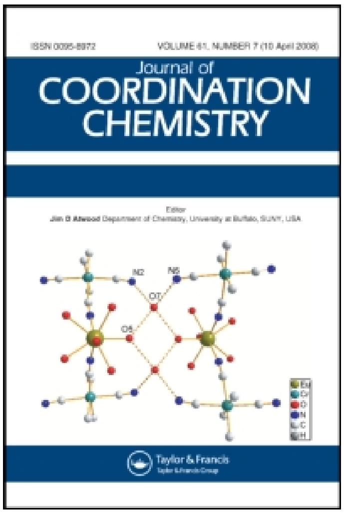

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Synthesis, Properties and X-ray Crystal Structures of Nickel(II) Complexes of a Hexaazamacrotetracyclic Ligand

Ki-Young Choi[a]
[a] Department of Chemistry Education, Kongju National University, Kongju, Korea

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SYNTHESIS, PROPERTIES AND X-RAY CRYSTAL STRUCTURES OF NICKEL(II) COMPLEXES OF A HEXAAZAMACROTETRACYCLIC LIGAND

KI-YOUNG CHOI*

Department of Chemistry Education,
Kongju National University, Kongju 314-701, Korea

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The complexes $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) and $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**) (L = 1,3,10,12,16,19-hexaazatetracyclo $[17,3,1,1^{12.16},0^{4.9}]$tetracosane) have been synthesized and structurally characterized by X-ray crystallography, spectroscopic and cyclic voltammetry. The crystal structure of **1** has a distorted octahedral geometry with two secondary and two tertiary amines of the macrocycle and two water molecules. In **2**, the coordination geometry around the nickel atom is square-planar with four nitrogen atoms of the macrocycle. The equilibrium $[Ni(L^2)]^{2+} + 2H_2O \rightleftharpoons [Ni(L^2)(H_2O)_2]^{2+}$ has been studied in aqueous solution over a temperature range, yielding $\Delta H^\circ = -19.0 \pm 0.2\,kJ\,mol^{-1}$ and $\Delta S^\circ = -56.0 \pm 0.4\,JK^{-1}\,mol^{-1}$. Cyclic voltammetry of the complexes give two one-electron waves corresponding to Ni(II)/Ni(III) and Ni(II)/Ni(I) processes. The electronic spectra and redox potentials of the complexes are influenced significantly by the geometry.

Keywords: Crystal structures; Nickel(II) complexes; Hexaazamacrotetracycle; Equilibrium

INTRODUCTION

Polyaza macrocyclic complexes with transition metal(II) ions have attracted considerable interest because the structural, equilibrium, and kinetic behavior of their metal complexes differ from those of the non-cyclic analogs [1–3]. Some of these ligands and metal complexes have potential applications, including metal ion-selective reagents [4–6] and models for metalloenzyme active site [7–9]. Metal-directed condensation reactions involving coordinated amines and formaldehyde have been employed in the synthesis of various saturated polyaza macrocyclic complexes [10–17]. For example, the square-planar nickel(II) complex $[Ni(L^1)]^{2+}$ (L^1 = 1,3,6,8,12,15-hexaazatricyclo$[13,3,1,1^{8.12}]$-eicosane) [14] containing $N–CH_2–N$ linkages has been prepared by the condensation reaction of formaldehyde and *N*,*N*′-bis(2-aminopropyl)ethylenediamine in the presence of $Ni(ClO_4)_2 \cdot 6H_2O$. However, the same condensation reaction of appropriate amines with formaldehyde and $NiCl_2 \cdot 6H_2O$ yields a six-coordinate octahedral complex

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*Tel./Fax: +82-41-8508284. E-mail: kychoi@kongju.ac.kr

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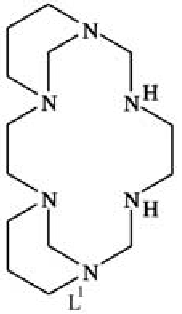
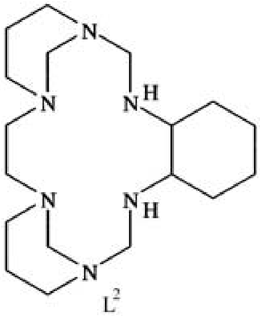
$[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) ($L^2 = 1,3,10,12,16,19$-hexaazatetracyclo$[17,3,1,1^{12.16},0^{4.9}]$tetracosane). Thus the formation of an octahedral complex as well as its properties is strongly affected by the anions.

