

## Preparation and Characterization of Nickel(II) and Copper(II) Tetraaza Macrocylic Complexes with Isonicotinate Ligands

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The complexes  $[\text{Ni}(\text{L})(\text{INT})_2] \cdot 5\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}(\text{L})(\text{H}_2\text{O})](\text{Cl})(\text{INT}) \cdot 3\text{H}_2\text{O}$  (**2**) (L = 3,14-dimethyl-2,6,13,17-tetraazatriacyclo[14,4,0<sup>1,18,0<sup>7,12</sup></sup>]docosane, INT = isonicotinate) have been prepared and characterized by X-ray crystallography, electronic absorption, and cyclic voltammetry. The crystal structure of **1** reveals an axially elongated octahedral geometry with two axial isonicotinate ligands. The electronic spectra, magnetic moment, and redox potentials of **1** also show a high-spin octahedral geometry. However, **2** shows that the coordination environment around the copper atom is a distorted square-pyramid with an axial water molecule. The spectra and electrochemical behaviors of **2** are also discussed.

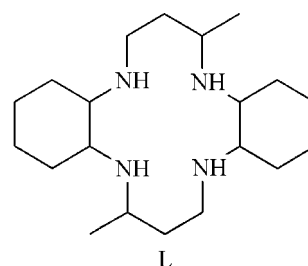
**Key words** : Crystal structures, Macrocycle, Isonicotinate, Nickel(II) and copper(II) complexes

### Introduction

There has been considerable interest in structural, thermodynamic, and kinetic studies of the metal complexes with polyaza macrocycles because of their significant implications in analytical, biological, and other application.<sup>1-9</sup> The structures of metal complexes with these ligands are affected by several factors, including the metal ion size and ligand topology, such as the cavity size, type and number of donor atoms, and stereochemical rigidity.<sup>7-9</sup> The coordination environments around the metal ion in these macrocyclic complexes are square-planar or octahedral. In a previous paper, we reported the synthesis and X-ray crystal structures of  $[\text{Ni}(\text{L})\text{X}_2]$  (X = N<sub>3</sub>, NCS, ONO, NCO),<sup>10,11</sup>  $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$ ,<sup>12</sup> and  $[\text{Cu}(\text{L})(\text{SCH}_3)_2] \cdot 2\text{H}_2\text{O}$ ,<sup>13</sup> in which the metal ion reveals an axially elongated octahedral geometry with two axial ligands. The compound  $[\text{Cu}(\text{L})\text{N}_3](\text{H}_2\text{O})(\text{ClO}_4)$  has a distorted square-pyramidal geometry, with four nitrogen atoms of the macrocycle and one nitrogen atom of the axial azido group.<sup>11</sup> However, an intra- and intermolecular two-dimensional chain compound  $[\text{Ni}(\text{L})(\text{BDC})] \cdot 2\text{H}_2\text{O}$  (BDC = 1,4-benzenedicarboxylate)<sup>13</sup> reveals a distorted octahedral coordination environment, in which the macrocycle, water molecules, and BDC anions have assembled around the nickel center. The BDC anion is a good candidate for a molecular building block because of its rigidity and stability in the resulting porous framework. However, the complex  $[\{\text{Ni}(\text{DL-Me}_6\text{cyclam})\}_2(\mu\text{-OCN})_2](\text{ClO}_4)_2$  (Me<sub>6</sub>cyclam = DL-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) shows that the cyanate group acts as end-to-end bridge with the nickel(II) ions in an NiN<sub>6</sub>O octahedral geometry.<sup>16</sup> The same synthetic strategy with the azido group leads to a *trans*-

monobridged one-dimensional network with Me<sub>6</sub>cyclam[15] and cyclam.<sup>17</sup> The different molecular topologies in the complexes may be due to the anionic effects such as stereochemical rigidity and different coordination modes of the anions.

