

Acetamide Coordination in a Nickel(I) Macrocyclic Complex: Synthesis, Properties, and X-ray Crystal Structure of a Five-Coordinate Nickel(I) Iminol Complex of 1,3,6,8,12,15-Hexaazatricyclo[13.3.1.1^{8,12}]jicosane

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Abstract: A five-coordinate Ni(I) macrocyclic complex, (R,S,R,S)-[Ni(L)(NHC(OH)CH₃)]ClO₄, where L is 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]jicosane, has been prepared by the reduction of Ni(II) complex (R,R,S,S)-[Ni(L)]-(ClO₄)₂·¹/₂H₂O with Na(Hg) in MeCN under a nitrogen atmosphere. In the formation of the complex, the solvent MeCN was hydrated to acetamide and coordinated to the Ni(I) ion. The complex shows rhombic EPR spectra with the powder sample or in the frozen MeCN solution. It equilibrates with four-coordinate (R,R,S,S)-[Ni(L)]⁺ in MeCN. [Ni(L)(NHC(OH)CH₃)]ClO₄ (NiC₁₆H₃₅N₇O₅Cl) crystallizes in the orthorhombic space group *Pbca* with *a* = 10.053(5) Å, *b* = 14.120(3) Å, *c* = 31.005(3) Å, and *Z* = 8. The structure was solved by the direct method and refined to *R* values of *R*₁ = 0.0500 and *ωR*₂ = 0.0983 for 2153 unique reflections measured with Mo Kα radiation on a CAD-4 diffractometer. The Ni(I) ion of the complex has square-pyramidal geometry with an acetamide coordinating in the iminol form at the apical position. The complex shows two sets of Ni–N(macrocycle) bond distances: 2.092(3) Å (av) for Ni–N(sec) and 2.135(3) Å (av) for Ni–N(tert), which are significantly longer than those of the square-planar Ni(I) complex (R,R,S,S)-[Ni(L)]ClO₄. The Ni–N(iminol) bond distance is 1.969(5) Å. The three bonds of Ni–N–C–O involving an iminol group have multiple bonding character.

Introduction

Recently, Ni(I) macrocyclic complexes have attracted considerable attention. This is because Ni(I) species were proposed to be involved in the electrochemical reduction of CO₂^{1–3} and alkyl halides,^{4–10} which was catalyzed by Ni(II) tetraaza macrocyclic complexes. Furthermore, F₄₃₀, a Ni(II) hydrocorphinoid complex, is a prosthetic group of *S*-methyl coenzyme M reductase which catalyzes the reductive cleavage of *S*-methyl coenzyme M to coenzyme M and methane in the final stage of carbon dioxide reduction in the methanogenic bacteria.^{11–14} An EPR signal detected with *Methanobacterium thermoautotrophicum* was attributed to a Ni(I) form of F₄₃₀ in intact active enzyme.^{15,16} However, only a few X-ray crystal structures of

Ni(I) complexes with macrocyclic ligands^{17–20} or porphyrin analogues²¹ have been reported so far, and thus the structures of Ni(I) complexes have not been well documented. All Ni(I) macrocyclic complexes whose structures have been determined so far are four-coordinate and show two different sets of Ni–N bond distances with^{17,19} or without^{18,20} an expansion of the macrocyclic core compared with the parent Ni(II) species. The results are in good agreement with the EXAFS data of Ni(I)-F₄₃₀²² and Ni(I) hydroporphyrins,^{23–25} although the distortion of the macrocyclic core in the Ni(I) species has not been properly explained yet. Furthermore, there has been no report on the X-ray crystal structures of five-coordinate Ni(I) complexes yet.

The nitrile hydration and the coordination chemistry of the metal–amide linkage are of interest also in their own rights and in the context of metal ion–peptide chemistry.^{26–28} The

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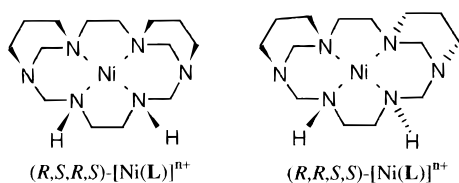
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Chart 1



coordination mode of amide has been known to depend on the acidity of the medium and the type and oxidation state of the metal ion. The complexes of O-bonded amide,^{29–34} anionic N-bonded amidate,^{34–39} N-bonded amide,^{40–42} and N-bonded iminol^{43,44} have been reported.

Here, we report the synthesis, properties, and structure of a five-coordinate Ni(I) macrocyclic complex coordinating acetamide in the iminol form, $(R,S,R,S)-[Ni(L)(NHC(OH)CH_3)]ClO_4$, where **L** is 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]icosane. This paper is significant in several respects: (i) it presents the first X-ray crystal structure of a five-coordinate Ni(I) macrocyclic complex, (ii) it gives the first example of acetamide coordination to a low-valent metal ion, binding through the N atom of iminol, and (iii) it provides an example of the hydration of nitrile. The configurational isomers for $[Ni(L)]^{II+}$ are shown in Chart 1 for clarity.

Experimental Section

General Procedures. As the Ni(I) complexes are air-sensitive, all preparation, experiments, and manipulations have to be conducted under strict exclusion of air by using a Schlenk line and tubes.

Reagents. All solvents and reagents were purified according to the literature.⁴⁵ Nitrogen gas was purified by passing it through a BASF column and a CaCl₂ column. Solvents were deaerated thoroughly prior to use. $(R,R,S,S)-[Ni^{II}(L)](ClO_4)_2 \cdot 1/2 H_2O$ ⁴⁶ and $(R,R,S,S)-[Ni^I(L)]ClO_4$ ^{18,20} were prepared according to the literature procedures previously reported.

Measurements. Infrared spectra were recorded with a JASCO IR 810 spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu UV-260 spectrophotometer. Electron spin resonance spectra were recorded on a Bruker ER 200E spectrometer. Elemental

analyses were performed by Galbraith Laboratories, Tennessee. Magnetic susceptibility was measured by the NMR method⁴⁷ on a VXR-200S FT-200 MHz NMR spectrometer.

Synthesis. Safety Note. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.

$(R,S,R,S)-[Ni(L)(NHC(OH)CH_3)]ClO_4$. Method 1. $(R,R,S,S)-[Ni(L)](ClO_4)_2 \cdot 1/2 H_2O$ (2 g)^{46,52} was stirred with Na(Hg) for 20 min in MeCN (50 mL) under a nitrogen atmosphere. The orange Ni(II) complex went into a deep blue solution. The solution was filtered, concentrated to ca. half of the initial volume, and then allowed to stand in a refrigerator for 7–10 days, during which time the solution turned green and green crystals formed. The green crystals were filtered, washed with MeCN, and dried *in vacuo*. Yield: ca. 70%.