In this article, we report the synthesis and crystal structures of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) and $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**). We have also investigated the equilibrium, spectroscopic and electrochemical properties of these complexes.



L^1



L^2

EXPERIMENTAL

Materials and Physical Measurements

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Electronic absorption spectra were obtained with a Jasco Uvidec 610 spectrophotometer. Magnetic moments were measured with a Johnson Matthey MK-II magnetic susceptibility balance. The diamagnetic corrections were estimated from Pascal's constants. Electrochemical measurements were accomplished with a three-electrode potentiostat BAS-100BW system. A hanging mercury dropping electrode was used as the working electrode. The counter electrode was a coiled Pt wire and a Ag/AgCl electrode was used as a reference electrode. Cyclic voltammetric data were obtained in dimethylformamide (DMF) solution with 0.10 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte at $20.0 \pm 0.1°C$. The solution was degassed with high purity nitrogen prior to carrying out the electrochemical measurements. Elemental analyses (C, H, N) were performed on a Perkin-Elmer CHN-2400 analyser.

Preparation of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (1)

Compound **1** was synthesized by the method of Kang *et al.* [18]. To a methanol solution (100 mL) of $NiCl_2 \cdot 6H_2O$ (11.9 g, 0.05 mol) was added *N*,*N*′-bis(2-aminopropyl)ethylenediamine (8.0 g, 0.05 mol), 1,2-diaminocyclohexane (5.7 g, 0.05 mol) and 37% formaldehyde (16.2 g, 0.2 mol). The solution was filtered and left at room temperature until the violet crystals formed. The product was filtered and recrystallized from a hot water–acetonitrile (1 : 1 v/v, 50 mL) mixture. Yield: 21%. Anal. Calcd. for $C_{36}H_{80}N_{12}Cl_4Ni_2O_4$ (%): C, 43.05; H, 8.03; N, 16.74. Found: C, 43.18; H, 8.15; N, 16.62. IR (KBr, cm^{-1}) 3256 (νNH), 1657 (νHOH). Magnetic moment (μ_{eff}): 2.92 μ_B at 20°C.

Preparation of $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (2)

To a methanol solution (20 mL) of **1** (251 mg, 0.5 mmol) was added an excess of $NaClO_4$ and the mixture refluxed for 1 h. The solution was filtered and allowed to stand for a few days, a quantity of yellow crystals precipitated. These were collected by filtration and dried in air. Yield: 78%. Anal. Calcd. for $C_{18}H_{40}N_6Cl_2NiO_{10}$ (%): C, 34.31; H, 6.40; N, 13.34. Found: C, 34.42; H, 6.31; N, 13.23. IR (KBr, cm^{-1}): 3252 (νNH) and 1094 ($\nu ClO_2{}^-$).

X-ray Crystallography

Single-crystals of **1** and **2** were mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected with graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å), using the ω-2θ scan mode. Unit cell parameters were determined from automatic centering of 25 reflections and refined by least-squares methods. The intensity data were corrected for Lorentz and polarization effects. The crystal intensity data appears to be weak. This fact may be due to the rather small crystal size and its poor quality. Empirical absorption corrections were carried out using φ-scan [19]. The structures were solved by direct methods [20] and the least-squares refinement of the structures was performed by the program SHELXL-97 [21]. The programs used to create the molecular graphics and prepare the material for publication were Ortep-3 [22] and WinGx [23]. For **1**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C atoms, with $U_{iso}(H) = 1.2U_{eq}$(C or N). The eight hydrogen atoms of Ow(1), Ow(2), Ow(3) and Ow(4) molecules were found from the difference Fourier map, and their positions were fixed and refined isotropically. For **2**, all atoms except for Ow(1) and Ow(1)′ including hydrogen atoms were refined anisotropically. All hydrogen atoms except for the water hydrogen atoms of Ow(1) and Ow(2) were placed in calculated positions with isotropic displacement parameters. The water Ow(1) atom is disordered over two positions and the split atoms, designated as Ow(1) and Ow(1)′, were refined isotropically. The final occupancy factors of Ow(1) and Ow(1)′ are 0.55 and 0.45, respectively. The hydrogen atoms of Ow(1) and Ow(2) were not found. A summary of the data collection and details of the structure refinement is listed in Table I.