In the present work, we report the synthesis and characterization of  $[\text{Ni}(\text{L})(\text{INT})_2] \cdot 5\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}(\text{L})(\text{H}_2\text{O})](\text{Cl})(\text{INT}) \cdot 3\text{H}_2\text{O}$  (**2**) (L = 3,14-dimethyl-2,6,13,17-tetraazatriacyclo[14, 4,0<sup>1,18,0<sup>7,12</sup></sup>]docosane, INT = isonicotinate). To evaluate the effect of the anionic groups, we have investigated the X-ray crystal structures, spectroscopic, and electrochemical properties of these complexes.



### Experimental Section

**Materials and Physical Methods.** All chemicals used in the synthesis were of reagent grade and were used without further purification. The macrocycle L was prepared according to the literature method.<sup>18</sup> Solid state electronic spectra were measured by the diffuse reflectance method on a Varian Cary 300 UV-Vis spectrophotometer. Solution spectra were obtained on a Jasco Uvidec-610 spectrometer. Infrared spectra were recorded as KBr disks on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Room-temperature magnetic susceptibility was measured with a Johnson

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Matthey MK-II magnetic balance. The diamagnetic corrections were evaluated from Pascal's constants. Electrochemical measurements were carried out with a BAS 100 BW electrochemical analyzer, using Pt auxiliary Ag/AgCl reference electrodes. A hanging mercury dropping electrode was used as the working electrode. All measurements were made on 0.01 M tetraethylammonium perchlorate (TEAP)-DMSO solution at  $20.0 \pm 0.1$  °C. Elemental analyses were carried out on a Perkin-Elmer 240C analyzer. FAB mass spectra were obtained using a Jeol JMS-HA 100A/100A spectrometer.

**Synthesis of [Ni(L)(INT)<sub>2</sub>·5H<sub>2</sub>O (1).** To a methanol solution (20 mL) of [Ni(L)]Cl<sub>2</sub>·2H<sub>2</sub>O (251 mg, 0.5 mmol) was added sodium isonicotinate (145 mg, 1.0 mmol). The mixture was heated to reflux for 1 h and then cooled to room temperature. The solution was allowed to stand for a few days, and a quantity of violet crystals formed. The product was filtered and recrystallized from a hot water-acetonitrile (1 : 1, 10 mL) mixture. Yield: 277 mg (76 %). Anal. Calcd for C<sub>32</sub>H<sub>38</sub>N<sub>6</sub>NiO<sub>9</sub>: C, 52.68; H, 8.01; N, 11.57. Found: C, 52.76; H, 8.12; N, 11.65. IR (KBr, cm<sup>-1</sup>): 3302, 3229, 3145, 2930, 1638, 1600, 1548, 1449, 1375, 1310, 1273, 1171, 1154, 1114, 1071, 1032, 1000, 967, 899, 842, 774, 711, 684. UV-Vis in CH<sub>3</sub>CN [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 525 (7.7); in CH<sub>3</sub>NO<sub>2</sub>: 526 (7.6); in diffuse reflectance ( $\lambda_{\text{max}}$ , nm): 522 nm. FAB mass (CH<sub>2</sub>Cl<sub>2</sub>, m/z): 730 (M)<sup>+</sup>,  $\mu_{\text{eff}}$ : 2.82  $\mu_{\text{B}}$  at 25 °C.

**Synthesis of [Cu(L)(H<sub>2</sub>O)](Cl)(INT)·3H<sub>2</sub>O (2).** This compound was prepared as violet crystals in a reaction similar to that of **1**, except for the use of [Cu(L)]Cl<sub>2</sub>·2H<sub>2</sub>O (254 mg, 0.5 mmol) instead of [Ni(L)]Cl<sub>2</sub>·2H<sub>2</sub>O. Yield: 220 mg (72%). Anal. Calcd for C<sub>26</sub>H<sub>52</sub>ClCuN<sub>5</sub>O<sub>6</sub>: C, 49.59; H, 8.32; N, 11.12. Found: C, 49.48; H, 8.23; N, 11.24. IR (KBr, cm<sup>-1</sup>): 3358, 3291, 3133, 2931, 1637, 1596, 1546, 1432, 1373, 1309, 1225, 1177, 1095, 1057, 1006, 992, 967, 904, 838, 776, 714, 669. UV-Vis in CH<sub>3</sub>CN [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 543 (98); in CH<sub>3</sub>NO<sub>2</sub>: 542 (96); in diffuse reflectance ( $\lambda_{\text{max}}$ , nm): 541 nm. FAB mass (CH<sub>2</sub>Cl<sub>2</sub>, m/z): 630 (M)<sup>+</sup>,  $\mu_{\text{eff}}$ : 1.84  $\mu_{\text{B}}$  at 25 °C.

