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Bis[(methanol){*N*-salicylidene-*N*′-(2-phenylimidazol-4-ylmethylidene)-1,3-propanediaminato}nickel(II)] Bridged by Di-μ-phenoxo Moiety and the Deprotonated Imidazolate-Bridged Cyclic-Tetranuclear Complex

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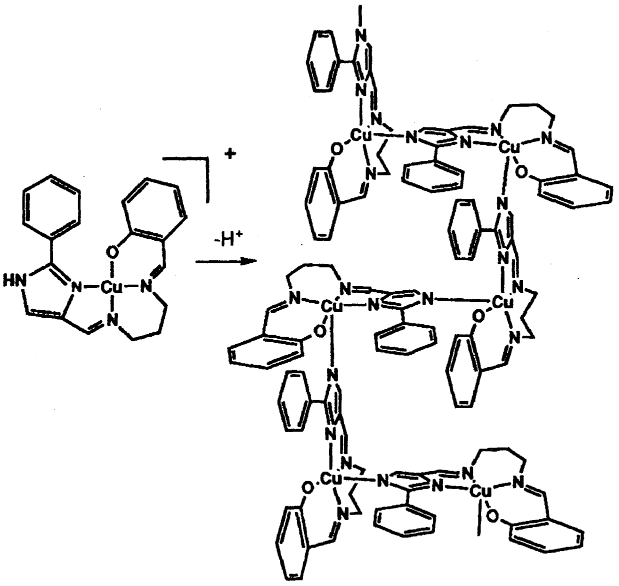
Protonated and deprotonated forms of nickel(II) complex with *N*-salicylidene-*N*′-(2-phenylimidazol-4-ylmethylidene)-1,3-propanediamine, **1** and **1′**, were synthesized and characterized. The X-ray crystal structures of $\mathbf{1}\cdot H_2O$ and **1′** were determined: $\mathbf{1}\cdot H_2O$, $P2_1/n$ (No. 14), $a=11.642(2)$, $b=12.908(3)$, $c=15.264(2)$ Å, $\beta=96.642(1)°$; **1′**, $I4_1/a$ (No. 88), $a=22.651(3)$, $c=13.950(7)$ Å. The crystal of $\mathbf{1}\cdot H_2O$ assumes a dinuclear structure bridged by the di-μ-phenoxo moiety in an out-of-plane fashion with Ni–Ni = 3.173(1) Å and Ni–O = 2.126(3) Å of the Ni_2O_2 core and two perchlorate ions as counter anions, in which the nickel(II) ion assumes an octahedral coordination geometry with N_3O_3 donor atoms consisting of four donor atoms of a quadridentate ligand, a bridging phenoxo-oxygen atom, and an oxygen atom of methanol. A ferromagnetic interaction with $J=+7.1\ \mathrm{cm}^{-1}$ operates between the two high-spin nickel(II) ions. **1** undergoes a deprotonation of the imidazole proton under basic conditions to give the deprotonated complex **1′**. The crystal of **1′** consists of an electrically-neutral imidazolate-bridged cyclic-tetranuclear molecule with Ni–Ni = 6.339(2) Å and Ni–N = 2.051(7) Å, in which the nickel(II) ion assumes a square-pyramidal geometry with N_4O donor atoms consisting of the quadridentate ligand and an imidazolate nitrogen of the adjacent nickel(II) complex. An antiferromagnetic interaction with $J=-6.3\ \mathrm{cm}^{-1}$ is observed between the adjacent nickel(II) ions through the imidazolate group. Since the corresponding deprotonated copper(II) complex with the same ligand assumed an imidazolate-bridged zigzag-chain structure, the result with the nickel(II) complex demonstrates a very marked influence of the metal ion on the formation of the assembly structure.

