⁱ, O8, and O8ⁱ) and two μ_2 -OH₂ (O9 and O9ⁱ)]. The Ni–O distances range from 1.998(5) to 2.143(6) Å, whereas the Ni–N bond lengths are 2.135(6) and 2.143(7) Å.

Diffuse reflectance spectra of **1** and **2** exhibit three absorption bands in the visible and near-infrared region which may be

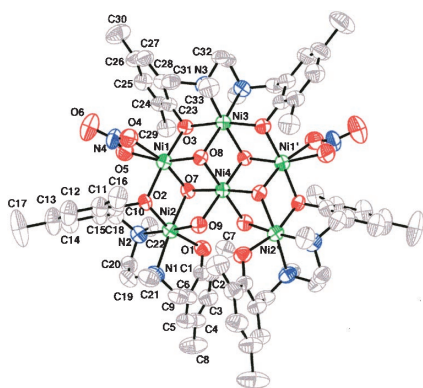


Figure 2. Perspective view of **2**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (*d*/Å) and angles (*φ*/°): Ni1–Ni2 3.182(3), Ni1–Ni3 3.200(3), Ni1–Ni4 2.930(3), Ni2–Ni4 3.093(3), Ni3–Ni4 3.036(3), Ni1–O2 2.085(5), Ni1–O3 2.046(5), Ni1–O4 2.098(6), Ni1–O5 2.143(6), Ni1–O7 1.998(5), Ni1–O8 2.020(5), Ni2–O1 1.999(5), Ni2–O2 2.037(5), Ni2–O7 2.052(5), Ni2–O9 2.132(5), Ni2–N1 2.143(7), Ni2–N2 2.095(6), Ni3–O3 2.032(5), Ni3–O8 2.102(5), Ni3–N3 2.135(6), Ni4–O7 2.023(5), Ni4–O8 2.003(5), Ni4–O9 2.084(5); Ni1–O2–Ni2 101.0(2), Ni1–O3–Ni3 103.4(2), Ni1–O7–Ni2 103.5(2), Ni1–O7–Ni4 93.6(2), Ni1–O8–Ni3 101.8(2), Ni1–O8–Ni4 93.5(2), Ni2–O7–Ni4 98.8(2), Ni2–O9–Ni4 94.4(2), Ni3–O8–Ni4 95.3(2). Symmetry code: *i*: $-x+3/2, y, -z+1/2$.

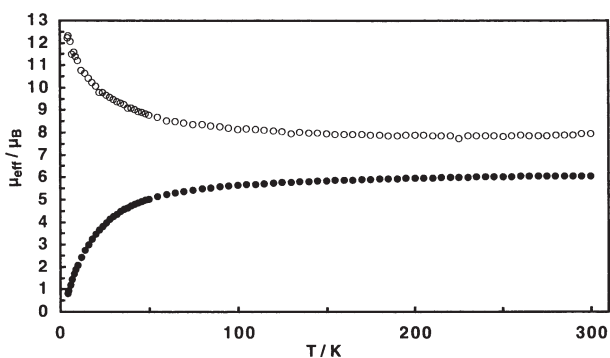


Figure 3. Temperature dependence of magnetic moments of **1** (●) and **2** (○).

assigned as d-d transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, ${}^3T_{1g}(F)$, and ${}^3T_{2g}$ for the high-spin nickel(II) ions.^{1,8}

The temperature dependence of the magnetic susceptibilities of **1** and **2** was measured in the range 4.5–300 K. The effective magnetic moment of **1** is $6.05 \mu_B$ per tetranuclear molecule at 300 K. This is a little higher than the spin-only value ($5.65 \mu_B$ for $g = 2$) for non-interacting four $S = 1$ spins. The magnetic moment gradually decreases with lowering of temperature until around 50 K (Figure 3). Upon further cooling, the magnetic moment decreases clearly, reaching a minimum value of $0.79 \mu_B$ at 4.5 K. This behavior is consistent with the presence of weak antiferromagnetic coupling between the nickel(II) ions. On the other hand, the magnetic moment of **2** ($7.92 \mu_B$ per hexanuclear molecule at 300 K) is significantly higher than the spin-only value ($6.93 \mu_B$ for $g = 2$) for non-interacting six $S = 1$ spins. The moment gradually increases with lowering of temperature and reaches a value of $12.22 \mu_B$ at 4.5 K. The magnetic behavior is indicative of ferromagnetic coupling between the nickel(II) ions in **2**. In the cluster **1**, there are two kinds of Ni–O–Ni angles, μ_2 -