Method 2. To the blue MeCN solution of $(R,R,S,S)-[Ni(L)]ClO_4$ ^{18,20} was added an MeCN solution of acetamide (aa/Ni^I = 2 mol/mol). The solution was allowed to stand at room temperature for 3 days, during which time the solution turned green and green crystals formed. The crystals were washed with MeCN and dried *in vacuo*. Yield: ca. 80%. Anal. Calcd for $[Ni(C_{14}H_{30}N_6)(CH_3CONH_2)]ClO_4$: C, 38.46; H, 7.06; N, 19.62. Found: C, 38.88; H, 7.07; N, 19.76. IR (cm⁻¹): $\nu(OH)$ 3345; $\nu[NH(\text{amide})]$ 3310; $\nu[NH(\text{mac})]$ 3200; $\nu(C=O, C=N)$ 1598 (vs). UV/vis (nm, with added acetamide in MeCN): 645 ($\epsilon = 53 \text{ cm}^{-1} \text{ M}^{-1}$); 401 ($\epsilon = 120 \text{ cm}^{-1} \text{ M}^{-1}$). EPR: $g_1 = 2.287$, $g_2 = 2.183$, $g_3 = 2.035$ for the powder sample at room temperature; $g_1 = 2.264$, $g_2 = 2.169$, $g_3 = 2.027$ in MeCN at 77 K. μ_{eff} (by the NMR method):⁴⁷ 1.46 μ_B .⁴⁷

$(R,R,S,S)-[Ni(L)(NHC(OH)CH_3)]ClO_4$. $(R,R,S,S)-[Ni(L)](ClO_4)_2 \cdot 1/2 H_2O$ (3 g)⁴⁶ was stirred with Na(Hg) for 20 min in MeCN (35 mL) under a nitrogen atmosphere. When the orange Ni(II) complex dissolved, a deep blue solution formed. The solution was filtered, and acetamide (0.5 g) dissolved in MeCN (15 mL) was added. The solution was concentrated to ca. half of the initial volume and then allowed to stand for 5 h, during which time pale blue crystals formed from the blue solution. The crystals were filtered, washed with MeCN, and dried *in vacuo*. The complex was recrystallized in MeCN. Yield: ca. 70%. Anal. Calcd for $[Ni(C_{14}H_{30}N_6)(CH_3CONH_2)]ClO_4$: C, 38.46; H, 7.06; N, 19.62. Found: C, 38.50; H, 7.24; N, 19.87. IR (cm⁻¹): $\nu(OH)$ 3330; $\nu[NH(\text{amide})]$ 3275; $\nu[NH(\text{mac})]$ 3150, 3060; $\nu(CO, C=N)$ 1670, 1585. UV/vis (nm, in MeCN saturated with acetamide): 588 ($\epsilon = 114 \text{ cm}^{-1} \text{ M}^{-1}$); 357 ($\epsilon = 280 \text{ cm}^{-1} \text{ M}^{-1}$). EPR (powder sample at room temperature): $g_{\parallel} = 2.245$, $g_{\perp} = 2.064$.

$(R,S,R,S)-[Ni(L)](ClO_4)_2$. Method 1. Green $(R,S,R,S)-[Ni(L)-NHC(OH)CH_3]ClO_4$ was dissolved in water or in MeCN with a trace amount of added HClO₄ in the air. The solution turned red, to which a saturated MeCN solution of LiClO₄ (LiClO₄/Ni^I = 1 mol/mol) was added. Red crystals formed from the solution, which were filtered, washed with water, and dried *in vacuo*. Yield: ca. 90%.

Method 2. Green $(R,S,R,S)-[Ni(L)(NHC(OH)CH_3)]ClO_4$ was dissolved in MeCN under a nitrogen atmosphere, and dry oxygen gas was bubbled through the solution for 1 h. The solution was allowed to stand at room temperature until it turned brown. A saturated MeCN solution of LiClO₄ (LiClO₄/Ni^I = 1 mol/mol) was added, and red crystals formed, which were filtered, washed with MeCN, and dried *in vacuo*. Yield: ca. 80%. Anal. Calcd. C, 31.14; H, 5.60; N, 15.56. Found: C, 31.22; H, 5.40; N, 15.57. IR (cm⁻¹): $\nu(NH)$, 3210, 3250, 3300; $\nu(ClO_4^-)$, 1100. UV/vis (nm): 490 ($\epsilon = 107 \text{ cm}^{-1} \text{ M}^{-1}$) in H₂O; 496 ($\epsilon = 106 \text{ cm}^{-1} \text{ M}^{-1}$) in MeCN; 489 ($\epsilon = 116 \text{ cm}^{-1} \text{ M}^{-1}$) in MeNO₂. ¹³C NMR (δ , ppm, in CD₃NO₂): 24.7, 48.2, 48.5, 56.5, 58.2, 70.9, 74.7.

X-ray Crystallography. A green crystal with approximate dimensions of 0.2 × 0.2 × 0.3 mm was sealed in a glass capillary under a nitrogen atmosphere. All X-ray data were collected at room temperature using graphite-monochromated Mo K α radiation on an Enraf-Nonius CAD4 diffractometer. The crystallographic data collection and refinement details are summarized in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered

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(47) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. The magnetic susceptibility was measured with an MeCN solution. The value of μ_{eff} is smaller than the expected 1.73 μ_B for the d⁹ system, which may be due to the experimental error. The error might come from the oxidation of the Ni(I) complex to diamagnetic $[Ni(L)]^{2+}$ and/or the inaccuracy of the concentration of the Ni(I) complex.

Table 1. Crystal Data and Data Collection for $(R,S,R,S)-[Ni(C_{14}H_{30}N_6)(NHC(OH)CH_3)]ClO_4$

formula	$C_{16}H_{34}N_7O_5ClNi$	μ , mm ⁻¹	1.046
FW	498.67	2θ range, deg	3–50
crystal system	orthorhombic	no. of data colld	2153
space group	<i>Pbca</i>	no. of unique data (all)	2153
<i>a</i> , Å	10.053(5)	no. of obsd data [$F > 4\sigma(F)$]	2025
<i>b</i> , Å	14.120(3)	no. of variable params	408
<i>c</i> , Å	31.005(3)	R^a (all data)	0.0500
<i>V</i> , Å ³	4401.1(24)	$wR(F^2)^b$ (all data)	0.0983
<i>Z</i>	8	GOF (all data)	1.104
ρ_{calc} , g cm ⁻³	1.508	$(\Delta/\sigma)_{max}$	0.095
temp, K	293 (2)	largest diff peaks, e Å ⁻³	0.323
λ , Å	0.71073		