A self-assembly process involving a metal ion has attracted much attention over the past decade, because a metal ion together with its ligand contains a variety of structural information to guide the self-assembly reaction.[1] Recent attention has focused particularly on the construction of various supramolecular structures,[2] such as molecular squares, cylindrical molecular boxes, molecular cages, and helical structures, as well as on supramolecules exhibiting a switching ability, whose structure and/or physicochemical properties change by an input of external information.[3] We have studied a self-assembly system of metal complexes involving an imidazole moiety; an example is given in Scheme 1, in which a protonated building unit and its deprotonated self-assembly oligomer or polymer are interconverted, depending on the pH.[4] A copper(II) complex with a quadridentate ligand involving an imidazole moiety potentially not only has donor ability at the imidazolate nitrogen atom, but also has an acceptor ability at the vacant or substitutable coordination site, so that such complexes can function as a building module for the process of assembly. The ligand framework and metal ion work cooperatively to determine the relative orientation and manner of linkage between the adjacent building modules, which would determined the final self-assembly structure. In other words, the self-assembly structure, stability, and reversibility can be controlled by both the ligand framework and metal ion. We have already shown several examples of the effect of the ligand framework on its self-assembly structure.[4] In this study, in order to investigate the effect of metal ion, nickel(II) and copper(II) complexes with the same ligand, H_2L=*N*-salicylidene-*N*′-(2-phenylimidazol-4-ylmethylidene)-1,3-propanediamine, were studied. For this ligand we previously reported that the copper(II) complex undergoes deprotonation to give an imidazolate-bridged zigzag-chain structure,[5] as shown in Scheme 1. In this paper we report on the syntheses, characterization, and structures of the protonated nickel(II) complex **1** and the deprotonated nickel(II) complex **1′**.

Experimental

Warning. Perchlorate salts are potentially explosive and should only be handled in small quantities.

General Procedures. All of the chemicals and solvents used for synthesis were of reagent grade. The reagents used for physical measurements were of spectroscopic grade.



Scheme 1. Structure of the protonated copper(II) complex and zigzag-chain structure of the deprotonated copper(II) complex.

[Ni(HL)(MeOH)]$_2$(ClO$_4$)$_2$, 1 (H$_2$L = *N*-Salicylidene-*N*′-(2-phenylimidazol-4-ylmethylidene)-1,3-propanediamine). Bis(*N*-salicylidene-1,3-propanediaminato)nickel(II) was prepared by a method of Elder.[6] To a solution of the nickel(II) complex (2.08 g, 5 mmol) in 50 ml of methanol, dimethylglyoxime (1.16 g, 10 mmol) was added, and the mixture was refluxed for 90 min. After cooling to room temperature, bis(dimethylglyoximato)nickel(II) precipitated, and was filtered out. A solution of 2-phenyl-4-formylimidazole (1.72 g, 10 mmol) in 10 ml of methanol was added to the filtrate. The solution was warmed to 50 °C for 30 min and then cooled to room temperature. To this solution, a solution of nickel(II) perchlorate hexahydrate (3.66 g, 10 mmol) in 20 ml of methanol was added, and the resulting solution was warmed for 10 min. The solution was filtered, and the filtrate was left to stand for several days. The light-green crystals which precipitated during that period were collected by suction filtration, washed with a small amount of methanol, and dried in vacuo. Yield: 1.25 g (23%). Anal. Calcd for $C_{20}H_{19}N_4O_5ClNi \cdot MeOH \cdot H_2O$: C, 46.74; H, 4.67; N, 10.39%. Found: C, 46.91; H, 4.75; N, 10.25%. IR (KBr) ν[N–H] 3150 cm^{-1}; ν[C=N] 1630 cm^{-1}; ν[Cl–O] 1090 cm^{-1}. Λ_{Ni} (in methanol) 100 S mol^{-1} cm^2. Mp > 280 °C.

[NiL]$_4$, 1′. To a solution of **1** (1.08 g, 2 mmol) in 30 ml of methanol a slight excess of triethylamine (0.30 g, 3 mmol) was added. After stirring the solution for several hours at room temperature, the bluish-green microcrystals which precipitated were collected by suction filtration, washed with methanol, and dried in vacuo. Yield: 0.69 g (89%). Recrystallization was performed by a mixed solution of methanol and dichloromethane at room temperature. Anal. Calcd for $C_{20}H_{18}N_4ONi$: C, 61.74; H, 4.66; N, 14.40%. Found: C, 61.63; H, 4.71; N, 14.33%. IR (KBr) ν[C=N] 1630 and 1615 cm^{-1}. Λ_{Ni} (in dichloromethane) 0 S mol^{-1} cm^2. Mp> 280 °C.

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Electrical-conductivity measurements were carried out on a Horiba DS-14 conductivity meter in ca. 10^{-3} mol dm^{-3} solution at room temperature. Infrared spectra were measured on KBr disks using JASCO A-102 spectrophotometers. The electronic absorption spectra of ca. 3×10^{-3} mol dm^{-3} solutions and the diffuse reflectance spectra of powdered samples were measured using a Hitachi U-4000 spectrophotometer. FAB-MS spectra were measured with a JEOL JMS-SX/SX102A Tanden Mass Spectrometer, in which a source potential of 6.0 kV was applied to produce a positive-ion current; 3-nitrobenzyl alcohol and methanol were used as the matrix and solvent, respectively. ^{1}H NMR spectra were measured with a JEOL GX-400 and an α-500.

