Di- and Trinuclear Nickel(II) Complexes Containing Tripodal Hexadentate Ligands

Hiromi Ohta, Kenji Harada, Koji Irie, Setsuo Kashino, Takashi Kambe,† Genta Sakane,†† Takashi Shibahara,††
Satoshi Takamizawa,††† Wasuke Mori,††† Matsuo Nonoyama,†††† Masakazu Hirotsu†††††, and Masaaki Kojima*
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530
†*Department of Physics, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530*
††*Department of Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005*
†††*Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293*
††††*Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602*
†††††*Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515*

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The reaction of Ni^{2+} with a tripodal hexadentate ligand (H_3L = 1,1,1-tris(*N*-salicylideneaminomethyl)ethane) afforded the O–H···O bridged dinuclear $[Ni_2(HL)_2]$ complex. When Ni^{2+} was allowed to react with H_3L in the presence of triethylamine (3 : 2 : 6), the linear trinuclear $[Ni_3(L)_2]$ complex formed, where the central nickel(II) ion is bridged by six phenolate oxygen atoms to the terminal nickel(II) ions.

Metal–metal interactions between paramagnetic metal centers through bridging atoms have been studied extensively in order to understand fundamental factors controlling the exchange interactions.[1] Although both oxygen (hard base) and sulfur (soft base) are Group 16 elements, their coordination abilities are quite different. It is interesting to compare the properties of complexes containing phenol groups with those of complexes containing thiophenol groups. Here, we report the preparation, structures, and magnetic properties of di- and trinuclear nickel(II) complexes containing tripodal hexadentate ligands, H_3L and $H_3L^{5\text{-MeO}}$ (Figure 1). The synthesis of the Ni^{II}–M^{II}–Ni^{II} type heterotrinuclear complexes is also reported.

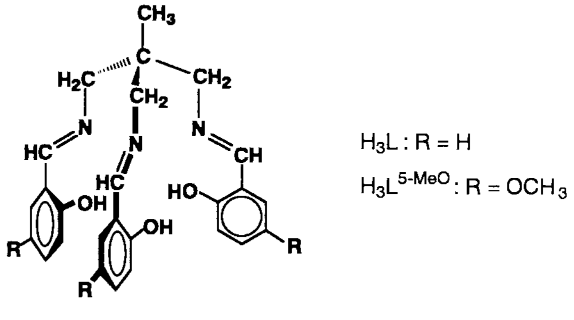

Figure 1. The H_3L and $H_3L^{5\text{-MeO}}$ ligands.

The bluish-green dinuclear complexes, $[Ni_2(HL)_2]$ (**1**) and $[Ni_2(HL^{5\text{-MeO}})_2]$ (**1'**), were prepared in the same manner and have very similar structures to each other; thus we describe only **1'** as a representative example. **1'** was prepared by the reaction of Ni^{2+} with the $H_3L^{5\text{-MeO}}$ ligand[2] in methanol in a 1 : 1 molar ratio without the addition of a base. Yield: 76%. The elemental analysis indicated that there are no counter ions.[3] Thus, one of the three acidic hydrogen atoms of $H_3L^{5\text{-MeO}}$ is not deprotonated and the empirical formula, $[Ni(HL^{5\text{-MeO}})]$ was suggested.

Figure 2 shows the X-ray structure of **1'**.[4] There are two independent mononuclear molecules in the unit cell, the two molecules being linked by hydrogen bonding between phenol and phenolate oxygen atoms. The distances between the hydrogen bonded oxygen atoms, O11···O22, 2.493(4); O12···O21, 2.490(4) Å, indicate a strong hydrogen bond. Each nickel atom is in an approximately octahedral environment composed of three facially coordinated imine nitrogen atoms and three phenolic oxygen atoms.