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]$ where $w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 1.7053P]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(R,S,R,S)-[Ni(C_{14}H_{30}N_6)(NHC(OH)CH_3)]ClO_4$

Ni–N3	2.099(4)	N1–C14	1.401(9)
Ni–N6	2.081(5)	N1–C2	1.429(8)
Ni–N10	2.151(4)	N1–C17	1.464(9)
Ni–N13	2.119(4)	N8–C7	1.435(7)
Ni–N24	1.969(5)	N8–C9	1.420(8)
C22–O23	1.242(7)	N8–C18	1.459(8)
C22–N24	1.314(7)	C22–C21	1.528(9)
N24–Ni–N6	109.9(2)	O23–C22–N24	122.8(5)
N24–Ni–N3	94.9(2)	O23–C22–C21	119.0(6)
N24–Ni–N13	105.7(2)	N24–C22–C21	118.2(6)
N6–Ni–N3	83.5(2)	C22–N24–Ni	124.6(4)
N6–Ni–N13	144.4(2)	C14–N1–C2	115.1(6)
N3–Ni–N13	93.1(2)	C14–N1–C17	112.1(6)
N24–Ni–N10	94.8(2)	C2–N1–C17	117.4(6)
N6–Ni–N10	92.6(2)	C9–N8–C7	116.3(6)
N3–Ni–N10	170.3(2)	C9–N8–C18	112.8(6)
N13–Ni–N10	84.9(2)	C7–N8–C18	116.1(6)

reflections with $16^\circ < 2\theta < 22^\circ$. Axial photographs were used to verify the unit cell choice. Data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied.⁴⁸ All calculations were carried out on a personal computer with use of SHELXS-86⁴⁹ and SHELXL-93⁵⁰ programs. The structure was solved by the direct method.⁵¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from the difference Fourier map, and their positional and isotropic displacement parameters except those for the hydroxyl hydrogen (H23) were refined. H23 was found from the difference Fourier map, but the isotropic displacement parameter was not refined satisfactorily. Therefore, the torsion angle was refined by the circular difference Fourier using the SHELXL93 HFIX147 option. Selected bond distances and bond angles are shown in Table 2.

The data were refined for both N-coordinated and O-coordinated acetamide complexes, and assignment of N and O atoms of acetamide was based on the comparison of the results of the final difference Fourier maps for the two possible structures. The refinement with the isotropic model for the non-hydrogen atoms without absorption correction gives $R(F) = 0.1215$ and $R(F^2) = 0.2977$ for the O-coordinated acetamide complex and $R(F) = 0.1205$ and $R(F^2) = 0.2957$ for the N-coordinated acetamide complex. The difference Fourier maps are reasonably good for the N-bonded acetamide complex while the O-bound acetamide complex shows peaks of +0.7 and -0.7 e/Å³ around the N atom and O atom, respectively. With the absorption

correction,⁴⁸ the N-bonded acetamide complex gives an $R(F)$ value of 0.098.

Measurement of Equilibrium between $(R,R,S,S)-[Ni(L)]^+$ and $(R,R,S,S)-[Ni(L)(CH_3CONH_2)]^+$. The UV/vis spectra were measured for a MeCN solution of $(R,R,S,S)-[Ni(L)]ClO_4$ by adding various amounts of a MeCN solution of acetamide under the strict exclusion of air. The concentrations of $[Ni(L)]^+$ and acetamide were 8.0×10^{-4} to 1.4×10^{-3} M and 0.017–0.27 M, respectively.

Results

Synthesis. The reduction of the yellow square-planar Ni(II) complex $(R,R,S,S)-[Ni(L)](ClO_4)_2 \cdot 1/2 H_2O$ with Na(Hg) in MeCN produced a blue solution from which square-planar $(R,R,S,S)-[Ni(L)]ClO_4$ was isolated.^{18,20} When the blue MeCN solution of $(R,R,S,S)-[Ni(L)]ClO_4$ was allowed to stand for several days under nitrogen, the color of the solution turned green. From the solution green five-coordinate Ni(I) acetamide complex $(R,S,R,S)-[Ni(L)(CH_3CONH_2)]ClO_4$ was isolated. In this reaction, MeCN was hydrated by OH⁻ ion, which was produced by the reaction between Na(Hg) and the lattice water contained in the starting Ni(II) complex. Exactly the same compound was obtained when a MeCN solution of acetamide (aa) was added to a MeCN solution of blue $(R,R,S,S)-[Ni(L)]ClO_4$ (aa/Ni^I = 2 mol/mol), and then the mixture was allowed to stand at room temperature for 3 days. However, the parent Ni(II) complex $(R,R,S,S)-[Ni(L)](ClO_4)_2 \cdot 1/2 H_2O$ ⁴⁶ or its configurational isomer $(R,S,R,S)-[Ni(L)](ClO_4)_2$ ⁵² did not react with acetamide either in the absence or in the presence of NEt₃ or BuLi (mole/mole ratio; Ni(II)/aa/base = 1/50/50), which was confirmed by the measurement of UV/vis spectra. This is in contrast to the fact that the oxygen-bonded or anionic nitrogen-bonded amide and urea complexes of 2+ or 3+ metal ions including $[Ni(H_2O)_2-(acetamide)_4]Cl_2$ were synthesized previously by the addition of amide without any added base.^{29,30,33,43,44,53} On the other hand, when the MeCN solution of the Ni(I) complex $(R,R,S,S)-[Ni(L)]ClO_4$ and that of acetamide were mixed, a pale blue acetamide adduct was produced. IR, UV/vis, EPR, and the results of elemental analysis (see the Experimental Section) indicate it to be $(R,R,S,S)-[Ni(L)(CH_3CONH_2)]ClO_4$, which is a macrocyclic configurational isomer of the green complex, although the bonding mode of acetamide is still less clear since the crystal structure has not been determined yet.

