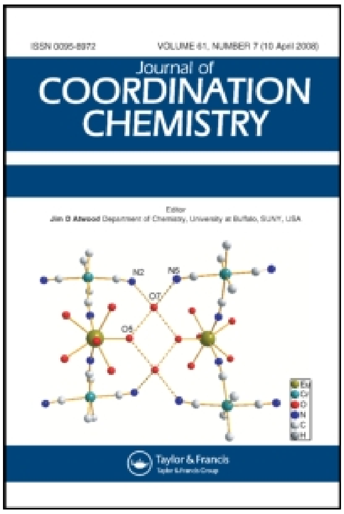


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Structure and properties of an oxalato-bridged dinickel(II) complex with a tetraazamacrocycle bearing an aminomethyl pendant arm, 5-aminomethyl-5*R*(*S*),12*R*(*S*)-dimethyl-1,4,8,11-tetraazacyclotetradecane

Katsura Mochizuki[a]; Yasunori Numata[a]; Yoshiko Kitazawa[a]; Atushi Ishii[a]
[a] Division of Chemistry, Graduate School of Integrated Science, Yokohama City University Seto 22-2, Kanazawa-ku, Yokohama 236-0027, Japan

To cite this Article Mochizuki, Katsura , Numata, Yasunori , Kitazawa, Yoshiko and Ishii, Atushi(2004) 'Structure and properties of an oxalato-bridged dinickel(II) complex with a tetraazamacrocycle bearing an aminomethyl pendant arm, 5-aminomethyl-5*R*(*S*),12*R*(*S*)-dimethyl-1,4,8,11-tetraazacyclotetradecane', Journal of Coordination Chemistry, 57: 7, 543 — 551

To link to this Article: DOI: 10.1080/00958970410001677042
URL: http://dx.doi.org/10.1080/00958970410001677042

J. Coord. Chem., Vol. 57, No. 7, 10 May 2004, pp. 543–551

Taylor & Francis
Taylor & Francis Group

STRUCTURE AND PROPERTIES OF AN OXALATO-BRIDGED DINICKEL(II) COMPLEX WITH A TETRAAZAMACROCYCLE BEARING AN AMINOMETHYL PENDANT ARM, 5-AMINOMETHYL-5*R*(*S*),12*R*(*S*)-DIMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECANE

KATSURA MOCHIZUKI*, YASUNORI NUMATA,
YOSHIKO KITAZAWA and ATUSHI ISHII

Division of Chemistry, Graduate School of Integrated Science,
Yokohama City University Seto 22-2, Kanazawa-ku, Yokohama 236-0027, Japan

(Received 16 June 2003; Revised 21 August 2003; In final form 12 February 2004)

The oxalato-bridged dinickel(II) complex with the title ligand, $[Ni_2(\mathbf{L^aH})_2(\mu\text{-ox})](ClO_4)_2 \cdot 2H_2O$ (**1**), was prepared and its structure was determined by X-ray crystallography, as well as that of the monomeric nickel(II) complex, $[Ni(\mathbf{L^aH})ox]ClO_4 \cdot 3H_2O$ (**2**). In Complexes **1** and **2**, the ligand, $\mathbf{L^a}$, is folded along the N(4)–Ni(1)–N(11) axis. The antiferromagnetic coupling between the two nickel(II) centers in **1** was revealed and the coupling constant, $J = -17.4\,\text{cm}^{-1}$, and $g = 2.11$ were estimated. It was found that the oxalato-bridged dimer **1** was readily converted to the mononuclear *cis*-nickel(II) complex $[Ni\mathbf{L^a}(OH_2)](ClO_4)_2$ (**3a**), in basic aqueous solution. In $[Ni\mathbf{L^a}(CH_3CN)]I_2$ (**3b**), which was derived from **3a**, the aminomethyl pendant arm is coordinated to the Ni(II) ion and $\mathbf{L^a}$ is folded along the N(1)–Ni(1)–N(8) axis.