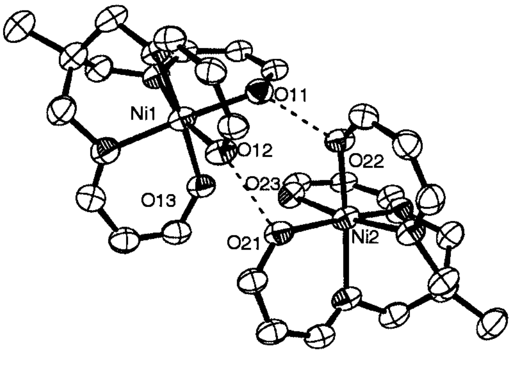

Figure 2. ORTEP view for **1'** with 50% probability ellipsoids. The H atoms and aromatic moieties are omitted for clarity. Selected bond distances (Å): Ni1–O11, 2.103(3); Ni1–O12, 2.044(3); Ni1–O13, 2.065(3); Ni2–O21, 2.119(3); Ni2–O22, 2.060(3); Ni2–O23, 2.069(3); O11···O22, 2.493(4); O12···O21, 2.490(4); O13···O23, 2.426(4); Ni1···Ni2, 4.763(1).

Temperature-dependent molar susceptibility measurements of powdered samples of the dinuclear complexes, **1** and **1'**, were carried out in the temperature range 5–300 K. The two complexes have very similar magnetic properties. The magnetic moments are almost constant above 50 K and drop sharply below 30 K. The magnetic data were analyzed using the isotropic spin exchange coupling model. The spin Hamiltonian in dinuclear complexes is expressed as $H = -2JS_1{\cdot}S_2$ ($S_1 = S_2 = 1$). The best fits were obtained with $J = -1.00\ cm^{-1}$ ($g = 2.02$) for **1**; $J = -1.02\ cm^{-1}$ ($g = 1.99$) for **1'**. The two Ni^{2+} are ca. 4.8 Å apart, and Ni–O–H···O–Ni superexchange pathways are possible. The small J values show that such pathways are not effective. Auerbach et al.[5] studied the magnetic properties of dimeric $[M_2(HL')_2](ClO_4)_2{\cdot}2H_2O$ (M = Cr, Fe; H_3L' = 1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane). They reported spin exchange coupling constants similar to ours: $[Cr_2(HL')_2](ClO_4)_2{\cdot}2H_2O$, $J = -0.93\ cm^{-1}$ ($g = 1.98$); $[Fe_2(HL')_2](ClO_4)_2{\cdot}2H_2O$, $J = -0.33\ cm^{-1}$ ($g = 1.98$). It is to be noted that the susceptibility data for in **1** and **1'** can also be accounted for by a single-ion zero-field splitting ($D = 9.71\ cm^{-1}$ and $g = 1.93$ for **1**, $D = 9.85\ cm^{-1}$ and $g = 1.90$ for **1'**).

The fact that the ligands are not fully deprotonated in **1** and **1'** indicates that the coordinated oxygen atoms still possess basicity. This residual basicity can be used for the formation of oxygen-bridged complexes. For the preparation of the trinuclear complexes, Ni^{2+} was allowed to react with H_3L or $H_3L^{5\text{-MeO}}$ in a 3 : 2 molar ratio in the presence of triethylamine to deprotonate the ligands. Orange complexes were obtained. Yield: 79% for **2** and 89% for **2'**. The elemental analyses indicated that the complexes have the trinuclear structure, $[Ni_3(L)_2]$ (**2**) and $[Ni_3(L^{5\text{-MeO}})_2]$ (**2'**).[6] The trinuclear structures were confirmed by X-ray crystallography.[7]

Figure 3 shows the molecular structure of **2'** viewed down the C_2 axis. The complex is a doubly face-sharing, trinuclear molecule. The coordination geometry around each Ni is approximately octahedral. Two terminal nickel(II) ions are coordinated by the hexadentate tripodal ligands, and the central and the terminal nickel(II) ions are bridged by six phenolate oxygen atoms ($Ni_t\cdots Ni_c$ 2.824(1) Å, $Ni_t\cdots Ni_t$ 5.648(3) Å). Thus, the terminal mononuclear units function as a tridentate ligand.