RESULTS AND DISCUSSION

Description of the Structures

An ORTEP drawing of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) with the atomic numbering scheme is shown in Fig. 1.

Selected bond distances and angles are listed in Table II. Two crystallographically independent complexes are present in each asymmetric unit. The ligand is tetradentate forming both five- and six-membered chelate rings which alternate on the equatorial plane of coordination about Ni(II) ion. The complex has a distorted octahedral coordination geometry with two secondary and two tertiary amines of the macrocyclic ligand and two axial water molecules. The macrocyclic ligand takes the most stable *trans*-III(*R*,*R*,*S*,*S*) configuration in the solid state. The 1,3-diazacyclohexane as well

TABLE I Crystallographic data

	1	*2*
Empirical formula	$C_{36}H_{80}N_{12}Cl_4Ni_2O_4$	$C_{18}H_{40}N_6Cl_2NiO_{10}$
Formula weight	1004.34	630.17
Temperature (K)	288	289
Wavelength (Å)	0.71069	0.71069
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	C_2/c
Unit cell dimensions		
a (Å)	10.617(1)	26.443(2)
b (Å)	15.135(1)	11.688(2)
c (Å)	16.173(3)	18.043(2)
α (°)	94.69(1)	
β (°)	89.98(1)	104.22(1)
γ (°)	110.52(1)	
V (Å^3)	2424.6(5)	5405.6(13)
Z	2	8
D_{calc} (Mg m^{-3})	1.376	1.549
Absorption coefficient (mm^{-1})	1.046	0.977
F(000)	1072	2656
Crystal size (mm^3)	0.26 × 0.26 × 0.13	0.26 × 0.26 × 0.23
θ range for data collection(°)	2.00–24.97	2.14–24.97
Index ranges	$-12 \le h \le 12$, $-17 \le k \le 17$, $0 \le l \le 19$	$0 \le h \le 31$, $0 \le k \le 13$, $-21 \le l \le 20$
Reflection collected/unique	8811/8483 ($R_{int} = 0.0382$)	4839/4732 ($R_{int} = 0.0397$)
Absorption correction	φ-scan	φ-scan
Max./min. transmission	0.8720 and 0.7727	0.7971 and 0.4037
Data/restraints/parameters	8483/0/524	4732/0/333
Goodness-of-fit on F^2	1.071	1.015
Final R indices ($I > 2\sigma(I)$)	$R_1^a = 0.0637$, $wR_2^b = 0.1662$	$R_1 = 0.0680$, $wR_2 = 0.1579$
R indices (all data)	$R_1 = 0.1125$, $wR_2 = 0.1891$	$R_1 = 0.1331$, $wR_2 = 0.1879$
Largest diff. peak and hole (eÅ^{-3})	1.711 and −0.403	0.651 and −0.344

$^aR_1 = \sum||F_0| - |F_c||/\sum|F_0|$; $^bwR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

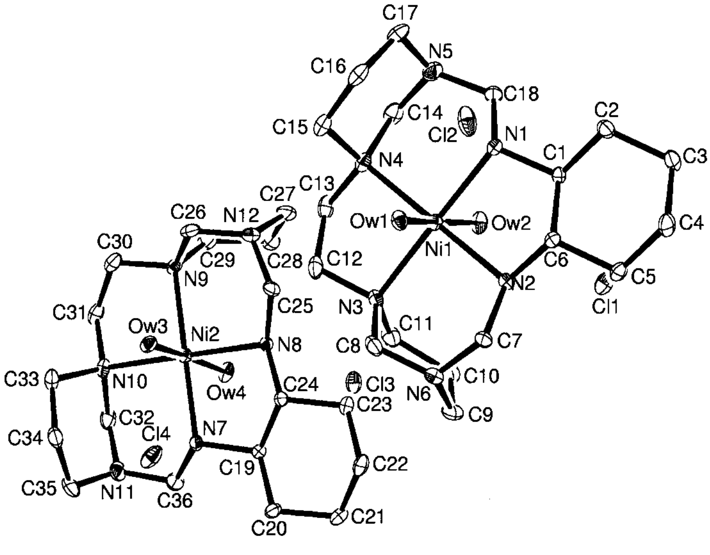


FIGURE 1 An ORTEP drawing of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) with the atomic numbering scheme (30% probability ellipsoids shown).