Keywords: Oxalato-bridged dinickel(II) complex; Folded macrocyclic ligand; Aminomethyl pendant arm

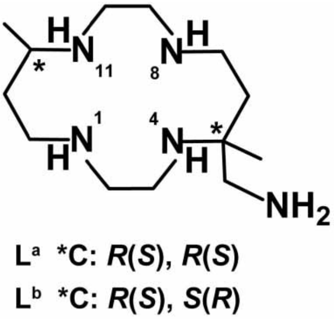
INTRODUCTION

Dinuclear complexes, in which the oxalate anion acts as a bis-bidentate bridging ligand, serve as good systems for the study of metal–metal interactions and of their structures and magnetic interactions. For tetraazamacrocyclic ligands, a number of oxalato-bridged dinuclear complexes have been synthesized, and magnetic properties of dinickel(II) complexes have been elucidated for the following; $[Ni_2(\textit{meso}\text{-tetd})_2(\mu\text{-ox})](ClO_4)_2$ (*meso*-tetd = *meso*-2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane) [1], $[Ni_2(cyclam)_2(\mu\text{-ox})](NO_3)_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) [2], $[Ni_2(Me_2cyclen)_2(\mu\text{-ox})](ClO_4)_2 \cdot 2H_2O$ (Me_2cyclen = 1,7-dimethyl-1,4,7,10-tetraazacyclododecane) [3], $[Ni_2(cyclen)_2(\mu\text{-ox})](NO_3)_2$ [3], $[Ni_2(macOH)_2(\mu\text{-ox})](NO_3)_2$

---

*Corresponding author. E-mail: katsura@yokohama-cu.ac.jp

ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00958970410001677042



(macOH = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane) [4], and $[Ni_2(rac\text{-cth})_2(\mu\text{-ox})](ClO_4)_2$ (*rac*-cth = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [5]. Herein we report the oxalato-bridged dinickel(II) complex with the title ligand ($\mathbf{L^a}$), which has an aminonomethyl pendant arm.

The nickel(II) complex with $\mathbf{L^a}$ was first prepared by Korybut-Daszkiewicz [6] by the reduction of the C=N bond in $[NiL](ClO_4)_2$ (L: 5-aminomethyl-5*R*(*S*),12-dimethyl-1,4,8,11-tetraazacyclotetradec-11-ene), as well as that with $\mathbf{L^b}$ (diastereoisomer; see the structural formula). Although the *trans*-structure of the nickel(II) complex with $\mathbf{L^b}$, where a macrocyclic N_4 ring occupies the equatorial plane, was confirmed by X-ray crystallography [7], no X-ray structure for the nickel(II) complex with $\mathbf{L^a}$ has been reported except for the brief description of the *cis*-structure of the nickel(II) complex with $\mathbf{L^a}$ based on preliminary X-ray data [8].

In this study, we have succeeded in carrying out the chromatographic separation of the isomers by applying the property that only the nickel(II) complex with $\mathbf{L^a}$ is able to form the above mentioned oxalato-bridged dinickel(II) complex. The X-ray structures of the di- and mononuclear nickel(II) complexes with $\mathbf{L^a}$ have been revealed, as well as the magnetic interaction between nickel(II) ions in the oxalato-bridged complex. Conversion behavior of the oxalato-bridged dinickel(II) complex in a basic aqueous solution has been also studied from the structural analysis of mononuclear nickel(II) complexes derived from the dinickel(II) complex.

EXPERIMENTAL

Synthesis of $[(NiL^aH)_2(\mu\text{-ox})](ClO_4)_2 \cdot 2H_2O$, 1

A mixture of nickel(II) complexes (perchlorate salts) with $\mathbf{L^a}$ and $\mathbf{L^b}$ was synthesized by the reported method [6]. To an aqueous solution (300 mL) of the mixture (20.04 g, 0.037 mol) was added an aqueous solution of sodium oxalate (5.04 g, 0.037 mol). The solution, adjusted to pH 4 with HCl, was heated at 40°C for 1 h. The resultant blue solution contained nickel(II) complexes with $\mathbf{L^a}$ and $\mathbf{L^b}$, which were separated by column chromatography using the cation exchange resin SP-Sephadex C25 and 0.1 M sodium oxalate as the eluent. Two bands were eluted, of which the first blue band was collected and evaporated to one-third its volume. An almost equal volume of ethanol was added to the concentrated aqueous solution to precipitate sodium oxalate, which was removed by filtration. Then, the solution was again evaporated to one-third its volume. After the removal of sodium oxalate had been repeated three times, the addition of sodium perchlorate to the solution gave a blue precipitate (yield: 6.0 g). Crystals of complex **1** were obtained by recrystallization from water. Found: C, 29.01; H, 5.57; N, 12.10%. Calcd for $C_{28}H_{64}N_{10}Ni_2Cl_4O_{20} \cdot 2H_2O$: C, 29.09; H, 5.93; N, 12.16%. FAB-mass: *m/z* 819 ($[M-2H^+-3ClO_4^-]^+$). IR (KBr): $1651\,cm^{-1}$. VIS (H_2O, 25°C): 942 nm (ε 38), 564 (37), 353 (65). Diffuse Reflectance Spectrum (powder): 585, 363 nm. The nickel(II) complex with $\mathbf{L^b}$ was obtained similarly from the violet second band.