Magnetic-susceptibility measurements were performed with a Faraday balance in the temperature range of 80—300 K and a MPMS5 SQUID susceptometer (Quantum Design Inc.) in the temperature range of 2—300 K The calibrations were made with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine) for the Faraday balance and with $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ for the SQUID susceptometer.[7] Corrections were made for the diamagnetism calculated from Pascal's constants.[8] The effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility per nickel atom. The magnetic data were fitted to a theoretical expression by minimizing the agreement factor, defined as $F = \sum_i (\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2 / \chi_i^{\text{obsd}}$ through a Levenberg–Marquart routine.

X-Ray Data Collection, Reduction, and Structure Determination. Since crystals of **1** gradually effloresce, a suitable crystal was selected and encapsulated in a Lindeman glass capillary containing a small amount of mother liquid. All of the measurements for **1** and **1′** were performed using a Rigaku AFC-7R diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 20±1 °C using a θ–2θ scan technique at a scan speed of 16.0 ° min^{-1}. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time to the background counting time was 2 : 1. The intensities of three representative reflections were measured after every 150 reflections, showing a good stability of intensities. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were also corrected for Lorentz and polarization effects.

The structures were solved by direct methods[9] and expanded using Fourier techniques.[10] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the ideal calculated positions were included in the structure-factor calculation, but were not refined. A full-matrix least-squares refinement based on the observed reflections ($I > 3.00\sigma(I)$) was employed using unweighed and weighed agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The weighing scheme was based on counting statistics. Neutral atomic-scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_{calcd}; the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[12] All of the calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.[13] Crystal data and details of the structure determination are summarized in Table 1. Tables of crystal data, atom coordinates, complete bond distances and angles, anisotropic displacement factors, and calculated hydrogen coordinates (21 pages) were deposited as Document No. 71039 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis and Characterization of 1 and 1′. The

Table 1. Crystallographic Data for **1**·H_2O and **1′**

	1·H_2O	**1′**
Formula	$C_{42}H_{50}N_8O_{14}Cl_2Ni_2$	$C_{80}H_{72}N_{16}O_4Ni_4$
FW	1079.20	1556.16
Space group	$P2_1/n$ (No. 14)	$I4_1/a$ (No. 88)
a/Å	11.642(2)	22.651(3)
b/Å	12.908(3)	22.651(3)
c/Å	15.264(2)	13.950(7)
β/Å	96.64(1)	—
V/Å	2278.3(6)	7156(2)
Z	2	4
ρ_{calcd}/g cm^{-3}	1.573	1.444
μ/cm^{-1}	10.20	11.01
R, R_w/%	4.0, 4.1	5.2, 3.6

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma(F_o)^2$.

half-unit ligand, *N*-salicylidene-1,3-propanediamine, was first prepared according to the procedure of Elder.[6] Then, the half-unit ligand and 2-phenyl-4-formylimidazole were mixed at a molar ratio of 1 : 1 in methanol. The resulting methanol solution containing the asymmetrical quadridentate ligand was used without isolation of the ligand for the synthesis of the nickel(II) complex **1**. The protonated nickel(II) complex **1** was obtained as light-green prisms. The IR spectrum showed characteristic bands which could be assigned to the C=N stretching vibration of the Schiff-base ligand at 1630 cm^{-1}, the imidazole N–H vibration at 3150 cm^{-1}, and the Cl–O vibration of the perchlorate ion at 1090 cm^{-1}.[14] The molar electrical conductivity per nickel atom was 100 S mol^{-1} cm^2 in methanol, which is within the expected range for 1 : 1 electrolytes.[15] The IR bands due to the imidazole N–H and the perchlorate ion as well as the electrical-conductivity data are indicative of the protonated form.

The deprotonated nickel(II) complex **1′** was obtained as bluish-green crystals when an equivalent or slightly excessive amount of triethylamine was added to the ca. 10^{-2} mol dm^{-3} solution of **1** in methanol; the resulting red solution was left to stand overnight at room temperature. The N–H and Cl–O (vibration) bonds observed for **1** were absent in the spectrum of **1′**. The electrical conductivity in dichloromethane was nearly zero. The diffuse reflectance spectrum of a powdered sample showed a broad d–d band at 634 nm, while that of **1** showed a d–d band maximum at 617 nm.