Magnetic susceptibility data for powdered samples of the trinuclear complexes were collected in the temperature range 2–300 K. In **2'**, the effective magnetic moment, $\mu_{\text{eff(Ni–Ni–Ni)}}$, increases gradually on decreasing the temperature and reaches a maximum at 7 K (7.63 μ_B), and then drops sharply (Figure 4).

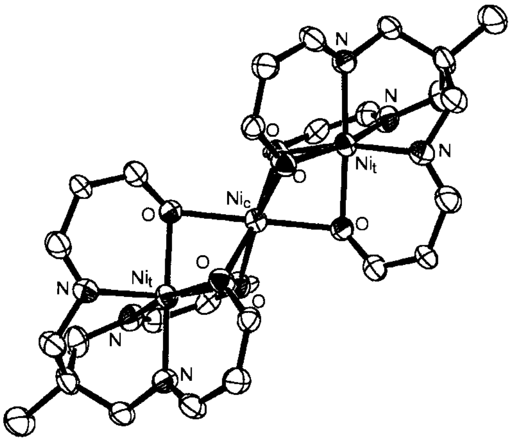

Figure 3. ORTEP view for **2'** with 50% probability ellipsoids. The H atoms and aromatic moieties are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni_t–O, av. 2.053(4); Ni_c–O, av. 2.081(4); $Ni_t\cdots Ni_c$, 2.824(1); $Ni_t\cdots Ni_t$, 5.648(3); Ni_t–O–Ni_c, 86.2(1).

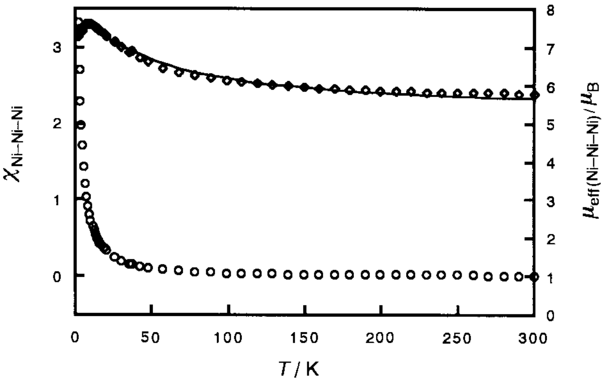

Figure 4. Temperature dependence of the magnetic moments (◇) and magnetic susceptibility (○) of **2'**.

The magnetic data were analyzed using the isotropic spin exchange coupling model. The spin Hamiltonian in linear trinuclear complexes is expressed as $H = -2(J_{12}S_1\cdot S_2 + J_{23}S_2\cdot S_3 + J_{13}S_1\cdot S_3)$, where $S_1 = S_2 = S_3 = 1$ for the S_1–S_2–S_3 arrangement. The terminal nickel(II) ions are crystallographically equivalent, and thus the spin exchange coupling constant for the interactions between the adjacent nickel(II) ions is expressed as $J = J_{12} = J_{23}$. The best fits were obtained with J = 14.8 cm^{-1}, J_{13} = –1.77 cm^{-1}, and g = 2.03 for **2**; J = 15.8 cm^{-1}, J_{13} = –2.61 cm^{-1}, and g = 2.19 for **2'**. These complexes have the S = 3 ground state. The structures and magnetic properties for **2** and **2'** are similar to those of $[Ni_3(acac)_6]$ (acac = 2,4-pentanedionate ion),[8] although the magnitude of the magnetic interactions is smaller for the present complexes. It should be noted that the linear homotrinuclear nickel(II) complex with 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane shows antiferromagnetic coupling between two adjacent nickel(II) ions (J = –28 cm^{-1}) and ferromagnetic coupling between terminal nickel(II) ions (J_{13} = 12 cm^{-1}), and indicates the S = 1 ground state.[9] The decrease in the magnetic moment of **2'** below 7 K (Figure 4) may be accounted for by zero-field splitting.

We have prepared the phenolate-bridged heterotrinuclear complexes, $[M(NiL^{5\text{-MeO}})_2]$ (M = Mn, Co)[10] by the reaction of $[Ni_2(HL^{5\text{-MeO}})_2]$ (**1'**) and M^{2+} in the presence of triethylamine. To avoid transmetallation, the reaction was carried out under mild conditions (room temperature). Their magnetic properties are under investigation.