Synthesis of $[Ni(L^aH)ox]ClO_4 \cdot 3H_2O$, 2

Recrystallization of **1** from an aqueous solution containing an excess of sodium oxalate gave crystals of **2**. FAB-mass: *m/z* 414 ($[M-H^+-C_2O_4^{2-}]^+$). IR (KBr): $1653\,cm^{-1}$, $1541\,cm^{-1}$.

Synthesis of $[NiL^a(OH_2)](ClO_4)_2$, 3a

To an aqueous solution (400 mL) of **1** (6.10 g, 0.005 mol) was added 6 M NaOH until the blue solution turned violet (pH ca. 9). The solution was evaporated to 50 mL, followed by the addition of $NaClO_4$, to give a violet precipitate of **3a** (yield: 3.96 g, 68%), which was recrystallized from water [9]. FAB-mass: *m/z* 414 ($[M-H_2O-ClO_4^-]^+$). VIS (H_2O, 25°C): 900 nm (ε 10), 532 (5.7), 341 (9.4).

Crystals of $[NiL^a(CH_3CN)]I_2$, **3b**, for X-ray crystallographic analysis, were obtained from the conversion of **3a** to the iodide salt, followed by recrystallization from acetonitrile.

Physical Measurements

Magnetic susceptibilities were measured using a Quantum SQUID magnetometer MPMS-XL. FAB-mass spectra were recorded using a JEOL DX-303 spectrometer and the VIS-absorption spectra were measured using a VARIAN Cary 500 spectrophotometer.

Crystallographic Study

X-ray crystallographic analysis of single crystals of **1** was carried out on a MAC Science MXC3k four-circle diffractometer with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) and the ω–2θ (**1**, **3b**) or ω scan (**2**) technique. The structures were solved by the direct method (SIR 92 [10] and Dirdif) and refined by the full-matrix least-squares method (SHELXL 97 [11]). All the nonhydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were attached according to SHELXL 97 [11]. All of the calculations were carried out using a Silicon Graphics O_2 work station (MaXus program system provided by MAC Science). The structural diagram was drawn using ORTEP-3 for Windows [12].

1: $_{28}H_{68}N_{10}Ni_2Cl_4O_{22}$; $FW = 1156.09$; $T = 298(2)$ K; 0.71073 Å; Monoclinic; $P2_1/n$; $a = 13.167(4)$ Å, $b = 21.915(8)$ Å, $c = 8.464(3)$ Å, $\beta = 96.56(3)°$; $V = 2426.3(14)$ Å^3; $Z = 4$; $D_{calcd} = 1.681$ Mg/m^3; $\mu = 1.082$ mm^{-1}; $F(000) = 1212$; Crystal size = 0.30 × 0.30 × 0.30 mm; $1.56 \leq \theta \leq 27.56°$; Decay collection applied; Independent reflections: 5583

TABLE I Selected bond lengths (Å) and angles (°) for **1**

Ni(1)–N(1)	2.085(5)
Ni(1)–N(4)	2.218(5)
Ni(1)–N(8)	2.081(4)
Ni(1)–N(11)	2.154(5)
Ni(1)–O(21)	2.091(3)
Ni(1)–O(23)	2.091(3)
Ni(1)···Ni(1′)	5.437(2)
N(1)–Ni(1)–N(8)	101.0(2)
N(4)–Ni(1)–N(11)	169.7(2)
N(8)–Ni(1)–O(23)	169.0(2)
N(1)–Ni(1)–O(21)	169.6(2)
O(21)–Ni(1)–O(23)	79.6(1)
N(4)–Ni(1)–O(21)	97.5(2)
N(4)–Ni(1)–O(23)	91.5(2)
N(11)–Ni(1)–O(21)	90.7(2)
N(11)–Ni(1)–O(23)	96.1(2)

TABLE II Selected bond lengths (Å) and angles (°) for **2**

Ni(1)–O(21)	2.054(3)
Ni(1)–O(23)	2.076(3)
Ni(1)–N(1)	2.081(3)
Ni(1)–N(8)	2.082(3)
Ni(1)–N(11)	2.149(4)
Ni(1)–N(4)	2.195(3)
O(21)–Ni(1)–O(23)	80.19(11)
O(21)–Ni(1)–N(1)	170.91(13)
O(23)–Ni(1)–N(8)	168.18(12)
N(1)–Ni(1)–N(8)	99.47(14)
O(21)–Ni(1)–N(4)	100.88(12)
N(11)–Ni(1)–N(4)	168.85(12)

($R_{\text{int}} = 0.0011$); Absorption correction: ψ-scan; One perchlorate disordered: Parameters: 325; Goodness-of-fit on F^2: 1.041; Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0657$, $wR_2 = 0.1710$; Largest diff. peak and hole: 0.836 and $-0.488\,\text{e}\,\text{Å}^{-3}$. Selected bond distances and angles are given in Table I.