Structural Description of 1·H_2O. The crystal of **1**·H_2O consists of a dinuclear cation bridged by the di-μ-phenoxo moiety $[Ni(HL)(MeOH)]_2^{2+}$, two perchlorate ions as the counter anion, and water molecules as the crystal solvent. An ORTEP drawing of the dinuclear molecule is shown in Fig. 1. Selected bond distances and angles for **1** and **1′** are given in Table 2, where the same atom numbering scheme is used for both compounds. The dinuclear molecule has a center of symmetry and assumes a di-μ-phenoxo structure with a Ni_2O_2 core in an out-of-plane fashion with dimensions of Ni(1)–O(1)* = 2.126(3) and Ni(1)–Ni(1)* = 3.173(1) Å. The nickel(II) ion assumes an octahedral coordination geometry with N_3O_3 donor atoms consisting of four donor atoms of a quadridentate ligand, a bridging phenoxo-oxygen atom, and an oxygen atom of methanol.

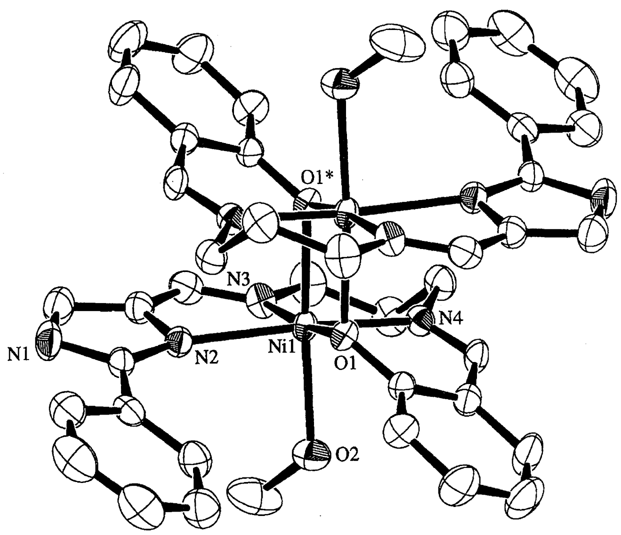


Fig. 1. An ORTEP drawing of dinuclear cation of **1**, showing 50% probability ellipsoids. The cation has an inversion center and the hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**·H_2O and **1′**

	1·H_2O	**1′**
	Bond distances (Å)	
Ni–O(1)	2.019(3)	1.964(6)
Ni–N(2)	2.167(3)	2.092(7)
Ni–N(3)	2.070(3)	2.062(7)
Ni–N(4)	2.041(3)	2.021(7)
Ni–O(2)	2.183(3)	—
Ni–O(1)*	2.126(3)	—
Ni–N(1)*	—	2.051(7)
Ni···Ni*	3.173(1)	—
O(1)···O(1)*	2.669(5)	—
	Bond angles (deg)	
O(1)–Ni–N(2)	100.1(1)	91.7(3)
O(1)–Ni–N(3)	172.2(1)	146.7(3)
O(1)–Ni–N(4)	87.8(1)	90.2(3)
N(2)–Ni–N(3)	79.0(1)	80.2(3)
N(2)–Ni–N(4)	170.6(1)	167.8(3)
N(3)–Ni–N(4)	93.8(1)	91.7(3)
Ni–O(1)–Ni*	99.9(1)	—
O(1)–Ni–O(1)*	80.1(1)	—

Structural Description of 1′. **1′** crystallizes in the tetragonal space group $I4_1/a$, where the asymmetric unit involves a fourth of the formula unit and the tetranuclear molecule possesses S_4 symmetry. ORTEP drawings of the tetranuclear molecule are given in Fig. 2. The structure can be described as a molecular square with a slight tetrahedral distortion. The side and diagonal Ni–Ni distances are 6.340(2) and 8.772(3) Å, respectively. The nickel(II) ion assumes a penta-coordinated environment with N_4O donor atoms consisting of four donor atoms of a quadridentate li-