Crystal Structure of Five-Coordinate Ni(I) Complex $(R,S,R,S)-[Ni(L)(NHC(OH)CH_3)]ClO_4$. An ORTEP plot of the cation in the green complex $[Ni(L)(NHC(OH)CH_3)]ClO_4$ is presented in Figure 1. The Ni(I) ion forms a square-pyramidal geometry, with the Ni(I) ion being 0.411(2) Å out of the square-coordination plane toward acetamide. The two 1,3-diazacyclohexane subring moieties of the macrocycle are situated to the direction of the apical ligand, resulting in an *R,S,R,S*-configuration, while the starting square-planar Ni(II)⁴⁶ and the corresponding square-planar Ni(I) complexes^{18,20} have the *R,R,S,S*-configuration. The dihedral angles between each six-membered diaza subring planes and the square coordination plane are 100.4(2)° and 112.4(2)°. The complex shows two sets of Ni–N(macrocycle) bond distances differentiated by the secondary and tertiary nitrogen donors; 2.092(3) Å (av) for Ni–N(sec) and 2.135(3) Å (av) for Ni–N(tert). These are significantly longer than 1.951 Å (av) for the parent Ni(II) complex⁴⁶ and 1.878(4) and 1.978(3) Å for the square-planar Ni(I) complex of **L**.^{18,20} Two sets of Ni–N bond distances have been commonly observed for all Ni(I) macrocyclic complexes in a square-planar geometry.^{17–20} The N–N bite distances are 2.783(7) and 2.883(6) Å for the five-membered chelate rings

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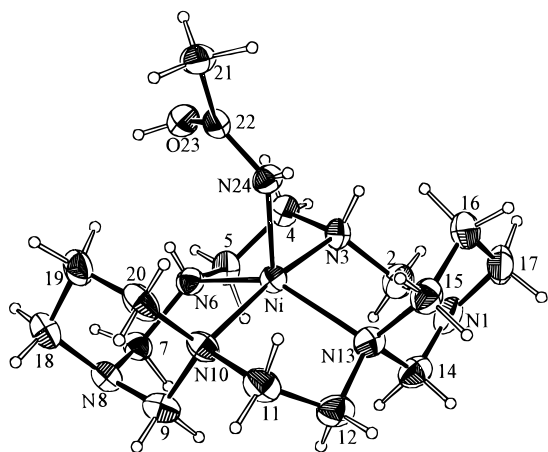
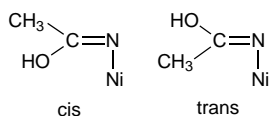


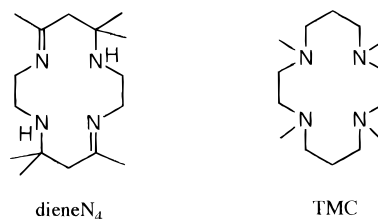
Figure 1. ORTEP drawing of the cation in (R,S,R,S) -[Ni(L)(NHC(OH)CH₃)]ClO₄ showing the atomic labeling scheme. The atoms are represented by 30% probable thermal ellipsoids.

and 3.059(7) and 3.063(6) Å for the six-membered chelate rings. The C–N bond distances involving uncoordinated bridgehead tertiary amines N1 and N8, ranging from 1.401(9) to 1.464(9) Å [average 1.435(3) Å], are shorter than normal aliphatic C–N bond distances (1.52 Å). The bond angles involving N1 and N8 are 112–117°. These indicate a significant contribution of sp² hybridization in the uncoordinated tertiary nitrogens. Similar shortening of the C–N bond distances involving uncoordinated tertiary nitrogens was also observed for [Ni(L)]ClO₄²⁰ and [Ni(L)](ClO₄)₂·1/2H₂O.⁴⁶

The bonding mode of acetamide, that is, nitrogen versus oxygen binding, was determined by the comparison of the final difference Fourier maps. The N-bonded structure shows lower *R* values and a better difference Fourier map. One hydrogen atom was located at N24 and another at O23 of acetamide from the difference Fourier map, indicating that acetamide binds the Ni(I) ion in the iminol form. In addition, hydrogen-bonding was found between the O atom of acetamide and H6–N6 of the macrocycle: O23···N6, 3.031(7) Å; O23···H6, 2.42(5) Å; ∠O23–H6–N6, 144(5)°. Although two isomers of *cis*- and *trans*-configuration are possible for the iminol complex with respect to the positions of the hydroxyl group and nickel atom, the complex has the *cis*-configuration, which may be attributed to this hydrogen-bonding.



The Ni–N(acetamide) bond distance is 1.969(5) Å, which is shorter than the equatorial Ni–N bond distances although it is significantly longer than the Ni(I)–CO bond distance (1.80 Å) in [Ni(dieneN₄)(CO)]ClO₄¹⁷ which was determined by the EXAFS analysis. The bond distances of C=O and C–N in the acetamide moiety are 1.242(7) and 1.314(7) Å, respectively. These are significantly longer and shorter, respectively, than the normal C=O (1.20 Å) and C–N (1.49 Å) bond distances. Compared with the C=O (1.233 Å) and C–N bond (1.333 Å) distances of free acetamide,⁵⁴ the C–O bond distance in the present complex is 0.01 Å longer and the C–N bond distance is 0.02 Å shorter than those of free acetamide. In addition, the four atoms C21, C22, O23, and N24 of acetamide make a perfect plane with a maximum deviation of 0.004 Å, and the Ni atom is located 0.574(11) Å out of the plane: the five atoms C21, C22, O23, N24, and Ni make a plane with a maximum deviation of 0.2 Å.



Properties and Spectra. The green complex (R,S,R,S) -[Ni(L)(NHC(OH)CH₃)]ClO₄ is oxygen-sensitive. As the green crystal was placed in the bottle filled with dry oxygen, it turned red in color. In addition, when the green MeCN solution of the compound was bubbled with dry oxygen or allowed to stand in air, it turned brown-red. From the solution a red Ni(II) complex was isolated, whose X-ray crystal structure indicates it to be (R,S,R,S) -[Ni(L)](ClO₄)₂, a configurational isomer of the starting orange complex.⁵² UV/vis spectra showing the oxygen sensitivity of the complex are presented in Figure S1 of the supporting information. When the complex was dissolved in degassed water under a nitrogen atmosphere, a redox reaction occurred between them and the red precipitate of the Ni(II) complex and hydrogen gas bubbles were produced.

The green complex (R,S,R,S) -[Ni(L)(NHC(OH)CH₃)]ClO₄ shows a rhombic EPR spectrum ($g_1 = 2.287$, $g_2 = 2.183$, and $g_3 = 2.035$ for the powder sample at room temperature and $g_1 = 2.264$, $g_2 = 2.169$, and $g_3 = 2.027$ for the frozen MeCN solution at 77 K) (Figure 2), demonstrating the d⁹ electronic state of five-coordinate nickel.^{18,55–57}

The infrared spectrum of the complex (Figure S2 of the supporting information) shows $\nu(\text{NH})$ of secondary nitrogens of the macrocycle at 3200 cm⁻¹ and $\nu(\text{OH})$, and $\nu(\text{NH})$, and $\nu(\text{CO}, \text{C}=\text{N})$ of the iminol at 3345, 3311, and 1598 cm⁻¹, respectively. The $\nu(\text{CO})$ value of 1598 cm⁻¹ is lower than that of free acetamide (1694 cm⁻¹),⁵⁸ those of N-bonded neutral amide (1710–1725 cm⁻¹),⁴² and those of O-bonded or anionic N-bonded complexes (1591–1675 cm⁻¹).^{31,32}