2: $C_{15}H_{38}ClN_5NiO_{11}$; $FW = 558.66$; $T = 298(2)$ K; 0.71073 Å; Orthorhombic; *Pbcn*; $a = 26.391(8)$ Å; $b = 14.251(5)$ Å; $c = 13.432(5)$ Å; $V = 5052(3)\,\text{Å}^3$; $Z = 8$; $D_{\text{calcd}} = 1.469\,\text{Mg/m}^3$; $\mu = 0.934\,\text{mm}^{-1}$; $F(000) = 2368$; Crystal size $= 0.40 \times 0.30 \times 0.30$ mm; $1.54 \le \theta \le 27.54$; ω scan; Independent reflections: 5830; Absorption correction: ψ-scan; Parameters: 298; Goodness-of-fit on F^2: 1.024; Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0565$, $wR_2 = 0.1282$; Largest diff. peak and hole: 0.606 and $-0.725\,\text{e}\,\text{Å}^{-3}$. Selected bond distances and angles are given in Table II.

3b: $C_{15}H_{34}I_2N_6Ni$; $FW = 610.97$; $T = 298(2)$ K; 0.71073 Å; Monoclinic; $P2_1/c$; $a = 10.050(7)$ Å, $b = 13.177(5)$ Å, $c = 17.176(5)$ Å, $\beta = 91.64(4)°$; $V = 2274(2)\,\text{Å}^3$; $Z = 4$; $D_{\text{calcd}} = 1.715\,\text{Mg/m}^3$; $\mu = 3.577\,\text{mm}^{-1}$; $F(000) = 1148$; Crystal size $= 0.40 \times 0.30 \times 0.30$ mm; Independent reflections: 5189 ($R_{\text{int}} = 0.0324$); Absorption correction: ψ-scan; Parameters: 217; Goodness-of-fit on F^2: 1.042; Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0464$, $wR_2 = 0.1104$; Largest diff. peak and hole: 1.377 and $-0.894\,\text{e}\,\text{Å}^{-3}$. Selected bond distances and angles are given in Table III.

TABLE III Selected bond lengths (Å) and angles (°) for **3b**

Ni(1)–N(1)	2.077(5)
Ni(1)–N(4)	2.105(4)
Ni(1)–N(8)	2.086(5)
Ni(1)–N(11)	2.147(4)
Ni(1)–N(16)	2.142(4)
Ni(1)–N(21)	2.098(5)
N(1)–Ni(1)–N(8)	170.3(2)
N(4)–Ni(1)–N(11)	100.1(2)
N(11)–Ni(1)–N(16)	175.8(2)
N(4)–Ni(1)–N(16)	79.9(2)
N(4)–Ni(1)–N(21)	168.4(2)

RESULTS AND DISCUSSION

The oxalato-bridged dinickel(II) complex with $\mathbf{L^a}$ was prepared from the reaction of sodium oxalate and the C=N reduction product of [NiL](ClO_4)$_2$, which was the mixture of nickel(II) complexes with the isomers $\mathbf{L^a}$ and $\mathbf{L^b}$. Only the nickel(II) complex with $\mathbf{L^a}$ reacted with an oxalate anion to form the blue complex, which was separated by column chromatography (cation-exchange resin: SP-Sephadex C25, 0.1 M sodium oxalate) and finally isolated as a perchlorate salt, $[(Ni\mathbf{L^aH})_2(\mu\text{-ox})](ClO_4)_2 \cdot 2H_2O$ (**1**). The removal of the sodium oxalate from the collected eluate is important during the isolation process of **1**. In the presence of excess oxalate, an oxalate anion may react with the nickel(II) complex to form the mononuclear nickel(II) complex predominantly. Indeed, the monomeric nickel(II) complex, $[Ni(\mathbf{L^aH})ox]ClO_4 \cdot 3H_2O$ (**2**) was also obtained from the column-eluted solution, when the sodium oxalate had not been removed sufficiently or when **1** had been recrystallized from a sodium oxalate aqueous solution. Complexes **1** and **2** can be easily distinguished by the differences in IR and VIS spectra.