TABLE II Selected bond distances (Å) and angles (°) of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**)

Ni(1)–N(1)	2.065(5)	Ni(2)–N(7)	2.061(5)
Ni(1)–N(2)	2.072(5)	Ni(2)–N(8)	2.074(5)
Ni(1)–N(3)	2.119(5)	Ni(2)–N(9)	2.115(5)
Ni(1)–N(4)	2.126(6)	Ni(2)–N(10)	2.126(5)
Ni(1)–Ow(1)	2.155(4)	Ni(2)–Ow(3)	2.165(4)
Ni(1)–Ow(2)	2.157(5)	Ni(2)–Ow(4)	2.162(5)
N(1)–C(1)	1.492(8)	N(7)–C(19)	1.492(8)
N(1)–C(18)	1.512(8)	N(7)–C(36)	1.504(8)
N(3)–C(8)	1.500(9)	N(9)–C(26)	1.497(9)
N(3)–C(11)	1.506(9)	N(9)–C(29)	1.503(9)
N(3)–C(12)	1.477(9)	N(9)–C(30)	1.480(9)
N(5)–C(14)	1.421(10)	N(11)–C(32)	1.418(10)
N(5)–C(17)	1.449(11)	N(11)–C(35)	1.460(11)
N(5)–C(18)	1.451(9)	N(11)–C(36)	1.446(9)
N(1)–Ni(1)–N(2)	85.6(2)	N(7)–Ni(2)–N(8)	85.4(2)
N(1)–Ni(1)–N(3)	179.3(2)	N(7)–Ni(2)–N(9)	179.2(2)
N(1)–Ni(1)–N(4)	94.2(2)	N(7)–Ni(2)–N(10)	94.1(2)
N(2)–Ni(1)–N(3)	93.7(2)	N(8)–Ni(2)–N(9)	93.8(2)
N(2)–Ni(1)–N(4)	179.5(2)	N(8)–Ni(2)–N(10)	179.6(2)
N(3)–Ni(1)–N(4)	86.5(2)	N(9)–Ni(2)–N(10)	86.6(2)
N(1)–Ni(1)–Ow(1)	88.2(2)	N(7)–Ni(2)–Ow(3)	88.2(2)
N(2)–Ni(1)–Ow(1)	86.9(2)	N(8)–Ni(2)–Ow(3)	87.5(2)
N(3)–Ni(1)–Ow(1)	91.6(2)	N(9)–Ni(2)–Ow(3)	91.5(2)
N(4)–Ni(1)–Ow(1)	92.7(2)	N(10)–Ni(2)–Ow(3)	92.5(2)
N(1)–Ni(1)–Ow(2)	87.2(2)	N(7)–Ni(2)–Ow(4)	87.2(2)
N(2)–Ni(1)–Ow(2)	88.6(2)	N(8)–Ni(2)–Ow(4)	88.2(2)
N(3)–Ni(1)–Ow(2)	93.0(2)	N(9)–Ni(2)–Ow(4)	93.1(2)
N(4)–Ni(1)–Ow(2)	91.8(2)	N(10)–Ni(2)–Ow(4)	91.8(2)
Ow(1)–Ni(1)–Ow(2)	173.7(2)	Ow(3)–Ni(2)–Ow(4)	174.0(2)
C(1)–N(1)–C(18)	113.1(5)	C(19)–N(7)–C(36)	112.3(5)
C(8)–N(3)–C(11)	106.1(6)	C(26)–N(9)–C(29)	106.8(6)
C(8)–N(3)–C(12)	111.9(5)	C(26)–N(9)–C(30)	111.8(5)
C(11)–N(3)–C(12)	109.0(6)	C(29)–N(9)–C(30)	108.6(6)
C(14)–N(5)–C(17)	111.2(7)	C(32)–N(11)–C(35)	111.5(7)
C(14)–N(5)–C(18)	117.2(6)	C(32)–N(11)–C(36)	117.3(6)
C(17)–N(5)–C(18)	117.3(7)	C(35)–N(11)–C(36)	117.2(7)