The color and UV/vis spectrum of five-coordinate (R,S,R,S) -[Ni(L)(NHC(OH)CH₃)]ClO₄ are similar to those of the five-coordinate Ni(I)–CO complex [Ni(dieneN₄)(CO)]⁺.^{19,55} The electronic spectrum of (R,S,R,S) -[Ni(L)(NHC(OH)CH₃)]⁺ depends on the amount of added acetamide as well as the temperature (Figure 3). The maximum absorption peaks of the complex appear at 628 nm ($\epsilon = 76 \text{ cm}^{-1} \text{ M}^{-1}$) and 389 nm ($\epsilon = 140 \text{ cm}^{-1} \text{ M}^{-1}$) in MeCN, which are 34–39 nm longer wavelengths compared with those of square-planar (R,R,S,S) -[Ni(L)]ClO₄¹⁸ (589 nm, $\epsilon = 620 \text{ cm}^{-1} \text{ M}^{-1}$; 355 nm, $\epsilon = 3020 \text{ cm}^{-1} \text{ M}^{-1}$) with remarkably decreased absorptivity. When excess acetamide (0.22 M) is added to the MeCN solution of the green complex ($3.03 \times 10^{-3} \text{ M}$), λ_{max} shifts to a 17 nm longer wavelength with further decreased intensity: $\lambda_{\text{max}} = 645 \text{ nm}$ ($\epsilon = 53 \text{ cm}^{-1} \text{ M}^{-1}$), 401 nm ($\epsilon = 120 \text{ cm}^{-1} \text{ M}^{-1}$). Furthermore, as the temperature increases, the maximum absorption of (R,S,R,S) -[Ni(L)(NHC(OH)CH₃)]⁺ moves to a shorter wavelength than 628 nm with increased intensity, and a new very intense peak appears at 358 nm which corresponds to the absorption maximum of four-coordinate (R,R,S,S) -[Ni(L)]⁺. The tendency of dissociation is increased as the temperature is elevated. It is estimated from Figure 3 that approximately 35% of the complex dissociates to (R,R,S,S) -[Ni(L)]⁺ at 80 °C. The spectrum changes reversibly as the

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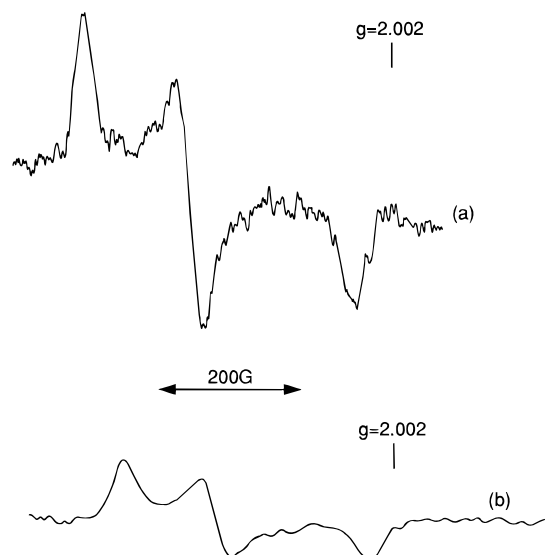


Figure 2. EPR spectra of (R,S,R,S) - $[\text{Ni}(\text{L})(\text{NHC}(\text{OH})\text{CH}_3)]\text{ClO}_4$: (a) powder sample at room temperature ($\nu = 9.775$ GHz), (b) frozen MeCN solution at 77 K ($\nu = 9.293$ GHz).

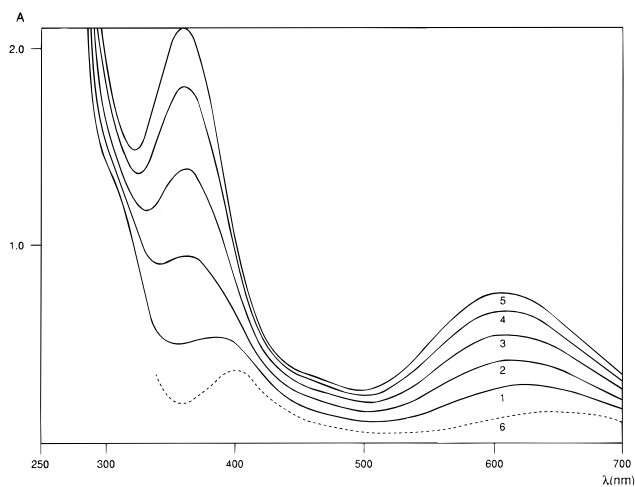
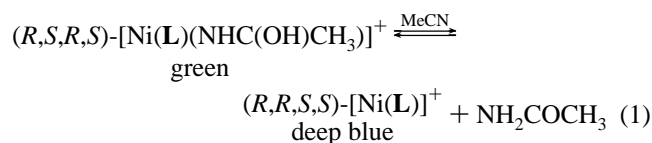


Figure 3. Electronic absorption spectra of (R,S,R,S) - $[\text{Ni}(\text{L})(\text{NHC}(\text{OH})\text{CH}_3)]\text{ClO}_4$ (3.03×10^{-3} M in MeCN) measured under N_2 : (1) 22 °C, (2) 48 °C, (3) 63 °C, (4) 74 °C, (5) 80 °C, (6) with added acetamide, $[\text{aa}] = 0.22$ M, at 18 °C.

solution is cooled. It is obvious that there exists an equilibrium between five-coordinate (R,S,R,S) - $[\text{Ni}(\text{L})(\text{NHC}(\text{OH})\text{CH}_3)]^+$ and four-coordinate (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ in MeCN (eq 1).



Spectral Titration of the Four-Coordinate Ni(I) Complex with Acetamide in MeCN. In order to examine the existence of the equilibrium between four-coordinate and five-coordinate Ni(I) complexes, acetamide was added to the MeCN solution of (R,R,S,S) - $[\text{Ni}(\text{L})]\text{ClO}_4$ ($\text{aa}/\text{Ni}^{\text{I}} \geq 100$ mol/mol). Figure 4 shows titration curves exhibiting the spectral changes of (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ upon addition of acetamide. The spectrum of (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ changes immediately upon addition of acetamide in a thermostated bath maintained at 20 °C. The spectral changes are associated only with the absorbance but not with the maximum wavelength. The intensity at λ_{max} (589 nm) of (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ decreases as the amount of added acetamide increases. The isosbestic points were not observed in the titration curves because the absorptivity of the five-