The X-ray crystal structure analysis of **1** clearly shows the oxalato-bridged nickel(II) dinuclear structure, where the tetraazamacrocycle, $\mathbf{L^a}$, is folded along with the N(4)–Ni(1)–N(11) axis (169.7(2)) with an angle of 101.0(2)° (N(1)–Ni(1)–N(8)) (Fig. 1). The oxalate anion acts as a bis-bidenate ligand to link the two *cis*-nickel(II) complexes, where an inversion center exists in the middle of the oxalato bridge. The aminomethyl pendant arms do not coordinate with the nickel(II) ions (arm-off) but are protonated, adopting an equatorial position with respect to the chair-shaped six-membered chelate ring consisting of Ni(1), N(4), C(5), C(6), C(7) and N(8). Two methyl groups adopt axial positions with respect to the six-membered chelate rings. The average Ni–N distance is 2.135 Å, typical for six-coordinate macrocyclic nickel(II) complexes [13]. The Ni(1)–N(4) distance (2.218(5) Å) is significantly longer than the others. The intramolecular distance of Ni(II)···Ni(II) is 5.437(2) Å, which is between those found in previously reported analogous dimeric nickel(II) complexes; $[Ni_2(cyclam)_2(\mu\text{-ox})](NO_3)_2$ [2]: 5.395(2) Å and $[Ni_2(Me_2cyclen)_2(\mu\text{-ox})](ClO_4)_2 \cdot 2H_2O$ [3]: 5.465(1) Å.

The X-ray structure of the cation part of the monomeric nickel(II) complex **2** (Fig. 2) is very similar to that found for the dimeric nickel(II) Complex **1**.

The close linkage of two nickel(II) ions by the oxalato-bridge leads to a magnetic interaction between the nickel(II) ions. The effective magnetic moment per nickel(II) of **1** in the solid state showed temperature dependence in the range of 5–300 K (Fig. 3); it gradually decreased with decrease in temperature from 2.94 B.M. at 300 K.

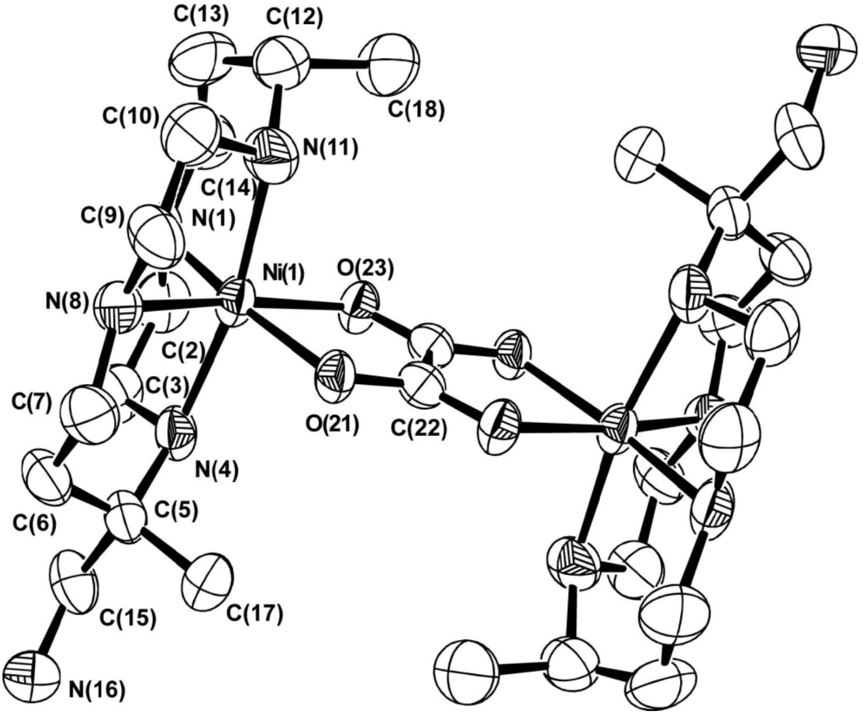


FIGURE 1 ORTEP drawing for the cation of **1**.