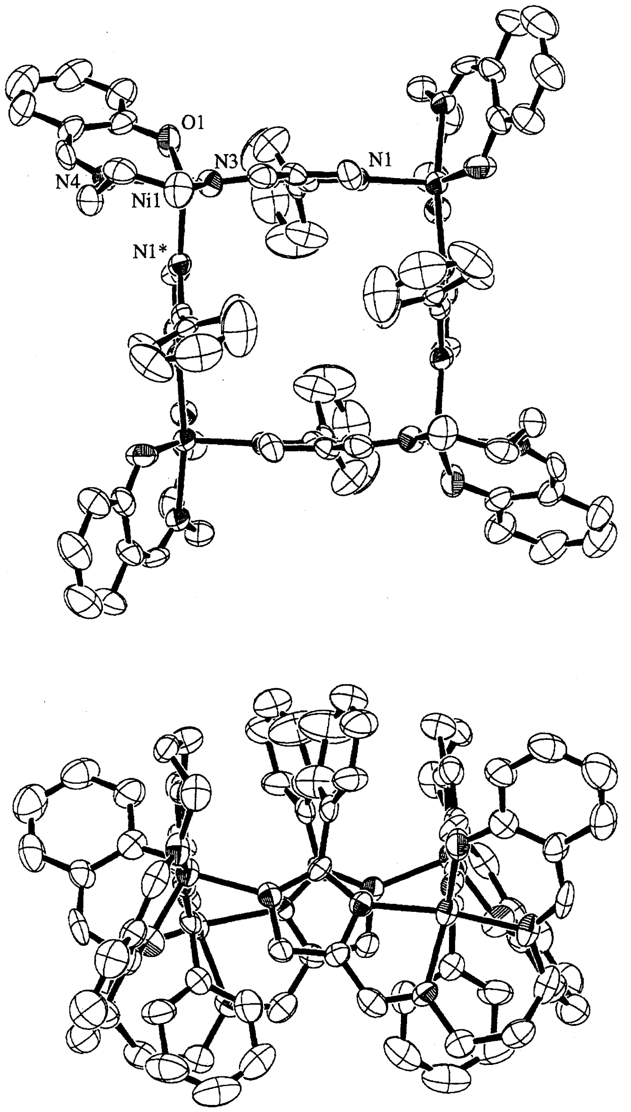


Fig. 2. ORTEP drawings of an imidazolate-bridged cyclic-tetranuclear nickel(II) complex **1′**, showing 50% probability ellipsoids. (top) view showing the cavity, (bottom) side view.

gand of a unit and an imidazolate nitrogen atom of the adjacent unit, where the Ni–O distance is 1.964(6) Å and the four Ni–N distances are within the range of 2.021(8) to 2.092(7) Å. These bond distances are shorter than the corresponding distances in **1**. The angle of O(1)–Ni–N(3) is 172.2(1)° and 146.7(3)° for **1** and **1′**, respectively, indicating that a molecular bend of the quadridentate ligand is substantially induced from **1** to **1′**. A structural index parameter for five-coordinated geometry introduced by Reedijk,[16] $\tau=(\beta-\alpha)/60$, is $\tau=0.35$, where α and β represent two basal angles ($\beta>\alpha$) and the parameters for ideal square-pyramid and trigonal-bipyramid are $\tau=0$ ($\alpha=\beta=180°$) and $\tau=1$ ($\alpha=120°$, $\beta=180°$), respectively, and $\alpha=$ O(1)–Ni–N(3) and $\beta=$ N(2)–Ni–N(4). The coordination geometry around nickel(II) of **1′** is described as a square-pyramid.

In a previous paper we reported on the crystal structure of a deprotonated copper(II) complex with the same quadridentate ligand.[5] The copper(II) complex assumed an imidazolate-bridged one-dimensional zigzag-chain structure[5] and in the crystal lattice two crystallographically independent copper(II) ions assumed a penta-coordinated environment with a substantial molecular bend of the quadridentate ligand. The degree of the molecular bend could be estimated by the angle of O–Cu–N. The angles for the two Cu(II) ions in the copper(II) complex are 144.8(3)° and 155.0(2)°, respectively; these values are compatible with 146.7(3)° of the nickel(II) complex **1′**. Although the copper(II) and nickel-