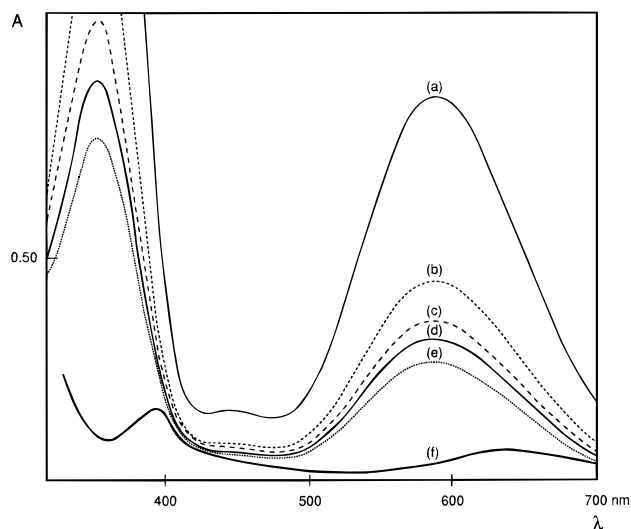
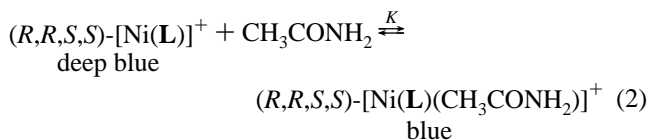


Figure 4. Spectral titration of (R,R,S,S) - $[\text{Ni}(\text{L})]\text{ClO}_4$ (1.41×10^{-3} M) with acetamide (aa) in MeCN at 20 °C: (a) $[\text{aa}] = 0$ M, (b) $[\text{aa}] = 0.106$ M, (c) $[\text{aa}] = 0.159$ M, (d) $[\text{aa}] = 0.212$ M, (e) $[\text{aa}] = 0.265$ M. (f) Spectrum of (R,S,R,S) - $[\text{Ni}(\text{L})(\text{NHC}(\text{OH})\text{CH}_3)]\text{ClO}_4$ (1.4×10^{-3} M) in MeCN for comparison.

coordinate acetamide adduct is too small compared with that of the four-coordinate complex, and the curves for the pure components do not cross. The acetamide adduct (R,R,S,S) - $[\text{Ni}(\text{L})(\text{CH}_3\text{CONH}_2)]\text{ClO}_4$ was isolated as a blue crystal although it eventually results in the green R,S,R,S -isomer after an extended period of time. The equilibrium constant of eq 2 and the absorptivity of blue (R,R,S,S) - $[\text{Ni}(\text{L})(\text{CH}_3\text{CONH}_2)]^+$ are estimated from the titration spectra. The plot of ϵ_{app} vs $(\epsilon_{\text{app}} - \epsilon_{\text{Ni(I)}})/[\text{CH}_3\text{CONH}_2]$ according to eq 3 gives $K = 15.6$ M $^{-1}$ and



$$\epsilon_{\text{app}} = (-1/K)\{(\epsilon_{\text{app}} - \epsilon_{\text{Ni(I)}})/[\text{CH}_3\text{CONH}_2]\} + \epsilon_{\text{Ni(I)(aa)}} \quad (3)$$

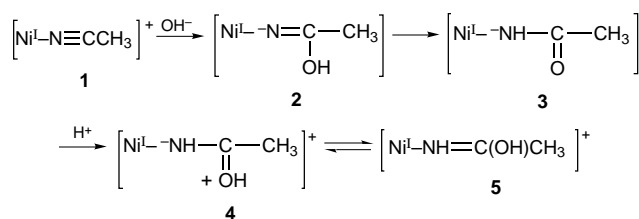
the limiting absorptivity of $\epsilon = 116$ cm $^{-1}$ M $^{-1}$ for (R,R,S,S) - $[\text{Ni}(\text{L})(\text{CH}_3\text{CONH}_2)]^+$ at 20 °C, where ϵ_{app} , $\epsilon_{\text{Ni(I)}}$, and $\epsilon_{\text{Ni(I)(aa)}}$ indicate the molar absorptivities of the equilibrium mixture and four-coordinate and five-coordinate Ni(I) acetamide complexes, respectively. The estimated limiting absorptivity of (R,R,S,S) - $[\text{Ni}(\text{L})(\text{CH}_3\text{CONH}_2)]^+$ is close to that ($\epsilon = 114$ cm $^{-1}$ M $^{-1}$) of the isolated (R,R,S,S) -Ni(I) acetamide complex measured in a saturated MeCN solution of acetamide.

The reactions of (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ with *N*-methylacetamide (NMA) and with *N,N*-dimethylacetamide (DMA) were also tested. A similar absorbance decrease of (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ in UV/vis spectra was observed with NMA, but there was no indication of a reaction with DMA. Probably steric hindrance between the two methyl groups of DMA and the macrocyclic ligand and/or the impossibility of DMA to form an iminol structure prohibits the formation of a Ni(I)–DMA complex.

Discussion

Formation of (R,S,R,S) - $[\text{Ni}(\text{L})(\text{NHC}(\text{OH})\text{CH}_3)]\text{ClO}_4$. The formation of a green acetamide complex from (R,R,S,S) - $[\text{Ni}(\text{L})](\text{ClO}_4)_2 \cdot 1/2\text{H}_2\text{O}$ in MeCN involves reduction of nickel and hydration of acetonitrile as well as changes in the coordination geometry from square-planar to square-pyramidal and the macrocyclic configuration from R,R,S,S to R,S,R,S . The formation of (R,S,R,S) - $[\text{Ni}(\text{L})(\text{NHC}(\text{OH})\text{CH}_3)]^+$ from (R,R,S,S) - $[\text{Ni}(\text{L})]^+$ in MeCN is very slow as it takes several days to obtain the green acetamide complex. The acetonitrile hydration by

Scheme 1

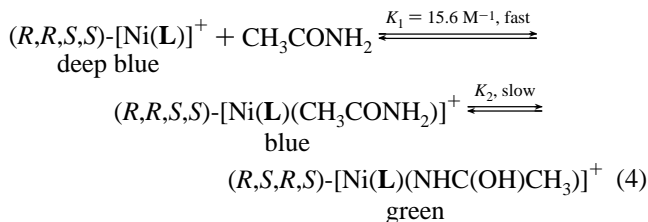


OH⁻ ion, which is produced by the reaction between Na(Hg) and the lattice water of the starting Ni(II) complex, might be promoted by the Ni(I) macrocyclic species. Hydration of nitrile promoted by the transition metal complexes in the 2+ or 3+ oxidation state such as Ni(II), Co(III), and Rh(III) has been well known.^{26,31,35-38,59-65} However, there has been no precedent example of nitrile hydration promoted by a macrocyclic complex or a low-valent metal complex. It has been known that nitriles are quite resistant to hydrolysis, and the second-order rate constant of OH⁻-catalyzed MeCN hydration is $1.6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.³⁶ Furthermore, the rate of hydration depends on the Lewis acidity of the metal ion. For example, the rate of nitrile hydration in [Ru(NH₃)₅NCR]²⁺ is much slower than that in [Co(NH₃)₅NCR]³⁺.⁶⁶ It also has been reported that the isomerization of the macrocycle in the Ni(I) complex is quite slow. It takes several hours in the case of the Ni(I)TMC complex although it is faster than in the corresponding Ni(II) complexes.^{9,10,67} The slow formation of the acetamide complex in the present study must be attributed to the slow hydration of MeCN promoted by the low-valent Ni(I) ion and to the fact that the reaction involves the configurational isomerization of the macrocycle.