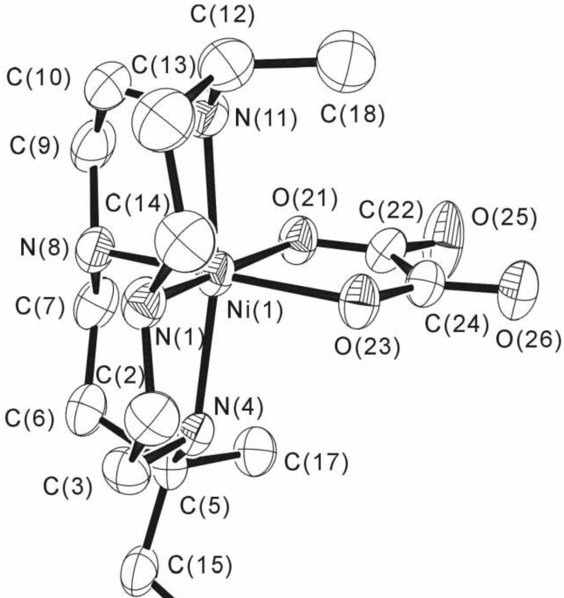


FIGURE 2 ORTEP drawing for the cation of **2**.

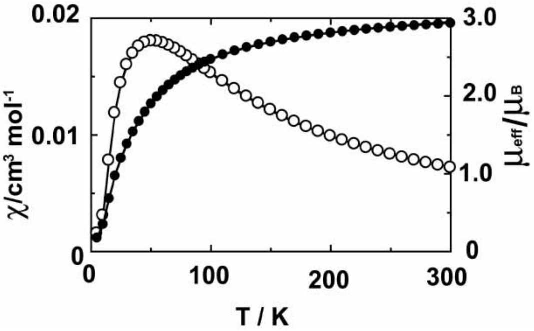


FIGURE 3 Temperature-dependence of molar magnetic susceptibility (○) and effective magnetic moment per nickel(II) (●) for **1**. Solid lines indicate the best-fit lines calculated from the theoretical equation.

This behavior obviously indicates that antiferromagnetic coupling exists between the two nickel(II) centers. The coupling constant, $J = -17.4\,\mathrm{cm}^{-1}$, and $g = 2.11$ were estimated ($\rho = 0.0043$, $R = \sum(\chi_{\mathrm{exptl}}(i) - \chi_{\mathrm{calcd}}(i))^2/\sum(\chi_{\mathrm{exptl}}(i))^2 = 3.83 \times 10^{-6}$) by fitting the experimental data to the following theoretical equation derived from the binuclear model (each symbol corresponds to commonly used parameters).

$$\begin{aligned}
\chi_{\mathrm{m}} &= (1-\rho)\chi_{\mathrm{dim}} + \rho\chi_{\mathrm{mono}} + TIP,\\
\chi_{\mathrm{dim}} &= (2N_{\mathrm{A}}g^2\mu_{\mathrm{B}}^2/kT)(\exp(2J/kT) + 5\exp(6J/kT))/\\
&\qquad (1 + 3\exp(2J/kT) + 5\exp(6J/kT)),\\
\chi_{\mathrm{mono}} &= 2N_{\mathrm{A}}g^2\mu_{\mathrm{B}}^2/3kT,\\
H &= -2JS_1S_2,\\
S_1 &= S_2 = 1.
\end{aligned}$$

The value of the coupling constant, J, found in this study is similar to those found for analogous oxalato-bridged dinickel(II) complexes; $[\mathrm{Ni_2}(meso\text{-tetd})_2(\mu\text{-ox})](\mathrm{ClO_4})_2$ [1]: $J = -18.4\,\mathrm{cm}^{-1}$, $g = 2.194$; $[\mathrm{Ni_2(cyclam)_2}(\mu\text{-ox})](\mathrm{NO_3})_2$ [2]: $J = -19.5\,\mathrm{cm}^{-1}$, $g = 2.33$; $[\mathrm{Ni_2(Me_2cyclen)_2}(\mu\text{-ox})](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$ [3]: $J = -17\,\mathrm{cm}^{-1}$, $g = 2.30$; $[\mathrm{Ni_2(cyclen)_2}(\mu\text{-ox})](\mathrm{NO_3})_2$ [3]: $J = -17.5\,\mathrm{cm}^{-1}$, $g = 2.15$; $[\mathrm{Ni_2}(rac\text{-cth})_2(\mu\text{-ox})](\mathrm{ClO_4})_2$ [5]: $J = -17\,\mathrm{cm}^{-1}$, $g = 2.07$.