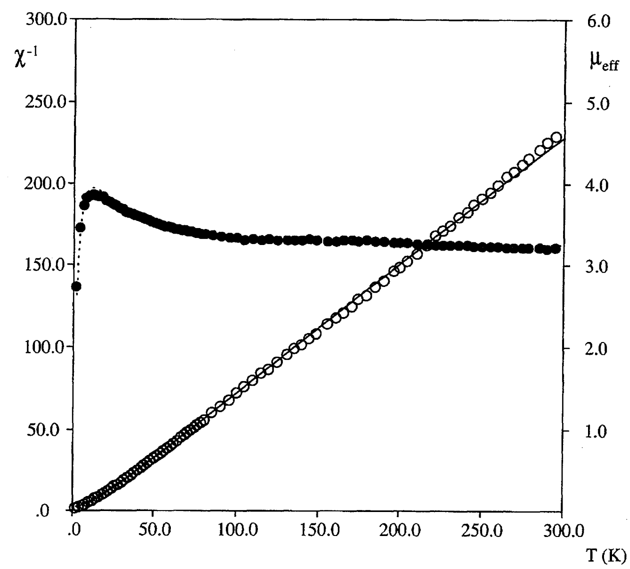


Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility and effective magnetic moment per nickel for **1**. The solid and dotted lines represent the best-fit calculated curves using the parameters $g=2.22$, $J=+7.1$ cm^{-1}, and $D=8.9$ cm^{-1}.

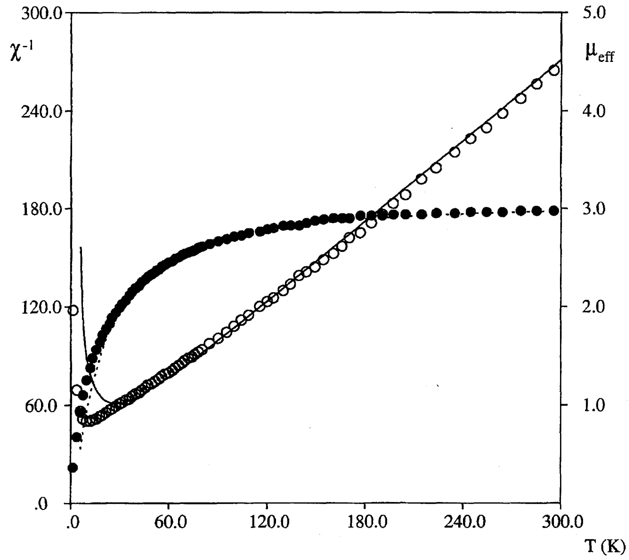


Fig. 4. Temperature dependence of the reciprocal magnetic susceptibility and effective magnetic moment per nickel for **1′**. The solid and dotted lines represent the best-fit calculated curves using the parameters $g=2.19$ and $J=-6.3$ cm^{-1}.

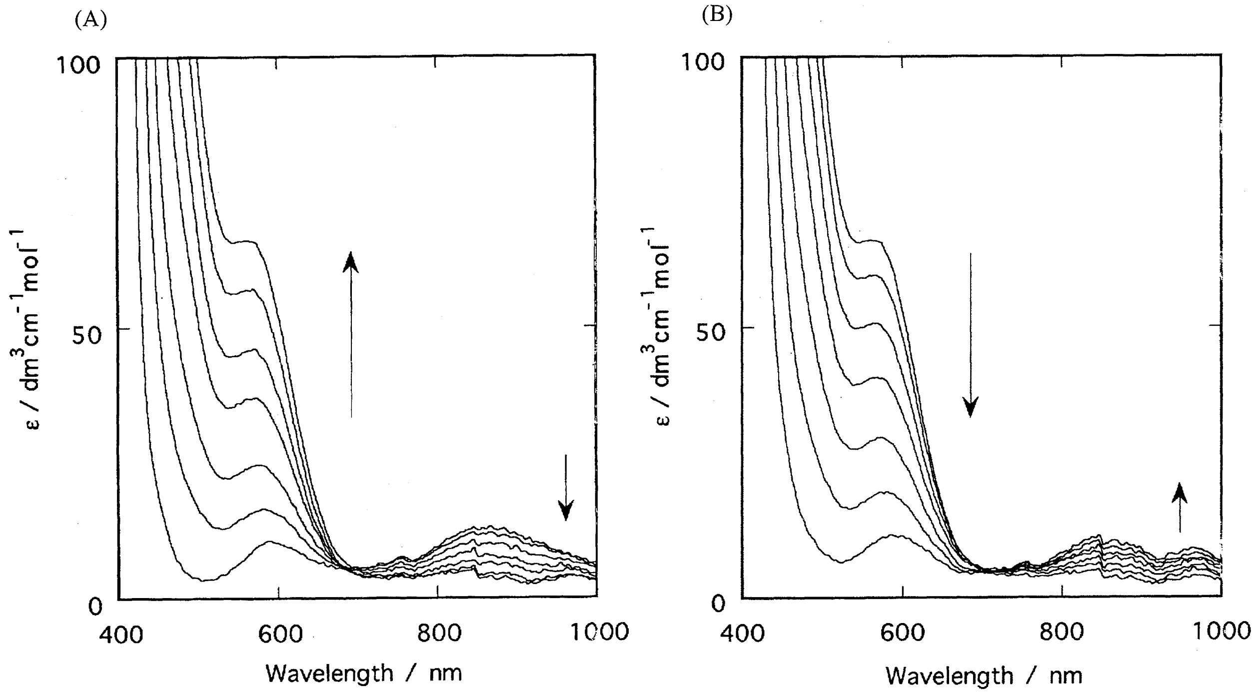
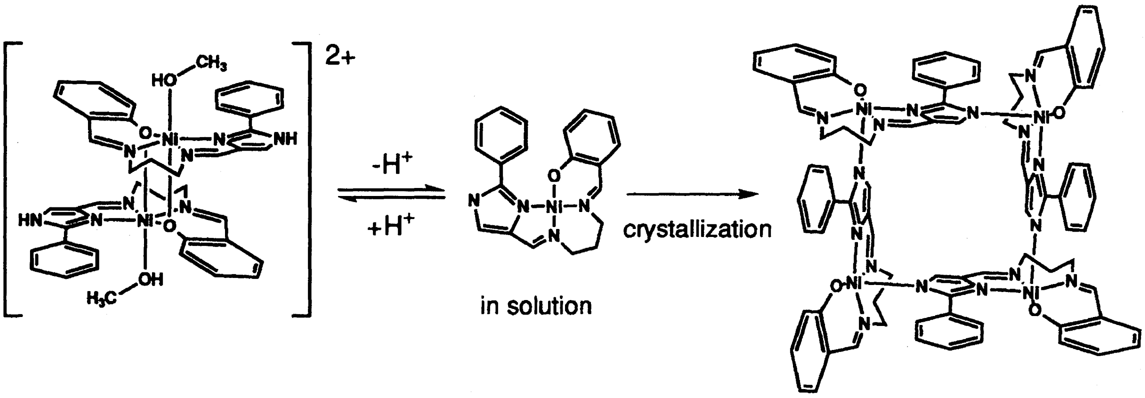