as the six-membered chelate rings has a chair conformation. The 1,3-diazacyclohexane subunits are also fused to each of the six-membered chelate rings and have an anti-configuration with respect to the macrocyclic plane. The Ni–N bond distances range from 2.061(5) to 2.126(6) Å, and are comparable to those of other octahedral Ni(II) complexes of 14-membered polyaza macrocyclic ligands [15,16,24,25]. The average Ni–N (secondary) distance of 2.068(3) Å is significantly shorter than the average Ni–N (tertiary) distance of 2.122(3) Å, indicating comparatively strong coordination. The average bond distance of two axial Ni(1)–Ow and Ni(2)–Ow is similar (2.156(3) and 2.164(3) Å) and longer than the average distance of Ni(1)N_4 and Ni(2)N_4 plane (2.096(3) and 2.094(3) Å), giving an axially elongated octahedral geometry. The axial Ni–Ow distances are similar to that found in $[Ni(cyclam)(H_2O)_2]Cl_2 \cdot 4H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) (2.176(2) Å) [26]. Furthermore, the axial Ni–Ow linkage is bent slightly off from the perpendicular axis to the NiN_4 plane by 1.4–3.1°. The N–Ni–N angles of the six-membered chelate ring are much larger than the N–Ni–N angles of the five-membered chelate rings, as usual. The C–N–C angles involving the uncoordinated tertiary nitrogen atoms are significantly larger than the ideal tetrahedral angles. Furthermore, C–N (tertiary) bond distances are much shorter than other C–N single bond distances. These results may be attributed to the sp^2-like hybridization of the uncoordinated tertiary nitrogen atoms [13,15,16]. The coordinated water molecules are hydrogen-bonded to the secondary amines of the macrocycle (N(1)···Ow(1) 2.937(7) Å, 100.2°; N(2)···Ow(2) 2.953(7) Å, 100.3°; N(7)···Ow(3) 2.943(7) Å, 100.4°; N(8)···Ow(4) 2.949(7) Å, 100.1°). Interestingly, the coordinated water molecules are also linked to the chloride ions through hydrogen bonds, which gives rise to a one-dimensional hydrogen-bonded network (Table III and Figs. 1 and 2).

TABLE III Hydrogen-bond parameters (Å,°) for **1**[a]

	D–H	*H···A*	*D–A*	*D–H···A*
N(1)–HN(1)···Ow(1)	0.91	2.64	2.937(7)	100.2
N(2)–HN(2)···Ow(2)	0.91	2.65	2.953(7)	100.3
N(7)–HN(7)···Ow(3)	0.91	2.64	2.943(7)	100.4
N(8)–HN(8)···Ow(4)	0.91	2.65	2.949(7)	100.1
Ow(1)–Hw(1B)···Cl(2)	0.959(4)	2.129(2)	3.084(5)	174.5(3)
Ow(1)–Hw(1A)···Cl(2)^{i}	0.979(4)	2.134(2)	3.109(5)	174.0(3)
Ow(2)–Hw(2A)···Cl(1)	0.974(5)	2.092(2)	3.062(5)	174.1(3)
Ow(2)–Hw(2B)···Cl(3)^{ii}	0.964(5)	2.128(2)	3.087(5)	173.1(3)
Ow(3)–Hw(3B)···Cl(4)	0.962(4)	2.149(2)	3.078(5)	161.8(3)
Ow(3)–Hw(3A)···Cl(4)^{iii}	0.961(4)	2.146(2)	3.091(5)	167.6(3)
Ow(4)–Hw(4B)···Cl(3)	0.974(4)	2.091(2)	3.058(5)	171.7(3)
Ow(4)–Hw(4A)···Cl(1)^{ii}	0.966(4)	2.128(2)	3.084(5)	170.2(3)