**X-ray Crystallography.** The X-ray single crystal data for the compounds were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystallographic data, conditions for the collection of intensity data, and some features of the structure refinements are listed in Table 1. Accurate cell parameters and an orientation matrix were determined by least-squares fit of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. No absorption correction was made during processing. The structure was solved by direct method<sup>19</sup> and refined by the full-matrix least-squares method with use of the SHELXL97 package program.<sup>20</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in calculated positions, allowing them to ride on their parent C atoms, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ , whereas the methyl groups were treated as rotating rigid groups with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ . For **1**, the hydrogen atoms of four water molecules were not

Table 1. Crystallographic data

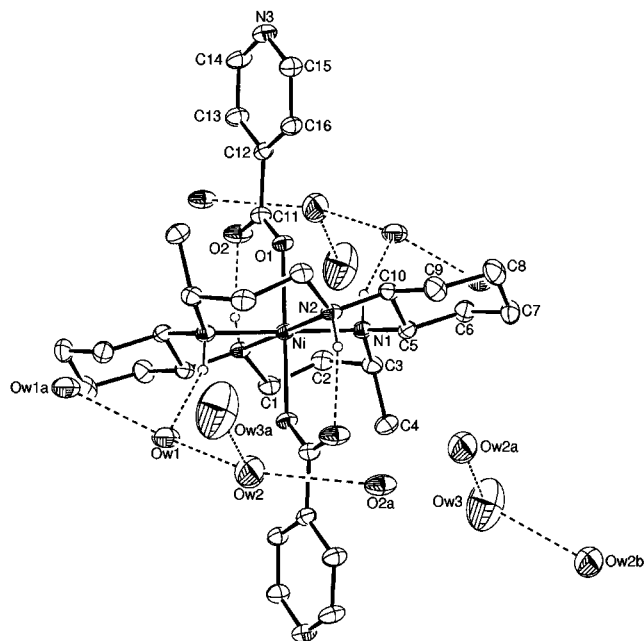
	1	2
empirical formula	C <sub>32</sub> H <sub>38</sub> N <sub>6</sub> NiO <sub>9</sub>	C <sub>26</sub> H <sub>52</sub> ClCuN <sub>5</sub> O <sub>6</sub>
formula weight	729.55	629.72
temperature (K)	293(2)	293(2)
crystal system	monoclinic	triclinic
space group	C2/c	P-1
<i>a</i> (Å)	12.460(5)	11.322(5)
<i>b</i> (Å)	16.441(5)	17.230(5)
<i>c</i> (Å)	17.719(5)	8.060(5)
$\alpha$ (°)		98.84(1)
$\beta$ (°)	91.30(1)	100.12(1)
$\gamma$ (°)		98.51(1)
<i>V</i> (Å <sup>3</sup> )	3629(2)	1504.5(12)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	1.335	1.390
absorption coefficient (mm <sup>-1</sup> )	0.593	0.862
<i>F</i> (000)	1568	674
crystal size (mm)	0.30×0.15×0.15	0.30×0.20×0.10
$\theta$ range (°)	2.05 to 24.97	1.22 to 24.97
limiting indices	$0 \leq h \leq 14$ , $-19 < k < 0$ , $-21 < l < 21$	$-13 \leq h \leq 13$ , $-20 < k < 20$ , $0 < l < 9$
reflection collected/unique	3352/3195	5703/5286
data/restraints/parameters	[ <i>R</i> <sub>int</sub> = 0.0273]	[ <i>R</i> <sub>int</sub> = 0.0957]
goodness of fit on <i>F</i> <sup>2</sup>	1.044	0.997
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> <sup>a</sup> = 0.0478, <i>wR</i> <sub>2</sub> <sup>b</sup> = 0.1142	<i>R</i> <sub>1</sub> = 0.0733, <i>wR</i> <sub>2</sub> = 0.1376
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0958, <i>wR</i> <sub>2</sub> = 0.1293	<i>R</i> <sub>1</sub> = 0.2031, <i>wR</i> <sub>2</sub> = 0.1752
largest difference peak and hole (eÅ <sup>-3</sup> )	0.402 and -0.251	0.577 and -0.623