Fig. 5. pH-dependent electronic spectra of **1** for the forward A(left) and reverse B(right) procedures. A methanol solution of the protonated complex **1** (0.12 mmol in 80 ml of methanol) was prepared. The spectrum was measured at every addition of 0.4 ml of 0.1 M NaOH solution. Then, to the final solution batches of 0.4 ml of 0.1 M HCl solution were added for the reverse procedure. The spectra were corrected by the volume deviation due to the addition of 0.1 M NaOH and HCl solutions.



Scheme 2. Schematic illustration of self-assembly process for nickel(II) complex.

(II) complexes have the same coordination number and a similar coordination geometry with a substantial molecular bend, a significant difference between them is found in the bond distance of the metal-imidazolate nitrogen atom. The distance of the nickel(II) complex is 2.050(7) Å, which is almost equivalent to the other four coordination bands. On the other hand, those of the copper(II) complex (2.228(6) and 2.461(6) Å) are considerably longer than those of the other coordination bonds, due to the Jahn-Teller effect of the Cu(II) ion. Further, the angle of N(1)–M–N(1),* which is the interunit bridging-angle and represents the relative orientation between the two adjacent units, is 94.6(3)° for **1′**. This value is smaller than that of the copper(II) complex (96.7(2)°) and closer to 90°. The relative orientation and dimension between the adjacent units would work cooperatively to produce the cyclic-tetranuclear of the nickel(II) complex. The result provides a good example that the nature of the metal ion can play an important role in determining the assembly structure, and a modification of the manner of linkage between the adjacent building units produces a distinctly different assembly structure.

Magnetic Properties of 1 and 1′. The magnetic behaviors of **1** and **1′** are shown in Figs. 3 and 4, respectively, in the forms of $1/\chi_A$ vs. T and μ_{eff} vs. T plots, where χ_A, μ_{eff}, and T denote the magnetic susceptibility per nickel atom, effective magnetic moment, and absolute temperature, respectively.