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

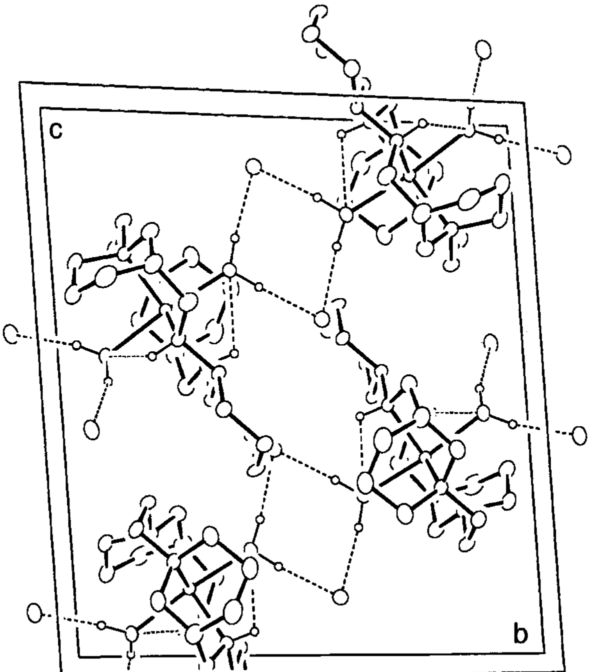


FIGURE 2 Crystal packing of **1**, showing the intermolecular hydrogen bonds as dotted lines.

An ORTEP drawing of $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**) with the atomic numbering scheme is shown in Fig. 3. Selected bond distances and angles are listed in Table IV. The nickel ion is coordinated to the two secondary and two tertiary nitrogen atoms with a square-planar geometry. The Ni–N (secondary) distances (1.955(5) and 1.950(5) Å) are somewhat shorter than the Ni–N (tertiary) distances (1.960(5) and 1.974(5) Å). The average Ni–N distance of 1.960(3) Å is similar to those of other related Ni(II) complexes with 14-membered tetraaza macrocycles [13,14]. The N–Ni–N bond angles (85.7(2) and 88.2(2)°) involved in the five-membered chelate ring are smaller than those (92.7(2) and 93.4(2)°) in the six-membered chelate ring, as usual. One of the interesting structural features of the complex is that the angles around the uncoordinated N(5) and N(6) atoms are distinctly larger than the ideal tetrahedral angles; the C(14)–N(5)–C(17) and C(7)–N(6)–C(9) angles are 112.4(6) and 116.4(6)°, respectively. It is also interesting to observed that the average N(5)–C (1.428(5) Å) and N(6)–C (1.438(5) Å) distance involving uncoordinated tertiary nitrogens is *ca.* 0.07 Å shorter than the average N(3)–C (1.500(5) Å) and N(4)–C (1.507(5) Å) distance involving coordinated

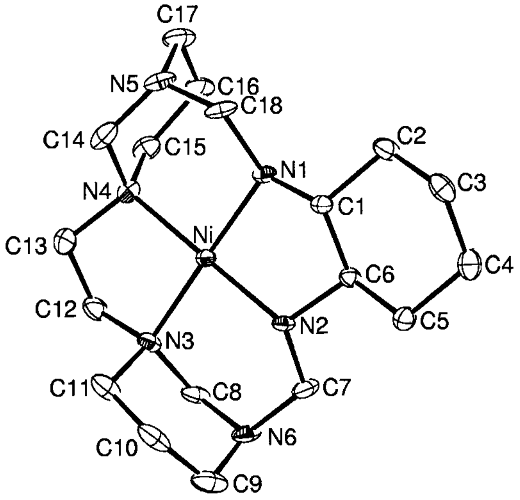


FIGURE 3 An ORTEP drawing of $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**) with the atomic numbering scheme (30% probability ellipsoids shown). The perchlorate anions and water molecules are omitted for clarity.

TABLE IV Selected bond distances (Å) and angles (°) of $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**)

Ni–N(1)	1.955(5)	N(3)–C(8)	1.490(8)
Ni–N(2)	1.950(5)	N(3)–C(11)	1.510(8)
Ni–N(3)	1.960(5)	N(3)–C(12)	1.499(8)
Ni–N(4)	1.974(5)	N(5)–C(14)	1.411(10)
N(1)–C(1)	1.487(7)	N(5)–C(17)	1.461(9)
N(1)–C(18)	1.521(7)	N(5)–C(18)	1.413(9)
N(1)–Ni–N(2)	85.7(2)	C(8)–N(3)–C(11)	107.6(5)
N(1)–Ni–N(3)	177.8(2)	C(8)–N(3)–C(12)	108.7(5)
N(1)–Ni–N(4)	93.4(2)	C(11)–N(3)–C(12)	107.6(5)
N(2)–Ni–N(3)	92.7(2)	C(14)–N(5)–C(17)	112.4(6)
N(2)–Ni–N(4)	178.5(2)	C(14)–N(5)–C(18)	114.0(6)
N(3)–Ni–N(4)	88.2(2)	C(17)–N(5)–C(18)	115.6(7)
C(1)–N(1)–C(18)	109.5(5)		

tertiary nitrogens. These results are consistent with the structure of **1** discussed previously. The secondary amine of the macrocycle forms the hydrogen bond with the perchlorate oxygen atom (N(1)···O(6) 3.156(7) Å, 116.5°).