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2))^2]^{1/2}$$

found. For **2**, the two hydrogen atoms of Ow(1) molecule were found from difference Fourier map and their positions were fixed and refined isotropically. The hydrogen atoms of Ow(2), Ow(3) and Ow(4) were not found. Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. CCDC 175427 for **1** and CCDC 175428 for **2**). The data can be obtained free via [www.ccdc.cam.ac.uk/perl-catreq.cgi](http://www.ccdc.cam.ac.uk/perl-catreq.cgi) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## Results and Discussion

**Crystal Structures.** An ORTEP drawing of **1** with the atomic labelling scheme is shown in Figure 1. The selected bond distances and angles are listed in Table 2. The ligand skeleton of the present compound takes the *trans*-III(R,R,S,S) configuration with two chair six-membered and two gauche five-membered chelate rings. An inversion center of complex **1** exists on the central nickel(II) ion. The structure of **1** shows that the nickel(II) ion is coordinated by the secondary amines of the macrocycle and that the axial



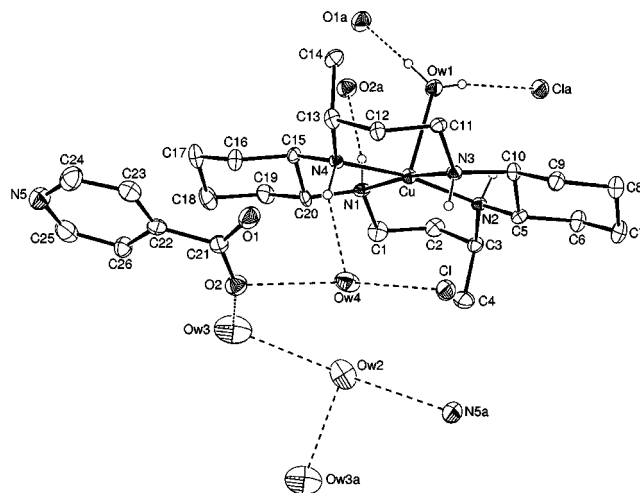
**Figure 1.** An ORTEP drawing of  $[\text{Ni}(\text{L})(\text{INT})_2] \cdot 5\text{H}_2\text{O}$  (**1**) with the atomic labelling scheme (30% probability ellipsoids shown). The dotted lines indicate the hydrogen bonds.