phenoxo [Ni1–O1–Ni2 $99.4(1)^\circ$] and μ_4 -acetato [Ni1–O3–Ni2 $93.2(1)^\circ$] bridges. The Ni–O distances are in the narrow range from 2.037(2) to 2.086(3) Å except for the Ni1–O3 distance [2.200(2) Å]. The magnetic interaction via the acetato-oxygen bridge can not be considered as the main contribution to the magnetic property, because this bridge has the longest Ni1–O3 bond. From this fact, it can be assumed that the main pathway for the magnetic exchange interaction should be via the phenoxo-oxygen bridges in **1** and thus, weak antiferromagnetism can be expected based on the relationship between the Ni–O–Ni angle and the magnetic exchange interaction.⁹ On the other hand, there are three kinds of Ni–O–Ni angles in the cluster **2**, which vary in the ranges $101.0(2)$ – $103.4(2)$, $93.5(2)$ – $103.5(2)$, and $94.4(2)^\circ$ corresponding to μ_2 -phenoxo, μ_3 -hydroxo, and μ_2 -aqua oxygen bridges, respectively. Among these bridges, the magnetic interaction between Ni1 and Ni4 via hydroxo-bridges (O7 and O8) must be important, because they contain shorter Ni–O bonds compared with those of the other Ni–O–Ni bridges. Thus, the Ni–O–Ni angles close to 90° [Ni1–O7–Ni4 $93.6(2)$, Ni1–O8–Ni4 $93.5(2)^\circ$] may contribute to the ferromagnetic behavior of **2** irrespective of the complicated situation. The present results show that metal-assembling by the non-Schiff-base ligand is promising to produce antiferromagnetic and ferromagnetic oligonuclear metal complexes. Further studies are now in progress.

References and Notes

- F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, "Advanced Inorganic Chemistry," 6th ed., Wiley-Interscience, New York (1999).
- M. Mikuriya, N. Tsuru, S. Ikemi, and S. Ikenoue, *Chem. Lett.*, **1998**, 879.
- R. E. P. Winpenny, *Adv. Inorg. Chem.*, **52**, 1 (2001).
- a) M. Mikuriya and K. Nakadera, *Chem. Lett.*, **1995**, 213. b) M. Mikuriya, Y. Hashimoto, and S. Nakashima, *Chem. Commun.*, **1996**, 29. c) M. Mikuriya and M. Fukuya, *Chem. Lett.*, **1998**, 421. d) M. Mikuriya, N. Nagao, and K. Kondo, *Chem. Lett.*, **2000**, 516. e) M. Mikuriya, S. Ikemi, and S. Yao, *Chem. Lett.*, **2000**, 538. f) M. Mikuriya and K. Minowa, *Inorg. Chem. Commun.*, **3**, 227 (2001). g) M. Mikuriya, S. Ikemi, and J.-W. Lim, *Bull. Chem. Soc. Jpn.*, **74**, 99 (2001). h) M. Mikuriya, K. Minowa, and N. Nagao, *Inorg. Chem. Commun.*, **4**, 441 (2001). i) T. Kotera and M. Mikuriya, *Chem. Lett.*, **2002**, 654.
- H₂L (72 mg, 0.20 mmol) was dissolved in THF (10 cm³). Then, nickel(II) acetate tetrahydrate (7 mg, 0.30 mmol) and six drops of triethylamine were successively added. The mixture was stirred and filtered. Yellowish-green crystals deposited from the filtrate upon layering with diethyl ether. Found: C, 54.35; H, 6.79; N, 4.51%. Calcd for C₆₀H₈₈N₄O₁₄Ni₄: C, 54.42; H, 6.70; N, 4.23%.
- H₂L (36 mg, 0.10 mmol) and nickel(II) nitrate hexahydrate (58 mg, 0.20 mmol) were dissolved in MeOH (5 cm³), then added three drops of triethylamine with stirring. The resulting green precipitate was collected by filtration. Recrystallization from Et₂O/DMF gave green crystals. Found: C, 48.27; H, 6.47; N, 8.29%. Calcd for C₇₂H₁₁₂N₁₀Ni₆O₂₀: C, 48.32; H, 6.31; N, 7.83%.
- Crystallographic data: for **1**: C₆₈H₁₀₄N₄Ni₄O₁₆, $M_r = 1468.39$, orthorhombic, space group *Fddd*, $a = 18.472(3)$, $b = 26.906(4)$, $c = 28.797(4)$ Å, $V = 14312(3)$ Å³, $Z = 8$, $D_{\text{calcd}} = 1.36$ Mg/m³, $\mu(\text{Mo K}\alpha) = 1.103$ mm⁻¹, 17578 reflections measured, 3058 independent reflections, $R1 = 0.0413$, $wR2 = 0.1116$ [$I \geq 2\sigma(I)$]. For **2**: C₇₂H₁₁₂N₁₀Ni₆O₂₀, $M_r = 1789.98$, monoclinic, space group *P21n*, $a = 17.447(17)$, $b = 15.148(14)$, $c = 17.901(15)$ Å, $\beta = 91.52(3)^\circ$, $V = 4729(7)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.26$ Mg/m³, $\mu(\text{Mo K}\alpha) = 1.233$ mm⁻¹, 20182 reflections measured, 6791 independent reflections, $R1 = 0.0708$, $wR2 = 0.2258$ [$I \geq 2\sigma(I)$]. Intensity data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K α radiation. All the structures were solved by the direct method and refined by the full-matrix least-squares method using the SHELXTL software package.
- Diffused reflectance spectra: λ_{max} **1**: 416, 740, 1206 nm; **2**: 420sh, 705, 1122 nm.
- K. K. Nanda, L. K. Thompson, T. N. Bridson, and K. Nag, *J. Chem. Soc., Chem. Commun.*, **1994**, 1337.