The effective magnetic moment of **1** gradually increased from 3.21 μ_B at 295 K to a maximum of 3.86 μ_B at 12 K, and then decreased at lower temperature. The magnetic moment demonstrated that the nickel(II) ion is in a high-spin state with $S = 1$. The increase in μ_{eff} suggests an intramolecular ferromagnetic coupling, and the decrease at low temperature is due to a zero-field splitting of the nickel(II) ion. The magnetic behavior was well reproduced by the following spin-Hamiltonian, based on a dinuclear structure with a spin system $(S_1, S_2)=(1, 1)$, including a zero-field splitting term:[17)]

$$H = g_{\mathrm{Ni}}\beta H\cdot (S_1 + S_2) - 2JS_1S_2 + D[S_{1z}^2 + S_{2z}^2].$$

The best-fit parameters were $g = 2.22$, J=+7.1 cm^{-1}, and D = 8.9 cm^{-1}. The theoretical curves are represented in Fig. 3. Although seemingly large, the calculated zero-field splitting is in the range observed for other Ni(II) complexes.[18,19)]

The effective magnetic moment of **1′** decreases monotonously from 2.98 μ_{B} at 295 K to 0.36 μ_{B} at 2 K, indicating the high-spin state of the nickel(II) ion and the operation of an antiferromagnetic coupling. A pronounced maximum in the χ_{A} vs. T curve was observed at 12 K. The magnetic behavior was fitted by the spin-Hamiltonian on the basis of a cyclic-tetranuclear structure,

$$H = g_{\mathrm{Ni}}\beta H\cdot (S_1 + S_2 + S_3 + S_4) - 2J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1).$$

No zero-field splitting was included, since its effect is qualitatively similar to that of the antiferromagnetic coupling at low temperature. A reasonably good fit was obtained for g=2.19 and J=−6.3 cm^{-1}, and the theoretical curves are given in Fig. 4. The effect of monomeric impurity and/or intermolecular interactions, which would improve the fit, were not included so as to avoid overparametrization.

Interconversion between Protonated and Deprotonated Species in Methanol. The solution of **1** (0.12 mmol in 80 ml of methanol) was prepared and the electronic absorption spectra were measured at every addition of 0.4 ml of 0.1 M NaOH aqueous solution (1 M = 1 mol dm^{-3}) until the total volume of the NaOH solution (2.4 ml) neutralized the imidazole proton. Then, to the final solution batches of 0.4 ml of 0.1 M HCl solution were added for the reverse procedure. The results for the forward and reverse procedures are shown in Fig. 5. The spectrum of **1** without NaOH exhibited two broad weak bands at 590 and 868 nm with the molar extinction coefficients of 10 and 13 dm^3 mol^{-1} cm^{-1}, respectively. These bands are both assignable to d–d bands of high-spin nickel(II) complex with an octahedral coordination geometry. Upon adding a 0.1 M NaOH solution, the color changed from green to brown and the spectrum changed with an isosbestic point at 690 nm. The band at 590 nm shifted to a lower wavelength with increasing intensity, while the band at 868 nm decreased in intensity. After complete deprotonation of the imidazole proton, the spectrum exhibited a d–d band with λ_{max}=560 nm and ε=70 dm^3 mol^{-1} cm^{-1}, resembling the spectrum of the deprotonated compound **1′** measured in dichloromethane (λ_{max}=560 nm, ε=100 dm^3 mol^{-1} cm^{-1}). Upon adding a 0.1 M HCl solution in the reverse procedure, the spectrum reached close to the original spectrum.

1′ had a d–d band at 634 nm in the powdered reflectance spectrum, indicating that the coordination geometry in the solid state was different from that in solution. The FABMS spectrum of **1** in methanol showed a molecular ion peak due to the dinuclear structure, indicating that the dinuclear structure confirmed in the crystalline state is at least partially retained in methanol. The FABMS spectrum of **1′** in CH_2Cl_2 showed molecular ion peaks attributable to a monomer as the main peak and a dimer as a trace, but no molecular ion peak attributable to a tetranuclear structure. The ^{1}H NMR spectra of **1′** measured in a ca. 10^{-3} mol dm^{-3} $CDCl_3$ solution indicated that the species is diamagnetic in solution. These data together with the electronic spectral data suggest that the tetranuclear nickel(II) molecule in the solid state dissociates to a diamagnetic mononuclear molecule with a square-planar coordination geometry in the 10^{-3} mol dm^{-3} solution.

On the basis of the above results, the interconversion behavior of the present nickel(II) complex between the protonated and deprotonated species is given in Scheme 2. The protonated species assumes a dinuclear structure in both the solid state and solution. The deprotonated species assumes a diamagnetic mononuclear structure in solution and crystallizes in an imidazolate-bridged cyclic-tetranuclear structure in the solid state.

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