**Table 2.** Selected bond lengths (Å) and angles (°) for **1**<sup>a</sup>

Ni-N(1)	2.084(3)	Ni-N(2)	2.052(3)
Ni-O(1)	2.126(2)	O(1)-C(11)	1.255(4)
O(2)-C(11)	1.240(4)	C(11)-C(12)	1.531(5)
N(3)-C(14)	1.328(4)	N(3)-C(15)	1.326(5)
N(1)-Ni-N(2)	84.3(1)	N(1)-Ni-N(2) <sup>i</sup>	95.7(1)
O(1)-Ni-N(1)	85.0(1)	O(1)-Ni-N(2)	87.9(1)
O(1)-Ni-N(1) <sup>i</sup>	95.1(1)	O(1)-Ni-N(2) <sup>i</sup>	92.1(1)
Ni-O(1)-C(11)	134.0(2)	Ni-N(1)-C(3)	121.1(2)
Ni-N(1)-C(5)	107.3(2)	Ni-N(2)-C(1) <sup>i</sup>	114.3(2)
Ni-N(2)-C(10)	108.0(2)	O(1)-C(11)-O(2)	127.2(3)
O(1)-C(11)-C(12)	115.2(3)	O(2)-C(11)-C(12)	117.7(3)
C(14)-N(3)-C(15)	116.6(3)		

<sup>a</sup>Symmetry code: (i)  $-x+3/2, -y+1/2, -z+1$ .

positions are bonded by the two carboxylate oxygen atoms of the isonicotinate ligands, which is a six-coordinated octahedral environment. The nickel atom and the four nitrogen atoms of the macrocycle (N(1), N(2), N(1'), N(2')) are exactly in a plane. The average Ni-N (secondary amine) distance of 2.068(2) Å is typical for high-spin octahedral nickel(II) complexes with 14-membered tetraaza macrocyclic ligands.<sup>21-24</sup> The N-Ni-N angles of the six-membered chelate rings (95.7(1)°) are larger than those of the five-membered chelate rings (84.3(1)°). The plane of the carboxylate group is nearly perpendicular to the NiN<sub>4</sub> plane, with a dihedral angle of 88.8(4)°. Furthermore, the dihedral angle between the plane of the carboxylate group and the aryl plane of the isonicotinate ligand is 84.9(1)°. The secondary amines of the macrocycle are hydrogen bonded to the carboxylate oxygen atom (N(1)⋯O(1)<sup>i</sup> 2.891(4) Å, 155.6°) and the water molecule (N(1)⋯Ow(1)<sup>i</sup> 3.173(4) Å,



**Figure 2.** An ORTEP drawing of  $[\text{Cu}(\text{L})(1\text{L}_2\text{O})](\text{Cl})(\text{INT}) \cdot 3\text{H}_2\text{O}$  (**2**) with the atomic labelling scheme (30% probability ellipsoids shown). The dotted lines indicate the hydrogen bonds.

**Table 3.** Selected bond lengths (Å) and angles (°) for **2**

Cu-N(1)	2.023(5)	Cu-N(2)	2.051(5)
Cu-N(3)	2.012(6)	Cu-N(4)	2.028(5)
Cu-Ow(1)	2.332(5)	O(1)-C(21)	1.236(9)
O(2)-C(21)	1.264(9)	N(5)-C(24)	1.321(11)
N(5)-C(25)	1.322(11)		
N(1)-Cu-N(2)	96.4(2)	N(1)-Cu-N(3)	171.7(2)
N(1)-Cu-N(4)	84.5(2)	N(2)-Cu-N(3)	84.4(2)
N(2)-Cu-N(4)	170.2(2)	N(3)-Cu-N(4)	93.3(2)
N(1)-Cu-Ow(1)	95.4(2)	N(2)-Cu-Ow(1)	88.5(2)
N(3)-Cu-Ow(1)	92.8(2)	N(4)-Cu-Ow(1)	101.2(2)
O(1)-C(21)-O(2)	125.5(8)	O(1)-C(21)-C(22)	117.0(7)
O(2)-C(21)-C(22)	117.5(7)	C(24)-N(5)-C(25)	116.7(8)

150.0°; the symmetry code (i) is  $-x+3/2, -y+1/2, -z+1$ ). Compound **1** was not assembled in the solid state to form multi-dimensional coordination polymer, even though the isonicotinate has a stereochemical rigidity as well as a BDC anion. This may be attributed to the different donor atoms on the *para* site of the isonicotinate anion.