Equilibrium Study of 1

Complex **1** dissolves in aqueous solution to give an equilibrium mixture of the square-planar $[Ni(L^2)]^{2+}$ and octahedral $[Ni(L^2)(H_2O)_2]^{2+}$ species according to Eq. (1) [26–29].

$$[Ni(L^2)]^{2+} + 2H_2O \overset{K}{\rightleftharpoons} [Ni(L^2)(H_2O)_2]^{2+} \qquad (1)$$

The equilibrium was studied at temperatures in the range 6.2–58.6°C as shown in Fig. 4. The equilibrium constants of the square-planar to octahedral conversion K and thermodynamic parameters are listed in Table V along with those for the complex of L^1 [14]. The conversion of the square-planar into the octahedral species shows an exothermic reaction, in good agreement with those previously reported for Ni(II)

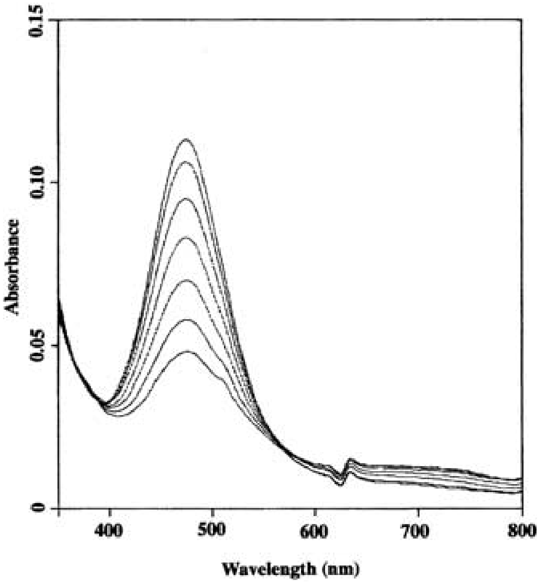


FIGURE 4 Electronic absorption spectra of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) in aqueous 0.10 M $NaClO_4$. [**1**] = 2.0×10^{-3} M. The spectra were determined (in terms of increasing absorbance) at 6.2, 15.1, 25.0, 35.0, 44.7, 53.1 and 58.6 ± 0.1°C.

TABLE V Thermodynamic parameters for the square-planar to octahedral conversion of nickel(II) complexes with macrocyclic tetraamines in aqueous 0.10 M $NaClO_4^a$

Ligand	*K*	ΔH° (kJ mol^{-1})	ΔS° (JK^{-1} mol^{-1})
$L^{1\,b}$	0.64	−24.7	−87.4
L^2	2.54	−19.0 ± 0.2	−56.0 ± 0.4

[a] Calculated from the ln K *vs* 1/T plot: 6.2°C ln K = 1.460; 15.1°C, 1.211; 25.0°C, 0.931; 35.0°C, 0.699; 44.7°C, 0.468; 53.1°C, 0.281; 58.6 ± 0.1°C, 0.165; [b] [14].

complexes of other macrocyclic ligands [14,27–30]. The value of K for $[Ni(L^2)]^{2+}$ is larger than that of $[Ni(L^1)]^{2+}$, indicating that formation of the octahedral species is not affected by steric repulsion of the cyclohexane ring on the macrocycle. However, the values of ΔH° and ΔS° for $[Ni(L^2)]^{2+}$ are considerably smaller than those of $[Ni(L^1)]^{2+}$. This may be due to the strongly hydrogen-bonding chelate rings involving the coordinated water molecules, secondary amines of the macrocycle and the central nickel(II) ion (Table III).