References and Notes

1 See, for example, O. Kahn, "Molecular Magnetism," VCH, Weinheim (1993).

2 The $H_3L^{5\text{-MeO}}$ ligand was prepared by condensation of 1,1,1-tris(aminomethyl)ethane and 5-methoxysalicylaldehyde in ethanol in a 1 : 3 molar ratio. Yield: 85%. Anal. Found: C, 66.86; H, 6.14; N, 8.10%. Calcd for $C_{29}H_{33}N_3O_6$: C, 67.04; H, 6.40; N, 8.09%.

3 Anal. Found: C, 56.58; H, 5.64; N, 6.64%. Calcd for $C_{58}H_{70}N_6Ni_2O_{16}$ = $[Ni_2(HL^{5\text{-MeO}})_2]\cdot 4H_2O$: C, 56.89; H, 5.76; N, 6.86%.

4 Bluish-green crystals of $[Ni_2(HL^{5\text{-MeO}})_2]\cdot 10H_2O$ were grown from a methanol solution. Crystallographic data: formula weight 1332.69, tetragonal, space group $P4/nnc$ (No. 126), a = 36.617(1), c = 21.4647(5) Å, V = 28779(1) Å^3, Z = 16, D_C = 1.231 Mg m^{-3}, μ(Mo Kα) = 0.59 mm^{-1}, 15872 unique reflections ($2\theta_{max}$ = 54.2°), R_1 (8449 reflections, $I > 2.0\sigma(I)$) = 0.070, R_w = 0.217.

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6 Anal. Found for **2**: C, 55.58; H, 4.19; N, 7.24%. Calcd for $C_{53}H_{49}Cl_3N_6Ni_3O_6$ = $[Ni_3(L)_2]\cdot CHCl_3$: C, 55.43; H, 4.30; N, 7.32%. Found for **2'**: C, 52.30; H, 4.48; N, 5.91%. Calcd for $C_{60}H_{64}Cl_4N_6Ni_3O_{12}$ = $[Ni_3(L^{5\text{-MeO}})_2]\cdot 2CH_2Cl_2$: C, 52.26; H, 4.68; N, 6.09%.

7 Orange crystals of $[Ni_3(L^{5\text{-MeO}})_2]\cdot 2CH_2Cl_2$ were grown from a dichloromethane–ethanol solution. Crystallographic data: formula weight 1379.11, monoclinic, space group $C2/c$ (No. 15), a = 19.886(7), b = 14.765(3), c = 23.211(7) Å, β = 115.08(2)°, V = 6172(3) Å^3, Z = 4, D_C = 1.48 Mg m^{-3}, μ(Mo Kα) = 1.144 mm^{-1}, 7347 unique reflections ($2\theta_{max}$ = 55.0°), 5557 ($I > 0.5\sigma(I)$) used in the refinement, R = 0.096, R_w = 0.140.

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9 T. Beissel, F. Birkelbach, E. Bill, T. Glaser, F. Kesting, C. Krebs, T. Weyhermüller, K. Wieghardt, C. Butzlaff, and A. X. Trautwein, *J. Am. Chem. Soc.*, **118**, 12376 (1996).

10 Anal. Found for the Mn complex: C, 53.60; H, 4.67; N, 6.34%. Calcd for $C_{59.5}H_{63}Cl_3MnN_6Ni_2O_{12}$ = $[Mn(NiL^{5\text{-MeO}})_2]\cdot 1.5CH_2Cl_2$: C, 53.62; H, 4.76; N, 6.31%. Found for the Co complex: C, 52.80; H, 4.66; N, 6.05%. Calcd for $C_{60}H_{64}Cl_4CoN_6Ni_2O_{12}$ = $[Co(NiL^{5\text{-MeO}})_2]\cdot 2CH_2Cl_2$: C, 52.25; H, 4.68; N, 6.09%.