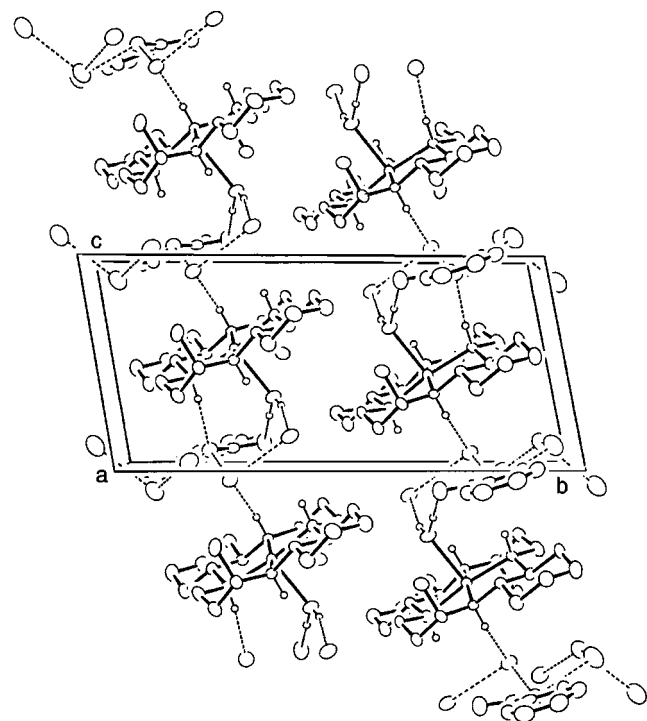
An ORTEP drawing of **2** with the atomic labelling scheme is shown in Figure 2, and the selected bond lengths and angles are listed in Table 3. The molecular structure of **2** consists of a  $[\text{Cu}(\text{L})(\text{H}_2\text{O})]^{2+}$  cation, isonicotinate anion and water molecules. Compound **2** also takes on a thermodynamically most stable *trans*-III(R,R,S,S) configuration in the solid state. The geometry of the copper center is effectively square pyramidal, with all equatorial Cu-N (secondary amine) bonds in the expected range (2.012(6)-2.051(5) Å), whereas the axially bound water oxygen is less strongly bound (2.332(5) Å). The long apical Cu-Ow(1) bond reflects a weak axial interaction, as expected for Jahn-Teller sensitive copper(II) complexes. The copper atom is displaced 0.126(2) Å from the least-squares plane defined by the N<sub>4</sub> basal plane toward the water molecule, and a slight distortion [deviation N(1) 0.017(3), N(2) 0.047(3), N(3)

**Table 4.** Hydrogen bonding parameters (Å, °) for **2**

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)-H(27)...O(2) <sup>i</sup>	0.91	2.19	3.09(1)	169.6
N(4)-H(30)...Ow(4)	0.91	2.15	2.98(1)	149.6
Ow(1)-H(31A)...O(1) <sup>i</sup>	1.01(1)	1.71(1)	2.72(1)	172.3(4)
Ow(1)-H(31B)...Cl <sup>i</sup>	0.75(1)	2.36(1)	3.08(1)	164.1(4)
Ow(2)...Ow(3) <sup>ii</sup>			2.77(1)	
Ow(2)...N(5) <sup>iii</sup>			2.99(1)	
Ow(3)...Ow(2)			2.98(1)	
Ow(3)...O(2)			2.79(1)	
Ow(4)...O(2)			2.79(1)	
Ow(4)...Cl			3.15(1)	

Symmetry codes: (i)  $x, y, z-1$ ; (ii)  $-x+1, -y, -z-2$ ; (iii)  $x+1, y, z$ .