Characterization of the Nickel(II) Complexes

The infrared spectra of **1** show a ν(NH) band at $3256\,cm^{-1}$ associated with secondary amines and a band at $1657\,cm^{-1}$ due to the HOH bending vibration of the coordinated water molecules. **2** Exhibits only ν(NH) and $\nu(ClO_4)$ bands at 3252 and $1094\,cm^{-1}$ associated with the secondary amines and perchlorate anion. The UV–Vis spectra of the complexes are listed in Table VI. The visible absorptions of **1** are found at 564 and 563 nm, respectively, in acetonitrile and DMF solution, which are *ca.* 90 nm longer than that of square-planar $[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**). The spectra are comparable to those of other octahedral nickel(II) complexes [17,26,29], indicating coordination of the water molecules. This was also confirmed by the magnetic moment ($2.92\,\mu_B$) and X-ray structure of **1**. However, this band shifts to higher energy (477 nm) in water, indicative of a significant structural change (square-planar geometry) in solution.

Cyclic voltammetric data for the Ni(II) macrotetracyclic complexes in DMF solution are given in Table VII. A typical cyclic voltammogram of **1** is shown in Fig. 5. The complexes exhibit two waves of a one-electron transfer corresponding to Ni(II)/Ni(III) and Ni(II)/Ni(I) processes. The redox potentials for **1** are distinctly more negative than those for square-planar complex **2**. The cathodic shift in redox potentials resulting from introduction of water molecules may be due to the longer Ni–N distance. The weaker Ni–N interaction for the axial water molecules results in stabilization of antibonding orbitals in the Ni(II) complex and makes removal of an electron a more

TABLE VI Electronic spectral data of the nickel(II) complexes[a]

Complex	λ_{max}, nm ($\varepsilon = M^{-1}\,cm^{-1}$)
$[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**)	477(61), 564(10)[b], 563(9)[c]
$[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**)	476(66), 478(68)[b], 477(67)[c]

[a]In water at 20.0±0.1°C; [b]In acetonitrile; [c]DMF.

TABLE VII Cyclic voltammetric data for the nickel(II) complexes[a]

Complex	*Potentials (Volt vs AgCl)*	
	Ni(II)/Ni(III)	*Ni(II)/Ni(I)*
$[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**)	+0.76	−1.15
$[Ni(L^2)](ClO_4)_2 \cdot 2H_2O$ (**2**)	+1.07(i)	−0.99(i)[b]

[a]Measured in 0.10 M TEAP-DMSO solution at 20.0 ± 0.1°C; [b]i = irreversible.

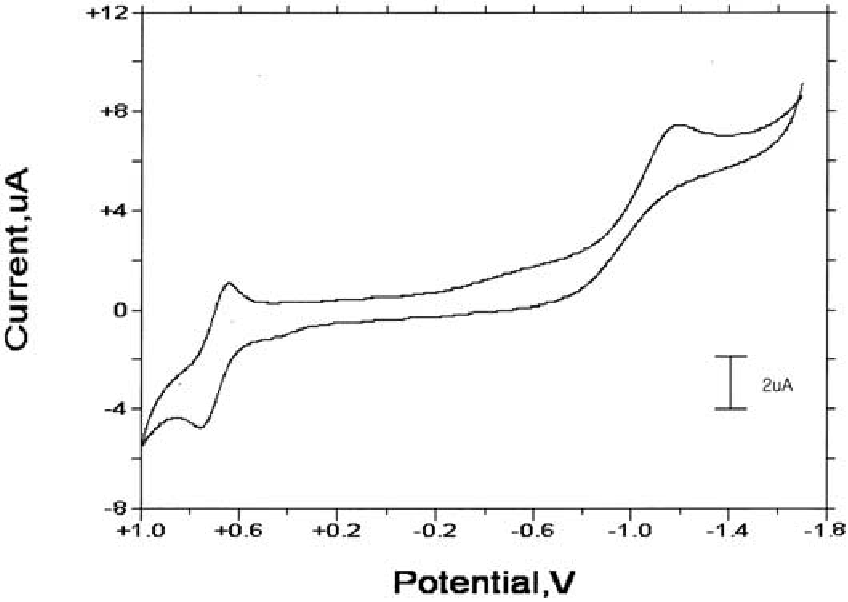


FIGURE 5 Cyclic voltammogram of $[Ni_2(L^2)_2(H_2O)_4]Cl_4$ (**1**) in 0.10 M TEAP–DMF solution at 20.0 ± 0.1°C. The scan rate is 100 mV/s.

unfavorable process. This is consistent with the crystal structures and spectral results discussed previously.

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 188650 for Compound **1** and 188651 for Compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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