The formation route of the acetamide complex from the hydration of MeCN is proposed in Scheme 1. The base-catalyzed hydrolysis of the nitrile promoted by a metal ion usually results in the anionic form of acetamide **3**.^{30,31,36-38,43,44,65} The anionic amide complexes are protonated at various pH values depending on the types of metal ions and amides,^{34,39,41,65} preferentially at the oxygen atom.^{34,39,68} The pK_a values reported for [Pt(dien)₂NHC(OH)Me]²⁺, [Pt(dien)₂NH₂CONMe₂]²⁺, and [(NH₃)₅Ru(NHC(OH)Ph)]²⁺ are 3.8, 5.6, and 8.0, respectively.^{39,41,43} Because the oxygen atom of iminol should be more basic in the Ni(I) complex than in the Pt(II) and Ru(II) complexes due to the lower oxidation state, the deprotonated amide complex **3** can be protonated at relatively high pH and is able to exist as the iminol complex **5**.

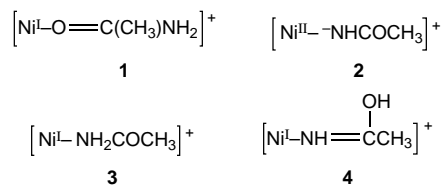
The (*R,S,R,S*)-Ni(I) green complex is assumed to be produced via the formation of an (*R,R,S,S*)-Ni(I) acetamide adduct followed by the isomerization of the macrocycle to the *R,S,R,S*-configuration because the (*R,R,S,S*)-acetamide adduct forms immediately upon the addition of acetamide to the four-coordinate (*R,R,S,S*)-[Ni(L)]⁺ and eventually changes to the green (*R,S,R,S*)-acetamide complex after an extended period of

time. The isomerization from the *R,R,S,S*- to the *R,S,R,S*-configuration in the Ni(I) acetamide complex may be extremely slow at room temperature. It has been observed for [Ni(L)]²⁺ that transformation from the *R,R,S,S*- to the *R,S,R,S*-configuration is too slow to be observed even at elevated temperature while that of *R,S,R,S* to *R,R,S,S* is relatively fast in the mixture of MeCN and H₂O (1/10 v/v).⁵² There exists an equilibrium between (*R,S,R,S*)-[Ni(L)(NHC(OH)CH₃)]ClO₄ and (*R,R,S,S*)-[Ni(L)]ClO₄ in MeCN as previously stated and shown in Figure 3. Since equilibrium exists between (*R,R,S,S*)-[Ni(L)]⁺ and (*R,R,S,S*)-[Ni(L)(CH₃CONH₂)]⁺ with $K = 15.6 \text{ M}^{-1}$ at 20 °C (eq 2), the whole equilibrium between deep blue (*R,R,S,S*)-[Ni(L)]⁺ and green (*R,S,R,S*)-[Ni(L)(NHC(OH)CH₃)]⁺ in MeCN can be described as follows (eq 4): the addition of acetamide



followed by the configurational isomerization of the macrocycle. A recent mechanistic study⁵² on the isomerization of (*R,S,R,S*)-[Ni(L)]²⁺ to the *R,R,S,S*-complex in MeCN-H₂O reveals that the isomerization occurs via the axial coordination of a water molecule followed by the Ni-N bond breaking. In the present complex, it is apparent that the axial acetamide ligand drives the isomerization of the macrocycle. When the thermodynamic parameters are estimated from Figure 3 on the basis of the absorbance change of the green acetamide complex in MeCN, $\beta = K_1K_2 = 5.5 \times 10^4 \text{ M}^{-1}$, $K_2 = 3500$, $\Delta H = -12 \text{ kcal mol}^{-1}$, and $\Delta S = -19 \text{ cal K}^{-1} \text{ mol}^{-1}$ are obtained at 22 °C for the whole equilibrium.

Bonding Mode of Acetamide. Amides and urea are known to coordinate 2+ or 3+ metal ions such as Ni(II),²⁹ Co(III),^{30,68,69} Cr(III),⁷⁰ Ru(III),^{39,71} and Rh(III)⁷² via the carbonyl oxygen or the anionic nitrogen. However, it has been reported recently that some Pt(II) complexes coordinate amide in the iminol form^{43,44} or in the NH₂-bonded neutral form.⁴² In this regard, four possible structures may be proposed for the green acetamide complex: **1**, a Ni(I) complex with O-bonded acetamide; **2**, a Ni(II) complex with a N-bonded anionic form of acetamide; **3**, a Ni(I) complex with N-bonded neutral acetamide; and **4**, a Ni(I) complex with N-bonded iminol.



Structure **1** is excluded unambiguously because (i) *R* values in the crystallographic refinement and the difference Fourier map are better for the N-bonded structure than for the O-bonded one, (ii) in all known O-bonded or anionic N-bonded acetamide complexes, C-O bond distances are ~0.7 Å shorter than C-N bond distances.³² If we assume an O-bonded structure for the present complex, the C-O bond becomes longer than the C-N bond, (iii) hydrogen-bonding was found between the O atom

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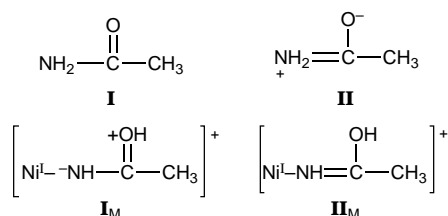
of acetamide and H6–N6 in the present complex, and (iv) the $\nu(\text{CO})$ value (1598 cm^{-1}) of acetamide in the present complex is relatively low. For the O-bonded or anionic N-bonded amide complexes with metal ions in the 2+ or 3+ oxidation state, $\nu(\text{CO})$ values are reported to be $1591\text{--}1675\text{ cm}^{-1}$.^{31,32} If Ni(I) is coordinated through O, the $\nu(\text{CO})$ value of the Ni(I) complex should be significantly greater than those values because of weaker interaction between Ni(I) and O than M(II) or M(III) and O.