The oxalato-bridged dimer **1** was found to change easily to the mononuclear nickel(II) complex **3a** in basic aqueous solution. The blue aqueous solution of the oxalato-bridged dimer turned violet immediately, when the solution was adjusted to over pH 9 by the addition of NaOH. This color change may correspond to the change in the coordination environment of nickel(II) ions from N4O2 to N5O1 donors; i.e., coordination of the aminomethyl pendant arm (arm-on). From the violet solution was isolated the monomeric nickel(II) complex, **3a**, as a perchlorate, which was converted to the iodide salt. The iodide was recrystallized from acetonitrile to give crystals suitable for X-ray crystallography, **3b** (Fig. 4). Although the macrocyclic ligand $\mathbf{L^a}$ also adopts a folded form in **3b**, the folded axis (N(1)–Ni(1)–N(8): 170.3(2)) is different from that found in **1**. The aminomethyl pendant arm coordinates to the nickel(II) ion, which is in a distorted octahedral geometry resulting from the pentadentate $\mathbf{L^a}$ ligand and one acetonitrile molecule. Contrary to the structures of the complexes **1** and **2**, the aminomethyl group of **3b** adopts an axial position of the

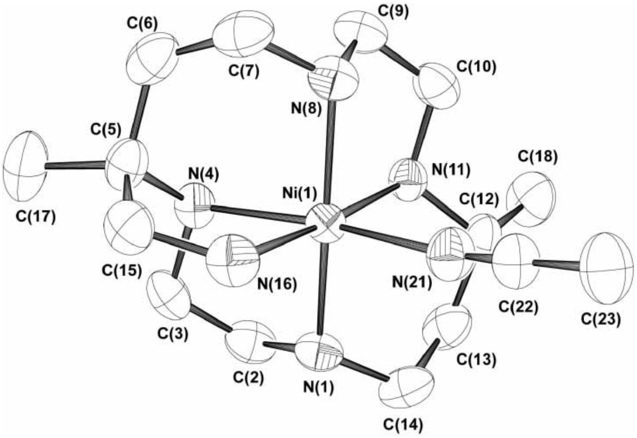
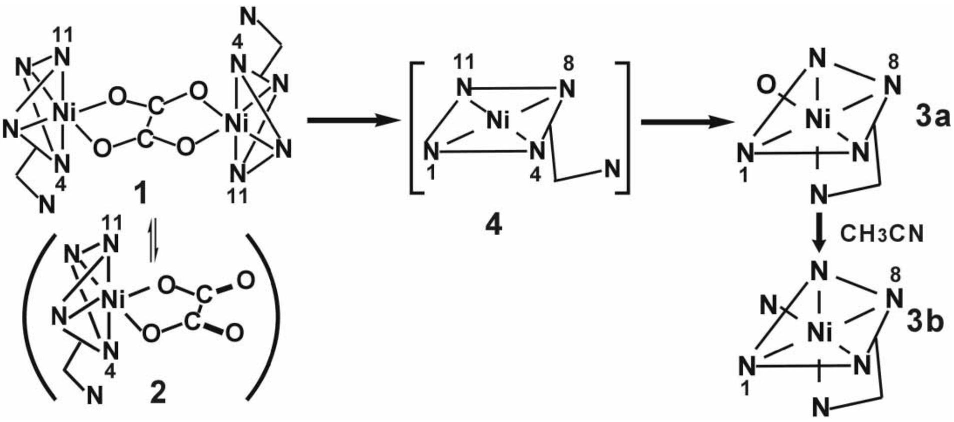


FIGURE 4 ORTEP drawing for the cation of 3**b**.



SCHEME 1.

chair-shaped six-membered chelate ring, whereas the two methyl groups are in equatorial positions. The Ni(1)–N(4) bond length (2.105(4) Å) is shortened markedly by the folding axis change and the aminomethyl pendant-arm coordination, compared with those of **1** (2.218(5) Å) and **2** (2.195(3) Å).

Thus, upon conversion from the oxalato-bridged complex, **1**, (and/or the oxalato complex **2**) to **3a**, deprotonation and coordination of the aminomethyl pendant arm occurred, which should be a significant driving force for the folding axis change of **L**$^{\mathbf{a}}$. The folding axis change is considered to proceed via the square planar complex, **4**, as an intermediate (see Scheme 1). In order to confirm the existence of Complex **4**, the protonation behavior of the complex **3a** was followed spectrophotometrically. Figure 5 shows the spectral change of **3a** in acidic aqueous media at pH 2. The absorption spectrum of **3a** was ascribable to a typical octahedral nickel(II) complex showing three absorption bands around 900, 550 and 350 nm, when it was measured just after dissolution. The absorption band around 900 nm decreased gradually as days passed, whereas the absorption spectrum around 450 nm, from the square-planar nickel(II)