0.016(3), N(4) 0.047(3) Å from the least-squares plane] of the macrocyclic donor atoms is observed. Average N-Cu-N angles of 84.5(1) and 94.9(1)° observed in this complex for the five- and six-membered chelate rings, respectively, are similar to those found in the 14-membered tetraaza macrocyclic complexes.<sup>14,25,26</sup> The *trans*-basal angles (N(1)-Cu-N(3) = 171.7(2) and N(2)-Cu-N(4) = 170.2(2)°) are similar to those expected for square-pyramidal copper(II) complexes.<sup>27</sup> The axial Cu-Ow(1) bond is not perfectly perpendicular to the CuN<sub>4</sub> plane, with the four N-Cu-Ow(1) angles ranging from 88.5(2) to 101.2(2)°. The coordinated water molecule Ow(1) forms hydrogen bonds with the carboxylate oxygen atom of the isonicotinate and chloride anion. The water molecules found in the lattice also form hydrogen bonds



**Figure 3.** The molecular packing diagram of [Cu(L)(H<sub>2</sub>O)](Cl)(INT)·3H<sub>2</sub>O (**2**). The hydrogen bonds are indicated by dotted lines. The hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

with the secondary amine of the macrocycle, with the carboxylate oxygen and nitrogen atom of the isonicotinate, with the chloride anion, and with other water inclusions. Furthermore, the secondary amine of the macrocycle forms a hydrogen bond with the carboxylate oxygen of the isonicotinate. Consequently, the copper atom occupies a distorted square-pyramid coordination environment in which the secondary amines of the macrocycle, coordinated and lattice water molecules, the isonicotinate, and chloride anions have assembled around each copper center. This interaction gives rise to a one-dimensional hydrogen-bonded network (Table 4 and Figure 3). Under this situation, the self-organization by the hydrogen bonding interaction seems to be stabilized although the isonicotinate anion is not coordinated to the central copper(II) ion.

**Characterization of the Nickel(II) and Copper(II) Complexes.** Compound **1** exhibits two  $\nu$  (N-H) infrared bands at 3229 and 3145 cm<sup>-1</sup> associated with the coordinated secondary amines of the macrocycle and two strong  $\nu$  (COO) bands at 1600 and 1548 cm<sup>-1</sup> consistent with the coordinated isonicotinate ligand at nickel center. **2** reveals two  $\nu$  (N-H) bands at 3291 and 3133 cm<sup>-1</sup> associated with the coordinated secondary amines. Two  $\nu$  (COO) bands, at 1596 and 1546 cm<sup>-1</sup>, confirm the lattice isonicotinate group. An absorption band at 1637 cm<sup>-1</sup> in **2** was assigned to the HOH bending vibration of the coordinated water molecule,<sup>28</sup> which is in agreement with the crystal structure of **2**. The effective magnetic moment ( $\mu_{\text{eff}}$ ) of **1** in the solid state is 2.82  $\mu_B$  at room temperature, which is consistent with a d<sup>8</sup> electron configuration in an octahedral geometry. The UV-visible spectra of the complexes in the solid state and various solutions are listed in Table 5. The visible absorption spectra of **1** are found at 522 nm in the solid, and at 525 and 526 nm respectively in acetonitrile and nitromethane solutions, consistent with the six-coordinate octahedral geometry. This band is at substantially lower energy than in [Ni(L)](ClO<sub>4</sub>)<sub>2</sub> (465 nm),<sup>18</sup> which has a square-planar nickel(II) center. The visible spectra of **2** in the solid and solutions show that the d-d bands ( $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ ) occur at 541 (solid), 543 (acetonitrile), and 542 nm (nitromethane), which are typical for copper(II) complexes with the square-pyramidal geometry.<sup>29</sup>

Cyclic voltammetric data for the Ni(II) and Cu(II) complexes in 0.01 M TEAP-DMSO solution are given in Table 6. A typical cyclic voltammogram of **1** is shown in Figure 4. The complexes **1** and **2** exhibit two one-electron waves corresponding to M(II)/M(III) and M(II)/M(I) processes. It is of interest to compare the redox potentials for the nickel