Structure **2** is also excluded according to the following arguments: (i) the compound is EPR active and oxygen-sensitive, (ii) the complex dissociates to four-coordinate (*R,R,S,S*)-[Ni(L)]⁺ in MeCN, (iii) the Ni(II) complex does not react with acetamide as evidenced by no spectral change in the UV/vis spectrum when acetamide is added to [Ni(L)]²⁺ with the *R,R,S,S*- or with *R,S,R,S*-configuration in the presence of NEt₃ or LiBu, and (iv) two peaks are observed around $3300\text{--}3350\text{ cm}^{-1}$ in the IR spectrum which correspond to $\nu(\text{OH})$ and $\nu(\text{NH})$.

Structure **3** is excluded although the neutral N-coordinated amide complexes of the Cu(II),⁴⁰ Ni(II),⁴⁰ and Pt(II)⁴² were reported previously. In these complexes, C–N bond distances are ca. $1.45\text{--}1.50\text{ \AA}$ which are ca. 0.2 \AA longer than that (1.22 \AA) of CO and the M–N–C angles are ca. $113\text{--}115^\circ$.^{40,42} The present complex [C–N, $1.314(7)\text{ \AA}$; C=O, $1.242(7)\text{ \AA}$; Ni–N–C, $124.6(4)^\circ$] has a significantly shorter C–N bond and larger M–N–C angle compared with them. Furthermore, this complex shows a $\nu(\text{CO})$ value (1598 cm^{-1}) which is significantly lower than those ($\sim 1710\text{ cm}^{-1}$) of N-coordinated amide complexes.^{40,42} It has been reported that Pt(II) ion forms a N-bonded neutral urea complex with NH₂CONMe₂ while it forms an iminol complex with acetamide.^{41–43}

Consequently, structure **4**, the Ni(I) complex with the iminol structure of acetamide is consistent with all spectroscopic results and crystal structural data.

Structure of (*R,S,R,S*)-[Ni(L)(NHC(OH)CH₃)]ClO₄. Free acetamide exists in resonance forms I and II. The increased bond distance and the decreased stretching frequency of carbonyl in acetamide compared with other carbonyl groups with pure double-bond character originate from this resonance. For N-bonded iminol complexes of Ni(I), the analogues are I_M and II_M. Since the iminol ligand has an empty π^* orbital which



can draw electron density from the filled d orbital of the metal, there must be $\pi\text{d}(\text{Ni})\text{--}\pi^*(\text{N})$ electron donation. Therefore, three bonds involving iminol, Ni–N–C–O, may have multiple bonding character. In fact, intermediate bond distances between normal single and double bonds were observed for N24–C22 and C22–O23 bonds, which are $1.314(7)$ and $1.242(7)\text{ \AA}$, respectively. The Ni–N24 bond distance [$1.969(5)\text{ \AA}$] is also short compared with the Ni–N(macrocyclic) bonds. In addition, the bond angle Ni–N24–C22 is $124.6(4)^\circ$, and the bond angles involving the C22 center are nearly 120° .

The fact that the four N24, C22, O23, and C21 atoms of acetamide make an almost perfect plane and the Ni atom is nearly in the plane (0.574 \AA out of the plane) also supports the multiple bonding character in them. When C–N and C–O bond distances and the $\nu(\text{CO})$ value of the complex are compared with those (1.333 \AA , 1.233 \AA , and 1694 cm^{-1})^{54,58} of free acetamide, it is seen that the contribution of II_M in the former

is greater than that of I in the latter. The unambiguous example of acetamide coordination in the iminol form is rare, and there is only one crystal structure of the Pt(II) iminol complex reported so far.⁴⁴ In this complex, the C–N bond is in the range $1.21\text{--}1.31\text{ \AA}$ which is even shorter than the C–O bond ($1.26\text{--}1.40\text{ \AA}$), and the M–N–C bond angles are in the range $125\text{--}130^\circ$.⁴⁴ As the Ni(I) ion in this study is more basic than the Pt(II) ion, it can donate more πd electron density to the π^* orbital of the iminol nitrogen. Therefore, the C–N bond distance increases and the C–O bond distance decreases in the Ni(I) complex compared with those in the Pt(II) complex.

The complex (*R,S,R,S*)-[Ni(L)(NHC(OH)CH₃)]ClO₄ shows two different sets of Ni–N bond distances: $2.092(3)\text{ \AA}$ (av) for Ni–N(sec) and $2.135(3)\text{ \AA}$ (av) for Ni–N(tert). These are significantly longer than those [$1.878(4)$ and $1.978(3)\text{ \AA}$]²⁰ of the four-coordinate (*R,R,S,S*)-[Ni(L)]ClO₄. All Ni(I) macrocyclic complexes including Ni(I)F₄₃₀ and Ni(I) hydroporphyrins have two sets of Ni–N bond distances,^{17–25} and the occurrence of two sets of Ni–N bond distances in this five-coordinate Ni(I) complex is consistent with the observations made with other Ni(I) macrocyclic complexes. However, the origin of the distortion of the macrocyclic core in Ni(I) complexes has not been properly explained yet. It has been argued recently by the comparison of the structures of Ni(I) and Cu(II) OEiBC complexes that it is not an electronic configuration effect.²⁵

In summary, the soft and electron-rich Ni(I) macrocyclic complex binds acetamide in the iminol form via the nitrogen atom which is a softer and weaker σ -donor than oxygen, although amides generally coordinate hard transition metal ions in the 2+ or 3+ oxidation state via the carbonyl oxygen or the anionic nitrogen.^{29,30,33,49–51,53,68} Referring to the fact that soft Pt(II) metal also binds amide in iminol or N-bonded neutral amide structures, it may be proposed that a polypeptide can bind soft metal ions through the nitrogen atom without deprotonation. The structure of the five-coordinate Ni(I) macrocyclic complex exhibits two sets of Ni–N bond distances, in accord with the observations previously made in four-coordinate Ni(I) complexes.^{17–20}

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Supporting Information Available: Tables S1–S5, listing positional parameters, anisotropic displacement parameters, and bond distances and angles of non-hydrogen atoms, hydrogen atom coordinates, and bond distances and angles involving hydrogen atoms for (*R,S,R,S*)-[Ni(C₁₄H₃₀N₆)(NHC(OH)CH₃)]ClO₄ and Figures S1–S3 showing UV/vis spectral changes upon exposure to dry oxygen, an IR spectrum, and a packing diagram for (*R,S,R,S*)-[Ni(C₁₄H₃₀N₆)(NHC(OH)CH₃)]ClO₄ (14 pages); table listing observed and calculated structure factors for (*R,S,R,S*)-[Ni(C₁₄H₃₀N₆)(NHC(OH)CH₃)]ClO₄ (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.