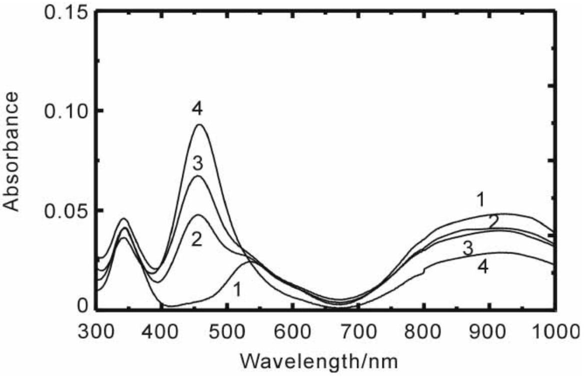


FIGURE 5 Absorption spectral change of 5×10^{-3} M **3a** in aqueous solution at pH 2 and at 25°C: after dissolution (1), 4 d (2), 6 d (3) and 14 d (4).

complex, increased. These spectral results strongly suggested the existence of the square-planar species **4**.

It is well known that some tetraazamacrocyclic ligands adopt folded forms to afford *cis*-nickel(II) complexes [13]. For the title tetraazamacrocyclic ligand, $\mathbf{L^a}$, there are two possible folded forms depending on the folding axis, i.e., N(1)–Ni(1)–N(8) or N(4)–Ni(1)–N(11), due to the asymmetric structure of the macrocycle $\mathbf{L^a}$ bearing an aminomethyl pendant arm. In the present study, we have actually found both folded forms of $\mathbf{L^a}$ in the nickel(II) complexes. The form folded along the N(4)–Ni(1)–N(11) axis was found in the μ-oxalato-bridged nickel(II) binuclear complex, $[(\mathrm{Ni}\mathbf{L^a}\mathbf{H})_2(\mu\text{-ox})](\mathrm{ClO_4})_2 \cdot 2\mathrm{H_2O}$ (**1**), in which the aminomethyl group was free from coordination (arm-off), and the other form with the N(1)–Ni(1)–N(8) folding axis in the mononuclear nickel(II) complex derived from **1**, $[\mathrm{Ni}\mathbf{L^a}(\mathrm{CH_3CN})]\mathrm{I_2}$ (**3b**), where the aminomethyl group was coordinated to the nickel(II) ion (arm-on). The ligand $\mathbf{L^a}$ can change its folding axis depending on the aminomethyl pendant arm coordination. This finding reflects a new property of a tetraazamacrocycle with a coordinating pendant arm.

References

[1] D.M. Duggan, E.K. Barefield and D.N. Hendrickson, *Inorg. Chem.* **12**, 985 (1973).

[2] L.P. Battaglia, A. Bianchi, A.B. Corradi, E. Garcia-España, M. Micheloni and M. Julve, *Inorg. Chem.* **27**, 4174 (1988).

[3] A. Bencini, A. Bianchi, E. Garcia-España, Y. Jeannin, M. Julve, V. Marcelino and M. Philoche-Levisa, *Inorg. Chem.* **29**, 963 (1990).

[4] H. Xiang, T.B. Lu, S. Chen, Z.W. Mao, X.L. Feng and K.B. Yu, *Polyhedron* **20**, 313 (2001).

[5] J.K. Tang, E.Q. Gao, L. Zhang, D.Z. Liao, Z.H. Jiang and S.P. Yan, *J. Coord. Chem.* **55**, 527 (2002).

[6] B. Korybut-Daszkiewicz, *J. Coord. Chem.* **19**, 101 (1988).

[7] J.W. Krajewski, P. Gluziń ski, B. Korybut-Daszkiewicz, A. Kemme and A. Mishnyov, *Bull. Pol. Acad. Sci. Chem.* **39**, 279 (1991).

[8] G. Rosloneck and J. Taraszewska, *J. Electroanal. Chem.* **325**, 285 (1992).

[9] The preliminary X-ray structural analysis of the perchlorate **3a** recrystallized from water suggested a folded form along the N(1)–Ni–N(8) axis and the coordination of H_2O.

[10] A. Altomare, G. Cascarno, C. Giacovazzo and A. Gualiardi, *J. Appl. Crystallogr.* **27**, 435 (1994).

[11] G.M. Sheldrick SHELX97. Programs for Crystal Structure Analysis (Release 97-2) (University of Göttingen, Germany, 1997 .

[12] L.J. Farrugia, *J. Appl. Crystallogr.* **30**, 565 (1997).

[13] N.F. Curtis, In: G.A. Melson (Ed.), Coordination Chemistry of Macrocyclic Compounds (Plenum Press, New York, 1979).