**Table 5.** Electronic spectral data<sup>a</sup>

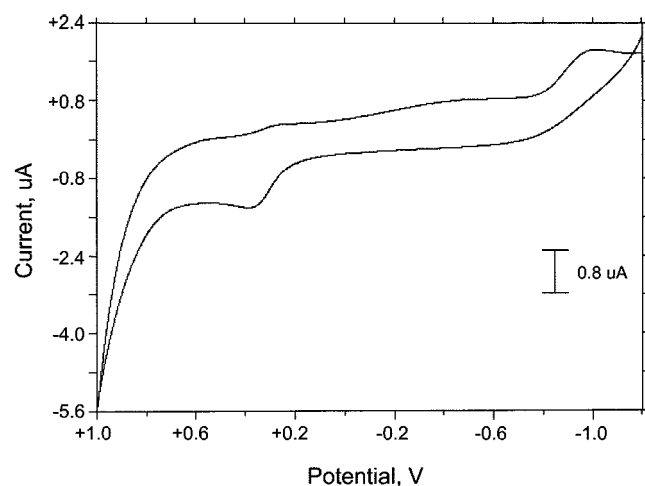
Complex	$\lambda_{\text{max}}$ (nm) ( $\epsilon - \text{M}^{-1} \text{cm}^{-1}$ )
[Ni(L)](ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	465(66), 463(73) <sup>c</sup>
[Ni(L)(INT) <sub>2</sub> ]·3H <sub>2</sub> O ( <b>1</b> )	525(7.7), 526(7.6) <sup>c</sup> , 522 <sup>d</sup>
[Cu(L)](ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	516(118), 518(128) <sup>c</sup>
[Cu(L)(H <sub>2</sub> O)](Cl)(INT)·3H <sub>2</sub> O ( <b>2</b> )	543(98), 542(96) <sup>c</sup> , 541 <sup>d</sup>

<sup>a</sup>In acetonitrile solution. <sup>b</sup>Ref. 18. <sup>c</sup>In nitromethane solution. <sup>d</sup>In diffuse reflectance.

**Table 6.** Cyclic voltammetric data for the nickel(II) and copper(II) complexes<sup>a</sup>

Complex	Potentials (Volt vs. Ag/AgCl)	
	M(II)/M(III)	M(II)/M(I)
[Ni(L)](ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	+0.73	-1.63
[Ni(L)(INT) <sub>2</sub> ]-5H <sub>2</sub> O ( <b>1</b> )	+0.38	-1.00(i) <sup>c</sup>
[Cu(L)](ClO <sub>4</sub> ) <sub>2</sub> <sup>b</sup>	+1.06	-1.27(i) <sup>c</sup>
[Cu(L)(1 <sub>2</sub> O)](Cl)(INT)-3H <sub>2</sub> O ( <b>2</b> )	+0.55	-0.83(i) <sup>c</sup>

<sup>a</sup>Measured in 0.01 M TFAP-DMSO solution at 20.0 ± 0.1 °C. <sup>b</sup>Ref. 18. These values are reduced from those of Ag/AgCl reference electrodes. <sup>c</sup> - irreversible.

**Figure 4.** Cyclic voltammogram of [Ni(L)(INT)<sub>2</sub>]-5H<sub>2</sub>O (**1**) in 0.01 M TFAP-DMSO solution at 20.0 ± 0.1 °C. The scan rate is 50 mV/s.

(II) and copper(II) complexes with the isonicotinate ligand. The oxidation and reduction potentials for **1** are considerably more negative and positive than those for the square-planar [Ni(L)](ClO<sub>4</sub>)<sub>2</sub>,<sup>18</sup> indicating that this complex makes the oxidation of Ni(II) to Ni(III) easier and the reduction to Ni(I) difficult. This fact may be attributed to the coordination of the axial isonicotinate group. A similar result is also observed for tetraaza macrocyclic nickel(II) complexes with the axial groups.<sup>11</sup> On the other hand, the oxidation and reduction potentials of **2** are also considerably more cathodic and anodic than those of [Cu(L)](ClO<sub>4</sub>)<sub>2</sub>.<sup>18</sup> This may result from the structural geometry (square-pyramidal vs square-plane). This is consistent with the crystal structures and spectroscopic data discussed previously.

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